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UNITED STATES AIR FORCE
611TH AIR SUPPORT GROUP
611TH CIVIL ENGINEER SQUADRON
ELMENDORF AFB, ALASKA

FINAL
QUALITY ASSURANCE
PROJECT PLAN

INSTALLATION RESTORATION
PROGRAM (IRP) REMEDIAL
INVESTIGATION/ FEASIBILITY STUDY

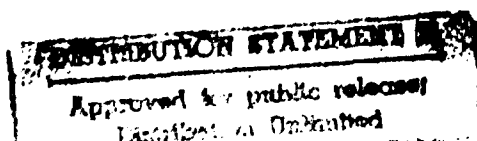
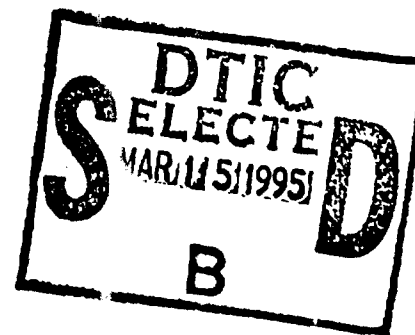
KOTZEBUE LONG RANGE
RADAR STATION, ALASKA

OCTOBER 1994

95-01106



VOLUME II
APPENDIX B



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ANALYTICAL STANDARD OPERATING PROCEDURES (SOPs) FOR ARI

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ANALYTICAL
RESOURCES
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Standard Procedure

Thermo Jarrell Ash
Graphite Furnace Analysis

503S

Revision 1

3/30/94

PROPRIETARY

Prepared By:

JPF James P. Fick

Approvals:

Jay Kuhn MGT
Section Manager

Don N. Seltman
Laboratory Manager

Michelle J. Turner 9/1/94
Quality Assurance Manager

Mark W. ...
Laboratory Director

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STANDARD OPERATING PROCEDURE Thermo Jarrell Ash Graphite Furnace

1.0 Scope and Application

This document describes methods for analyzing samples on the Thermo Jarrell Ash Smith-Hieftje 11 and Video 22E graphite furnaces. While drinking waters may be analyzed directly, other types of samples require some sort of digestion preparatory step. Samples are run first on an analytical curve using an instrument spike. Those samples failing to show sufficient spike recovery are either diluted and rerun and/or run by the method of standard additions.

2.0 Definitions

GFAAS - Graphite Furnace Atomic Absorption Spectrometry

ICV and CCV - Initial and Continuing Calibration Verification - An independent standard at a concentration other than that used for instrument calibration run to verify the accuracy of the calibration.

ICB and CCB - Initial and Continuing Calibration Blank - A calibration blank run immediately after the ICV and CCV to verify the baseline of the calibration.

CRA - A standard made at twice the IDL run to check the accuracy of results that are close to the detection limit.

IDL - Instrument Detection Limit - As defined in the EPA-CLP SOW; three times the standard deviation of seven replicate measurements averaged over three non-consecutive days.

MDL - Method Detection Limit - As defined in 40 CFR; three times the standard deviation of seven replicate measurements of a low level standard or sample that has gone through a preparation step.

MSA - Method of Standard Additions - To correct for the fact that a sample may have a different response slope than the calibration standards, three additions of known amount of analyte are added to the sample, and the results of those analyses plus the unspiked sample are extrapolated using a linear least squares fit to determine the sample's concentration.

SD - Standard Deviation

RSD - Relative Standard Deviation - The SD divided by the mean, multiplied by 100.



RPD - Relative Percent Difference - The absolute difference between two numbers, divided by the average of the two numbers, multiplied by 100.

%R - Percent Spike recovery - The difference between the matrix spike concentration and the original sample concentration divided by the concentration of the spike added multiplied by 100.

3.0 Equipment

3.1 Instrument

One TJA S/H 11 or Video 22E atomic absorption spectrometer equipped with a CTF 188 graphite furnace, FASTAC deposition system and an autosampler.

3.2 Gas supply

Argon supply from Dewar flask, 99.997% pure (High purity grade). A large number of Ar tank backups of the same purity are kept. Compressed air from an air compressor.

3.3 Consumables

A large supply of graphite tubes and other furnace parts to minimize the possibility of downtime due to lack of inventory.

Lab consumables include 13 X 100 mm sample tubes, lens paper, cotton swabs, and kimwipes.

3.4 Reagents

Matrix modifiers - These are prepared and stored according to the instructions in the modifier preparation section.

Nitric Acid - (HNO_3) 70%. Trace Grade that has Lot QC documentation to verify that it is contamination free.

De-ionized water - Water that is ion free.

Stock Standards and Independent check standards - Stock standards and independent check standards from many different sources are used. A file of their certified concentrations and other documentation is kept.

3.5 Labware

Assorted volumetric flasks, both glass and plastic, glass class A volumetric pipettes, air-displacement pipettes with disposable tips covering a wide volume range, and plastic beakers of various sizes are available for use.



4.0 Documentation

4.1 During instrument setup, the TJA instrument setup log is completed. The GFAA summary logbook and TJA sample logbook are filled out during the run. Any event or observation or action that is worth noting should be recorded in the appropriate instrument maintenance hardbound logbook, and on the instrument set-up logbook page. When the analytical day is complete, a data package for review consists of all raw data, and copies of all related logbook pages. All logbook pages should have unused portions 'z'-ed out by the analyst, initialed, and dated.

5.0 Inhouse Modifications to Referenced Method

5.1 Method 7000A 7/92 - 7.3.5 Calls for serial dilution analysis of one sample per batch to check for matrix interferences. Instead we analytically spike (equivalent to single addition MSA) every sample to test for matrix interferences.

5.2 Method 7000A 7/92 - 8.3 Calls for continuing calibration verification sample result to be within an acceptance limit of 20%. Instead we use an acceptance limit of 10% for the continuing calibration verification sample result.

5.3 Method 7000A 7/92 - 8.4 Calls for a MSD and a LCS with every sample batch. Instead of a MSD we do a duplicate. Per client request we will do a MSD instead of a duplicate. We do not do a LCS with every batch. Per client request we will do a LCS with every batch.

5.4 Method 7041 9/86 (Sb) - Does not specify a matrix modifier is needed. We use a 0.5% KMnO_4 solution as a matrix modifier.

5.5 Method 7060A 11/92 (As) - 7.1.3 Calls for NiNO_3 to be added to the sample as a matrix modifier. Instead we use a Pd/Mg solution as a matrix modifier. 7.5 Calls for certain types of samples to be analyzed for by using the MSA. Instead we analyze every sample by using the single addition MSA.

5.6 Method 7421 9/86 (Pb) - 3.3 Calls for H_3PO_4 to be added to the sample as a matrix modifier *if needed*. Instead we use a Pd/Mg solution as a matrix modifier.

5.7 Method 7841 9/86 (Ti) - 5.3 Calls for PdCl_2 to be added to the sample as a matrix modifier. Instead we use a Pd/Mg solution as a matrix modifier.

6.0 Procedure

6.1 Method Description

A representative aliquot of sample is deposited on a platform in a graphite tube and evaporated to dryness. Once dried the sample is pretreated in an ashing step which is designed to minimize the interference effects caused by the sample matrix. The ash step is followed by atomization. Atomization is characterized by rapid heating of the furnace to a temperature at which the analyte is atomized from the pyrolytic graphite surface. The resulting atomic cloud absorbs the element specific atomic emission



produced by a hollow cathode lamp (HCL). Because the resulting absorbance usually has a nonspecific component associated with the actual analyte absorbance, an instrumental background correction device is necessary to subtract from the total signal the component which is nonspecific to the analyte. Thermo Jarrell Ash Smith-Hieftje 11 and Video 22 E utilize deuterium background correction and Smith-Hieftje background correction. A monochromator isolates the analytic line emission from the hollow cathode lamp and a photomultiplier tube measures the absorbance by the sample.

6.2 Procedure

FURNACE SET-UP

6.2.1 Turn on all necessary equipment in the following order: a.)cooling water, b.)CTF 188 (FURNACE), c.)printer, d.)auto sampler, e.)AA power (Red button), f.)AA operate knob (This knob should be on "Restart/Stand-by" when not in use)

6.2.2 Install the appropriate hollow cathode lamp and set the timer to begin warm-up. Allow approximately 30 minutes for adequate warm-up.

6.2.3 Adjust the wavelength, bandwidth, high voltage, background and other specifications to their proper settings as found in the individual element sheets in this document.

6.2.4 Go to the "I/O" menu on the keyboard. Input the correct date and time.

6.2.5 Exit the "I/O" menu. Go to "MODE" on the keyboard. Input the correct element to be run.

6.2.6 Exit "MODE". Go to "RECALL" and input the correct furnace method from its computer memory. See the individual element sheets for specific information. After recalling the correct program, print the program by pressing the decimal point button on the keypad.

6.2.7 While the lamp is warming up, clean the furnace.

6.2.7.1 Unhook the FASTAC, remove the jet tip and set it aside. Remove the workhead and place it in the bracket on the left side of the furnace. Remove the sapphire window, quartz window caps, electrode inserts, ceramic washer, pressure washer, cell body and the cuvette from the workhead. Store cuvettes in ziplock bags according to the element run. It is helpful to keep a rough track of how many firings each cuvette has gone through.

6.2.7.2 Use cotton swabs dipped in deionized water to clean the inside surface of the electrodes, cell door, cell body tray, IR window and sapphire window bracket. Allow ample drying time before replacing the parts.

6.2.7.3 Use cotton swabs dipped in deionized water to clean all surfaces of the electrode inserts, the ceramic washer, the pressure washer, and the cell body. Set them aside to dry until needed.



6.2.7.4 Remove the quartz lenses from the window caps. Use cotton swabs dipped in deionized water to clean both sides of each lens. Use lens paper to dry and buff the surfaces. Inspect each lens for smudges and fibers before re-inserting the lenses into the window caps.

6.2.7.5 To minimize dust build-up on the lenses, re-install the right and left electrode inserts and window caps into their respective electrodes. Make sure all surfaces of the electrodes are dry before replacement.

6.2.7.6 Use cotton swabs dipped in deionized water to clean the sapphire window. Use lens paper to dry and buff the surfaces. Inspect the window for smudges and fibers.

6.2.7.7 Re-insert the sapphire window into its bracket on the workhead.

6.2.7.8 Replace the cell body into the workhead.

6.2.7.9 Insert the proper cuvette into the workhead. Some left electrode inserts have two position options. Make sure that the jet tip hole in the cuvette is facing you after installation. If not, adjust the left electrode insert to the correct cuvette position.

6.2.7.10 Re-insert the pressure washer and the ceramic washer onto the right electrode insert and close the workhead.

6.2.7.11 Clean the aerosol jet tip with a 10% HNO_3 solution. Rinse it with deionized water. Dry it thoroughly and re-install it in the sample injector. Check the alignment of the aerosol jet tip with the hole in the cuvette. If the alignment is severely off, refer to cleaning guideline number nine above.

6.2.7.12 Remove the silicon sample delivery tubing from the FASTAC assembly. Clean it with a 10% HNO_3 solution and rinse it with deionized water. Dry it thoroughly and re-install it on the FASTAC.

6.2.7.13 Clean the windows on both sides of the workhead compartment with lens paper.

6.2.7.14 Replace the workhead to the workhead bracket and secure tightly.

6.2.7.15 Replace the FASTAC and attach the power supply cord and all tubing.

6.2.7.16 Place the sample probe in a 20% $\text{HCL}/20\% \text{HNO}_3$ solution. (This is kept in the "Acid Rinse" cup on the autosampler.) By pushing the "Neb Air" button on the furnace, flush the sample tubing and FASTAC assembly for approximately twenty seconds. Let the solution sit for at least one minute and then repeat this step again.

6.2.7.17 Place the sample probe in a cup of fresh deionized water. This cup is also located on the autosampler. Neb Air again for approximately two minutes.



6.2.8 Once the lamp has had adequate warm-up time, its signal must be optimized. With the workhead in place, a good peak should lie mid-scale in the green sector on the high voltage energy meter.

6.2.8.1 Confirm required specifications for the element you plan to run, i.e. wavelength, bandwidth, high voltage setting, background etc.

6.2.8.2 Peak the signal to background current. Consult the individual element sheets for recommended currents. Set your background current according to specifications. By adjusting the signal current, a balance is achieved when there is no variation between the two on the high voltage energy meter.

6.2.8.3 Peak the wavelength. The reading on the wavelength dial for a particular element may not agree with its actual measurement. Watch the high voltage meter as you adjust the wavelength dial for the optimum energy peak. Lock the dial upon optimization.

6.2.8.4 Optimize the lamp position. Open the hood and spin the lamp in its bracket until the peak on the high voltage meter is reached. If necessary, the bracket screws can be adjusted.

6.2.8.5 Though it shouldn't change position often, the workhead is also adjustable. Periodically, or when high voltage energy is low, with the workhead in place, check its position by adjusting the black knobs for height, tilt and depth.

6.2.9 Before attempting calibration, the calibration blank should be run to ensure that there is no contamination in the cuvette and to set the baseline. This also provides the opportunity to view deposit and adjust the jet tip if necessary.

6.2.9.1 Go to "MODE" on the keyboard. Enter "4. RESULTS" and recall S/E 1.0 (scale expansion). Enter "5. STATISTICS". Program to run samples using two burns.

6.2.9.2. Place the probe in the "A/Z" cup located on the autosampler. Manually run the calibration blank for two burns to decontaminate the cuvette and furnace cell. Repeat the process if a measurable analyte persists.

6.2.9.3 Enter A/Z on the keyboard and manually run the calibration blank to set the baseline to zero. If the baseline is much above or below the baseline on the graphics screen repeat the procedure to confirm that the baseline is properly set.

6.2.9.4 When the baseline is set, go to "MODE". Enter "4. RESULTS" and recall "CONC." (concentration).

6.2.9.5 To prepare for calibration, enter "7. AUTOSAMPLER". Enter "1. AUTOSAMPLER ON".

6.2.9.6 Enter "2. CALIBRATE WITH AUTOSAMPLER". Refer to the individual element methods regarding standard values for each element.



6.2.9.7 Enter the necessary standard values as prompted. First, enter the Autozero value followed by the Autocal value. The remaining calibration values should be entered from low standard to high.

6.2.9.8 Follow the prompts and load the standards in the positions indicated on the screen and run.

6.2.10 Prepare standards (except Calibration Blank and Auto-calibration) and samples as follows.

6.2.10.1 Pipette the appropriate amount and type of modifier into 13 x 100 mm sample tube (See individual element methods).

6.2.10.2 Pipette 2 mL of sample or standard into the tube. It may be necessary to dilute the sample due to high analyte levels, in which case be sure that the final volume is 2 mL.

6.2.10.3 For each sample run it is necessary to run an instrument spike which is prepared in the same manner as the sample with the addition of a known amount of the intermediate standard. (see individual element methods for spiking levels).

6.2.10.4 Begin each run with a detection limit check (CRA) sample and an independent QC solution sample. The analytical run order of 10 samples would be as follows: ICV, ICB, CRA, indep QC, 3 samples, CCV, CCB, 5 samples, CCV, CCB.

MONITORING THE RUN

6.3.1 During the run, the instrument condition and sample results are monitored so appropriate actions can be performed. Follow the instructions below as appropriate when encountered.

6.3.1.1 Calibration: The calibration curve, run at the start of the analytical run to relate sample absorbance to concentration, should show consistent sensitivity from day to day. Check that a mid-level standard, usually 10 or 20 ppb, has a similar absorbance reading to what is typical for that element. If the absorbance is much lower than expected, check the instrument for uptake problems, graphite condition, optical alignment, deposition, etc.

Check that the calibration curve is smooth and free from dips. Check the apparent concentration of each standard. Each standard should deviate no more than 5% from their true value, except the lowest standard, which should deviate no more than 10%. The correlation coefficient (r), should be greater than or equal to 0.995.

6.3.1.2 All analysis should fall within the calibration curve range. If any analysis result, including the analytical spike, is greater than the highest calibration standard level, dilute the sample and rerun. The only exception would be an analytical spike of a matrix spike, because one is not required to be run.



6.3.1.3 Autozeroing the instrument. If during the run the calibration blank starts to drift up or down toward the IDL, it may be necessary to reset the baseline. Run a manual auto zero by placing the probe in the calibration blank tube and enter A/Z on the keyboard, nebulize some of the solution to fill the capillary, then press run. After autozeroing manually it is necessary to nebulize air to clear the capillary of the blank solution. If the baseline drift is greater than 1.4 times the detection limit it will be necessary to rerun the last set of samples. Be sure to start the next run with a CV and CB.

6.3.1.4 Resloping the instrument. If during the run the calibration verification result starts to drop off or drift upward toward the 10% limit, start the next run with an A/Z and A/C and be sure to begin the run with a CV and CB. If the CV has gone out of control it will be necessary to rerun the last set of 5 samples.

Resloping involves running a specified mid-range standard and adjusting the calibration curve slope to the new instrument response result for that standard. Check that the reslope result is between 80% to 120% of the calibration curve value.

6.3.1.5 Fill out the logbooks as the run progresses. Check the ICV and CCV recovery, independent QC solution recovery, duplicate RPD, matrix spike %R, and reference recovery 'real time'. Indicate on the summary logbooks that the above were checked and/or write the results in the comments section.

6.3.1.6 QC CHECKS

ICV & CCVs

A calibration verification standard is run at the start of the run immediately after calibration, every 5 samples (20 burns), and at the end of the analytical run to verify calibration stability. The same solution is used for both the initial calibration verification (ICV) and the continuing calibration verification (CCV). QC acceptance limits for the CV are 90% to 110% of the true value. If a CV result is outside of the limits, perform an autozero and autocal (reslope), and rerun all samples since the last acceptable CV.

ICB & CCBs

A calibration blank is run after every analysis of a calibration verification standard to check for baseline drift and sample carry-over. An initial calibration blank (ICB) is run immediately after the ICV and a continuing calibration blank (CCB) is run immediately after each CCV. The acceptance limits for the CB are negative 1 IDL to positive 1 IDL with rounding (i.e. if IDL is 1.0 ug/L, then limits would be -1.4 to +1.4 ug/L). If a CB is outside the limits, run an autozero (A/Z) and rerun samples since the last acceptable CB.⁵

CRA

The CRA (Contract Required Detection Limit standard for GFAA) prepared at 2 times the IDL, is a QC check sample run after the ICV and ICB. Although there are no acceptance limits for the CRA, it should run within 1 IDL of its true value. It should be run with an analytical spike as an analytical spike check.



INDEPENDENT QC SOLUTION (currently APG7878)

The APG solution is run as an independent QC sample, a source separate from the calibration standards and the CV, usually immediately after the CRA. Since no preparation steps are required to run this solution, other than routine dilution for some elements, this solution is used as a double check of the calibration standards preparation.

IVPC

The IVPC (Inorganic Ventures Performance Check) solution is a 1/100 dilution of the IVCV INT (Inorganic Ventures Calibration Verification Intermediate). It can be used to verify CV preparation or for a non-calibration curve MSA QC check.

6.3.1.7 PRECISION CRITERIA

All GFA analyses are double burn/injections, except for MSA and IDL determinations. The precision criteria between the 2 burns is based on the concentration result. If the mean concentration is less than or equal to 4 times the IDL, then the standard deviation should be less than or equal to 0.7 ppb. If the concentration is greater than 4 times the IDL, then the RSD should be less than or equal to 20%. If either limit is exceeded, then the sample should be rerun once. If the sample precision is still bad, a dilution might possibly be run to dilute a matrix problem if one exists, or the number with the better RPD is reported.

6.3.1.8 ANALYTICAL SPIKE

Each GFA sample is run with an analytical spike (sometimes referred to as an instrument spike) to determine if sample matrix effects are occurring during analysis. The acceptance limits for the analytical spike recovery are based on the concentration result. If the concentration result is greater than or equal to 2.5 times the IDL, then the recovery acceptance limits are 85% to 115%. If the concentration is less than 2.5 times the IDL, then the analytical spike recovery should be greater than or equal to 40%. If either limit is not met, then an appropriate dilution should be prepared and run, or, if the analytical spike recovery is close to meeting the acceptance limits, the sample may be rerun once at the same dilution. If the sample result rounds to greater than 2.5 times the IDL and the analytical spike recovery is not acceptable, a dilution of the sample (or a further dilution) should be run, unless the resulting concentration would be less than 5 times the IDL. The dilution factors we analyze samples at are 1/2, 1/5, 1/10, 1/20, 1/40, 1/50, 1/100. Perform a MSA on the sample using three additions of analyte at the current sample dilution after the above actions fail to produce an acceptable result.

When comparing dilutions keep in mind that the accuracy of the concentration result may be affected by matrix effects/low spike recovery. If a sample is run initially at a dilution in anticipation of matrix interference, the lowest possible dilution with acceptable instrument spike recovery should be attempted.



DILUTION GUIDELINES FOR INSTRUMENT SPIKE RECOVERY

CONCENTRATION	% RECOVERY	DILUTION
any	0 - 39 %	1/5 or greater
greater than 2.5 IDL	40-69, >130	1/5
greater than 2.5 IDL	70-80, 120-130	1/2
greater than 2.5 IDL	borderline acceptable	rerun at same dilution

6.3.1.9 DIGESTION/BATCH QC SAMPLES

METHOD BLANK

A method blank (MB) is run with every client group of samples or every sample digestion group (SDG). The method blank concentration should be less than 1 IDL. All method blanks should have analytical spike recovery from 85% to 115%. The following rerun guidelines apply. If the analyte is detected in the method blank, then it should be rerun. If the method blank is still detectable, check the digestion log for other method blanks from the same digestion group and run one (or more if necessary). If this method blank is still detectable, then all the samples in the client job must be redigested with a new method blank unless all samples are greater than 10X the detected method blank concentration. A corrective action form should be filled out by the analyst and the supervisor should be informed.

MATRIX/DIGESTION DUPLICATE

A duplicate sample is digested to test the reproducibility of the method. The acceptance limits are based on the concentration result. If both original and duplicate sample concentrations are greater than or equal to 5 times the IDL, then the relative percent difference (RPD) should be less than 20%. If either the original or duplicate sample concentration is less than 5 times the IDL, then the absolute difference between the two concentration results should be 1 IDL or less. For soil or tissue samples, the sample concentrations must be calculated in mg/kg units. If a duplicate RPD is outside the acceptance limits, then a corrective action form should be filled out by the analyst and the supervisor should be informed.

MATRIX/DIGESTION SPIKE

A matrix spike sample is spiked before digestion to detect analyte losses during digestion and matrix effects on digestion efficiency. Usually the matrix duplicate and the matrix spike are performed on the same sample. The acceptance limits for spike recovery are 75% to 125%, if the original sample concentration is less than 4 times the spike added. If the original sample concentration is greater than 4 times the spike added, there is no acceptance criteria. For soil or tissue samples, the sample concentrations must be calculated in mg/kg units, including the spike added. Antimony recoveries on soil or sludge samples typically range between 15% and 65%. Except for Antimony, if the matrix spike recovery is outside the acceptance limits then a corrective action form should be filled out by the analyst, and the supervisor should be informed.



REFERENCE SAMPLES

A reference sample is a sample of known and/or certified analyte concentration, which is digested with a group of samples to verify digestion recovery in the appropriate matrix. Water, soil, and tissue references are used. The water reference recovery acceptance limits are 80% to 120%. For a soil reference the certified ranges are used as recovery limits. For soil or tissue samples, the reference concentration must be calculated in mg/kg units. If the recovery is outside the acceptance limits, then a corrective action form should be filled out by the analyst, and the supervisor should be informed.

6.3.1.10 GRAPHICS

Graphics should be reviewed for analyte peak appearance time shifts. This is especially important for peak area integration methods as the entire peak must be in the integration window for the result to be valid. The background + signal trace can be useful for predicting the appropriate dilution necessary for matrix interferences, but a low background + signal trace may also appear with low spike recovery. Peak shapes should also be watched for any anomalies.

6.3.1.11 CARRY-OVER

Very high samples can affect the samples run after them. This effect, called carry-over, is usually apparent as a high burn followed by successively lower burns. Samples suspected of carry-over effects should be rerun. Pipetting carry-over can also occur after very high samples, so samples suspected of this should be reprepared and rerun.

6.3.1.12 MSA

The method of standard additions (MSA) is a method of adjusting sample concentration result for spike recovery at three spike levels. Sample concentration is extrapolated by linear regression from the absorbance result of the unspiked sample and the sample spiked at three levels. Ideally the spiking levels are 50%, 100% and 150% of the sample concentration.

For the elements with an IDL of 1 ug/L, and additions of 5, 10, 15 ug/L, the MSA calculated concentration should be less than 20 ug/L, or the sample should be diluted and run by MSA again. For the elements with an IDL of 0.2 ug/L, and additions of 0.5, 1.0, 1.5 ug/L, the MSA calculated concentration should be less than 2.0 ug/L, or the sample should be diluted and run by MSA again.

Linear regression of the MSA can be calculated using HP calculators or EXCEL software. r (correlation coefficient) should be greater than or equal to 0.995, or the sample should be rerun once. If both r values are less than 0.995, then the analysis with the better r value is used. A single burn is used for MSA.

6.3.1.13 ROUNDING RULES

The routine rounding rule is to round up if the digit following those to be retained is 5 (i.e. 40.55 would round up to 40.6).



6.4 SHUT DOWN PROCEDURES

6.4.1 When the instrument is done analyzing samples turn off all equipment in the following order: a.)printer, b.)auto sampler, c.)AA operate knob to "Restart/Stand-by," d.)AA power (Red button), e.)CTF 188 (FURNACE), f.)cooling water.

7.0 Review

Refer to procedures section for review during the run instructions.

8.0 Quality Control

Refer to procedures section for QC acceptance criteria.

9.0 Corrective Actions

9.1 Calibration

If the calibration does not meet the criteria in section 6.3.1.1, then corrective action should be taken before proceeding with re-calibration, unless the graphite cuvette is new and may have needed some conditioning. If the cuvette is new, then recalibration can be attempted without taking corrective action first.

9.2 QC checks

If a QC check is out of control, then corrective action should be taken before proceeding with analysis. This could involve re-preparing the solution, rerunning the solution, checking instrument conditions, etc.

9.3 Instrument malfunctions

Consult other experienced Varian 300Z operators or the supervisor for guidance. The maintenance logbook and the service manual could be helpful for troubleshooting.

10.0 Miscellaneous Notes and Precautions

10.1 The analyst should be aware of the sensitivity differences of the various GFAAS elements as they typically run on the instrument. If calibration absorbances start at the lower end of acceptability, then the percentage of reslope absorbance acceptability should be adjusted. Also a lower reslope value also affects the precision criteria on low level samples.

10.2 GFAAS low detection limits require that contamination potential be minimized. The samples preparation area should be kept clean and the autosampler should be wiped down regularly. Standards should be segregated at all times from samples, blank, and modifier. Re-use of pipet tips and beakers should be clearly identified and segregated.



11.0 Method References

USEPA SW-846 Method 7000A 7/92.
USEPA SW-846 Method 7041 9/86.
USEPA SW-846 Method 7060A 11/92.
USEPA SW-846 Method 7131A 11/92.
USEPA SW-846 Method 7421 9/86.
USEPA SW-846 Method 7740 9/86.
USEPA SW-846 Method 7761 9/86.
USEPA SW-846 Method 7841 9/86.

12.0 Appendices

12.1 Standard and Modifier Preparation

12.2 Instrument Parameters - All Methods

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Appendix

12.1 Standard and Modifier Preparation



STANDARDS PREPARATION

Weekly:

Seven Element Intermediate Standard: To a 100 mL volumetric flask containing approximately 80 mL de-ionized water, add 2 mL Fisher Trace Metal Grade HNO_3 , 1.0 mL GFA calibration stock and 0.200 mL 1000 mg/L Sb stock. Dilute to volume with de-ionized water.

Calibration Standards: All calibration standards are made up in 100 ml volumetric flasks with 0.5% HNO_3 (add 0.5 ml Fisher Trace Metal Grade HNO_3 to the volumetric flask containing about 80 ml de-ionized water then dilute to volume with de-ionized water after intermediate standard has been added). Numbers in parentheses refer to Ag and Cd concentrations.

75 (7.5) mg/L: Add 3.75 mL intermediate std. Used for Pb (Varian and TJA).

50 (5.0) mg/L: Add 2.50 mL intermediate std. Used for all elements and instruments. For TJA Pb analysis, this is used for the Autocal solution and the flask should have 1.0 mL modifier added to it after dilution.

20 (2.0) mg/L: Add 1.00 mL intermediate std. Used for all TJA elements. For TJA Ti and Sb this standard level is used for the Autocal solution and should have the appropriate level of modifier add after dilution.

10 (1.0) mg/L: Add 0.50 mL intermediate std. Used for all TJA elements.

3.0 (0.3) mg/L: Add 0.150 mL intermediate std. Used for TJA Pb.

CRA: These solutions are made in the same manner and the calibration standards.

2.0 mg/L: Add 0.100 ml intermediate std. Used for As, Pb, Sb, Se and Ti.

0.4 mg/L: Add 0.200 ml intermediate std. Used for Cd and Ag.

IDL Standards: These standards are made in the same manner as the calibration standards.

For As, Pb, Sb, Se and Ti use the 3 mg/L standard.

For Cd and Ag use a 0.6 mg/L standard made by using 0.300 ml intermediate std.

Daily

Calibration Verification Standards (CV): These standards are made in the same manner as the calibration standards, in 0.5% HNO_3 and using the Calibration Verification intermediate solution.

Ag: Add 1.00 ml CV intermediate std. 3 mg/L

Cd: Add 1.25 ml CV intermediate std. 2.5 mg/L

Pb: Add 1.60 ml CV intermediate std. 40 mg/L

As, Se, Sb and Ti: Add 0.5 ml intermediate std. 25 mg/L



MODIFIER PREPARATION

Pd/Mg modifier: For Tl and Pb. For a final concentration of 500 mg/L Pd and 1000 mg/L Mg: Mix equal amounts Environmental Express 1% Pd concentrate and 20,000 mg/L Mg solution, dilute to volume.

20,000 mg/L Mg solution: To a 200 mL volumetric flask with about 100 mL de-ionized water in it, add 42 g Ultra Pure ALFA $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Dilute to volume with de-ionized water.

KMnO_4 modifier: For Sb. Add 0.5g KMnO_4 to a volumetric flask containing 50 ml de-ionized water, dilute to volume.

Cd-free 0.64% $(\text{NH}_4)_2\text{HPO}_4$: For Cd. In a 100 ml volumetric flask, dilute 4 ml stock Cadmium free $(\text{NH}_4)_2\text{HPO}_4$ to volume with de-ionized water.

Stock Cd-free $(\text{NH}_4)_2\text{HPO}_4$: Dissolve 32 g $(\text{NH}_4)_2\text{HPO}_4$ in de-ionized water, bring to volume in a 200 ml volumetric flask. Add 10 drops saturated APDC solution and extract three times with 20 ml MIBK (methyl isobutyl ketone).

Saturated APDC solution: Dissolve about 2 g Ammonium Pyridine Dithionate in approximately 30 ml deionized water to make a saturated solution. Refrigerate.



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Appendix

12.2 Instrument Parameters - All Methods



ANTIMONY METHOD

INSTRUMENT PARAMETERS

Background Method	Smith Hieftje
Hollow Cathode Lamp Current	Match background signal
~3.0mA	
Background Lamp Current	2.0 mA
Slit Width	0.3nm
Wavelength	217.6 nm
High Voltage	~ 800 V
Cuvette Type	Uncoated

FURNACE PARAMETERS

Step	Dry	Pyrolysis 1	Pyrolysis 2	Atomize	Clean
Temp --C	150	550	700	2000	2500
Ramp (Sec)	2	10	5	0	
Hold (Sec)	0	0	10	3	2
Purge	1	2	2	0	3

INTEGRATE

Peak Height	2.5 Sec Integration Delay
0.5 Sec	
FASTAC Delay	10.0 Sec
	Deposit 12.0 Sec

STANDARDS

Standard Z	0.0
Standard C	20.0
Standard 1	10.0
Standard 2	50.0
Concentration Units	mg/L
Reslope Standard	C



SAMPLE PARAMETERS

Volumes

Sample Preparation 2 mL sample + 0.020 ml 0.5% KMnO_4
Analytical Spike 2 ml sample + 0.020 ml 0.5% KMnO_4 +
 0.020 ml GFA Intermediate Solution

QC PROTOCOLS

QC Standard Concentration	25	mg/L
Required Detection Limits	1.0	mg/L
Analytical Spike Concentration	20	mg/L



CADMIUM METHOD

INSTRUMENT PARAMETERS

Background Method	Smith Hieftje
Hollow Cathode Lamp Current	Match background signal
~3.0mA	
Background Lamp Current	0.7 mA
Slit Width	1.0nm
Wavelength	228.8 nm
High Voltage	~ 530 V
Cuvette Type	Uncoated

FURNACE PARAMETERS

Step	Dry	Pyrolysis 1	Pyrolysis 2	Atomize	Clean
Temp °C	150	400	600	2000	2500
Ramp (Sec)	2	10	10	0	
Hold (Sec)	0	5	5	2	2
Purge	1	2	2	0	3

INTEGRATE

Peak Area	2.0 Sec Integration
Delay	0.3 Sec
FASTAC Delay	10.0 Sec
	Deposit 5.0 Sec

STANDARDS

Standard Z	0.0
Standard C	2.00
Standard 1	1.00
Standard 2	5.00
Concentration Units	mg/L
Reslope Standard	C



SAMPLE PARAMETERS

Volumes

Sample Preparation 2 ml sample + 0.025 ml 0.64% Cd-free $(\text{NH}_4)_2\text{HPO}_4$

Analytical Spike 2 ml sample + 0.025 ml 0.64% Cd-free
 $(\text{NH}_4)_2\text{HPO}_4$ + 0.020 ml GFA Intermediate Solution

QC PROTOCOLS

QC Standard Concentration 2.5mg/L

Required Detection Limits 0.2 mg/L

Analytical Spike Concentration 1.0 mg/L



LEAD METHOD

INSTRUMENT PARAMETERS

Background Method	Smith Hieftje
Hollow Cathode Lamp Current	Match background signal
~2.5mA	
Background Lamp Current	1.5 mA
Slit Width	0.5nm
Wavelength	283.3 nm
High Voltage	~ 700 V
Cuvette Type	Uncoated

FURNACE PARAMETERS

Step	Dry	Pyrolysis 1	Pyrolysis 2	Atomize	Clean
Temp °C	150	600	200	2000	2500
Ramp (Sec)	2	15	10	1	
Hold (Sec)	0	5	5	3	3
Purge	1	2	2	0	3

INTEGRATE

Peak Area	2.4 Sec Integration
Delay	1.6 Sec
FASTAC Delay	12.0 Sec
	Deposit 7.0 Sec

STANDARDS

Standard Z	0.0
Standard C	50.0
Standard 1	3.00
Standard 2	10.0
Standard 3	20.0
Standard 4	75.0
Concentration Units	mg/L
Reslope Standard	C



SAMPLE PARAMETERS

Volumes

Sample Preparation 2 ml sample + 0.020 ml Pd/Mg solution
Analytical Spike 2 ml sample + 0.020 ml Pd/Mg solution +
 0.020 ml GFA Intermediate Solution

QC PROTOCOLS

QC Standard Concentration	40.0mg/L
Required Detection Limits	1.0 mg/L
Analytical Spike Concentration	20.0 mg/L



THALLIUM METHOD

INSTRUMENT PARAMETERS

Background Method	Smith Hieftje
Hollow Cathode Lamp Current	Match background signal
~4.0mA	
Background Lamp Current	2.0 mA
Slit Width	1.0nm
Wavelength	276.6 nm
High Voltage	~ 620 V
Cuvette Type	Uncoated

FURNACE PARAMETERS

Step	Dry	Pyrolysis 1	Pyrolysis 2	Atomize	Clean
Temp °C	150	250	400	2000	2500
Ramp (Sec)	2	10	10	0	
Hold (Sec)	0	5	5	2	2
Purge	1	2	2	0	3

INTEGRATE

Peak Height	1.8 Sec Integration
Delay	0.5 Sec
FASTAC Delay	12.0 Sec
	Deposit 12.0 Sec

STANDARDS

Standard Z	0.0
Standard C	20.0
Standard 1	10.0
Standard 2	50.0
Concentration Units	mg/L
Reslope Standard	C



SAMPLE PARAMETERS

Volumes

Sample Preparation 2 ml sample + 0.020 ml Pd/Mg solution
Analytical Spike 2 ml sample + 0.020 ml Pd/Mg solution +
 0.020 ml GFA Intermediate Solution

QC PROTOCOLS

QC Standard Concentration	25.0mg/L
Required Detection Limits	1.0 mg/L
Analytical Spike Concentration	20.0 mg/L



Standard Operating Procedure

Graphite Furnace Analysis - Thermo Jarrell Ash
Method Series 7000 - (United States Air Force)

503S

Revision 1

3/30/94

Prepared By:

James P. Fick

Approvals:

Jay L. Loh
Section Manager

Don M. DeBru
Laboratory Manager

Michelle J. Turner
Quality Assurance Manager

Mark W. Ward
Laboratory Director



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Standard Operating Procedure

Graphite Furnace Analysis - Varian 300Z
Method Series 7000 - (United States Air Force)

502S

Revision 1

3/30/94

PROPRIETARY

Prepared By:

James P. Sick

Approvals:

Ray Kuhn
Section Manager

Don W. Baker
Laboratory Manager

Michelle J. Turner
Quality Assurance Manager

Mark V. ...
Laboratory Director

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Standard Procedure

Varian 300Z
Graphite Furnace Analysis

502S

Revision 1

3/30/94

Prepared By:

JFF James L. Fick

Approvals:

Jay Kuhn ngt
Section Manager

Don N. Allen
Laboratory Manager

Michelle J. Turner 11/1/94
Quality Assurance Manager

Mark W. [Signature]
Laboratory Director



STANDARD PROCEDURE 300Z GRAPHITE FURNACE ANALYSIS

1.0 Scope and Application

This document describes methods for analyzing samples on the Varian 300 graphite furnace. While drinking waters may be analyzed directly, other types of samples require some sort of digestion preparatory step. Samples are run first on an analytical curve using an instrument spike. Those samples failing to show sufficient analytical spike recovery are either diluted and rerun and/or run by the method of standard additions.

2.0 Definitions

GFAAS - Graphite Furnace Atomic Absorption Spectrometry

ICV and CCV - Initial and Continuing Calibration Verification - An independent standard at a concentration other than that used for instrument calibration run to verify the accuracy of the calibration.

ICB and CCB - Initial and Continuing Calibration Blank - A calibration blank run immediately after the ICV and CCV to verify the baseline of the calibration.

CRA - A standard made at twice the IDL run to check the accuracy of results that are close to the detection limit.

IDL - Instrument Detection Limit - As defined in the EPA-CLP SOW; three times the standard deviation of seven replicate measurements averaged over three non-consecutive days.

MDL - Method Detection Limit - As defined in 40 CFR; three times the standard deviation of seven replicate measurements of a low level standard or sample that has gone through a preparation step.

MSA - Method of Standard Additions - To correct for the fact that a sample may have a different response slope than the calibration standards, three additions of known amount of analyte are added to the sample, and the results of those analyses plus the unspiked sample are extrapolated using a linear least squares fit to determine the sample's concentration.

SD - Standard Deviation

RSD - Relative Standard Deviation - The SD divided by the mean, multiplied by 100.

RPD - Relative Percent Difference - The absolute difference between two numbers, divided by the average of the two numbers, multiplied by 100.



%R - Percent Spike recovery - The difference between the matrix spike concentration and the original sample concentration divided by the concentration of the spike added multiplied by 100.

3.0 Equipment

3.1 Instrument

One Varian 300Z graphite furnace equipped with a direct deposit autosampler, MS-DOS based computer data system, superlamp power supply system, and featuring the Zeeman background correction technique.

3.2 Gas supply

Argon supply from Dewar flask, 99.997% pure (High purity grade). A large number of Ar tank backups of the same purity are kept. Also, as required per element, a 95% Ar/5% H₂ mix gas from a compressed gas tank.

3.3 Consumables

A large supply of graphite tubes, platforms, and other furnace parts to minimize the possibility of downtime due to lack of inventory.

Lab consumables include sample cups, 13 X 100 mm sample tubes, lens paper, cotton swabs, kim-wipes, plastic syringes and syringe filters.

3.4 Reagents

Matrix modifiers - These are prepared and stored according to the section below.

Nitric Acid - (HNO₃) 70%. Trace Grade that has Lot QC documentation to verify that it is contamination free.

De-ionized water - Water that is ion free.

Stock Standards and independent check standards - Stock standards and independent check standards from many different sources are used. A file of their certified concentrations and other documentation is kept.

3.5 Labware

Assorted volumetric flasks, both glass and plastic, glass class A volumetric pipettes, air-displacement pipettes with disposable tips covering a wide volume range, and plastic beakers of various sizes are available for use.

4.0 Documentation

4.1 During instrument setup, the VARIAN instrument setup log is completed. During the instrument set-up, the clipboard for recording the PMT voltages is filled out. The GFAA summary logbook is filled out during the run. Any event or observation or action that is worth noting should be recorded in the appropriate instrument maintenance hardbound logbook, and on the instrument set-up logbook page. When the analytical day is



complete, a data package for review consists of all raw data, and copies of all related logbook pages. All logbook pages should have unused portions 'z'-ed out by the analyst, initialed, and dated. A diskette containing the file ZDATA.TXT should be included for use in the data loading process.

5.0 In-house Modifications to Referenced Method

5.1 Method 7000A 7/92 - 7.3.5 Calls for serial dilution analysis of one sample per batch to check for matrix interferences. Instead we analytically spike (equivalent to single addition MSA) every sample to test for matrix interferences.

5.2 Method 7000A 7/92 - 8.3 Calls for continuing calibration verification sample result to be within an acceptance limit of 20%. Instead we use an acceptance limit of 10% for the continuing calibration verification sample result.

5.3 Method 7000A 7/92 - 8.4 Calls for a MSD and a LCS with every sample batch. Instead of a MSD we do a duplicate. Per client request we will do a MSD instead of a duplicate. We do not do a LCS with every batch. Per client request we will do a LCS with every batch.

5.4 Method 7041 9/86 (Sb) - Does not specify a matrix modifier is needed. We use a Pd/Mg/Citric Acid solution as a matrix modifier.

5.5 Method 7060A 11/92 (As) - 7.1.3 Calls for NiNO_3 to be added to the sample as a matrix modifier. Instead we use a Pd/Mg/Citric Acid solution as a matrix modifier. 7.5 Calls for certain types of samples to be analyzed for by using the MSA. Instead we analyze every sample by using the single addition MSA.

5.6 Method 7421 9/86 (Pb) - 3.3 Calls for H_3PO_4 to be added to the sample as a matrix modifier *if needed*. Instead we use a Pd/Mg/Citric Acid solution as a matrix modifier.

5.7 Method 7740 9/86 (Se) - 7.1.3 Calls for NiNO_3 to be added to the sample as a matrix modifier. Instead we use a Pd/Mg/Citric Acid solution as a matrix modifier. 8.2 Calls for recalibrating every hour. Instead we calibrate daily and also if continuing calibration sample results indicate recalibration is needed.

5.8 Method 7761 9/86 (Ag) - Does not specify a matrix modifier be added to the samples. We use a 1% $\text{NH}_4\text{H}_2\text{PO}_4$ solution as a matrix modifier. 7.2 & 7.3 Calls for a separate sample preparation digestion procedure for Ag furnace analysis. Instead we use Method 3020 (ARI precode TWN) for Ag analysis or we analyze the preserved sample without digestion if it meets the criteria for not requiring digestion. 7.9 Calls for certain types of samples to be analyzed for by using the MSA. Instead we analyze every sample by using the single addition MSA.

5.9 Method 7841 9/86 (Ti) - 5.3 Calls for PdCl_2 to be added to the sample as a matrix modifier. Instead we use a Pd/Mg/Citric Acid solution as a matrix modifier.

6.0 Procedure



6.1 Method Description

A representative aliquot of sample is deposited on a platform in a graphite tube and evaporated to dryness. Once dried the sample is pretreated in an ashing step which is designed to minimize the interference effects caused by the sample matrix. The ash step is followed by atomization. Atomization is characterized by rapid heating of the furnace to a temperature at which the analyte is atomized from the pyrolytic graphite surface. The resulting atomic cloud absorbs the element specific atomic emission produced by a hollow cathode lamp (HCL) or a boosted intensity Super Lamp. Because the resulting absorbance usually has a nonspecific component associated with the actual analyte absorbance, an instrumental background correction device is necessary to subtract from the total signal the component which is nonspecific to the analyte. The Varian SpectrAA 300Z utilizes Zeeman background correction. A monochromator isolates the analytic line emission from the hollow cathode lamp and a photomultiplier tube measures the absorbance by the sample.

6.2 Procedure

FURNACE SET-UP

6.2.1 Turn on the cooling water, and the alternate gas cylinder, if required.

6.2.2 Make sure the Super Lamp power supply is turned off and the boost current knob is turned fully counterclockwise. Turn unit on in the following order: a.) spectrometer, b.) GTA, c.) power strip, which turns on the printer, screen, and computer. The Super Lamp power supply is also plugged into a timer on this power strip; bypass the timer using the switch on the timer.

6.2.3 Place the appropriate hollow cathode lamp in the lamp turret. Use position 1 for Super Lamps (As, Sb, Tl and Se), and position 2 for normal Hollow Cathode Lamps.

6.2.4 Place a floppy disc labeled with the day of the week corresponding to the day of the ~~last~~ analytical run in the appropriate disk drive of the computer. At the DOS prompt type COPY ZDATA.TXT A: to copy the data from the last analytical run to disc. When the data has been copied, remove the disc from the drive and at the DOS prompt, type DEL ZDATA.TXT.

6.2.5 At the DOS prompt, enter SGLRUNZ. When the Varian software is loaded press F10 to access the index. Go to page 10 (Sequence Selection) and press F1 to clear the sequence. Enter the required program number to turn on the lamp to start it warming up. The program numbers are in appendix 12.1. The instrument and element specific conditions are found in the Methods part of this document. Press F10 to access the index and select page 6 (Optimization). Allow the lamp the warm up for 10 to 15 minutes.

6.2.6 While the lamp is warming up, clean the furnace:

6.2.6.1 Remove the autosampler and place it on the autosampler rack. Tip the furnace forward and remove the window caps. Open the furnace by turning the toggle lever on top of the furnace clockwise and remove the cuvette. Remove the stainless steel



chimney insert from the top of the furnace. Open the left side of furnace by lifting the catch on the top left side of the unit.

6.2.6.2 Use cotton swabs dipped in deionized water to clean the inside and top of the furnace, including all graphite surfaces, the inside of the electrode assemblies, and the chimney. Leave open to dry.

6.2.6.3 Inspect each lens for smudges and fibers. If necessary, remove the quartz lenses from the window caps. Use a cotton swab dipped in deionized water to clean both surfaces of each lens. Use lens paper to dry and buff the surfaces. Replace the lenses in the lens caps.

6.2.6.4 Replace the chimney and close the electrode assemblies. Replace the lens caps in furnace, making sure to align the grooves in the washer of the right lens cap horizontally for visual reference later when determining the horizontal alignment of the platform with the mirror.

6.2.7 Optimization: The lamp should be warmed up for at least 15 minutes before optimization. If using a Super Lamp, turn the Super Lamp power supply on at this time and after about 5 seconds turn up to the usual operating boost current for that lamp. Allow the Super Lamp another 15 minutes warm up time with the boost current on.

6.2.7.1 On the lamp turret, with the lamp in position, turn the horizontal adjustment screw (top knob) fully clockwise. Turn the horizontal adjustment screw counterclockwise slowly until the signal bar on the computer screen peaks. If the adjustment screw is turned counterclockwise past the first peak a second peak will appear—do not align on the second peak. As the signal bar reaches maximum press F1 to rescale the signal bar. It may be necessary to press F1 several times during the optimization process.

6.2.7.2 Peak the signal bar with the vertical adjustment screw (bottom knob).

6.2.7.3 After optimizing, press F1 and record the final PMT voltage on the clipboard in the 'PMT voltage without furnace' column.

6.2.7.4 Replace the furnace and insert a cuvette. For long runs, use a new cuvette. Also, selenium and thallium runs usually require a new cuvette. For shorter runs a used cuvette may be used. If using a plateau tube with a platform make sure that the platform is horizontal (check with the mirror). Use the knob at the bottom of the furnace to adjust the height of the furnace until the signal bar peaks. If the signal bar peak is passed, back the knob off and return to the signal bar peak from the same direction as before. Press F1 and record the final PMT reading in the 'PMT voltage with furnace' column. The two PMT readings should be within 30 mV of each other. If the difference between the two PMT voltage readings is greater than 30 mV, check the quartz lenses for smudges, recheck the alignment of the cuvette, and the furnace height.

6.2.8 Replace the autosampler, making sure the white adjustment knob is properly seated on the right side of the furnace compartment. Fill the rinse bottle on the bottom of the unit with acidified deionized water. On the computer, go to page 8 (Sampler).



6.2.9 If a silver run is planned, the dedicated silver capillary should be installed. Remove the capillary in use by loosening the capillary sleeve from its holder, remove the sleeve, and unscrew the other end of the capillary from the syringe. Pull out the capillary from the syringe fitting end. To install the silver capillary, thread the tubing end through the black sleeve inside the autosampler (behind the syringe holder). Attach the capillary sleeve to the deposition end and replace it in the holder.

6.2.10 Remove the bubbles from the syringe by pressing F3 (wait until the rinsing action starts), remove the plunger from the syringe. Hold a folded paper towel to catch the rinse water. Press F3 several times until all bubbles are purged from the syringe. Replace the plunger and draw it back and forth a couple of times to draw any bubbles remaining in the capillary. Replace the plunger while rinse water is still flowing from the syringe to keep new bubbles from entering the syringe. If the plunger fit feels loose, gently press the end on a clean, flat surface to flare the Teflon before replacing the plunger. Carefully replace the syringe into the syringe compartment. Press F3 a couple more times to clear any bubbles in the sample delivery capillary. At this time check the rinse flow by lifting the capillary arm and observing the rinse flow. If it seems slow, tighten the rinse bottle.

6.2.11 To align the probe, press F2 once to place the probe in an empty sample cup. The capillary should be about 5 mm from the bottom of the cup. Press F2 again to move the probe to the cuvette. Stop the capillary from lowering into the cuvette with your hand. Gently lower it to be sure it goes into the hole on the cuvette. Center it using the adjustment knobs on the side and front of the sampler. Adjust the depth of the probe using the height adjusting screw on the sampler arm. Go through the sampler alignment process again to make sure the capillary alignment is correct.

6.2.12 Go to page 11 (Sequence Control) and set the analytical run sequence. Enter two tube cleans, the starting and ending sample numbers and start the run with a calibration.

6.2.13 Go to Error Protocol (F6). If the graphite furnace is to be left unattended operating overnight, verify that Exit to DOS is set at YES.

6.2.14 Go to QC Protocols (F5). Verify that QC Protocol is set to ON and that all options and limits are correct (see below). The error protocol should be set at RESLOPE AND REPEAT. For all analyses the QC Spike limits should be set at 85 - 115%, the Recovery Minimum Limit should be set at 40%, the Replicate RSD Limit should be set at 100% and Correlation Coefficient at 0.995.



6.2.15 From the index, go to page 13 (Report Format). Enter your initials, date and batch name (format for batch name is: element symbol/yr/mo/day). Other settings should be as follows:

Format	Sequential
Data Printed	EachReading
Print	DuringRun
Instrument Status	Yes
Notes	Yes
Calibration Results	Yes
Calibration Graph	Yes
Sample Labels	Yes
Lines per Report Page	66
Printer Type	LX800

6.2.16 Go to Sample Labels (F6) and enter the sample labels. Begin each run with a detection limit check (CRA) sample and an independent QC solution sample. The analytical run order of 10 samples would be as follows: ICV, ICB, CRA, indep QC, 3 samples, CCV, CCB, 5 samples, CCV,CCB. Print the table using the "Print Screen" key. At this time fill out the instrument setup logbook, and start filling out the summary logbook.

6.2.17 Aliquot the samples into 2 ml polystyrene autosampler cups that are labelled with the sample ID. Take care to avoid particulates. If cadmium is requested, use the cadmium-free autosampler cups. If a dilution is required, use a 13 X 100 mm test tube to prepare a 2 ml volume dilution (eg. for a 1/5 dilution use 1.6 ml of 0.5% nitric acid and 0.4 ml of sample for a total volume of 2 ml). Vortex the diluted sample before pouring an aliquot into an autosampler cup.

6.2.18 Make new standards as appropriate according to the instructions in the standards preparation section. Fill the autosampler with samples, standards and modifier in the correct positions with the QC spike standard solution in position 44 and the Calibration Verification solution in position 45.

6.2.19 Go to page 18 (Signal Graphics). Do an instrument zero (Alt/F10) and press F11 twice to start the automatic run.

6.2.20 If over-night operation is required using a Super Lamp, set the timer on the power strip to the required length of time.

6.3 MONITORING THE RUN

6.3.1 During the run, the instrument condition and sample results are monitored so appropriate actions can be performed as needed. Follow the instructions below as appropriate when encountered.

6.3.1.1 Calibration: The calibration curve, run at the start of the analytical run to relate sample absorbance to concentration, should show consistent sensitivity from day to day. Check that a mid-level standard, usually 10 or 20 ppb, has a similar absorbance reading to what is typical for that element. If the absorbance is much lower than



expected, check the instrument for correct capillary alignment, platform alignment, graphite condition and contact, correct standards, etc. Check that the calibration curve is smooth and free from dips. Calculate % deviation from linearity for each standard relative to the other standards. Each standard should deviate no more than 5% from their true value, except the lowest standard which should deviate no more than 10%. The correlation coefficient (r), should be greater than or equal to 0.995.

6.3.1.2 All analysis should fall within the calibration curve range. If any analysis result, including the analytical spike, is greater than the highest calibration standard level, dilute the sample and rerun. The only possible exception would be an analytical spike of a matrix spike, because one is not required to be run on matrix spikes.

6.3.1.3 Autozeroing the instrument. If during the run the calibration blank starts to drift up or down toward the IDL, pressing F12(stop) followed by F11(start) will pause the run and restart with an autozero to reset the baseline. It is best to do this immediately after the CB is run or else the samples run since the last CB will have to be rerun. If the baseline drift is greater than 1.4 times the detection limit it will be necessary to rerun the last set of samples. In this case after pausing the run (F12), go to the index (F10) and select page 11 (Sequence Control). At the bottom of the page change the starting sample number to the one after the last valid CB. Then press F11 to start the run. After the autozero the run will automatically begin with a CV and CB.

6.3.1.4 Resloping the instrument. If during the run the calibration verification result starts to drop off or drift upward toward the 10% limit, reslope the calibration curve. Pause the run (F12). From the index (F10) select page 11 (Sequence Control). At the bottom of the page, cursor over to the last column (First Measurement) and toggle it to RESLOPE with the Home key. Then return to the Signal Graphics page and press F11 to restart the run. The instrument will perform an autozero and reslope then restart the run with a CV and CB. If the CV has gone out of control the instrument will automatically perform a reslope and rerun the last set of 5 samples.

Resloping involves running a specified mid-range standard and adjusting the calibration curve slope to the new instrument response result for that standard. Check that the reslope result is between 80% to 120% of the calibration curve value.

6.3.1.5 Adding samples to the analytical sequence.

Pause the run (F12). Go to page 14 (Sample Labels), delete the sample labels that have already been run and add the new samples to be run. Go to page 11 (Sequence Control). At the bottom set the sample number to start with and the First Measurement (i.e. sample or reslope - the instrument will run an autozero automatically in any case). If necessary, change the last sample to be run in the top line of this page. Remove the old samples from the sampler tray and add any new ones to be run. Go to page 18 (Signal Graphics) and press F11 (Start).

6.3.1.6 Fill out the logbooks as the run progresses. Check the ICV and CCV recovery, independent QC solution recovery, duplicate RPD, matrix spike %R, and reference recovery 'real time'. Indicate on the summary logbooks that the above were checked and/or write the results in the comments section.



6.3.1.6 QC CHECKS

ICV & CCVs

A calibration verification standard is run at the start of the run immediately after calibration, every 5 samples (20 burns), and at the end of the analytical run to verify calibration stability. The same solution is used for both the initial calibration verification (ICV) and the continuing calibration verification (CCV). QC acceptance limits for the CV are 90% to 110% of the true value. If a CV result is outside of the limits, the instrument will perform an autozero and a reslope, and rerun all samples since the last acceptable CV.

ICB & CCBs

A calibration blank is run after every analysis of a calibration verification standard to check for baseline drift and sample carry-over. An initial calibration blank (ICB) is run immediately after the ICV and a continuing calibration blank (CCB) is run immediately after each CCV. The acceptance limits for the CB are negative 1 IDL to positive 1 IDL with rounding (i.e. if IDL is 1.0 ug/L, then limits would be -1.4 to +1.4 ug/L). If a CB is outside the limits, run an autozero (A/Z) and rerun samples since the last acceptable CB.

CRA

The CRA (Contract Required Detection Limit standard for GFAA) prepared at 2 times the IDL, is a QC check sample run after the ICV and ICB. Although there are no acceptance limits for the CRA, it should run within 1 IDL of its true value. It should be run with an analytical spike as an analytical spike check.

INDEPENDENT QC SOLUTION (currently APG7878)

The APG solution is run as an independent QC sample, a source separate from the calibration standards and the CV, usually immediately after the CRA. Since no preparation steps are required to run this solution, other than routine dilution for some elements, this solution is used as a double check of the calibration standards preparation.

IVPC

The IVPC (Inorganic Ventures Performance Check) solution is a 1/100 dilution of the IVCV INT (Inorganic Ventures Calibration Verification Intermediate). It can be used to verify CV preparation or for a non-calibration curve MSA QC check.

6.3.1.7 PRECISION CRITERIA

All GFA analyses are double burn/injections, except for MSA and IDL determinations. The precision criteria between the 2 burns is based on the concentration result. If the concentration is less than or equal to 4 times the IDL, then the absolute difference between the two burns' absorbance readings should be less than or equal to the absorbance amount equivalent of 1 IDL. The absorbance amount that is equal to 1 IDL is calculated from the calibration curve or the latest reslope. If the concentration is greater than 4 times the IDL, then the RSD should be less than or equal to 20%. If either limit is exceeded, then the sample should be rerun once. A dilution might possibly be run to dilute a matrix problem, if one exists.



ELEMENTS	IDL	2 X IDL	4 X IDL
Ag, Cd	0.2 ug/L	0.4 ug/L	0.8 ug/L
As, Pb, Sb, Se, Tl	1.0	2.0	4.0

6.3.1.8 ANALYTICAL SPIKE

Each GFA sample is run with an analytical spike (sometimes referred to as an instrument spike) to determine if sample matrix effects are occurring during analysis. The acceptance limits for the analytical spike recovery are based on the concentration result. If the concentration result is greater than or equal to 2.5 times the IDL, then the recovery acceptance limits are 85% to 115%. If the concentration is less than 2.5 times the IDL, then the analytical spike recovery should be greater than or equal to 40%. If either limit is not met, then an appropriate dilution should be prepared and run, or, if the analytical spike recovery is close to meeting the acceptance limits, the sample may be rerun once at the same dilution. If the sample result rounds to greater than 2.5 times the IDL and the analytical spike recovery is not acceptable, a dilution of the sample (or a further dilution) should be run, unless the resulting concentration would be less than 5 times the IDL. The dilution factors we analyze samples at are 1/2, 1/5, 1/10, 1/20, 1/40, 1/50, 1/100. Perform a MSA on the sample using three additions of analyte at the current sample dilution after the above actions fail to produce an acceptable result.

When comparing dilutions keep in mind that the accuracy of the concentration result may be affected by matrix effects/low spike recovery. If a sample is run initially at a dilution in anticipation of matrix interference, the lowest possible dilution with acceptable instrument spike recovery should be attempted.

DILUTION GUIDELINES FOR INSTRUMENT SPIKE RECOVERY

CONCENTRATION	% RECOVERY	DILUTION
any	0 - 39 %	1/5 or greater
greater than 2.5 IDL	40-69, >130	1/5
greater than 2.5 IDL	70 -80, 120-130	1/2
greater than 2.5 IDL	borderline acceptable	rerun at same dilution

6.3.1.9 DIGESTION/BATCH QC SAMPLES

METHOD BLANK

A method blank (MB) is run with every client group of samples or every sample digestion group (SDG). The method blank concentration should be less than 1 IDL. All method blanks should have analytical spike recovery from 85% to 115%. The following rerun guidelines apply. If the analyte is detected in the method blank, then it should be rerun. If the method blank is still detectable, check the digestion log for other method blanks from the same digestion group and run one (or more if necessary). If this method blank is still detectable, then all the samples in the client job must be redigested with a new method blank unless all samples are greater than 10X the detected method blank



concentration. A corrective action form should be filled out by the analyst and the supervisor should be informed.

MATRIX/DIGESTION DUPLICATE

A duplicate sample is digested to test the reproducibility of the method. The acceptance limits are based on the concentration result. If both original and duplicate sample concentrations are greater than or equal to 5 times the IDL, then the relative percent difference (RPD) should be less than 20%. If either the original or duplicate sample concentration is less than 5 times the IDL, then the absolute difference between the two concentration results should be 1 IDL or less. For soil or tissue samples, the sample concentrations must be calculated in mg/kg units. If a duplicate RPD is outside the acceptance limits, then a corrective action form should be filled out by the analyst and the supervisor should be informed.

MATRIX/DIGESTION SPIKE

A matrix spike sample is spiked before digestion to detect analyte losses during digestion and matrix effects on digestion efficiency. Usually the matrix duplicate and the matrix spike are performed on the same sample. The acceptance limits for spike recovery are 75% to 125%, if the original sample concentration is less than 4 times the spike added. If the original sample concentration is greater than 4 times the spike added, there is no acceptance criteria. For soil or tissue samples, the sample concentrations must be calculated in mg/kg units, including the spike added. Antimony recoveries on soil or sludge samples typically range between 15% and 65%. Except for Antimony, if the matrix spike recovery is outside the acceptance limits then a corrective action form should be filled out by the analyst, and the supervisor should be informed.

REFERENCE SAMPLES

A reference sample is a sample of known and/or certified analyte concentration, which is digested with a group of samples to verify digestion recovery in the appropriate matrix. Water, soil, and tissue references are used. The water reference recovery acceptance limits are 80% to 120%. For a soil reference the certified ranges are used as recovery limits. For soil or tissue samples, the reference concentration must be calculated in mg/kg units. If the recovery is outside the acceptance limits, then a corrective action form should be filled out by the analyst, and the supervisor should be informed.

6.3.1.10 GRAPHICS

Graphics should be reviewed for analyte peak appearance time shifts. This is especially important for peak area integration methods as the entire peak must be in the integration window for the result to be valid. The background + signal trace can be useful for predicting the appropriate dilution necessary for matrix interferences, but a low background + signal trace may also appear with low spike recovery. Peak shapes should also be watched for any anomalies. On the VARIAN GFAAS, Zeeman background correction over-correction appears as a negative concentration. Samples that show over-correction may require sample dilution.



6.3.1.11 CARRY-OVER

Very high samples can affect the samples run after them. This effect, called carry-over, is usually apparent as a high burn followed by successively lower burns. Samples suspected of carry-over effects should be rerun. Pipetting carry-over can also occur after very high samples, so samples suspected of this should be reprepared and rerun.

3.1.12 MSA

The method of standard additions (MSA) is a method of adjusting sample concentration result for spike recovery at three spike levels. Sample concentration is extrapolated by linear regression from the absorbance result of the unspiked sample and the sample spiked at three levels. Ideally the spiking levels are 50%, 100% and 150% of the sample concentration.

For the elements with an IDL of 1 ug/L, and additions of 5, 10, 15 ug/L, the MSA calculated concentration should be less than 20 ug/L, or the sample should be diluted and run by MSA again. For the elements with an IDL of 0.2 ug/L, and additions of 0.5, 1.0, 1.5 ug/L, the MSA calculated concentration should be less than 2.0 ug/L, or the sample should be diluted and run by MSA again.

Linear regression of the MSA can be calculated using HP calculators or EXCEL software. r (correlation coefficient) should be greater than or equal to 0.995, or the sample should be rerun once. If both r values are less than 0.995, then the analysis with the better r value is used. A single burn is used for MSA.

6.3.1.13 ROUNDING RULE

The routine rounding rule is to round up if the digit following those to be retained is 5 (i.e. 40.55 would round up to 40.6).

6.4 SHUT DOWN PROCEDURES

6.4.1 When the instrument is done analyzing samples the software will exit to DOS. Turn the boost current knob of the Super Lamp power supply fully counterclockwise and switch the power off. Turn off the unit in the following order: a.) the power strip, b.) the GTA furnace power supply, c.) the spectrometer.

6.4.2 Turn off the cooling water, and the alternate gas cylinder (if required).

6.4.3 Turn off the exhaust fan switch.

7.0 Review

Refer to procedures section for review during the run instructions.

8.0 Quality Control

Refer to procedures section for QC acceptance criteria.



9.0 Corrective Actions

9.1 Calibration

If the calibration does not meet the criteria in section 6.3.1.1, then corrective action should be taken before proceeding with re-calibration, unless the graphite cuvette is new and may have needed some conditioning. If the cuvette is new, then recalibration can be attempted without taking corrective action first.

9.2 QC checks

If a QC check is out of control, then corrective action should be taken before proceeding with analysis. This could involve repreparing the solution, rerunning the solution, checking instrument conditions, etc.

9.3 Instrument malfunctions

Consult other experienced Varian 300Z operators or the supervisor for guidance. The maintenance logbook and the service manual could be helpful for troubleshooting.

10.0 Miscellaneous Notes and Precautions

10.1 The analyst should be aware of the sensitivity differences of the various GFAAS elements as they typically run on the instrument. If calibration absorbances start at the lower end of acceptability, then the percentage of reslope absorbance acceptability should be adjusted. Also a lower reslope value also affects the precision criteria on low level samples.

10.2 GFAAS low detection limits require that contamination potential be minimized. The samples preparation area should be kept clean and the autosampler should be wiped down regularly. Standards should be segregated at all times from samples, blank and modifier. Re-use of pipet tips and beakers should be clearly identified and segregated.

11.0 Method References

USEPA SW-846 Method 7000A 7/92.
USEPA SW-846 Method 7041 9/86.
USEPA SW-846 Method 7060A 11/92.
USEPA SW-846 Method 7131A 11/92.
USEPA SW-846 Method 7421 9/86.
USEPA SW-846 Method 7740 9/86.
USEPA SW-846 Method 7761 9/86.
USEPA SW-846 Method 7841 9/86.

12.0 Appendices

12.1 Varian Program Directory

12.2 Standard and Modifier Preparation

12.3 Instrument Parameters - All Elements

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Appendix

12.1 Varian Program Directory

APPENDIX 12.1

VARIAN PROGRAM DIRECTORY

1. Cu	16. Pb ROUTINE
2. Cu BC OFF	17. Pb CLP
3. Ag ROUTINE	18. Pb IDL
4. Ag CLP	19. Pb CURVE MSA
5. Ag IDL	20. As ROUTINE
6. Ag CURVE MSA	21. As CLP
7. Ag HF DIGEST	22. As IDL
8. Sb ROUTINE	23. As CURVE MSA
9. Sb CLP	24. Se ROUTINE
10. Sb IDL	25. Se CLP
11. Sb CURVE MSA	26. Se IDL
12. Ti ROUTINE	27. Se CURVE MSA
13. Ti CLP	28. Cd ROUTINE
14. Ti IDL	29. Cd CLP
15. Ti CURVE MSA	30. Cd IDL
31. Cd CURVE MSA	50. Cd Pd MOD/PLAT/WBH
32. Cd HF DIGEST	
34. Be	
35. Ni	
36. Cr	



**ANALYTICAL
RESOURCES
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Appendix

12.2 Standards Preparation



STANDARDS PREPARATION

Weekly:

Seven Element Intermediate Standard:

To a 100 mL volumetric flask containing approximately 80 mL de-ionized water, add 2 mL Trace Metal Grade HNO_3 , 1.0 mL GFA calibration stock and 0.200 mL 1000 mg/L Sb stock. Dilute to volume with de-ionized water.

Calibration Standards:

All calibration standards are made up in 100 mL volumetric flasks with 0.5% HNO_3 (add 0.5 mL Trace Metal Grade HNO_3 to the volumetric flask containing about 80 mL de-ionized water then dilute to volume with de-ionized water after intermediate standard has been added). Numbers in parentheses refer to Ag and Cd concentrations.

75 (7.5) mg/L: Add 3.75 mL intermediate std. Used for Pb (Varian and TJA).

50 (5.0) mg/L: Add 2.50 mL intermediate std. Used for all elements and instruments.

25 (2.5) mg/L: Add 1.25 mL intermediate std. Used for Varian spiking solution.

3.0 (0.3) mg/L: Add 0.150 mL intermediate std. Used for IDL determinations.

CRA: These solutions are made in the same manner as the calibration standards.

2.0 mg/L: Add 0.100 mL intermediate std. Used for As, Pb, Sb, Se and Ti.

0.4 mg/L: Add 0.200 mL intermediate std. Used for Cd and Ag.

IDL Standards: These standards are made in the same manner as the calibration standards.

For As, Pb, Sb, Se and Ti use the 3 mg/L standard.

For Cd and Ag use a 0.6 mg/L standard made by using 0.300 mL intermediate std.

Daily

Calibration Verification Standards (CV): These standards are made in the same manner as the calibration standards in a 0.5% HNO_3 matrix and using the Calibration Verification intermediate solution as a source.

Ag: Add 1.00 mL CV intermediate std. 3 mg/L

Cd: Add 1.25 mL CV intermediate std. 2.5 mg/L

Pb: Add 1.60 mL CV intermediate std. 40 mg/L

As, Se, Sb and Ti: Add 0.5 mL intermediate std. 25 mg/L



MODIFIER PREPARATION

Pd/Mg/Citric Acid modifier: Used for As, Se, Ti, Pb, Sb. To make a final concentration of 500 mg/L Pd, 1000 mg/L Mg and 1% Citric Acid, to a 100 mL volumetric flask with about 50 mLs de-ionized water in it, add 5 mLs Environmental Express 1% Pd concentrate and 5 mL 20,000 mg/L Mg solution and 1 gram Baker Analyzed Citric Acid Monohydrate. Dilute to volume with de-ionized water.

20,000 mg/L Mg solution: To a 200 mL volumetric flask with about 100 mL de-ionized water in it, add 42 g Ultra Pure ALFA $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Dilute to volume with de-ionized water.

Cadmium-free $(\text{NH}_4)_2\text{HPO}_4$: Used for Cd. In a 100 mL volumetric flask, dilute 4 mL stock Cadmium free $(\text{NH}_4)_2\text{HPO}_4$ to volume with de-ionized water.

Stock Cadmium-free $(\text{NH}_4)_2\text{HPO}_4$: Dissolve 32g $(\text{NH}_4)_2\text{HPO}_4$ in de-ionized water, bring to volume in a 200 mL volumetric flask. Add 10 drops saturated APDC solution and extract three times with 20 mL MIBK (methyl isobutyl ketone).

Saturated APDC solution: Dissolve about 2g Ammonium Pyridine Dithionite in approximately 30 mL deionized water to make a saturated solution. Keep refrigerated.

1% $\text{NH}_4\text{H}_2\text{PO}_4$: Used for Ag. Dissolve 1.00 g of ultrex Ammonium Phosphate, Monobasic in deionized water. Dilute to volume in a 100 mL flask.



Appendix

12.3 Instrument Parameters



INSTRUMENT PARAMETERS FOR ALL ELEMENTS

Measurement Mode	Peak Area
Slit Height	Normal
Measurement time (sec.)	1.0
Background Correction	On
Cuvette Type	Coated Plateau with Platform
Replicates	
Routine	2
IDL	1
MSA	1
Recalibration Rate	0
Reslope Rate	0
Multiple Inject	No
Hot Inject	Yes
Temp	150
Inject Rate	5
QC Standard Sampler Position	45
QC Standard Rate	
Routine	5
IDL	0
MSA	20
QC Standard Limits	90-110%
QC Standard Volume (mL)	15
QC Spike Sampler Position	44
QC Spike Rate	
Routine	1
IDL	0
MSA	0
QC Spike Limits (for samples > 2.5xIDL)	85-115%
QC Spike Minimum (for samples < 2.5xIDL)	40%
QC Spike Volume (mL)	6
Overrange Volume Reduction	1
RSD Limit	100% (No automatic rerun for RSD over 20%)



ANTIMONY METHOD

INSTRUMENT PARAMETERS

Lamp Current	10mA
Slit Width	0.2nm
Wavelength	217.6nm
Sample Introduction	Sampler Automix

FURNACE PARAMETERS

Step No.	Temperature (°C)	Time (sec)	Gas Flow (L/min)	Gas Type	Read Command
1	300	35.0	3.0	alternate	no
2	600	10.0	3.0	alternate	no
3	1200	5.0	3.0	alternate	no
4	1200	5.0	3.0	alternate	no
5	1200	1.0	0.0	normal	no
6	2500	0.6	0.0	normal	yes
7	2500	2.0	0.0	normal	yes
8	2500	1.0	3.0	normal	no
9	2600	2.0	3.0	normal	no
10	40	12.8	3.0	normal	no

STANDARDS

Standard 1	10.0
Standard 2	20.0
Standard 3	50.0
Concentration Units	mg/L
Reslope Standard	2

SAMPLER PARAMETERS

Volumes (uL)

Type	Solution	Blank	Modifier
Blank		15	5
Standard 1	3	12	5
Standard 2	6	9	5
Standard 3	15	0	5
Sample	15	0	5



QC PROTOCOLS

QC Standard Concentration	25mg/L
QC Spike Concentration	25.0mg/L
Required Detection Limit	1.0 mg/L

MATRIX MODIFIER

500mg/LPd,
1000ug/LMG,
and 1% Citric Acid



ARSENIC METHOD

INSTRUMENT PARAMETERS

Lamp Type	PhotronSuperLamp
Lamp Current	15mA
Slit Width	1.0nm
Wavelength	193.7nm
Sample Introduction	Sampler Automix

FURNACE PARAMETERS

Step No.	Temperature (C)	Time (sec)	Gas Flow (L/min)	Gas Type	Read Command
1	300	35.0	3.0	alternate	no
2	600	10.0	3.0	alternate	no
3	1300	5.0	3.0	alternate	no
4	1300	5.0	3.0	alternate	no
5	1300	1.0	0.0	normal	no
6	2500	0.6	0.0	normal	yes
7	2500	2.0	0.0	normal	yes
8	2500	1.0	3.0	normal	no
9	2600	2.0	3.0	normal	no
10	40	12.8	3.0	normal	no

STANDARDS

Standard 1	10.0
Standard 2	20.0
Standard 3	50.0
Concentration Units	mg/L
Reslope Standard	2

SAMPLER PARAMETERS

Volumes (mL)

Type	Solution	Blank	Modifier
Blank		15	5
Standard 1	3	12	5
Standard 2	6	9	5
Standard 3	15	0	5
Sample	15	0	5



QC PROTOCOL

QC Standard Concentration	25mg/L
QC Spike Concentration	25mg/L
Required Detection Limit	1.0 mg/L

MATRIX MODIFIER

500mg/LPd,
100mg/LMg and
1%citricacid.



CADMIUM METHOD

INSTRUMENT PARAMETERS

Lamp Current	5mA
Slit Width	0.5nm
Wavelength	228.8nm
Sample Introduction	SamplerAutomix

FURNACE PARAMETERS

Step No.	Temperature (C)	Time (sec)	Gas Flow (L/min)	Gas Type	Read Command
1	300	35.0	3.0	normal	no
2	600	10.0	3.0	normal	no
3	900	5.0	3.0	normal	no
4	900	5.0	3.0	normal	no
5	900	1.0	0.0	normal	no
6	1900	0.5	0.0	normal	yes
7	1900	2.0	0.0	normal	yes
8	1900	1.0	3.0	normal	no
9	2600	2.0	3.0	normal	no
10	40	12.8	3.0	normal	no

STANDARDS

Standard 1	1.00
Standard 2	2.00
Standard 3	5.00
Concentration Units	mg/L
Reslope Standard	2

SAMPLER PARAMETERS

Volumes (uL)

Type	Solution	Blank	Modifier
Blank		15	5
Standard 1	3	12	5
Standard 2	6	9	5
Standard 3	15	0	5
Sample	15	0	5

QC PROTOCOLS

QC Standard Concentration	2.5mg/L
QC Spike Concentration	2.5mg/L
Required Detection Limit	0.2 mg/L

MATRIX MODIFIER

Cadmium free $(\text{NH}_4)_2\text{HPO}_4$



LEAD METHOD

INSTRUMENT PARAMETERS

Lamp Current	5mA
Slit Width	0.5 nm
Wavelength	283.3nm
Sample Introduction	Sampler Automix

FURNACE PARAMETERS

Step No.	Temperature (C)	Time (sec)	Gas Flow (L/min)	Gas Type	Read Command
1	300	35.0	3.0	alternate	no
2	600	10.0	3.0	alternate	no
3	1000	5.0	3.0	alternate	no
4	1000	30.0	3.0	alternate	no
5	150	4.3	0.0	normal	no
6	2300	1.1	0.0	normal	yes
7	2300	2.0	0.0	normal	yes
8	2300	1.0	3.0	normal	no
9	2700	2.0	3.0	normal	no
10	40	13.3	3.0	normal	no

STANDARDS

Standard 1	15.0
Standard 2	30.0
Standard 3	45.0
Standard 4	60.0
Standard 5	75.0
Concentration Units	ug/L
Reslope Standard	2

SAMPLER PARAMETERS

Volumes (uL)

Calibration

Type	Solution	Blank	Modifier
Blank	0	15	5
Standard 1	3	12	5
Standard 2	6	9	5
Standard 3	9	6	5
Standard 4	12	3	5
Standard 5	15	0	5
Sample	15	0	5



QC PROTOCOL

QC Standard Concentration

40mg/L

QC Spike Concentration

50mg/L

Required Detection Limit

1.0 mg/L

MATRIX MODIFIER

500mg/LPd,

100mg/LMg, and

1%citricacid



SELENIUM METHOD

INSTRUMENT PARAMETERS

Lamp Type	PhotronSuperLamp
Lamp Current	18mA
Slit Width	1.0nm
Wavelength	196.0nm
Sample Introduction	Sampler Automix

FURNACE PARAMETERS

Step No.	Temperature (C)	Time (sec)	Gas Flow (L/min)	Gas Type	Read Command
1	300	35.0	3.0	alternate	no
2	600	10.0	3.0	alternate	no
3	1300	5.0	3.0	alternate	no
4	1300	5.0	3.0	alternate	no
5	1300	1.0	0.0	normal	no
6	2500	0.7	0.0	normal	yes
7	2500	2.0	0.0	normal	yes
8	2500	1.0	3.0	normal	no
9	2600	2.0	3.0	normal	no
10	40	12.8	3.0	normal	no

STANDARDS

Standard 1	10.0
Standard 2	20.0
Standard 3	50.0
Concentration Units	mg/L
Reslope Standard	2

SAMPLER PARAMETERS

Volumes (uL)

Calibration

Type	Solution	Blank	Modifier
Blank		15	5
Standard 1	3	12	5
Standard 2	6	9	5
Standard 3	15	0	5
Sample	15	0	5



QC PROTOCOL

QC Standard Concentration	25.0mg/L
QC Spike Concentration	25.0mg/L
Required Detection Limit	1.0 mg/L

MATRIX MODIFIER

500mg/LPd,
1000mg/LMg.and
1%CitricAcid.



SILVER METHOD

INSTRUMENT PARAMETERS

Lamp Current	4mA
Slit Width	0.5nm
Wavelength	328.1nm
Sample Introduction	Sampler Automix

FURNACE PARAMETERS

Step No.	Temperature (C)	Time (sec)	Gas Flow (L/min)	Gas Type	Read Command
1	300	35.0	3.0	normal	no
2	600	10.0	3.0	normal	no
3	1000	5.0	3.0	normal	no
4	1000	5.0	3.0	normal	no
5	1000	1.0	0.0	normal	no
6	1900	0.5	0.0	normal	yes
7	1900	2.0	0.0	normal	yes
8	1900	1.0	3.0	normal	no
9	2600	2.0	3.0	normal	no
10	40	12.8	3.0	normal	no

STANDARDS

Standard 1	1.00
Standard 2	2.00
Standard 3	5.00
Concentration Units	mg/L
Reslope Standard	2

SAMPLER PARAMETERS

Volumes (uL)

Type	Solution	Blank	Modifier
Blank		15	5
Standard 1	3	12	5
Standard 2	6	9	5
Standard 3	15	0	5
Sample	15	0	5



QC PROTOCOLS

QC Standard Concentration	3.0mg/L
QC Spike Concentration:	2.5mg/L
Required Detection Limit	0.2 mg/L

MATRIX MODIFIER

1% $\text{NH}_4\text{H}_2\text{PO}_4$



THALLIUM METHOD

INSTRUMENT PARAMETERS

Lamp Type	Photron Super Lamp
Lamp Current	10mA
Slit Width	0.5nm
Wavelength	276.8nm
Sample Introduction	Sampler Automix

FURNACE PARAMETERS

Step No.	Temperature (C)	Time (sec)	Gas Flow (L/min)	Gas Type	Read Command
1	300	35.0	3.0	alternate	no
2	600	10.0	3.0	alternate	no
3	1100	5.0	3.0	alternate	no
4	1100	5.0	3.0	alternate	no
5	1100	1.0	0.0	normal	no
6	2300	0.6	0.0	normal	yes
7	2300	2.0	0.0	normal	yes
8	2300	1.0	3.0	normal	no
9	2600	2.0	3.0	normal	no
10	40	12.8	3.0	normal	no

STANDARDS

Standard 1	10.0
Standard 2	20.0
Standard 3	50.0
Concentration Units	mL/L
Reslope Standard	2

SAMPLER PARAMETERS

Volumes (uL)

Type	Solution	Blank	Modifier
Blank		15	5
Standard 1	3	12	5
Standard 2	6	9	5
Standard 3	15	0	5
Sample	15	0	5



QC PROTOCOLS

QC Standard Rate Concentration	25.0mg/L
QC Spike Concentration	25.0mg/L
Required Detection Limit	1.0 mg/L

MATRIX MODIFIER

500 mg/L Pd,
1000 ug/L Mg, and
1% Citric Acid



ANALYTICAL
RESOURCES
INCORPORATED

Standard Operating Procedure

ICP Analysis - Thermo Jarrell Ash ICAP61
Method 6010A - (United States Air Force)

504S

Revision 1

3/30/94

PROPRIETARY

Prepared By:

Christine I. Gebel

Approvals:

[Signature]
Section Manager

[Signature]
Laboratory Manager

[Signature]
Quality Assurance Manager

[Signature]
Laboratory Director

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ANALYTICAL
RESOURCES
INCORPORATED

Standard Procedure

Thermo Jarrell Ash
ICAP61 Analysis

504S

Revision 1

3/30/94

Prepared By:

JPF James P. Fick & CT6 Christine Gebel

Approvals:

Jay Kuhn MGT
Section Manager

Bruce N. Chesser
Laboratory Manager

Michelle J. Turner 4/1/94
Quality Assurance Manager

Mark Wilson
Laboratory Director



STANDARD OPERATING PROCEDURE

Thermo Jarrell Ash ICAP61 Analysis

1.0 Scope and Application

This document will cover the optimization, daily set-up, operation and maintenance of the ARI's Thermo-Jarrell Ash ICAP61 (TJA ICAP61). The TJA ICAP61 is a simultaneous ICP allowing the detection of 28 to 31 elements simultaneously by the arrangement of separate photomultiplier tube detectors for each analytical line along an arc. An autosampler allows for unattended operation of the ICP, although ARI does not operate the ICP overnight or completely unattended for extended periods of time. For each analytical sample run, the ICP is first standardized, then QC solutions are checked. After the standardization and QC solutions are verified to be in control, samples are prepared for analysis. Optimization of the ICP torch and optics will be described in detail. The quarterly procedures for linear range checks, IEC checks and IDL determinations are also described. Maintenance is detailed for both daily and less frequent intervals.

2.0 Definitions

- 2.1 ICP-OES: Inductively Coupled Argon Plasma - Optical Emission Spectrometry
- 2.2 ICP: Abbreviated ICP-OES to ICP for this document.
- 2.3 IDL: Instrument Detection Limit. As defined in the EPA-CLP SOW, three times the standard deviation of seven replicate measurements averaged over three non-consecutive days.
- 2.4 MDL: Method Detection Limit. As defined in 40 CFR; three times the standard deviation of seven replicate measurements of a low level standard or sample that has gone through a preparation step.
- 2.5 ICV: Initial Calibration Verification. An independent standard at a concentration other than that used for instrument standardization, run immediately after standardization to verify the accuracy of the standardization.
- 2.6 CCV: Continuing Calibration Verification. An independent standard at a concentration other than that used for instrument standardization, run after every group of 10 samples and at the end of the day to verify standardization accuracy during the analytical run.
- 2.7 ICB: Initial Calibration Blank. A standardization blank run immediately after the ICV to verify the baseline of the standardization.
- 2.8 CCB: Continuing Calibration Blank. A standardization blank run immediately after every CCV to verify the baseline of the standardization.



2.9 LCS: Laboratory Control Sample. A reference sample of known concentration processed along with the samples to test the digestion procedure for accuracy. Both solid references and method blank spikes are LCSs.

2.10 ICSA, ICSAB: Interference Check Solutions ICSA and ICSAB. The ICSA solution contains minerals at high concentrations. The ICSAB contains the same minerals as the ICSA at the same concentrations, and also twelve elements at moderate levels.

2.11 CRI: A solution to check the results of concentrations near the detection limit for several analytes.

2.12 SD: Standard Deviation

2.13 RSD: Relative Percent Standard Deviation. The SD divided by the mean, multiplied by 100.

2.14 RPD: Relative Percent Difference. The absolute difference between two numbers, divided by the average of the two numbers, multiplied by 100.

2.15 %R: Percent Spike Recovery. The difference between the matrix spike concentration and the original sample concentration divided by the concentration of the spike added multiplied by 100.

2.16 DI water: de-ionized water

2.17 IEC: Inter-element correction factor

3.0 Equipment

3.1 Instrument

The Thermo-Jarrell Ash ICAP61, a simultaneous 34 channel inductively coupled argon plasma optical emission spectrometer, is equipped with an IBM PS2 computer loaded with Thermospec ICP software, a 300 sample and 18 standard capacity autosampler, a Tylan mass flow controller and a Rainin peristaltic pump. The TJA ICAP61 consists of a 0.75 meter polychromator, an RF generator, an inductively coupled argon plasma excitation source, and a data acquisition system.

3.2 Argon Supply

Argon is supplied from a liquid argon dewar of high purity (99.997% pure). Reserve compressed argon tanks of the same purity are in-line to substitute during liquid argon dewar changes.

3.3 Consumables

At least two of each type of ICP glassware are kept in the lab to minimize downtime in case of ICP glassware breakage. Two of the ICP torch bodies have two to four spare quartz tips since the build-up of deposits on the tips requires semi-monthly replacement. A spare cross flow nebulizer, spray chamber, and torch bonnet are stored in the lab.



Lab consumables include 13 X 100 mm sample tubes, kimwipes, pipet tips, plastic beakers Gelman IC syringe filters, polyethylene syringes, 50 ml polyethylene centrifuge tubes, blue-yellow peristaltic pump tubing, tubing/tubing connectors and autosampler probes.

3.4 Reagents

- Fisher trace grade concentrated nitric acid
- Fisher trace grade concentrated hydrochloric acid
- De-ionized water produced by the Technic/Barnstead system

3.5 Labware

- glass volumetric flasks, class A
- glass volumetric pipets, class A
- polypropylene volumetric flasks, class B
- Rainin Pipetman Pipets:
 - Two each of P-20, P-1000, and P-5000
 - One each of P-100, P-200, and P-10 ml

3.6 De-ionized Water system

The Technic/Barnstead de-ionized water system consists of two de-ionizing cartridges and two particulate pre-filters. Weekly monitoring of the de-ionized water quality is performed on the ICP.

4.0 Documentation

The following logbooks and files are set-up to document all actions and procedures related to ICP operation. For daily analysis runs, the ICP sample logbook should be used as a run sequence log, for sample specific notes, for QC limit notes and for any notes pertaining to the run. For periodic checks of instrument performance, the ICP instrument logbook should be used. The ICP maintenance logbook is used for all maintenance procedures except the daily set-up cleaning. The daily standardization summary table is filed in the standardization summary file. The torch position optimization file contains all the raw data and related graphs from the torch position optimization process. The inter-element corrections and linear ranges file contains all the raw data and calculations related to their determinations. The instrument detection limits file contains the calculations for IDL determinations. The Inorganic Ventures standards certificates notebook contains all the certificates for the Inorganic Ventures stock standards. The ICP methods file contains all method updates.



5.0 Inhouse Modifications to Referenced Method

5.1 EPA SW-846 Method 6010A.

5.1.1 Section 5.6. States that the instrument check standard, which is referred to as the ICP CV, should be "at concentrations equivalent to the midpoint of their respective calibration curves." ARI's instrument check standard or CV (see table 2) is at concentrations several hundred times the IDLs for accurate quantitation and for minimizing carry-over effects. Most of these concentrations are below the standardization standards' concentrations (see tables 1 and 2).

5.1.2 Section 7.1. States that water samples which have been prefiltered and acidified will not need acid digestion as long as the samples and standards are matrix matched. ARI does not matrix match undigested water samples for ICP; they are preserved with 0.5% nitric acid.

5.1.3 Section 7.3. Recommends calibration according to the instrument manufacturer's recommended procedures using a blank and three standards. As recommended by TJA, ARI standardizes the ICP at the beginning of each analysis run and as needed during the run. Standardization consists of a blank and one standard level for each analyte. Four multiple element standardization standards are used based on chemical and spectral compatibility (see table 1).

5.1.4 Section 7.4. States that the highest mixed calibration standard should be run as if it were a sample at the beginning of the sample run and that it should read within 5% of its true values. ARI runs an instrument check standard, called the ICV (see table 2), after standardization. The ICV should read within 10% of true values for each requested element, although typically the values are within 5% of true values.

5.1.5 Section 7.5. Recommends flushing the system with the calibration blank solution. ARI uses a rinse solution of 6% nitric acid and 6% hydrochloric acid.

5.1.6 Section 8.5. Recommends that whenever a new or unusual sample matrix is encountered, a serial dilution and post digestion spike should be performed. A serial dilution and a post digestion spike of a new or unusual sample matrix is not always performed.

5.1.7 Section 8.6.2. States that the laboratory should verify the inter-element and background correction factors at the beginning and end of an analytical run or twice during every 8 hour work shift, whichever is more frequent. ARI runs the interference check samples (ICSA and ICSAB) during specific runs, after every torch change and after IEC changes.



6.0 Procedure

This section will describe the ICP technique, the required steps for daily operation, the procedures for periodic checks of ICP performance, such as linear limit checks, IEC checks, IDL determinations, and finally maintenance procedures, such as torch replacement and autosampler cleaning.

6.1 Method Description

Inductively coupled argon plasma spectrometry is an analytical technique based on the measurement of atomic emission of trace elements by optical spectrometry. By employing a high energy excitation source, a radio-frequency inductively coupled argon plasma, efficient atomization (and ionization) is achieved. A peristaltic pump evens the flow of sample to the nebulizer, which forms an aerosol that is transported to the plasma torch where desolvation and excitation occur. Characteristic atomic-line spectra are produced by this process. The spectra enters the spectrometer through an entrance slit, then is dispersed by a diffraction grating into separate lines to each element's entrance slit and photomultiplier tube (PMT) detector. These PMTs, except for potassium which is on its own mount, are arranged along a thermally stable 0.75 meter arc, called the Rowland circle. This arrangement of separate detectors allows for the simultaneous reading of the 28 to 31 elements. The signal from each detector is measured by each channel card, then is processed by the computer. Background correction and inter-element correction factors are applied for each analytical line before the reading for each element is displayed. The complexity of the emission spectra and background requires extensive characterization research. The wide dynamic range of the ICP technique allows for the measurement of concentrations ranging from 1 ppb to hundreds or thousands ppm.

6.2 Daily ICP Set-up

6.2.1 Preparing the uptake system and the torch.

6.2.1.1 First check that the argon dewar is at least 1/8 full (see the float gauge on top of the dewar), the autosampler rinse bottle is at least half full, and the waste carboy is lower than 2 inches below the shoulder of the carboy. Turn on the cooling water at the manifold on the south west corner of the metals instrument lab and turn on the argon supply toggle valve at the back right side of the ICP. The blue RF power off button should light when both cooling water and argon supplies are on.

6.2.1.2 Push the red RF power button. Turn on the computer printer, the computer monitor, and then the computer. The computer will start-up with date and time prompts, then the TJA ThermoSpec software will start.

6.2.1.3 Place each peristaltic pump tubing line in the guides of the pump beds. The top one is the sample line and the bottom one is the rinse solution line. Clamp the tubings in place with the tensioned pump bed clamps.



6.2.1.4 Prepare the autosampler by raising the probe in its holder, so that the bottom of the probe is near the top of the probe holder, then turn on the autosampler using the power switch on bottom of the back panel. Place a 13 X 100 mm polystyrene sample tube filled with 0.5% Triton-X solution in position 1 of the left rear sample rack (rack number 2).

6.2.1.5 From the ThermoSpec main menu, choose Operation / Analysis / type (method name)/ at the "command" prompt (command line), type IA (to initialize autosampler) / type SRT70SRN2MA1/ <enter>. The method name will depend on the elements required or not required. Typically method ICP30X (X takes the place of the letter of the revision, the latest revision will have the later alphabet letter) is used; it includes all the elements except lithium. Method ICP31X would be used if lithium is requested. Method MICRO# (# takes the place of the number of the revision, the latest revision will have the highest number) would be used if total digestates were analyzed; this method does not read boron and silicon since they are at high levels due to the digestion matrix.

6.2.1.6 To open the argon valves, turn up toggle switches 1 and 2 on the Tylan mass flow controller (located on top of the ICP) and turn up all three toggle switches on the right front argon panel.

6.2.1.7 Manually position the probe down to the bottom of the 0.5% Triton-X tube, then raise it 5 mm. Turn the peristaltic pump toggle on switch to the left to begin aspirating this solution. Daily adjustment of the pump bed tension or pump speed is not usually required except immediately after the weekly pump tubing replacement. The usual uptake rate is 1.6 to 1.8 ml/min. To adjust the pump bed tension after new pump tubing is attached, use the adjustment screw on the pump bed clamp. Loosen the adjustment screw until an air gap does not proceed through the tubing, then tighten the adjustment screw until flow begins. Typically a half turn tighter of the adjustment screw beyond this point is sufficient for a stable setting (look for a smooth flow rate). Aspirate 0.5% Triton-X for 5 minutes.

6.2.1.8 At the command line, type SRT95SRN1MA11 to place the autosampler probe in a DI water vial at position 11 of the standards/QC rack (the L-shaped rack). Aspirate for DI water for 5 minutes.

6.2.1.9 During the de-ionized water aspiration, clean all uptake lines' connectors using a fine tip deionized water bottle and clean the nebulizer intake capillary using the cleaning wire (checking for clogs).

6.2.1.10 Turn off the peristaltic pump, then purge the torch with argon for 5 minutes by setting the auxiliary flow on at 3.0 L/min (use the auxiliary flow knob on the right front panel).

6.2.2 Lighting the torch

6.2.2.1 Turn off the sample argon by toggling switch 1 down on the mass flow controller. Turn down the auxiliary argon flow to between 0.8 to 0.9 L/min. Check that the automatic power control switch is set to manual and the load control tuning switch is set to automatic.



6.2.2.2 Increase the "power" knob (RF power) until reflected power meter reads about 50 watts. Tap the ignitor button once per second while turning the power knob up. Observe the torch through the round front viewing window. As the forward power is increased the plasma first appears as a faint filamentary swirling. As soon as the plasma "lights," which appears as a self sustaining "flame" (usually accompanied by a whirring sound of the tuner mechanism), stop turning the power knob, turn the automatic power control switch to automatic, turn the "power" knob fully clockwise, and turn the sample argon switch on (switch 1 up on the mass flow controller). As soon as the sample argon reaches the specified flow (see the label on the mass flow controller, typically about 0.62 to 0.65 L/min), turn down the auxiliary argon toggle (on the right front panel) and turn on the peristaltic pump.

6.2.2.3 At the command line, type RA (to aspirate rinse solution). The rinse station contains a 6% nitric acid and 6% hydrochloric acid solution. The reflected power meter should read less than 50 watts, typically it is less than 10 watts.

6.2.2.4 Observe the plasma periodically during the first 5 minutes. The plasma position should be above the inner concentric about 1 to 2 mm and the torch glass should not be glowing orange or red. If any orange or red glowing is observed, turn off the torch immediately, by opening the front access door. Check the argon flows and the torch position before relighting the torch.

6.2.2.5 During the warm-up period, stronger acid rinse solutions can be aspirated to clean the uptake system, the nebulizer and the spray chamber. Warm-up the instrument for 30 to 45 minutes. The warm-up is adequate when the forward power meter reads 1.10 kilowatts.

6.2.3 Profiling the optics

For optimum performance of the ICP, each spectral line must be centered on its exit slit which is positioned before its photomultiplier tube. This optics profiling procedure is achieved by adjusting the entrance slit refractor plate using its micrometer. The built-in mercury lamp is usually used for profiling, although any channel can be used for profiling using an appropriate single element standard.

6.2.3.1 Place the mercury lamp in front of the entrance slit. To start a mercury automatic profile: F5 (profile) / F3 (automatic profile) / F1 (run profile). 5

6.2.3.2 After the instrument reads the mercury emission, a peak is displayed. The peak position should be close to zero. A shift of greater than 0.5 (positive or negative) moves the spectrum shifter refractor plate to compensate, which is an undesirable analytical condition.

6.2.3.3 To adjust the peak position, move the micrometer 1 unit for each 0.05 of peak position measurement (eg. for a peak position of 0.25, dial the micrometer 5 units down). After this micrometer adjustment, run another automatic profile to check the setting. It should be from -0.1 to +0.1 (this is adequate as the noise of the peak position measurement is 0.05 to 0.1).



6.2.3.4 When the profiling process is complete, remove the mercury lamp from the light path. Press ESC to return to the analysis mode.

6.3 Standardization

Standardization is the process of establishing a linear relationship between intensity and concentration by analyzing a blank and a single standard. For most environmental ICP applications, standardization is sufficient to establish this correlation as the ICP technique has been established to be linear over several orders of magnitude. Calibration with three or more standards levels of each analyte is used for applications in which a wider dynamic range is required and curvature of the calibration curve is expected.

6.3.1 Working Standards Preparation.

The working standards are diluted to working levels (see table 1 for the elements and the concentrations of each working standard) on the first day of the work week. Four multiple element standards are prepared using the ICP blank solution as a diluent. The ICP blank solution is 5% concentrated hydrochloric acid and 1% concentrated nitric acid. For total digestion analysis, standards are matrix matched to the total digestate matrix. The multiple element stocks are prepared based on chemical stability and on spectral compatibility. They are prepared from Inorganic Ventures ICP grade (at least 99.9 % purity, ideally 99.999 % purity) single element 10,000 mg/L stocks. Class A glass volumetric flasks and glass volumetric pipets are used for diluting 1000 mg/L stocks from the 10,000 mg/L stocks. Polypropylene volumetric flasks are used for the working standards preparation. For standards 2, 3 and 4 use 2.0 ml of the appropriate stock in 100 ml volume. For standard 5 use 4.0 ml of stock in 100 ml volume.

6.3.2 Standardization analysis

6.3.2.1 At the command line, type SRT95SRN1MA5 to place autosampler probe in the ICP blank vial at position 5 of the standards/QC rack (the L-shaped rack). Aspirate the ICP blank for 2 minutes, then start the blank analysis: F3 (standardization)/ highlight STD1-BLANK / F1 (run). If the intensities of the blank are acceptable (see previous ICP standardizations), continue standardization.

6.3.2.2 Place STD4 in position 1, STD5 in position 2, STD2 in position 3, and STD3 in position 4 of the standards/QC rack. Continue the standardization using the autosampler: F9 (autosampler) / type STDIZE / F1 (run).

6.3.2.3 After the standards have run, aspirate a strong acid rinse solution (10% concentrated nitric acid and 10% concentrated hydrochloric acid) for 10 to 15 minutes.



6.3.2.4 Print a standardization summary: F3 (standardization) / F9 (done) / F2 (print) / F9 (done). Compare the slope for each element to previous ones in the standardization file. The slopes should be within 10 % of previous values, although this may be greater after a torch replacement. The performance of the QC solutions will dictate the slope acceptance limits. Watch for long term gradual slope changes as these may be indicative of impending instrument failure. File the printed summary in the standardization summary file. Keep the standardization raw data with the samples raw data.

6.4 Samples Analysis

6.4.1 Samples Selection and Preparation.

To select samples for a daily analysis run, refer to both the ICP worklist and the magnetic job tags on the ICP samples scheduling calendar. Prioritize samples by due date and other considerations such as elements requested, digestion matrix, CLP, etc. A typical analytical run will be started with water samples and leachates, then soil samples; queued from low levels to high levels to provide some predictability for setting the rinse times. Typically a group of twenty samples is set-up at a time.

6.4.1.1 Arrange each group of 10 samples beginning with suspected low level samples such as method blanks and ending with higher level samples such as matrix spikes. A digestion QC group will typically be run in the following order to facilitate acceptance limit checking: matrix duplicate, background sample, matrix spike, and reference (if requested).

6.4.1.2 Label 20 - 13 X100 mm polystyrene test tubes with the sample ID in the order in which they will be run. Pre-rinse the test tubes with 10 % nitric acid, then with deionized water.

6.4.1.3 Transfer each sample by pipet into a pre-rinsed test tube taking care to avoid transferring particulates. Filtration of digestates is required when suspended particulates are present with flotation characteristics that are not responsive to centrifugation. Often these particulates are a light color that is difficult to see against the white sample bottle; viewing the sample in its bottle on the black countertop often will improve particulate spotting. Since the uptake system is susceptible to clogging in the tubing connectors or in the intake capillary to the nebulizer, care should be taken to notice which samples require filtration. Centrifugation of digestates is required when uniformly opaque digestates are encountered; an example of this would be a silty soil which must be analyzed soon after digestion (usually fine particulates will settle overnight). To centrifuge, pour about 30 ml of each sample into a centrifuge tube, and centrifuge at 2000 to 2500 rpm for 5 minutes.

6.4.1.4 Samples requiring dilution, i.e. samples with element(s) above linear range or with high levels that are likely to have carry-over effects, can often be anticipated by the appearance of the sample. Also, a review of the job list can indicate clients' projects with histories of high level samples. Soil digestates with a dark yellow, green or orange color can be high in iron, aluminum, copper, chromium, etc.; these samples are



typically first run at a 1/5 or greater dilution. TCLP leachates prepared with extraction fluid #2 are often high in calcium and typically require a 1/5 or greater dilution. Water digestates are often less predictable: color is often an indicator of potential high analyte levels, although some industrial dyes or paints are colored but are detected at relatively low levels. Also, viscosity during the pipet transfer from the sample bottle to the sample tube can be an indicator of high salts.

6.4.1.5 Developing and fixing solutions for film or X-rays are a special case: these solutions are diluted immediately before analysis in de-ionized water only (typically starting at 1/100) and the uptake system is pre-flushed for 5 minutes with 10% nitric acid followed by a 5 minute de-ionized water flush.

6.4.1.6 Instrument or Analytical Spiking. TCLP leachates, undigested water samples and digestates requiring post-digestion spiking are spiked at the instrument before the sample is analyzed. For TCLP leachates and undigested water samples, a 10 ml aliquot of sample is pipetted into a tube and 0.1 ml of the appropriate spiking solution is added: the TCLP spike solution for TCLP extracts and the ICP Routine spike solution for waters. For post-digestion spikes, the amount of spike solution added is calculated based on the background level of analyte.

6.4.2 Autosampler table preparation.

After standardization, the sample autosampler table is prepared.

6.4.2.1 From the ThermoSpec main menu, choose Operation / Autosampler set-up / type (table name) / F3 (add a new set). The table name format is table number/month/day, eg. 1stJAN01 is the 1st table of January 1. For default operator, type in the analyst's initials; for rinse time, type in an appropriate rinse time (60 to 120 seconds based on suspected sample levels and torch tip condition). Delete the default sample name and set auto-increment to NO.

6.4.2.2 The analytical run order of 20 samples would be as follows: ICV, ICB, 10 samples, CCV, CCB, 10 samples, CCV, CCB.

6.4.2.3 Use F1 (edit samples) to start your first set of the autosampler table. To insert ahead of the highlighted sample, use F3 (insert QC) for adding a CV, use F7 (insert blank) for adding a CB and use F8 (insert rinse) for adding an extra rinse. To insert after the highlighted sample, use ALT + an F key. The extra rinse is used between the CV and CB, after matrix spikes, and when a low level sample follows a higher level one.

6.4.2.4 The Edit Sample Info menu, ALT + F2, is useful for editing the sample labels. Use F2 as many times as needed to copy a sample label, then use the F1 edit mode key to toggle on the edit function of the labels or comments. Use F9 to return to the table and add the CVs and the CBs. Use F9 twice to store the set and then the table.

6.4.2.5 The autosampler rack positions of the samples and QC solutions should be noted when the table is prepared. A list of the positions can be printed using F2 (print table).



6.4.2.6 Check the mercury profile as described in section 6.2.3. Start the autosampler run after the standardization is verified by using F9 (autosampler) / type (table name)/ F1 run.

6.4.3 Monitoring the Analysis Run.

Periodically during the operation of the ICP check the argon flows, the sample uptake flow, the appearance of the plasma, the level of solution in the autosampler QC vials, and the rinse solution level.

6.4.3.1 Monitoring QC samples.

Analysis QC samples such as the CV and the CB (see sections 6.5.1 and 6.5.2) should be monitored closely during the run to check for standardization stability and baseline drift. If the CV and/or CB are outside the QC limits, then corrective action should be taken as soon as possible to minimize sample reruns.

6.4.3.2 Monitoring High Levels and Carry-over.

If high level samples (above the linear limit) are observed during the run, the autosampler can be paused and the high level sample diluted and rerun (see table 6 for the linear limits). The ICP system software checks automatically for results greater than the current linear range and will flag the data with an "H." Often a single high level sample will indicate that dilution is required for the entire job. Saturated photomultiplier tube response is indicated as either a "s" or "S" before the mean concentration (the degree of saturation is indicated by the size of the "s" or "S"). If saturation happens, the autosampler run should be paused for at least 10 minutes to allow the photomultiplier tube to return to normal. If high levels are observed, copper and zinc are especially prone to carry-over. Carry-over can often be minimized by pausing the autosampler after the high level sample and rinsing as needed.

6.5 ICP QC checks

6.5.1 Calibration Verification solution.

The calibration verification (CV) solution is a custom second source multiple element solution from Inorganic Ventures (certified second source from the manufacturer) which is analyzed to verify standardization stability. There are two CV stock solutions (two are required due to chemical compatibility) which are diluted to working levels as needed (typically monthly). The levels for the CV solution were chosen at several hundred times the IDLs for quantitation and for minimizing carry-over effects. The same solution is used for both the initial calibration verification (ICV), run immediately after standardization, and for the continuing calibration verification (CCV), run after every group of 10 samples. The CV is run at least every 10 samples. QC limits for the CV are 90% to 110% of true values for each requested analyte. See table 2 for the concentrations of the CV solution elements.

6.5.2 Calibration Blank Verification.

The calibration blank (CB) solution is run at least every 10 samples to check for baseline drift and to check for carry-over. The initial calibration blank (ICB) is run immediately after the ICV and the continuing calibration blank (CCB) is run immediately after each CCV. The limits for the CB are -2 times the IDL to +2 times the IDL for each requested analyte (see table 6 for IDLs).



6.5.3 Independent QC solutions.

Independent QC solutions are used to check standardization standards' stability, concentrations and preparation. They are run as samples after new working standards are prepared; the levels should be within the certified ranges. See table 3 and 4 for the current independent QC solutions elements and concentrations.

6.5.4 Interference Check Solutions.

The interference check solutions ICSA and ICSAB are run during CLP runs, after every torch change and after IEC changes. The ICSA solution contains aluminum, calcium, iron and magnesium (some common interferent elements) at high levels. The ICSAB contains these interferent elements and 12 analytes at moderate levels (see table 5 for the solutions' elements and concentrations). Typically the ICSA is run after the ICV/ICB/CRI group, followed by the ICSAB and again at the end of the run after the CRI and before the last CCV/CCB. If the analysis run is longer than 8 hours, then the CRI, ICSA and ICSAB will be run before 8 hours into the run. They are prepared from multiple element stocks which are dilutions of Inorganic Ventures ICP grade single element 10,000 mg/L stocks. These solutions check some of the spectral interferences that are commonly present in environmental samples. For both solutions, QC limits are 80% to 120% of the true values for both interferents and analytes.

6.5.5 CRI Solution.

The CRI solution is run to check the detection limits of some analytes at low concentrations. It is prepared from a multiple element stock which is prepared from dilutions of Inorganic Ventures ICP grade single element 10,000 mg/L stocks. There are no acceptance limits set for this solution, typically the CRI is within an IDL of the true value except for the elements that are below 2 times the IDL.

6.5.6 Digestion / Batch QC Samples

6.5.6.1 Method Blanks.

A method blank (MB) is run with every client group of samples or every sample digestion group (SDG). The method blank should be less than 1 IDL for every element. Typically Zn, Na, Fe, Cu, and Ca are sometimes detected at levels of up to about 5 times the IDL. If the analyte is detected in the method blank at high levels, then it should be rerun. If the method blank is still detectable, then all the samples in the client job must be redigested with a new method blank unless all samples are greater than 10 times the detected method blank concentration. A corrective action form should be filled out by the analyst and the supervisor should be informed.

6.5.6.2 Matrix / Digestion Duplicate.

A duplicate sample is digested to test the reproducibility of the results. The acceptance limits are based on the concentration result. If both original and duplicate sample concentrations are greater than or equal to 5 times the IDL, then the relative percent difference (RPD) should be less than 20%. If either the original or duplicate sample concentration is less than 5 times the IDL, then the absolute difference between



the two concentrations should be 1 IDL or less. For soil/tissue samples, the sample concentrations must be calculated in mg/Kg units. If a duplicate RPD is outside the acceptance limits, then a corrective action form should be filled out by the analyst and the supervisor should be informed.

6.5.6.3 Matrix / Digestion Spike.

A matrix spike sample is spiked before digestion to detect losses during digestion and matrix effects on digestion efficiency. Usually the matrix duplicate and the matrix spike are performed on the same sample. The acceptance limits for spike recovery are 75% to 125%, if the original sample concentration is less than 4 times the spike added. If the original sample concentration is greater than 4 times the spike added, then there is no acceptance criteria. For soil/tissue samples, the sample concentrations must be calculated in mg/Kg units, including the spike added. If the matrix spike recovery is outside the acceptance limits, then a corrective action form should be filled out by the analyst, and the supervisor should be informed.

6.5.6.4 References.

A reference sample is a sample of known and/or certified analyte concentrations, which is digested with a group of samples to verify digestion recovery in the appropriate matrix. Water, soil, and tissue references are used. The recovery acceptance limits are 80% to 120% for a water reference, and for a soil reference the certified ranges are used as recovery limits. For soil/tissue samples, the reference concentrations must be calculated in mg/Kg units. If the recovery is outside the acceptance limits, then a corrective action form should be filled out by the analyst, and the supervisor should be informed.

6.6 Daily End of Analysis Run Procedures

6.6.1 ICP Shutdown.

6.6.1.1 Rinse the uptake system with DI water for 10 minutes.

6.6.1.2 Extinguish the plasma by slowly turning down the RF "power" knob down, turn the automatic power control to manual as power begins to drop; if the reflected power alarm sounds push the reset button. Push the blue RF off button. Turn on the auxiliary argon toggle and turn up the flow to 3.0 L/min.

6.6.1.3 After allowing 10 minutes to cool the torch, turn off the peristaltic pump, loosen the pump bed clamps and watch the air space following the DI water move through the tubing: It should move smoothly, if not a tubing connector clog or nebulizer clog could be indicated.

6.6.1.4 Prepare the autosampler for a power-down by moving the the probe "home:" at the command line type MH. Turn off the autosampler power switch at the bottom left back panel.

6.6.1.5 Turn off the cooling water. Turn off the argon supply at the back right side of the ICP, turn off the mass flow controller and turn off all argon toggles on the front right panel.



6.6.2 Data storage

6.6.2.1 Place the appropriate day of the week diskette in disc drive A.

6.6.2.2 From the ThermoSpec main menu, choose Operation / Analysis / type (method name)/ type xp"command" (to access DOS).

6.6.2.3 At the DOS prompt, type BACK, then <enter>. The computer will display filenames as they are copied.

6.6.2.4 After this is complete, at the DOS prompt type EXIT (to return to ThermoSpec software). Also, eject the diskette from disc drive A.

6.6.2.5 Turn off the printer, the monitor and then the computer.

6.7 Torch Replacement.

6.7.1 ICP Glassware Cleaning. Follow the ICP glassware cleaning instructions as described in section 6.11.1.

6.7.2 Assembling the Glassware.

6.7.2.1 Reassemble the torch body and tip using a very light application of silicone grease on the ground glass joints, and then secure with small rubber bands around the glass nlbs.

6.7.2.2 Attach the tesla coil wiring loop to the top argon side-arm of the torch, and attach the argon lines (labelled top and bottom) to the appropriate side-arms of the torch after replacing the rubber tubing connectors with new rubber tubing.

6.7.2.3 Check that the nebulizer is thoroughly dry and examine the glass inside the nebulizer with a magnifier for clarity.

6.7.2.4 Check that the baffle in the spray chamber is 2 1/4 inches from the end before carefully attaching the nebulizer; this is a tight fit so care should be taken to avoid bending the intake capillary on the nebulizer. Also, orient the nebulizer label "top" correctly.

6.7.2.5 Using a very light application of silicone grease on the ground glass joint, connect the spray chamber to the torch using the spring clamp.

6.7.2.6 Position the torch in the center of the copper work coil. Set the height of the inner concentric at 3 to 4 mm below the coil; adjust the spray chamber tray height if necessary. Notice that the height will change as the yoke around the upper torch and as the spray chamber clamp are tightened.

6.7.2.7 Observe the torch and spray chamber as a unit. The unit should be straight from the top of the torch to the top of the spray chamber, or conversely, the joint between the spray chamber and the torch body should not be bent.



6.7.3 Initial lighting. Light the torch and observe any unusual effects. If the torch lighting is particularly difficult, then the torch position may need adjustment. Allow the usual warm-up of 30 to 45 minutes.

6.7.4 Optimizing the torch position.

The torch position is critical to trace metals ICP analysis. Different torch positions will be optimized for different elements; if the torch position is kept as consistent as possible, then IEC accuracy and IDLs should remain constant.

6.7.4.1 Profile with the mercury channel.

6.7.4.2 Start a manual Cd profile with an 8 mg/L cadmium solution, optimizing the signal on the meter on the controller panel by turning the horizontal adjustment micrometer (using the bottom knob) on the D mirror mount. The D mirror micrometer is located in the top right side of the torch compartment, accessed through the right side door. To minimize retinal exposure to UV, use UV protective eyeglasses and use the offset dental mirror to read the micrometer

6.7.4.3 To optimize the verticle position, review the last torch change to find the range of micrometer settings that should be measured for cadmium S/N (if a different torch body is used, then a wider range of settings could be measured). Set the verticle adjustment micrometer (using the top knob) to the lowest micrometer setting required by turning down to at least 20 units below the setting, then back up to the required setting in one movement. Using the CDVERT method, take a measurement of the 8 mg/L cadmium solution at each micrometer setting.

6.7.4.4 For the next required setting, dial directly up to the setting; avoid dialing up and down in short increments as poor micrometer accuracy will result. Take a cadmium reading at each setting.

6.7.4.5 Rinse for 10 minutes. Aspirate blank solution and take the same measurements, as with cadmium, starting at the lowest micrometer setting.

6.7.4.6 Calculate S/N for each micrometer setting, the 8 mg/L cadmium intensity divided by the blank intensity, then plot the verticle micrometer setting vs the S/N for each setting. From this graph, find the peak to determine the optimum verticle micrometer setting.

6.7.4.7 Set the micrometer to this optimum setting. Fill out the ICP instrument logbook with the optimization data. File the raw data and graph in the torch position optimization file.

6.7.4.8 Run a standardization. Compare the slope for each element to previous ones in the standardization file; especially the standardization prior to the torch change, and also the standardizations immediately after previous torch changes. The slopes should be within 15 % of previous values. The performance of the QC solutions will dictate the slope acceptance limits.



6.8 Background Correction.

Background correction is required for many elements due to background interferences. Single element solutions at or near the top of the linear range are scanned. The resulting intensity vs. wavelength plots display that background will vary depending on the elements present or matrix of the sample. Overlays of the plots reveal where background correction points can be set with minimal interference. One effect other elements have on a given analyte is a constant elevation of the background continuum emission spectrum. It is virtually impossible to set a background correction position(s) free from line interferences. Also, the use of numerous background correction positions must be limited as the analysis time can become unacceptably time consuming. The best compromise is to choose a background correction position(s) that is optimized for the major elements' interferences: aluminum, calcium, iron, magnesium, manganese and sodium. The background correction positions we use are +11, +18 and -18 spectrum shifter units. No background correction is required for lithium and strontium.

6.9 Inter-element correction factors and Linear limit verification.

6.9.1 Inter-element correction factors.

Due to the spectral complexity of emission spectra, spectral overlap must be identified and corrected by the appropriate factors. These inter-element correction factors (IECs) are checked quarterly for each element. After each torch change the IECs are checked for the eight most common interferent elements: Al, As, Ca, Cr, Fe, Mg, Pb and V. The extent of spectral overlap is determined by analyzing an ICP grade single element standard and identifying apparent concentrations of other elements. The apparent concentrations should be at least positive 2 IDL or negative 2 IDL to be considered significant. ICP grade standards must be at least 99.9 % purity, ideally 99.999 % purity. The concentration of the standards for IEC determinations is at the linear limit as this maximizes the potential to detect minor interferences. For some of ARI's early IEC determinations, three levels of each element were analyzed and the IECs were determined to be linear. Provided the concentration of the standard is within 5% of true value, the apparent elements' concentrations are divided by the true value of the standard to determine the IEC (usually an EXCEL spreadsheet is used for IEC calculations). The IEC data is compared to previous determinations, to spot any discrepancies; any new apparent concentration is considered a possible standard contaminant. If contamination is suspected, first check the Inorganic Ventures standard certificate to find out if this is a known contaminant. If not, reprepare the standard and reanalyze. If the possible contaminant is confirmed again, then depending on the magnitude of the IEC, a new lot of stock standard may be required. The tabulated IECs are loaded into the current methods and the method is printed. The IEC entries are verified by the supervisor. File the raw data in the IECs and linear ranges file, and the method in the ICP methods file.

6.9.2 Linear Ranges.

ICP is a method known for its wide dynamic range. Linear ranges were first determined when the ICP was initially set up using three or more levels for each element and constructing a graph of true value vs read value. The linear limit was set at the



concentration at which the curve deviated 2 to 3% (see table 6). Linear limits are verified at least quarterly, simultaneously with IEC checks, by analyzing each element at the linear limit and verifying that the concentration at the linear limit is linear, within 5 % of the true value. File the raw data in the IECs and linear ranges file.

6.10 Detection Limits.

6.10.1 Instrument Detection Limits.

The instrument detection limit (IDL) is determined quarterly for each element as described by CLP protocols. A multi-element IDL solution is prepared at 3 to 5 times IDLs, and analyzed as a sample seven times each day on three non-consecutive days. The standard deviation is calculated for each element on each day, and the sum of the three days' standard deviation is the IDL. In actuality, the IDL determination for most elements is below our conservatively stated IDLs (see table 6 and the IDL file).

6.11 Maintenance.

All maintenance, except daily maintenance, should be noted in the ICP maintenance logbook in the appropriate section.

6.11.1 Daily Maintenance.

Clean all of the sample uptake lines' connectors and the nebulizer intake capillary of clogs (use the cleaning wire and a fine tip deionized water bottle). Lightly wipe the exposed rails of the ICP autosampler with a dry kimwipe to remove dust and corrosion. Also wipe the autosampler probe holder with a damp kimwipe to remove dust.

6.11.1 ICP glassware cleaning.

The torch tip is changed as needed, typically every two months. Orange deposits accumulate on the tip resulting in increased carry-over effects. Two torch bodies have custom matched tips to minimize the time required to replace the torch and optimize the torch position; this is important as IECs and IDLs could be dependent on a consistent torch position. Used torch tips are sent to Precision Glassblowing of Colorado for re-tipping. In-house cleaning with hydrofluoric acid can be performed, but the inherent damage to the tip surface results in decreased usage before new deposits adsorb. The torch and the spray chamber are cleaned in an ultrasonic bath with dilute Citranox followed by an acid soak in 10% nitric acid and 10% hydrochloric acid, followed by deionized water rinsing. The nebulizer, after the o-ring is removed, is also cleaned in the ultrasonic bath with dilute Citranox, followed by deionized water rinsing. Thoroughly dry the torch in a drying oven and thoroughly dry the nebulizer using argon and kimwipes; it is not necessary to dry the spray chamber. See torch replacement section 6.7.

6.11.2 Autosampler.

The autosampler requires daily wiping of the exposed metal rails; the slightest amount of dust or corrosion can cause the rails to bind against the probe holder. Weekly, the inside rails and the outside rails are lubricated with a teflon containing grease.



6.11.3 Peristaltic Pump.

The blue-yellow tubings of the peristaltic pump are replaced at the same time as the weekly autosampler maintenance. Wipe the outer surfaces of the pump with water and kimwipes.

6.11.4 Air Filters.

When the torch is replaced, two screen filters on the high voltage power supply and one large air filter on the RF power supply (both on the back of the ICP) are cleaned with warm water. Air dry and dry with paper towels before replacing.

6.11.5 Entrance slit.

The entrance slit is located to the left of the mercury lamp in a grooved slot. Pull the entrance slit up and out of the slot, then clean it with a strong blast of argon or compressed air along its entire length.

7.0 Review

ICP data is reviewed by the analyst periodically during the sample analysis run. For each sample, the raw data printout is highlighted with the client requested elements. The raw data is reviewed for high levels, carry-over, poor precision, method blank contamination and any anomalies. The QC samples are reviewed to check the QC limits.

7.1 Raw Data Review

Look through the raw data printout, highlighting the requested elements of every client sample. Note on the raw data any comments on instrument problems, delays, unusual occurrences, etc. Check for all the potential problems listed in section 6.4.3. Especially check the instrument QC checks, matrix duplicates RPD, matrix spike %R, and reference recoveries, as described in section 6.5.

7.2 ICP Sample Logbook Review

Xerox the appropriate ICP sample logbook pages which correspond with the raw data. Check every sample label (job number, sample letter, precode) and dilution factor. Highlight the client sample edits, sample analysis deletions, and dilution factor edits so they are not missed during the data loading process.

7.3 QC Samples Review

Check QC samples as described in section 6.5

7.4 Samples Review

7.4.1 Precision Criteria

For elements that occur in samples at high concentration levels, the RSD of the three or four exposures (three or four depending upon which ICP method is being used) should not exceed about three percent. RSD values of one and a half percent or less are



typical. For elements that occur in samples at low concentration levels, nominally at 10 times the IDL and below, the SD should not be much greater than the IDL. The typical SD on low samples varies with each element, but most run at about half the IDL.

7.4.2 Carry-over

Examination of the data could show that a sample containing a significantly lower concentration of an element than the previous sample has carry-over. The symptom of carry-over to look for is the concentration result decreasing throughout the three or four exposures. The RSD will sometimes be higher than normal in these cases. Samples that are affected by possible carry-over should be rerun.

7.4.3 Linear Range.

All acceptable samples results must be less than the specified linear range for each element in the sample. The ICP system software checks automatically for results greater than the current linear range and will flag the data with an "H". Samples that have analyte concentrations greater than the linear range should be diluted and rerun.

7.4.4 Inter-element Correction Factors.

In all samples, it is important to look for inter-element correction factors that may need slight adjusting. A good way to spot potential problems is to look for samples that contain high levels of one element, and low amounts of other elements. Any other elements that have concentrations that are negative lower than one IDL could indicate that an IEC of the high element needs adjustment. This is especially true if the high element already has an IEC on the affected element. Notify the analyst and the supervisor of the potential problem so it can be checked.

8.0 Quality Control

See section 6.5 for the QC limits specific to each QC solution or QC sample.

9.0 Corrective Actions

9.1 Standardization.

If the standardization does not meet the criteria in section 6.3.2.4, then corrective action should be taken before proceeding with re-standardization. This could involve uptake rate optimization, optics profiling, re-preparation of standardization standards, etc.

9.2 QC solutions.

If a QC solution is out of control, then corrective action should be taken before proceeding with analysis. This could involve re-preparation of standardization standards and re-standardization, analysis of an alternate independent QC solution, re-standardization of the blank (resetting the baseline), etc.

9.3 Instrument malfunctions.

When instrument malfunctions occur, consult with other experienced ICP operators or the supervisor for guidance. The maintenance logbook and the service manual could be helpful for troubleshooting.



10.0 Miscellaneous Notes and Precautions

10.1 Contamination.

ICP low detection limits require that contamination potential be minimized. The samples preparation area should be kept clean and the autosampler should be wiped regularly. Standards should be segregated from samples, blank solution and QC solutions. Dedicated pipet tips and beakers should be clearly identified.

10.2 Clogs.

The uptake lines should be monitored for clogs, which may form from minute sample particulates and due to the nature of the open autosampler vials.

10.3 Autosampler.

The autosampler should be monitored for probe misses and tubing disconnections. The time that the torch is running without any aerosol should be minimized.

10.4 Argon Supply.

During an argon dewar change or during the automatic switching from an argon dewar to compressed argon tanks, the torch may be extinguished. If this occurs, re-light the torch and continue analysis after a 15 minute warm-up period.

11.0 Method References

USEPA SW-846 Method 6010A

12.0 Appendices

12.1 TJA ICAP61 specifications

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Appendix

12.1 TJA ICAP61 Specifications

ICP STANDARDIZATION STANDARDS
ALL CONCENTRATIONS IN mg/L

STD 2	STOCK CONC	FINAL CONC	STD 4	STOCK CONC	FINAL CONC
Ba	500	10.00	Mo	500	10.00
Ca	500	10.00	Sb	500	10.00
Cd	500	10.00	Si	500	10.00
Co	500	10.00	Sn	500	10.00
Cr	500	10.00	Ti	500	10.00
Cu	500	10.00			
Li	500	10.00			
Mn	500	10.00			
V	500	10.00			

STD 3	STOCK CONC	FINAL CONC	STD 5	STOCK CONC	FINAL CONC
Ag	5	1.00	Fe	2500	100
Al	500	10.00	K	2500	100
As	500	10.00	Na	2500	100
B	500	10.00			
Be	500	10.00			
Fe	500	10.00			
Mg	500	10.00			
Na	500	10.00			
Ni	500	10.00			
Pb	500	10.00			
Se	500	10.00			
Sr	500	10.00			
Tl	500	10.00			
Zn	500	10.00			

TABLE 1

ICP CALIBRATION VERIFICATION SOLUTION (CV)
 FROM INORGANIC VENTURES
 1/100 DILUTION OF AR-A-3 AND AR-B-3

ELEMENT	CONC mg/L	ELEMENT	CONC mg/L
Ag	1.00	Mn	1.00
Al	5.00	Mo	1.00
As	5.00	Na	5.00
B	1.00	Ni	1.00
Ba	1.00	Pb	5.00
Be	1.00	Sb	5.00
Ca	5.00	Se	5.00
Cd	0.50	Si	2.00
Co	1.00	Sn	1.00
Cr	0.50	Sr	1.00
Cu	0.50	Ti	1.00
Fe	2.00	Tl	5.00
K	50.00	V	1.00
Li	1.00	Zn	1.00
Mg	5.00		

TABLE 2

APG TRACE METALS SOLUTION 7879

ICP QC SOLUTION

LOT#12286-12288

	TRUE VALUE mg/L	95% CONFIDENCE INTERVAL mg/L	
Ag	0.3029	0.2623 -	0.3381
Al	0.3903	0.3036 -	0.4495
As	0.2502	0.2219 -	0.2909
B	0.9896	0.909 -	1.042
Ba	2.005	1.777 -	2.172
Be	0.3769	0.3443 -	0.409
Cd	0.2769	0.2432 -	0.3024
Co	0.4197	0.3737 -	0.4759
Cr	0.1617	0.1306 -	0.1863
Cu	0.2425	0.2207 -	0.2635
Fe	0.5047	0.4416 -	0.5718
Hg	0.00286	0.00186 -	0.00434
Mn	0.2377	0.2118 -	0.2608
Mo	0.4221	0.3515 -	0.4722
Ni	0.259	0.2282 -	0.2831
Pb	0.3122	0.2863 -	0.345
Sb	1.678	1.574 -	2.016
Se	0.1145	0.0889 -	0.1505
Tl	0.7094	0.5692 -	0.7945
V	1.825	1.67 -	1.947
Zn	0.1642	0.1445 -	0.1907

TABLE 3

SPEX ICP QC SOLUTION: ICP-1
PREPARED AT 1/4 DILUTION OF CERTIFIED TRUE VALUE

	TRUE VALUE mg/L	95% CONFIDENCE INTERVAL mg/L
As	1.00	0.85 - 1.11
Be	1.00	0.85 - 1.13
Ca	1.00	0.85 - 1.29
Cd	1.00	0.84 - 1.12
Co	1.00	0.9 - 1.09
Cr	1.00	0.89 - 1.11
Cu	1.00	0.91 - 1.07
Fe	1.00	0.91 - 1.1
Li	1.00	data not available
Mg	1.00	0.87 - 1.14
Mn	1.00	0.93 - 1.06
Mo	1.00	0.78 - 1.17
Ni	1.00	0.88 - 1.09
Pb	1.00	0.88 - 1.1
Sb	1.00	0.83 - 1.24
Se	1.00	0.8 - 1.14
Sr	1.00	0.85 - 1.17
Ti	1.00	0.9 - 1.09
Tl	1.00	0.81 - 1.15
V	1.00	0.91 - 1.09
Zn	1.00	0.91 - 1.08

SPEX ICP QC SOLUTION: ICP-2

	TRUE VALUE mg/L	95% CONFIDENCE INTERVAL mg/L
Ag	0.50	0.44 - 0.56
Al	1.00	0.87 - 1.1
B	1.00	data not available
Ba	1.00	0.89 - 1.07
K	10.00	8.75 - 11.1
Na	1.00	0.83 - 1.47
Si	5.00	data not available

TABLE 4

CLP ICP CHECK SOLUTIONS
FROM INORGANIC VENTURES SINGLE ELEMENT STOCK

CRI: CRDL STANDARD

ELEMENT	CONC mg/L	ELEMENT	CONC mg/L
Ag	0.02	Ni	0.08
As	0.02	Pb	0.006
Be	0.01	Sb	0.12
Cd	0.01	Se	0.01
Co	0.1	Tl	0.02
Cr	0.02	V	0.1
Cu	0.05	Zn	0.04
Mn	0.03		

ICSA: INTERFERENT CHECK

ELEMENT	CONC mg/L
Al	500
Ca	500
Fe	200
Mg	500

ICSAB: INTERFERENTS WITH ANALYTES CHECK

ELEMENT	CONC mg/L	ELEMENT	CONC mg/L
Al	500	Ag	1.00
Ca	500	Ba	0.50
Fe	200	Be	0.50
Mg	500	Cd	1.00
		Co	0.50
		Cr	0.50
		Cu	0.50
		Mn	0.50
		Ni	1.00
		Pb	1.00
		V	0.50
		Zn	1.00

TABLE 5

ICP LINES AND THEIR CHARACTERISTICS
THERMO JARRELL ASH ICAP61

ELEMENT	EMISSION LINE nm	IDL mg/L	LINEAR LIMIT mg/L
Ag	328.068	0.003	40
Al	308.215	0.02	750
As	197.197	0.05	750
B	249.678	0.006	500
Ba	455.495	0.001	300
Be	313.042	0.001	20
Ca	317.933	0.01	500
Cd	228.802	0.002	150
Co	228.616	0.003	300
Cr	267.716	0.005	500
Cu	324.754	0.002	60
Fe	259.94	0.005	
Fe	271.441		500
K	766.491	0.4	500
Li	670.784	0.004	100
Mg	279.079	0.02	750
Mn	257.61	0.001	80
Mo	202.03	0.005	150
Na	588.995	0.01	
Na	330.298		5000
Ni	231.604	0.01	50
Pb	220.353	0.02	500
Sb	206.838	0.05	275
Se	196.022	0.05	300
Si	288.158	0.02	100
Sn	189.989	0.01	75
Sr	421.552	0.001	100
Ti	334.941	0.005	50
Tl	190.864	0.05	250
V	292.402	0.002	30
Zn	213.856	0.004	100

TABLE 6

1.1 ICAP 61 TECHNICAL SPECIFICATIONS

Optics: 0.75 ^m~~mm~~ Rowland Circle, Paschen-Runge mount. 1510 or 2400 grooves/mm ruled grating at 500 nm.

	1510 g/mm grating	2400 m/mm grating	
Linear Dispersion:	0.84 nm/mm 0.42 nm/mm, 0.28 nm/mm	0.53 nm/mm 0.26 nm/mm	first order second order third order
Resolution:	.048 nm .024 nm .016 nm, third order	0.031 nm 0.015 nm	first order second order
Wavelength Range:	190-800 nm 170-800 nm (Special channels are available for K, Li and Na determinations with 2400 g/mm grating.)	190-500 nm 170-500 nm	Air Vacuum

Dynamic Range (electronics): > 8 X 10⁶

Variable Wavelength Channel: 0.5 meter Ebert.
190-900 nm.

Internal Standards: Up to 7 maximum.

Background Correction: 63 available steps on a computer controlled scanning refractor plate covering a 0.5 nm range, (1st order).

Source: 2.5 kw R.F. generator operating at 27.12 MHz with automatic power control and automatic tuning. Housed in spectrometer cabinet.

Nebulizer: Cross-flow pneumatic.

Torch: Quartz

Argon Consumption: 10-15 lpm. Constant flow control.

Coolant Water Flow: 0.4 lpm minimum.

Electrical Requirements: Spectrometer: 220 volt, single phase, 50/60 Hz
R.F. Generator: 220 volt, three phase, 50/60 Hz

Dimensions: Spectrometer: 63.5"(161 cm)W X 62"(158 cm)H X 45"(114 cm)D.

DATA ACQUISITION SYSTEM

Controller: Microcomputer controlled individual integrators with multiplexed A/D converter.

User Interface: Thermo Jarrell Ash ThermoSPECTTM Spectrometer Operation System, running on either an IBM PC-AT or an IBM Personal System 2 computer.

Power requirements: 110V, 3A, 50/60 Hz single phase



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Standard Operating Procedure

Ferrous Iron (Fe^{2+})
Method 3500 Fe D - (United States Air Force)

600S

Revision 1

3/31/94

PROPRIETARY

Prepared By:

McLukin

Approvals:

Jay Kuhn
Section Manager

Don R. Baker
Laboratory Manager

Michelle J. Turner
Quality Assurance Manager

Mark W. Turner
Laboratory Director

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Standard Procedure

Ferrous Iron (Fe^{2+})

600S

Revision 1

3/31/94

Prepared By:

McPike

Approvals:

Jay Kuhn ngt
Section Manager

Don V. Luber
Laboratory Manager

Michelle J. Turner 4/1/94
Quality Assurance Manager

Mark V. ...
Laboratory Director



STANDARD OPERATING PROCEDURE FERROUS IRON (Fe^{2+})

METHOD: COLORIMETRIC, PHENANTHROLINE

RANGE: 0.04 - 2.0 mg Fe^{2+} /liter (undiluted)

HOLDING TIME: ASAP (<24 hours)

PRESERVATIVE: Collect in clean acid rinsed 250ml amber glass bottles containing 5 mL concentrated HCl (2mL/ 100 mL sample). Avoid atmospheric contact and keep samples in dark.

1.0. Scope and Application

Iron in natural waters may exist in either the ferrous (Fe^{2+}) or ferric (Fe^{3+}) oxidation state. Well oxygenated surface waters usually have iron in the ferric state predominantly as insoluble particulate and colloidal complexes with dissolved iron concentrations generally <1 mg/L. Ferrous iron is more typical in ground waters and/or waters which are highly reducing. Ferrous iron is rapidly oxidized to ferric iron and its complexes upon exposure to air.

The colorimetric phenanthroline method is specific for Fe^{2+} . Ferrous iron forms an orange-red cheleated complex (3 molecules phenanthroline per atom of iron) with 1,10-phenanthroline in a pH range of 3.0 - 3.5. Phenanthroline must be present in excess for the following protocol. Measured concentrations must be less than 2.0 mg/L for the conditions outlined. Absorbance of the colored solution is measured at 510 nm in a 1cm cell.

2.0. Definitions

N/A

3.0. Supplies and Equipment

3.1. Glassware

Volumetric flask (100 mL)
50 mL, graduated Folin tubes
pipettors and tips
Spectrophotometer fitted for 1 cm cuvette.

3.2. Reagents

3.2.1. AMMONIUM ACETATE BUFFER : Dissolve 250 grams ammonium acetate ($\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$) in 150 mL DI water. Add 700 mL glacial Acetic Acid.



3.2.2. PHENANTHROLINE SOLUTION. Dissolve 100 mg 1,10-phenanthroline monohydrate ($C_{12}H_8N_2 \cdot H_2O$) in 100 mL DI. Add 2 drops concentrated HCl and mix to dissolve (slight heating if necessary). Store in amber glass bottle. Discard solution if it darkens.

3.2.3. STOCK FERROUS IRON STANDARD (200 mg /l Fe^{2+}). Carefully add 20 mL concentrated H_2SO_4 to 50 mL DI contained in a 1000 mL volumetric flask. Add 1.404 grams ferrous ammonium sulfate ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, FW= 392.13, 14.24% Fe) and mix to dissolve. Dilute to 1000 mL with DI and mix. Store in tightly capped amber glass bottle away from direct light. Do not use the permanganate oxidation as described in SM as this will convert Fe^{2+} to Fe^{3+} . Verify that there is no precipitation in the standard bottle before use. If there is, you must prepare a new stock solution. Intermediate and calibration verification standards must be prepared fresh with each days use.

3.2.3.1. Intermediate Iron Standard (10 mg /l Fe^{2+}). Add 5 mL stock iron solution to a 100 mL volumetric flask and dilute to volume. Prepare fresh daily and store in a tightly capped amber glass bottle. Avoid any unnecessary exposure to the atmosphere.

3.2.3.2. Calibration verification standard (1.00 mg/L Fe^{2+}). This is a standard which will be used to verify the performance of the standard curve for estimating sample concentrations. The verification standard should be prepared from the Stock Ferrous Iron Standard which is traceable back to the original weight of ferrous ammonium sulfate used in it's preparation. Add 0.5 mL of the stock iron solution to 50 mL DI water contained in a 100 mL volumetric flask, mix and dilute to a 100 mL volume. Store in a tightly capped amber glass bottle and avoid any unnecessary exposure to the atmosphere. Do not use the Intermediate Standard to prepare the verification standard!

4.0. Documentation

Ferrous Iron (Fe^{2+}) Benchsheet

5.0. In-house Modifications to Referenced Method

N/A

6.0. Procedure

6.1. Analytical sequence. Every batch run will be conducted in the following sequence:

- Step 1. Run Standard Curve
- Step 2. Run Initial Calibration Verification (ICV) standard
- Step 3. Run Initial Calibration Blank (ICB)
- Step 4. Confirm that all QC requirements are within acceptable limits
- Step 5. Process 10 analytical samples, including any duplicates, spikes and dilutions
- Step 6. Run a Continuing Calibration Verification (CCV) standard



- Step 7. Run a Continuing Calibration Blank (CCB)
Step 8. Confirm that QC requirements are within acceptable limits
Step 9. Process another 10 analytical samples
Step 10. Repeat CCV, CCB and confirmation
Step 11. End each run with a CCV, CCB

6.2. Prepare a series of Fe^{2+} standards by adding set volumes of the working standard to graduated Folin tubes and diluting to the 25 mL mark with DI. Add 20 mL phenanthroline and 5 mL ammonium acetate buffer, mix and allow 5 minutes for color development and then read absorbance at 510 nm in a 1 cm cell. Use the standard series as indicated below:

mL Intermediate Std	Final volume (mL)	Conc. (mg/L)
0.00	25	0.00
0.10	25	0.04
0.25	25	0.10
0.50	25	0.20
1.25	25	0.50
2.50	25	1.00
5.00	25	2.00

Process a calibration blank and a calibration verification standard along with the standard curve.

6.3. Enter the data for the standard curve into the computer and verify an r^2 value of at least 0.99 (a comment will appear automatically regarding the status of the r^2 value). Verify blank value less than lowest point on curve and recovery of verification standard ($\pm 10\%$ of "true value").

6.4. Mix sample and withdraw 25 mL aliquots (or dilutions to 25 mL). Add 20 phenanthroline and 5 mL buffer, mix, allow five minutes and read. Record all data including sample dilutions (expressed as mL sample/25 mL) on the benchsheet. If samples are turbid or colored, take a separate aliquot or dilution and substitute 20 mL DI for the 20 mL phenanthroline (DO NOT ADD PHENANTHROLINE!!) and use this sample as a background absorbance.

6.5. For each batch of samples or job number, process at least 1 blank, 1 duplicate and 1 spiked sample for every 20 samples analyzed. Spike at + 0.2 mg/l (add 0.5 mL of intermediate standard to 25 mL sample or dilution). Spike recoveries should be in the range of 85 to 115 %. If they fall outside of this range, dilute the sample and reanalyze. The 20 mL of phenanthroline is suitable for approximately 50 μg of iron. Therefore, if measured concentration exceeds 2 mg/l you must dilute the sample (i.e. make sure absorbencies fit within the range of the curve).



6.6. Record all data and notes on benchsheets and enter data into computer. Place a copy of the computed data reduction into every Job File run. The original is placed in chronological sequence in the Methods file.

7.0. Review

7.1. The supervisor reviews Service Request, enters information into the Conventional database and assigns samples to the analyst.

7.2. The analyst verifies Service Request, reviews the SOP and proceeds with the analysis.

7.3. The final computer generated result is placed into the method folder in chronological sequence and a copy is placed into the job folder.

7.4. The supervisor reviews the job folder for completeness of analysis (all requested parameters have been run) and sufficiency of Quality Control.

7.5. Completed analysis is given to the Data Section for final report preparation.

7.6. The final report is reviewed for accuracy and completeness and then signed by the Division Manager or other authorized person.

8.0. Quality Control

8.1. The regression coefficient, r^2 should be greater than 0.99.

8.2. Initial Calibration Verification (ICV) and Calibration Blank (ICB) must be run at the beginning of each batch. Continuing Calibration Verification standards and blanks (CCV, CCB) must be run after every ten analytical samples in the batch and at the end of each run. The calibration verification standards must agree within $\pm 10\%$ of the "true" value and the concentration of the blanks should be less than the detection limit (the lowest point on the standard curve). Record the results of CV and CB on the daily run summary benchsheets.

8.3. All sample absorbencies must fit within the range of the standard curve. Matrix spike and duplicate analyses are run with each job number or once for every 20 samples in a job.

8.3.1. Duplicate analysis. If both the original and duplicate sample concentrations are greater than 5X the detection limit, the calculated RPD should be less than 20%. If either concentration is less than 5X the detection limit, then the absolute difference between the two should be less than or equal to the detection limit. If these criteria are not satisfied, corrective actions must be taken.



8.3.2. Matrix Spikes. The acceptance limits for matrix spike recoveries are $\pm 25\%$ if the original concentration is less than 4X the spike concentration added. If the original concentration is greater than 4X the added spike level, the spike is invalid and must be repeated.

9.0. Corrective Actions

9.1. If r^2 is less than 0.99, new calibration standards must be prepared and the calibration repeated. The supervisor will be notified and no samples will be processed if this condition is not satisfied.

9.2. If Initial Calibration Verification (ICV) and Initial Calibration Blank (ICB) are out of QC limits, new calibration standards or new ICV solution should be made. If the Continuing Calibration Verification (CCV) and Continuing Calibration Blank (CCB) are out of QC limits, all samples between the last in control condition and the out of control condition must be re-run. All samples in any batch run must be bracketed by in control verification standards.

9.3. After the above two corrective actions, if the results are still outside the limits, the supervisor will review the entire procedure with the analyst to verify that correct procedures are being followed or check the instrument to make sure it is working properly.

9.4. Any sample having its absorbance greater than the highest point on the standard curve will be diluted and rerun. If the absorbance is less than the lowest point on the curve, that sample will be flagged as being less than the lowest standard concentration. If RPD or matrix spike recoveries are outside the prescribed limits, the analysis will be repeated to confirm the outlying condition. The sample analysis will be flagged and reported in the final report to the client.

9.5. If any of the following situations arises, the supervisor will be immediately notified and the project manager be informed for resolution with the client:

Samples have exceeded holding times.

Samples have been improperly preserved.

There is insufficient sample to run the analysis.

10.0. Miscellaneous Notes and Precautions

N/A

11.0. Method Reference

Standard Method for the Examination of Water and Wastewater. 1992. 18th ED. Method 3500-Fe.D.

12.0 Appendices

N/A

Ferrous Iron (Fe^{2+})
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FERROUS IRON (Fe +2) BENCHSHEET
1,10-phenanthroline colorimetric

DATE: _____
 ANALYST: _____

CALIBRATION DATA

Ferrous ammonium sulfate Stock Soln				Intermediate Std (Prepare fresh)	
Fe(NH ₄) ₂ (SO ₄) ₂ • 6H ₂ O	1.404 grams			mL stock =	5
volume =	1000 mL			volume =	100 mL
Conc =	200 mg/L Fe+2			Conc =	10.0 mg/L Fe+2
Prep Date: _____					

Standard Curve Data				Regression Data	
ml inter. Std to 25 mL	CONC (mg/L)	Absorbance (510 nm, 1cm cell)		AVG	CONC = (ABS-a)/ b
0.00	0.00			#DIV/0!	intercept = #DIV/0!
0.10	0.04			#DIV/0!	slope = #DIV/0!
0.25	0.10			#DIV/0!	r ² = #DIV/0!
0.50	0.20			#DIV/0!	Comment: #DIV/0!
1.25	0.50			#DIV/0!	
2.50	1.00			#DIV/0!	
5.00	2.00			#DIV/0!	

Calibration Verification Standard					
Source	in house			Stock Conc =	200 mg/L Fe+2
Dilution	0.50	ml stock to	100	mL =	1.00 mg/L Fe+2

SAMPLE DATA

SAMPLE ID	SAMPLE DILUTION	ABS	Bkg ABS	CONC (mg/l)	ORIG CONC (mg/l)	NOTES
ICB	1		0.000	#DIV/0!	#DIV/0!	
ICV	1		0.000	#DIV/0!	#DIV/0!	#DIV/0!
	1		0.000	#DIV/0!	#DIV/0!	
	1		0.000	#DIV/0!	#DIV/0!	
	1		0.000	#DIV/0!	#DIV/0!	
	1		0.000	#DIV/0!	#DIV/0!	
	1		0.000	#DIV/0!	#DIV/0!	
	1		0.000	#DIV/0!	#DIV/0!	
	1		0.000	#DIV/0!	#DIV/0!	
	1		0.000	#DIV/0!	#DIV/0!	
	1		0.000	#DIV/0!	#DIV/0!	
	1		0.000	#DIV/0!	#DIV/0!	
	1		0.000	#DIV/0!	#DIV/0!	
OCB	1		0.000	#DIV/0!	#DIV/0!	
CCV	1		0.000	#DIV/0!	#DIV/0!	#DIV/0!
	1		0.000	#DIV/0!	#DIV/0!	
	1		0.000	#DIV/0!	#DIV/0!	
	1		0.000	#DIV/0!	#DIV/0!	
	1		0.000	#DIV/0!	#DIV/0!	
	1		0.000	#DIV/0!	#DIV/0!	
	1		0.000	#DIV/0!	#DIV/0!	
	1		0.000	#DIV/0!	#DIV/0!	
	1		0.000	#DIV/0!	#DIV/0!	
OCB	1		0.000	#DIV/0!	#DIV/0!	
CCV	1		0.000	#DIV/0!	#DIV/0!	#DIV/0!



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Standard Operating Procedure

Metals Preparation
Method 3020 (TWN)

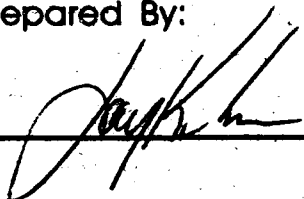
505S

Revision 3

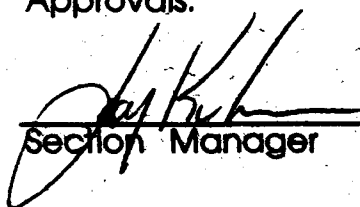
5/5/94

PROPRIETARY

Prepared By:



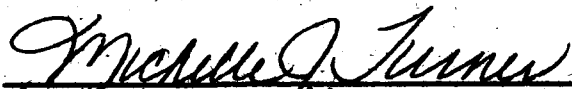
Approvals:



Section Manager



Laboratory Manager



Quality Assurance Manager



Laboratory Director

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Standard Operating Procedure - Metals

SW-846 Method 3020

ARI Prep Code: TWN

1.0 Scope and Application

This is the digestion method identified in the SW-846 USEPA Solid Waste manual as Method 3020. It is intended for preparing waste water samples and liquid wastes that contain suspended solids for analysis by graphite furnace atomic absorption spectroscopy (GFAA). Samples prepared by this method will be labeled with the preparation code "TWN".

2.0 Definitions

N/A

3.0 Equipment

- 3.1 Beakers, 150 mL.
- 3.2 Watch glasses, 65 mm flat and 75 mm ribbed.
- 3.3 Concentrated nitric acid (HNO_3 70%): Use trace metal grade nitric acid that has been lot QC checked.
- 3.4 Hot plate
- 3.5 Polyethylene bottles, 125 mL: Use only acid-rinsed HDPE bottles.

4.0 Documentation

- 4.1 Water Sample Digestion Log.

5.0 Inhouse Modifications to Referenced Method

N/A

6.0 Procedures

- 6.1 Fill out digestion log, entering header information, prep. code, date, analyst name, SOP revision date, sample number, and beaker number.



- 6.2 Transfer 100 mL of sample to a 150 mL beaker.
 - 6.2.1 Using pH paper, verify that the sample has been preserved properly ($\text{pH} \leq 2$), and mark digestion log with a check mark. If the sample has not been preserved, add appropriate preservative. (See section 9.1)
 - 6.2.2 Mix the sample thoroughly before transferring.
 - 6.2.3 Tare an empty beaker and add 100.0 g of sample. Record exact amount on digestion log.
- 6.3 Add 3 mL of concentrated HNO_3 .
- 6.4 Cover with a ribbed watch glass and digest on a hot plate.
 - 6.4.1 Evaporate the sample down to a volume of 5 mL.
 - 6.4.2 Do not boil the sample.
 - 6.4.3 Do not allow any part of the bottom of the beaker to dry. If the beaker does go dry, see section 9.2.
- 6.5 Cool the sample.
- 6.6 Add 3 mL of concentrated HNO_3 .
- 6.7 Cover with a flat watch glass and return to the hot plate.
 - 6.7.1 Increase the heat on the hot plate to gently reflux the sample.
 - 6.7.2 Continue heating, adding acid as necessary, until the digestion is complete. This is generally indicated when the digestate is light in color or does not change in appearance with continued refluxing.
- 6.8 Cover with a ribbed watch glass and continue heating.
 - 6.8.1 Evaporate down to a volume of 3 mL.
 - 6.8.2 Do not allow the sample to boil.
 - 6.8.3 Do not allow any part of the bottom of the beaker to dry. If the beaker does go dry, see section 9.2.
- 6.9 Add 10 mL deionized water and warm for 10 - 15 minutes.
- 6.10 Cool the sample.
- 6.11 Prepare a polyethylene bottle.
 - 6.11.1 Use an acid-rinsed HDPE bottle.
 - 6.11.2 Label the bottle with the sample number.
 - 6.11.3 Mark the bottle with the preparation code "TWN".



- 6.12 Dilute to 100 mL with deionized water.
- 6.12.1 Tare a labeled, empty, acid-rinsed HDPE bottle on the balance.
 - 6.12.2 Rinse the digested sample into the bottle.
 - 6.12.3 Add enough deionized water to make 100.0 g total weight, and record the exact amount added on the digestion log.
- 6.13 Centrifuge the sample.
- Alternatively, allow the sample to settle overnight. This step is unnecessary if there are no insoluble materials.
- 6.14 Take digested samples to the instrument lab and record in the appropriate logbook.
- 7.0 Review**
- 7.1 Verify that all information has been properly entered in the digestion log.
 - 7.2 All unused space in the digestion log must be crossed out and initialed by the analyst.
- 8.0 Quality Control**
- 8.1 All quality control samples are assigned by the supervisor/manager when samples are logged into the metals data base.
 - 8.2 Verify the following:
 - 8.2.1 Method blanks are processed with each analytical batch, or every twenty samples, as assigned on the Sample Log Form.
 - 8.2.2 Other QC samples, spikes, duplicates, and reference materials are processed as assigned on the Sample Log Form.
- 9.0 Corrective Actions**
- 9.1 If samples were not preserved properly, adjust to $\text{pH} \leq 2$ with nitric acid according to the Sample Preservation SOP.
 - 9.2 If a beaker goes dry, notify the supervisor/manager and reprep the sample.
 - 9.3 Any unusual sample or problem that arises must be noted on the digestion log or on an Analyst Notes Form and also brought to the attention of the supervisor/manager.



10.0 Miscellaneous Notes and Precautions

- 10.1 Concentrated acids are very dangerous. Follow proper safety procedures according to the ARI Chemical Hygiene Plan. Always wear gloves, eye protection, and a lab coat.

11.0 Method References

- 11.1 USEPA, Test Methods for Evaluating Solid Waste, SW-846, Volume IA, Method 3020, July 1992.

12.0 Appendices

N/A

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Standard Operating Procedure

Metals Preparation
Method 3050 (SWC)

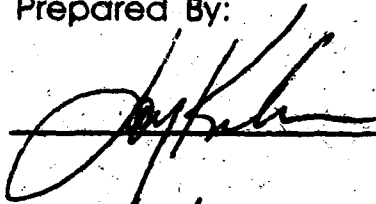
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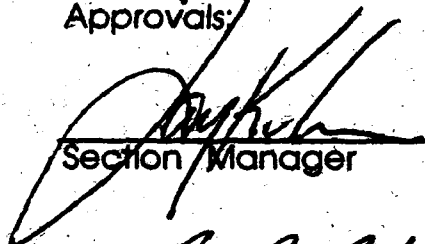
5/5/94

PROPRIETARY

Prepared By:



Approvals:



Section Manager

 5/11/94

Laboratory Manager



Quality Assurance Manager



Laboratory Director

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Standard Operating Procedure - Metals

SW-846 Method 3050

ARI Prep Code: SWC

1.0 Scope and Application

This is the sediment digestion procedure identified in the SW-846 USEPA manual as Method 3050. It is intended for preparing soil, sludge, and sediment samples for analysis by either flame atomic absorption spectroscopy (FLAA) or by inductively coupled argon plasma spectroscopy (ICP). This is also the digestive use when antimony is being analyzed by graphite furnace atomic absorption (GFAA). Samples prepared by this method will be labeled with the preparation code "SWC".

2.0 Definitions

N/A

3.0 Equipment

- 3.1 Beakers, 250 mL, conical.
- 3.2 Watch glasses, 65 mm flat and 75 mm ribbed.
- 3.3 Concentrated hydrochloric acid (HCL 37%): Use trace metal grade hydrochloric acid that has been lot QC checked.
- 3.4 Concentrated nitric acid (HNO₃ 70%): Use trace metal grade nitric acid that has been lot QC checked.
- 3.5 (1+1) Nitric acid (HNO₃ 1:1): Use trace metal grade nitric acid that has been lot QC checked, diluted 1:1 with deionized water, and stored in Teflon bottles.
- 3.6 Hydrogen peroxide solution, 30% (H₂O₂ 30%).
- 3.7 Hotplate
- 3.8 Polyethylene bottles, 125 mL: Use only acid-rinsed HDPE bottles.

4.0 Documentation

- 4.1 Soil Sample Digestion Log.



5.0 Inhouse Modifications to Referenced Method

N/A

6.0 Procedures

- 6.1 Fill out digestion log, entering header information, prep. code, date, analyst name, SOP revision date, sample number, and beaker number.
- 6.2 Mix the sample thoroughly to achieve homogeneity.
- 6.3 Weigh 1.00 to 2.00 g of wet sample and place in a beaker. Record the weight to the nearest 0.01 g. If samples have a low percent solids a larger sample size may be used.
- 6.4 At the same time weigh another portion of sample for determining the percent solids. If more than one soil prep is being performed per sample only one solids determination is required.
 - 6.4.1 Tare balance to achieve a zero reading.
 - 6.4.2 Weigh an empty weighing tin and record weight to the nearest 0.001 g.
 - 6.4.3 Fill the weighing tin (10.000 to 20.000 g) with wet sample. Less sample can be used if necessary. Record the exact weight to the nearest 0.001g.
 - 6.4.4 Place tins in oven at 104°C for 24 hours or until sample is dry.
 - 6.4.5 Remove from oven, cool, and weigh. Record exact weight to the nearest 0.001 g.
- 6.5 Add 10 mL of (1+1) HNO₃ and mix.
- 6.6 Cover with a flat watch glass and heat on a hot plate 10 - 15 minutes. The recommended temperature is 95°C. Do not allow the sample to boil.
- 6.7 Cool the sample.
- 6.8 Add 5 mL of concentrated HNO₃.
- 6.9 Replace the flat watch glass and reflux the sample for 30 minutes without boiling.
- 6.10 Cool the sample.
- 6.11 Add another 5 mL of concentrated HNO₃.
- 6.12 Replace the flat watch glass and reflux for 30 minutes, again without boiling.
- 6.13 Change to a ribbed watch glass and continue digestion. Evaporate the sample to a volume of 5 mL. Make sure the sample does not boil, and that no part of the bottom of the beaker dries.
- 6.14 Cool the sample.



- 6.15 Add 2 mL of deionized water.
 - 6.16 Add 3 mL of 30% H₂O₂ solution.
 - 6.17 Cover with a flat watch glass and return to the hotplate. Heat until the peroxide reaction starts. Do not allow sample to froth over; remove the sample temporarily if necessary. Continue heating until the reaction ends.
 - 6.18 Cool the sample.
 - 6.19 Add additional 1 mL aliquots of H₂O₂ solution and heat. Continue additions until sample appearance does not change and digestion is complete. Add no more than 7 aliquots of H₂O₂.
 - 6.20 Cool the sample.
 - 6.21 Add 5 mL of concentrated HCl.
 - 6.22 Add 10 mL of deionized water.
 - 6.23 Cover with a flat watch glass and return to hotplate for 10-15 minutes. Do not allow sample to boil.
 - 6.24 Cool the sample.
 - 6.25 Prepare a polyethylene bottle.
 - 6.25.1 Use an acid-rinsed HDPE bottle.
 - 6.25.2 Label the bottle with the sample number.
 - 6.25.3 Mark the bottle with the preparation code "SWC".
 - 6.26 Dilute to 100 mL with deionized water.
 - 6.26.1 Tare a labeled, empty, acid-rinsed HDPE bottle on the balance.
 - 6.26.2 Rinse the digested sample into the bottle.
 - 6.26.3 Add enough deionized water to make 100.0 g total weight, and record exact amount added on the log.
 - 6.27 Centrifuge the sample, or allow it to settle overnight. This step is unnecessary if there are no insoluble materials.
 - 6.28 Transfer digested samples to the instrument lab and record them in the appropriate logbook.
-
- 7.0 **Review**
 - 7.1 Verify that all information has been properly entered in the digestion log.
 - 7.2 All unused space in the log must be crossed out and initialed by the analyst.



8.0 Quality Control

8.1 All quality control samples are assigned by the supervisor/manager when samples are logged into the metals data base.

8.2 Verify the following:

8.2.1 Method blanks are processed with each analytical batch, or every twenty samples, as assigned on the Sample Log Form.

8.2.2 Other QC samples, spikes, duplicates, and reference materials are processed as assigned on the Sample Log Form.

9.0 Corrective Actions

9.1 If a beaker goes dry, notify the supervisor/manager and reprep the sample.

9.2 Any unusual sample or problem that arises must be noted on the digestion log or on an Analyst Notes Form and also brought to the attention of the supervisor/manager.

10.0 Miscellaneous Notes and Precautions

10.1 Concentrated acids are very dangerous. Follow proper procedures according to the ARI Chemical Hygiene Plan. Always wear gloves, eye protection, and a lab coat.

11.0 Method References

11.1 USEPA, Test Methods for Evaluating Solid Waste, SW-846, Volume IA, Method 3050, July 1992.

12.0 Appendices

N/A

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Standard Operating Procedure

Metals Preparation
Method 3010 (TWC)

510S

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PROPRIETARY

Prepared By:

John K. H.

Approvals:

John K. H.
Section Manager

Don N. Steu 5/11/94
Laboratory Manager

Michelle I. Turner
Quality Assurance Manager

Michelle I. Turner 5/12/94
Laboratory Director

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Standard Operating Procedure - Metals

SW-846 Method 3010

ARI Prep Code: TWC

1.0 Scope and Application

This is the digestion method identified in the SW-846 USEPA Solid Waste manual as Method 3010. It is intended for preparing wastewater samples and TCLP extracts for analysis by inductively coupled argon plasma spectroscopy (ICP) or flame atomic absorption spectroscopy (FLAA). Samples prepared by this method will be labeled with the preparation code "TWC".

2.0 Definitions

N/A

3.0 Equipment

3.1 Beakers, 150 mL.

3.2 Watch glasses, 65 mm flat and 75 mm ribbed.

3.3 Concentrated nitric acid (HNO_3 70%): Use trace metal grade nitric acid that has been lot QC checked.

3.4 1 + 1 hydrochloric acid (HCL 1:1): Use trace metal grade hydrochloric acid that has been lot QC checked, diluted 1:1 with DI water, and stored in a teflon-lined bottle.

3.5 Hotplate

3.6 Polyethylene bottles, 125 mL: Use only acid-rinsed HDPE bottles.

4.0 Documentation

4.1 Water Sample Digestion Log.

5.0 Inhouse Modifications to Referenced Method

N/A



6.0 Procedures

- 6.1 Fill out digestion log, entering header information, prep. code, date, analyst name, SOP revision date, sample number, and beaker number.
- 6.2 Transfer 100 mL of sample to a 150 mL beaker.
 - 6.2.1 Using pH paper, verify that the sample has been preserved properly ($\text{pH} \leq 2$), and mark log with a check mark. If sample has not been preserved, add appropriate preservative. (See section 9.1)
 - 6.2.2 Mix the sample thoroughly before transferring.
 - 6.2.3 Tare an empty beaker and add 100.0 g of sample. Record exact amount on log.
- 6.3 Add 3 mL of concentrated HNO_3 .
- 6.4 Cover with a ribbed watch glass and digest on a hot plate.
 - 6.4.1 Evaporate the sample down to a volume of 5 mL.
 - 6.4.2 Do not boil the sample.
 - 6.4.3 Do not allow any part of the bottom of the beaker to dry. If beaker does go dry, see section 9.2.
- 6.5 Cool the sample.
- 6.6 Add 3 mL of concentrated HNO_3 .
- 6.7 Cover with a flat watch glass and return to the hot plate.
 - 6.7.1 Increase the heat on the hot plate to gently reflux the sample.
 - 6.7.2 Continue heating, adding acid as necessary, until the digestion is complete. This is generally indicated when the digestate is light in color or does not change in appearance with continued refluxing.
- 6.8 Cover with a ribbed watch glass and continue heating.
 - 6.8.1 Evaporated down to a volume of 3 mL.
 - 6.8.2 Do not allow the sample to boil.
 - 6.8.3 Do not allow any part of the bottom of the beaker to dry. If beaker does go dry, see section 9.2.
- 6.9 Cool the sample.
- 6.10 Add 10 mL 1:1 HCL and warm for 10 - 15 minutes.
- 6.11 Cool the sample.



- 6.12 Prepare a polyethylene bottle.
 - 6.12.1 Use an acid-rinsed HDPE bottle.
 - 6.12.2 Label the bottle with the sample number.
 - 6.12.3 Mark the bottle with the preparation code "TWC".
- 6.13 Dilute to 100 mL with deionized water.
 - 6.13.1 Tare a labeled, empty, acid-rinsed HDPE bottle on the balance.
 - 6.13.2 Rinse the digested sample into the bottle.
 - 6.13.3 Add enough deionized water to make 100.0 g total weight, and record exact amount added on the digestion log.
- 6.13 Centrifuge the sample.

Alternatively, allow the sample to settle overnight. This step is unnecessary if there are no insoluble materials.
- 6.14 Take digested samples to the instrument lab and record in the appropriate logbook.

7.0 Review

- 7.1 Verify that all information has been properly entered in the digestion log.
- 7.2 All unused space in the log must be crossed out and initialed by the analyst.

8.0 Quality Control

- 8.1 All quality control samples are assigned by the supervisor/manager when samples are logged into the metals data base.
- 8.2 Verify the following:
 - 8.2.1 Method blanks are processed with each analytical batch, or every twenty samples, as assigned on the Sample Log Form.
 - 8.2.2 Other QC samples, spikes, duplicates, and reference materials are processed as assigned on the Sample Log Form.

9.0 Corrective Actions

- 9.1 If samples were not preserved properly, adjust to $\text{pH} \leq 2$ with nitric acid, according to the Sample Preservation SOP.
- 9.2 If a beaker goes dry, notify the supervisor/manager and reprep the sample.



9.3 Any unusual sample or problem that arises must be noted on the digestion log and brought to the attention of the supervisor/manager.

10.0 Miscellaneous Notes and Precautions

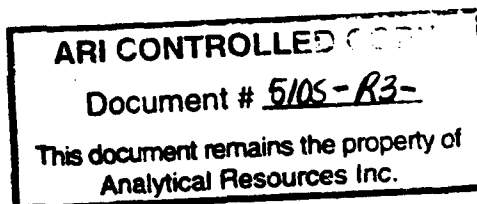
10.1 Concentrated acids are very dangerous. Follow proper safety procedures according to the ARI Chemical Hygiene Plan. Always wear gloves, eye protection, and a lab coat.

11.0 Method References

11.1 USEPA, Test Methods for Evaluating Solid Waste, SW-846, Volume IA, Method 3010, November 1986.

12.0 Appendices

N/A





Prep Code: _____

Date: _____

Analyst: _____

SOP Revision Date:

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Standard Operating Procedure

Metals Preparation
Method 7470 (TMM)

512S

Revision 4

7/7/94

PROPRIETARY

Prepared By:

Approvals:

Section Manager

Laboratory Manager

Quality Assurance Manager

Laboratory Director

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Standard Operating Procedure - Metals

SW-846 Method 7470

ARI Prep Code: TMM

1.0 Scope and Application

This is the digestion procedure identified in the SW-846 USEPA Solid Waste manual as Method 7470. This digestion is applicable to water samples, wastewaters, and industrial wastewaters for mercury analysis by the cold vapor atomic absorption method (CVA). Samples prepared by this method will be labeled with the preparation code "TMM".

2.0 Definitions

N/A

3.0 Equipment

- 3.1 Concentrated sulfuric acid (H_2SO_4 96.8%): Use trace metal grade sulfuric acid.
- 3.2 Concentrated nitric acid (HNO_3 70%): Use trace metal grade nitric acid that has been lot QC checked.
- 3.3 Potassium permanganate solution (KMnO_4): Dissolve 50 g of KMnO_4 in 1000 mL of deionized water.
- 3.4 Potassium persulfate solution ($\text{K}_2\text{S}_2\text{O}_8$): Dissolve 50 g of $\text{K}_2\text{S}_2\text{O}_8$ in 1000 mL of deionized water.
- 3.5 Water bath maintained at 95°C.
- 3.6 300 mL borosilicate BOD bottles.
- 3.7 BOD bottle rack.

4.0 Documentation

- 4.1 Mercury Digestion Log
- 4.2 Mercury Standard Preparation Log

5.0 Inhouse Modifications to Referenced Method

- 5.1 Method section 7.2: ARI does not use a 10 $\mu\text{g/L}$ Hg standard during calibration as the instrument is not linear past 5 $\mu\text{g/L}$ Hg.



6.0 Procedures

6.1 Standard Preparation.

- 6.1.1 Calibration stock solution (1000 mg/L Hg): certified stock standard solutions are purchased.
- 6.1.2 Intermediate calibration standard solution (1.00 mg/L Hg): Pipet 0.100 mL of 1000 mg/L Hg stock standard into a 100-mL glass volumetric flask. Dilute to 100 mL with 0.50% HNO₃ solution. Make this standard fresh daily.
- 6.1.3 Calibration Standard: Add the following amounts of 1.00 mg/L intermediate mercury solution to 300 mL BOD bottles containing 100 mL of deionized water in order to make the indicated calibration standards:

<u>µg/L Hg</u>	<u>mL intermediate std.</u>
0.0	0.00
0.5	0.05
1.0	0.10
2.0	0.20
5.0	0.50

- 6.1.3.1 Add 5.0 mL of concentrated H₂SO₄ and mix.
- 6.1.3.2 Add 2.5 mL of concentrated HNO₃ and mix.
- 6.1.3.3 Add 15.0 mL of KMNO₄ solution and mix.
- 6.1.3.4 Let the standards stand for at least 15 minutes.
- 6.1.3.5 Add 8 mL of K₂S₂O₈ solution to each standard and mix.
- 6.1.3.6 Heat in a 95°C water bath for 2 hours.
- 6.1.3.7 Cool to room temperature before analyzing.
- 6.1.4 Calibration Verification Standards
- 6.1.4.1 Intermediate CV standard solution (1.00 mg/L Hg): Pipet 0.100 mL of 1000 mg/L Hg CV stock standard into a 100 mL glass volumetric flask. Dilute to 100 mL with 0.50% HNO₃ solution. Make this standard fresh each time analysis is performed.
- 6.1.4.2 Calibration Verification Standards (3.0 µg/L Hg): To make each CV standard, add 0.30 mL of 1.00 mg/L intermediate CV mercury solution to 300 mL BOD bottles containing 100 mL of deionized water. Follow steps 6.1.3.1 to 6.1.3.7 for each CV bottle.



6.2 Sample Preparation

- 6.2.1 Fill out the digestion log, entering header information, prep. code, date, analyst name, SOP revision date, sample number, and beaker number.
- 6.2.2 Transfer 100 mL of sample to a 300 mL BOD bottle.
 - 6.2.2.1 Using pH paper, verify that the sample has been preserved properly ($\text{pH} \leq 2$), and mark the digestion log with a check mark. If the sample has not been preserved, add appropriate preservative. (See section 9.1)
 - 6.2.2.2 Mix the sample thoroughly before transferring.
 - 6.2.2.3 A smaller aliquot diluted to 100 mL may be used.
 - 6.2.2.4 Tare an empty BOD bottle and add 100.0 grams of sample.
- 6.2.3 Add 5.0 mL of concentrated H_2SO_4 and mix.
- 6.2.4 Add 2.5 mL of concentrated HNO_3 and mix.
- 6.2.4 Add 15.0 mL of KMnO_4 solution and mix. Add additional aliquots until the purple color persists for 15 minutes. No more than 3 aliquots may be added.
- 6.2.5 Add 8 mL of $\text{K}_2\text{S}_2\text{O}_8$ solution and mix.
- 6.2.6 Heat in a 95° C water bath for 2 hours.
- 6.2.7 Cool to room temperature before analyzing.

7.0 Review

- 7.1 Verify that all information has been properly entered in the digestion log.
- 7.2 All unused space in the log must be crossed out and initialed by the analyst.

8.0 Quality Control

- 8.1 All quality control samples are assigned by the supervisor/manager when samples are logged into the metals database.
- 8.2 Verify the following:
 - 8.2.1 Method blanks are processed with each analytical batch, or every twenty samples, as assigned on the Sample Log Form.
 - 8.2.2 Other QC samples, spikes, duplicates, and reference materials are processed as assigned on the Sample Log Form.



9.0 Corrective Actions

- 9.1 If samples were not preserved properly, adjust to pH $\leq$ 2 with nitric acid, according to the Sample Preservation SOP.
- 9.2 Any unusual sample or problem that arises must be noted on the digestion log or on an Analyst Notes Form and also brought to the attention of the supervisor/manager.

10.0 Miscellaneous Notes and Precautions

- 10.1 Concentrated acids are very dangerous. Follow proper safety procedures according to the ARI Chemical Hygiene Plan. Always wear gloves, eye protection, and a lab coat.

11.0 Method References

- 11.1 USEPA, Test Methods for Evaluating Solid Waste, SW-846, Volume IA, Method 7470, November 1990.

12.0 Appendices

N/A



MERCURY SAMPLE DIGESTION LOG

Preparation Code: _____

Date: _____

Analyst: _____

SOP Revision Date:

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MERCURY STANDARD PREP LOG

Preparation Code: _____

Date: _____

Analyst: _____

SOP Revision Date: _____

Calibration Stock Standard: _____

ICV/CCV Stock Standard: _____

Standard Type	True Value (µg/L)	Intermediate Standard (mL)	Number Made	Digest Start	Digest End
STD0	0	0.000			
STD1	0.5	0.050			
STD2	1.0	0.100			
STD3	2.0	0.200			
STD4	5.0	0.500			
ICB/CCB	0	0.000			
ICV/CCV	3.0	0.300			

Preparation Code: _____

Date: _____

Analyst: _____

SOP Revision Date: _____

Calibration Stock Standard: _____

ICV/CCV Stock Standard: _____

Standard Type	True Value (µg/L)	Intermediate Standard (mL)	Number Made	Digest Start	Digest End
STD0	0	0.000			
STD1	0.5	0.050			
STD2	1.0	0.100			
STD3	2.0	0.200			
STD4	5.0	0.500			
ICB/CCB	0	0.000			
ICV/CCV	3.0	0.300			



Standard Operating Procedure

Metals Preparation
Method 7471 (SWM)

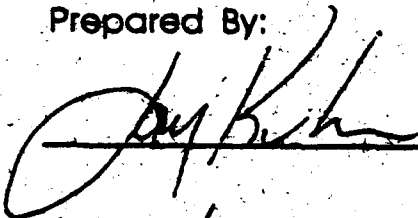
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Revision 3

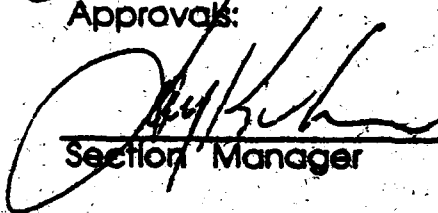
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PROPRIETARY

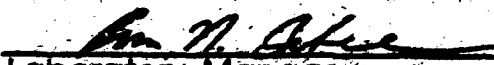
Prepared By:



Approvals:



Section Manager



Laboratory Manager



Quality Assurance Manager



Laboratory Director

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Standard Operating Procedure - Metals

SW-846 Method 7471

ARI Prep Code "SWM"

1.0 Scope and Application

- 1.1 This is the digestion procedure identified in the SW-846 USEPA Solid Waste manual as Method 7471. This digestion is applicable to soil, sediments, and sludge type materials for mercury analysis by the cold vapor atomic absorption method (CVA). Samples prepared by this method will be labeled with the "SWM" preparation code.

2.0 Definitions

N/A

3.0 Equipment

- 3.1 Concentrated sulfuric acid (H_2SO_4 96.8%): Use trace metal grade sulfuric acid.
- 3.2 Concentrated nitric acid (HNO_3 70%): Use trace metal grade nitric acid that has been lot QC checked.
- 3.3 Potassium permanganate solution (KMnO_4): Dissolve 50 grams of KMnO_4 in 1000 mL of deionized water.
- 3.4 Potassium persulfate solution ($\text{K}_2\text{S}_2\text{O}_8$): Dissolve 50 grams of $\text{K}_2\text{S}_2\text{O}_8$ in 1000 mL of deionized water.
- 3.5 Water bath maintained at 95°C.
- 3.6 300 mL borosilicate BOD bottles.
- 3.7 BOD bottle rack.

4.0 Documentation

- 4.1 Mercury Digestion Log
- 4.2 Mercury Standard Preparation Log



5.0 Inhouse Modifications to Referenced Method

- 5.1 Method section 7.1: Triplicate analysis is not performed. Also, ARI substitutes 5 mL H_2SO_4 and 2 mL HNO_3 for the 5 mL DI water and 5 mL aqua regia specified in the method. ARI adds 8 mL $\text{K}_2\text{S}_2\text{O}_8$ along with the KMnO_4 before heating.
- 5.2 Method section 7.3: ARI does not use a 10 $\mu\text{g/L}$ Hg standard during calibration because the instrument is not linear past 5 $\mu\text{g/L}$.

6.0 Procedure

6.1 Standard Preparation

- 6.1.1 Calibration stock solution (1000 mg/L Hg): Certified stock standard solutions are purchased.
- 6.1.2 Intermediate calibration standard solution (1.00 mg/L Hg): Pipet 0.100 mL of 1000 mg/L Hg standard into a 100 mL glass volumetric flask. Dilute to 100 mL with 0.50% HNO_3 solution. Make this solution fresh daily.
- 6.1.3 Calibration Standard: Add the following amounts of 1.00 mg/L intermediate mercury solution to 300 mL BOD bottles containing 100 mL of deionized water in order to make the indicated calibration standards:

$\mu\text{g/L}$ Hg	mL Intermediate std.
0.0	0.00
0.5	0.05
1.0	0.10
2.0	0.20
5.0	0.50

- 6.1.3.1 Add 5.0 mL of concentrated H_2SO_4 and mix.
- 6.1.3.2 Add 2.5 mL of concentrated HNO_3 and mix.
- 6.1.3.3 Add 15.0 mL of KMnO_4 solution and mix.
- 6.1.3.4 Let the standards stand for at least 15 minutes.
- 6.1.3.5 Add 8 mL of $\text{K}_2\text{S}_2\text{O}_8$ solution to each standard and mix.
- 6.1.3.6 Heat in a 95°C water bath for 30 minutes.
- 6.1.3.7 Cool to room temperature before analyzing.
- 6.1.4 Calibration Verification Standards
- 6.1.4.1 Calibration verification stock solution (1000 mg/L Hg): Certified stock standard solutions are purchased.



- 6.1.4.2 Intermediate CV standard solution (1.00 mg/L Hg): Pipet 0.100 mL of 1000 mg/L Hg CV stock standard into a 100-mL glass volumetric flask. Dilute to 100 mL with 0.50% HNO₃ solution. Make this solution fresh daily.
- 6.1.4.3 Calibration Verification Standards (3.0 µg/L Hg): To make each CV standard, add 0.30 mL of 1.00 mg/L Intermediate CV mercury solution to 300 mL BOD bottles containing 100 mL of deionized water. Follow steps 6.1.3.1 to 6.1.3.7 for each CV bottle.

6.2 Sample Preparation

- 6.2.1 Weigh out 0.2 grams of wet sample into a BOD bottle. Mix the sample thoroughly before transferring. Weigh the sample to the nearest 0.001 grams. If samples have a low percent solids a larger sample size may be used.
- 6.2.2 At the same time weigh another portion of sample for determining the percent solids. If more than one soil prep is being performed per sample only one solids determination is required.
- 6.2.2.1 Tare balance to achieve a zero reading.
- 6.2.2.2 Weigh an empty weighing tin and record weight to the nearest 0.001 gram.
- 6.2.2.3 Fill the weighing tin (10.000 to 20.000 grams) with wet sample. Less sample can be used if necessary. Record the exact weight to the nearest 0.001 gram.
- 6.2.2.4 Place tins in oven at 104°C for 24 hours or until sample is dry.
- 6.2.2.5 Remove from oven, cool, and weigh. Record exact weight to the nearest 0.001 grams.
- 6.2.3 Add 5.0 mL of concentrated H₂SO₄ and mix.
- 6.2.4 Add 2.5 mL of concentrated HNO₃ and mix.
- 6.2.5 Heat in a 95°C water bath for 2 minutes.
- 6.2.6 Cool the samples.
- 6.2.7 Add 50 mL of deionized water and mix.
- 6.2.8 Add 15.0 mL of KMNO₄ solution and mix.
- 6.2.9 Add 8 mL of K₂S₂O₈ solution and mix.
- 6.2.10 Heat in a 95°C water bath for 30 minutes.



- 6.2.11 Cool the samples.
- 6.2.12 Add 50 mL deionized water.
- 6.2.13 Cool to room temperature before analyzing.

7.0 Review

- 7.1 Verify that all information has been properly entered in the digestion log.
- 7.2 All unused space in the log must be crossed out and initialed by the analyst.

8.0 Quality Control

- 8.1 All quality control samples are assigned by the supervisor/manager when samples are logged into the metals data base.
- 8.2 Verify the following:
 - 8.2.1 Method blanks are processed with each analytical batch, or every twenty samples, as assigned on the Sample Log Form.
 - 8.2.2 Other QC samples, spikes, duplicates, and reference materials are processed as assigned on the Sample Log Form.

9.0 Corrective Actions

- 9.1 Any unusual sample or problem that arises must be noted on the digestion log or on an Analyst Notes Form and also brought to the attention of the supervisor/manager.

10.0 Miscellaneous Notes and Precautions

- 10.1 Concentrated acids are very dangerous. Follow proper safety procedures according to the ARI Chemical Hygiene Plan. Always wear gloves, eye protection, and a lab coat.

11.0 Method References

- 11.1 USEPA, Test Methods for Evaluating Solid Waste, SW-846, Volume IA, Method 7471, November 1990.

12.0 Appendices

N/A



Preparation Code:

Date: _____

Analyst:

SOP Revision Date:

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MERCURY STANDARD PREP LOG

Preparation Code: _____

Date: _____

Analyst: _____

SOP Revision Date: _____

Calibration Stock Standard: _____

ICV/CCV Stock Standard: _____

Standard Type	True Value (µg/L)	Intermediate Standard (mL)	Number Made	Digest Start	Digest End
STD0	0	0.000			
STD1	0.5	0.050			
STD2	1.0	0.100			
STD3	2.0	0.200			
STD4	5.0	0.500			
ICB/CCB	0	0.000			
ICV/CCV	3.0	0.300			

Preparation Code: _____

Date: _____

Analyst: _____

SOP Revision Date: _____

Calibration Stock Standard: _____

ICV/CCV Stock Standard: _____

Standard Type	True Value (µg/L)	Intermediate Standard (mL)	Number Made	Digest Start	Digest End
STD0	0	0.000			
STD1	0.5	0.050			
STD2	1.0	0.100			
STD3	2.0	0.200			
STD4	5.0	0.500			
ICB/CCB	0	0.000			
ICV/CCV	3.0	0.300			



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Standard Operating Procedure

Metals Preparation
Method 3050 (SWN)

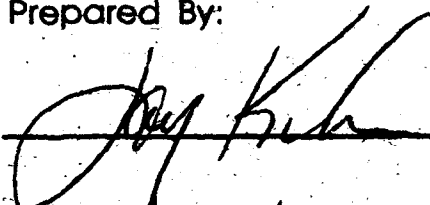
5095

Revision 3

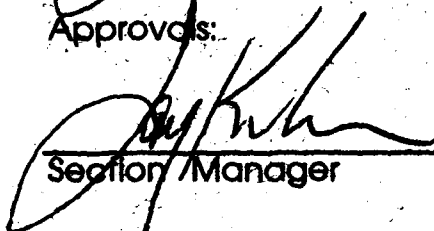
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PROPRIETARY

Prepared By:



Approvals:



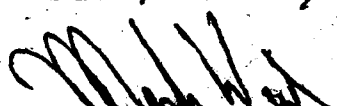
Section Manager


_____ 5/11/94

Laboratory Manager



Quality Assurance Manager



Laboratory Director

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Standard Operating Procedure - Metals

SW-846 Method 3050

ARI Prep Code: SWN

1.0 Scope and Application

This is the sediment digestion procedure identified in the SW-846 USEPA manual as Method 3050. It is intended for preparing soil, sludge, and sediment samples for analysis by graphite furnace atomic absorption (GFAA). Samples prepared by this method will be labeled with the preparation code "SWN".

2.0 Definitions

N/A

3.0 Equipment

3.1 Beakers, 250 mL, conical.

3.2 Watch glasses, 65 mm flat and 75 mm ribbed.

3.3 Concentrated nitric acid (HNO_3 70%): Use trace metal grade nitric acid that has been lot QC checked.

3.4 (1+1) Nitric acid (HNO_3 , 1:1): Use trace metal grade nitric acid that has been lot QC checked, diluted one-to-one with deionized water, and stored in Teflon bottles.

3.5 Hydrogen peroxide solution, 30% (H_2O_2 30%).

3.6 Hotplate

3.7 Polyethylene bottles, 125 mL: Use only acid-rinsed HDPE bottles.

4.0 Documentation

4.1 Soil Sample Digestion Log.

5.0 Inhouse Modifications to Referenced Method

N/A



6.0 Procedures

- 6.1 Fill out digestion log, entering header information, prep. code, date, analyst name, SOP revision date, sample number, and beaker number.
- 6.2 Mix the sample thoroughly to achieve homogeneity.
- 6.3 Weigh 1.00 to 2.00 g. of wet sample and place in a beaker. Record the weight to the nearest 0.01 g. If samples have a low percent solids a larger sample size may be used.
- 6.4 At the same time weigh another portion of sample for determining the percent solids. If more than one soil prep is being performed per sample only one solids determination is required.
 - 6.4.1 Tare balance to achieve a zero reading.
 - 6.4.2 Weigh an empty weighing tin and record weight to the nearest 0.001 g.
 - 6.4.3 Fill the weighing tin (10.000 to 20.000 g.) with wet sample. Less sample can be used if necessary. Record the exact weight to the nearest 0.001 g.
 - 6.4.4 Place tins in oven at 104°C for 24 hours or until sample is dry.
 - 6.4.5 Remove from oven, cool, and weigh. Record exact weight to the nearest 0.001 g.
- 6.5 Add 10 mL of (1+1) HNO₃ and mix.
- 6.6 Cover with a flat watch glass and heat on a hot plate 10 - 15 minutes. The recommended temperature is 95°C. Do not allow the sample to boil.
- 6.7 Cool the sample.
- 6.8 Add 5 mL of concentrated HNO₃.
- 6.9 Replace the flat watch glass and reflux the sample for 30 minutes without boiling.
- 6.10 Cool the sample.
- 6.11 Add another 5 mL of concentrated HNO₃.
- 6.12 Replace the flat watch glass and reflux for 30 minutes, again without boiling.
- 6.13 Change to a ribbed watch glass and continue digestion. Evaporate the sample to a volume of 5 mL. Make sure the sample does not boil, and that no part of the bottom of the beaker dries.
- 6.14 Cool the sample.
- 6.15 Add 2 mL of deionized water.
- 6.16 Add 3 mL of 30% H₂O₂ solution.



- 6.17 Cover with a flat watch glass and return to the hotplate. Heat until the peroxide reaction starts. Do not allow sample to froth over; remove the sample temporarily if necessary. Continue heating until the reaction ends.
- 6.18 Cool the sample.
- 6.19 Add additional 1 mL aliquots of H_2O_2 solution and heat. Continue additions until sample appearance does not change and digestion is complete. Add no more than 7 aliquots of H_2O_2 .
- 6.20 Cover with a ribbed watch glass and return to hotplate. Evaporate to about 5 mL. Do not allow sample to boil or the bottom of the beaker to dry.
- 6.21 Cool the sample.
- 6.22 Prepare a polyethylene bottle.
 - 6.22.1 Use an acid-rinsed HDPE bottle.
 - 6.22.2 Label the bottle with the sample number.
 - 6.22.3 Mark the bottle with the preparation code "SWN".
- 6.23 Dilute to 100 mL with deionized water.
 - 6.23.1 Tare a labeled, empty, acid-rinsed HDPE bottle on the balance.
 - 6.23.2 Rinse the digested sample into the bottle.
 - 6.23.3 Add enough deionized water to make 100.0 g. total weight, and record exact amount added on the log.
- 6.24 Centrifuge the sample, or allow it to settle overnight. This step is unnecessary if there are no insoluble materials.
- 6.25 Transfer digested samples to the instrument lab and record them in the appropriate logbook.

7.0 Review

- 7.1 Verify that all information has been properly entered in the digestion log.
- 7.2 All unused space in the log must be crossed out and initialed by the analyst.

8.0 Quality Control

- 8.1 All quality control samples are assigned by the supervisor/manager when samples are logged into the metals data base.



8.2 Verify the following:

8.2.1 Method blanks are processed with each analytical batch, or every twenty samples, as assigned on the Sample Log Form.

8.2.2 Other QC samples, spikes, duplicates, and reference materials are processed as assigned on the Sample Log Form.

9.0 Corrective Actions

9.1 If a beaker goes dry, notify the supervisor/manager and reprep the sample.

9.2 Any unusual sample or problem that arises must be noted on the digestion log or on an Analyst Notes Form and also brought to the attention of the supervisor/manager.

10.0 Miscellaneous Notes and Precautions

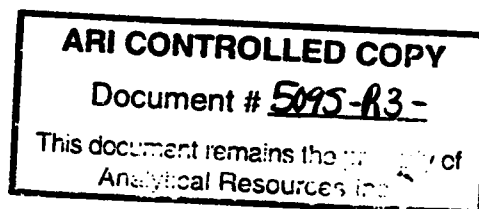
10.1 Concentrated acids are very dangerous. Follow proper procedures according to the ARI Chemical Hygiene Plan. Always wear gloves, eye protection, and a lab coat.

11.0 Method References

11.1 USEPA, Test Methods for Evaluating Solid Waste, SW-846, Volume IA, Method 3050, July 1992.

12.0 Appendices

N/A





ANALYTICAL
RESOURCES
INCORPORATED

Standard Operating Procedure

Metals Preparation
Method 3005 (RWC)

508S

Revision 3

5/5/94

PROPRIETARY

Prepared By:

Jay Kahn

Approvals:

Jay Kahn
Section Manager

Ch. W. Allen 5/11/94
Laboratory Manager

Michelle J. Turner
Quality Assurance Manager

Mark W. Allen
Laboratory Director

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Standard Operating Procedure - Metals

SW-846 Method 3005

ARI Prep Code: RWC

1.0 Scope and Application

This is the method identified in the SW-846 USEPA Solid Waste manual as Method 3005. It is intended for preparing surface and ground water samples for trace metal analysis by either flame atomic absorption spectroscopy (FLAA) or by inductively coupled argon plasma spectroscopy (ICP). This is also the preferred digestion to use when antimony is being analyzed by graphite furnace atomic absorption (GFAA). Samples prepared by this method will be labeled with the preparation code "RWC".

2.0 Definitions

N/A

3.0 Equipment

- 3.1 Beakers, 250 mL.
- 3.2 Watch glasses, 75 mm ribbed.
- 3.3 Hotplate
- 3.4 Concentrated nitric acid (HNO_3 70%): Use trace metal grade nitric acid that has been lot QC checked.
- 3.5 Concentrated hydrochloric acid (HCl 37%): Use trace metal grade hydrochloric acid that has been lot QC checked.
- 3.6 Polyethylene bottles 125-mL: Use only acid-rinsed HDPE bottles.

4.0 Documentation

- 4.1 Water Sample Digestion Log.

5.0 Inhouse Modifications to Referenced Method

N/A



6.0 Procedures

- 6.1 Fill out the digestion log, entering header information, prep. code, date, analyst name, SOP revision date, sample number, and beaker number.
- 6.2 Transfer 100 mL of sample to a 250 mL beaker.
 - 6.2.1 Using pH paper, verify that the sample has been preserved properly ($\text{pH} \leq 2$), and mark the digestion log with a check mark. If the sample has not been preserved, add appropriate preservative. (See section 9.1)
 - 6.2.2 Mix the sample thoroughly before transferring.
 - 6.2.3 Tare an empty beaker and add 100.0 g of sample. Record the exact amount on the log.
- 6.3 Add 2 mL of concentrated nitric acid.
- 6.4 Add 5 mL of concentrated hydrochloric acid.
- 6.5 Cover with a ribbed watch glass and digest on a hotplate.
 - 6.4.1 Heat the sample at approximately 95°C for 2 hours, until the sample volume is reduced to slightly less than 15-20 mL. Do not allow the sample to boil.
- 6.6 Cool the sample.
- 6.7 Prepare a polyethylene bottle.
 - 6.7.1 Use an acid-rinsed HDPE bottle.
 - 6.7.2 Label the bottle with the sample number.
 - 6.7.3 Mark the bottle with the prep. code, "RWC".
- 6.8 Dilute to 100 mL with deionized water.
 - 6.8.1 Tare a labeled, empty, acid-rinsed HDPE bottle on the balance.
 - 6.8.2 Rinse the digested sample into the bottle.
 - 6.8.3 Add enough deionized water to make 100.0 g total weight, and record the exact amount added in the log.
- 6.9 Centrifuge the sample.

Alternatively, allow the sample to settle overnight. This step is unnecessary if there are no insoluble materials.
- 6.10 Take digested samples to the instrument lab and record in the appropriate logbook.



7.0 Review

- 7.1 Verify that all information has been properly entered in the digestion log.
- 7.2 All unused space in the log must be crossed out and initialed by the analyst.

8.0 Quality Control

- 8.1 All quality control samples are assigned by the supervisor/manager when samples are logged into the metals data base.
- 8.2 Verify the following:
 - 8.2.1 Method blanks are processed with each analytical batch, or every twenty samples, as assigned on the Sample Log Form.
 - 8.2.2 Other QC samples, spikes, duplicates, and reference materials are processed as assigned on the Sample Log Form.

9.0 Corrective Actions

- 9.1 If the samples were not preserved properly, adjust to pH ≤ 2 with nitric acid, according to the Sample Preservation SOP.
- 9.2 If a beaker goes dry, notify the supervisor/manager and reprep the sample.
- 9.3 Any unusual sample or problem that arises must be noted on the digestion log or on an Analyst Notes Form and also brought to the attention of the supervisor/manager.

10.0 Miscellaneous Notes and Precautions

- 10.1 Concentrated acids are very dangerous. Follow proper procedures according to the ARI Chemical Hygiene Plan. Always wear gloves, eye protection, and a lab coat.

11.0 Method References

- 11.1 USEPA, Test Methods for Evaluating Solid Waste, SW-846, Volume 1A, Method 3005, July 1992.

12.0 Appendices

N/A

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Prep Code: _____

Date: _____

Analyst: _____

SOP Revision Date: _____

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Standard Operating Procedure

Metals Preparation
Methods 7060 and 7740 (RMA)

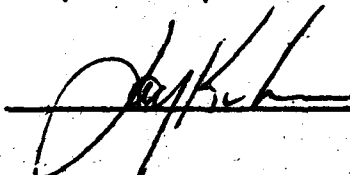
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Revision 3

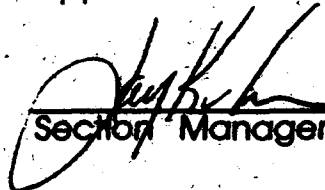
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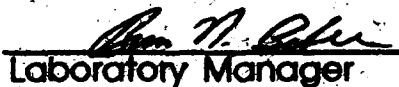
Prepared By:



Approvals:



Section Manager

 5/11/94

Laboratory Manager



Quality Assurance Manager



Laboratory Director

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Standard Operating Procedure - Metals

SW-846 Methods 7060 and 7740

ARI Prep Code: RMA

1.0 Scope and Application

This is the digestion method identified in the SW-846 USEPA Solid Waste manual as Methods 7060 and 7740. It is intended for preparing water and liquid waste samples for analysis by graphite furnace atomic absorption spectroscopy (GFAA) for arsenic and selenium. Samples prepared by this method will be labeled with the preparation code "RMA".

2.0 Definitions

N/A

3.0 Equipment

3.1 Beakers, 250 mL.

3.2 Concentrated nitric acid (HNO_3 70%): Use trace metal grade nitric acid that has been lot QC checked.

3.3 Hydrogen peroxide solution, (H_2O_2 30%).

3.4 Hotplate

3.5 Polyethylene bottles, 125 mL: Use only acid-rinsed HDPE bottles.

4.0 Documentation

4.1 Water Sample Digestion Log.

5.0 Inhouse Modifications to Referenced Methods

N/A

6.0 Procedures

6.1 Fill out the digestion log, entering header information, prep. code, date, analyst name, SOP revision date, sample number, and beaker number.



- 6.2 Transfer 100 mL of sample to a 250 mL beaker.
 - 6.2.1 Using pH paper, verify that the sample has been preserved properly ($\text{pH} \leq 2$), and mark the digestion log with a check mark. If the sample has not been preserved, add appropriate preservative. (See section 9.1)
 - 6.2.2 Mix the sample thoroughly before transferring.
 - 6.2.3 Tare an empty beaker and add 100.0 g of sample. Record the exact amount on the log.
- 6.3 Add 0.5 mL of concentrated nitric acid.
- 6.4 Add 2 mL of 30% H_2O_2 solution.
- 6.4 Cover with a ribbed watch glass and digest on a hotplate.
 - 6.4.1 Heat the sample at approximately 95°C for 1 hour, or until the sample volume is reduced to slightly less than 50 mL. Do not allow the sample to boil.
- 6.5 Cool the sample.
- 6.6 Prepare a polyethylene bottle.
 - 6.6.1 Use an acid-rinsed HDPE bottle.
 - 6.6.2 Label the bottle with the sample number.
 - 6.6.3 Mark the bottle with the prep. code, "RMA".
- 6.7 Dilute to 100 mL with deionized water.
 - 6.7.1 Tare a labeled, empty, acid-rinsed HDPE bottle on the balance.
 - 6.7.2 Rinse the digested sample into the bottle.
 - 6.7.3 Add enough deionized water to make 100.0 g total weight, and record the exact amount added in the log.
- 6.8 Centrifuge the sample.

Alternatively, allow the sample to settle overnight. This step is unnecessary if there are no insoluble materials.
- 6.9 Take digested samples to the instrument lab and record in the appropriate logbook.
- 7.0 Review**
 - 7.1 Verify that all information has been properly entered in the digestion log.
 - 7.2 All unused space in the log must be crossed out and initialed by the analyst.



8.0 Quality Control

8.1 All quality control samples are assigned by the supervisor/manager when samples are logged into the metals database.

8.2 Verify the following:

8.2.1 Method blanks are processed with each analytical batch, or every twenty samples, as assigned on the Sample Log Form.

8.2.2 Other QC samples, spikes, duplicates, and reference materials are processed as assigned on the Sample Log Form.

9.0 Corrective Actions

9.1 If the samples were not preserved properly, adjust to $\text{pH} \leq 2$ with nitric acid, according to the Sample Preservation SOP.

9.2 If a beaker goes dry, notify the supervisor/manager and reprep the sample.

9.3 Any unusual sample or problem that arises must be noted on the digestion log or on an Analyst Notes Form and also brought to the attention of the supervisor/manager.

10.0 Miscellaneous Notes and Precautions

10.1 Concentrated acids are very dangerous. Follow proper procedures according to the ARI Chemical Hygiene Plan. Always wear gloves, eye protection, and a lab coat.

11.0 Method References

11.1 USEPA, Test Methods for Evaluating Solid Waste, SW-846, Volume IA, Method 7060, November 1990.

11.2 USEPA, Test Methods for Evaluating Solid Waste, SW-846, Volume IA, Method 7740, September 1986.

12.0 Appendices

N/A

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Prep Code: _____

Date: _____

Analyst: _____

SOP Revision Date: _____

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ANALYTICAL
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Standard Operating Procedure

Mercury Cold Vapor Analysis
Method Series 7470/7471

513S

Revision 2

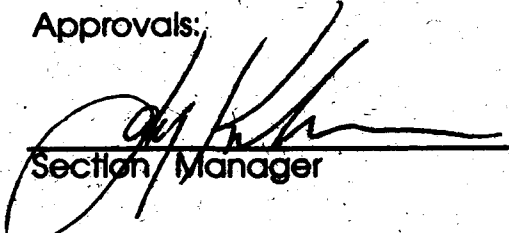
7/5/94

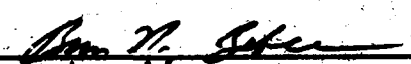
PROPRIETARY

Prepared By:

Jay Kuhn / Jim Fick

Approvals:


Section Manager


Laboratory Manager


Quality Assurance Manager


Laboratory Director

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STANDARD OPERATING PROCEDURE MERCURY COLD VAPOR ANALYSIS

1.0 Scope and Application

This document describes the cold vapor atomic absorption analysis of mercury in previously digested water, soil or tissue samples. Unknown samples are run against a calibration curve generated by standards of known concentration. Standards and sample preparation is covered in the appropriate digestion standard operating procedure.

2.0 Definitions

- 2.1 CVAAS - Cold Vapor Atomic Absorption Spectroscopy.
- 2.2 IDL - Instrument Detection Limit - As defined in the EPA-CLP SOW; three times the standard deviation of seven replicate measurements averaged over three non-consecutive days.
- 2.3 MDL - Method Detection Limit - As defined in 40 CFR; three times the standard deviation of seven replicate measurements of a low level standard or sample that has gone through a preparation step.
- 2.4 SD - Standard Deviation
- 2.5 RSD - Relative Standard Deviation - The SD divided by the mean, multiplied by 100.
- 2.6 RPD - Relative Percent Difference - The absolute difference between two numbers, divided by the average of the two numbers, multiplied by 100.
- 2.7 %R - Percent Spike Recovery - The difference between the matrix spike concentration and the original sample concentration divided by the concentration of the spike added multiplied by 100.

3.0 Equipment

- 3.1 Buck 400 mercometer with aerator apparatus, interfaced with a controlling IBM-compatible PC with printer and an A/D converter.
- 3.2 Compressed nitrogen cylinder with regulator.
- 3.3 5-ml air displacement pipette with disposable tips.



3.4 Reagents

- 3.4.1 14% Hydroxylamine hydrochloride/sodium chloride solution - Dissolve 144 grams of hydroxylamine hydrochloride (or 144 grams of hydroxylamine sulfate) and 144 grams of sodium chloride in deionized water and dilute to 1000 mL with deionized water. Use reagents that have been certified to be low in mercury.
- 3.4.2 10% Stannous chloride solution - make fresh daily - Dissolve 75 grams of stannous chloride in 500 ml of deionized water. Add 10.5 ml of concentrated sulfuric acid and dilute to 750 ml with deionized water. Adjust reagent amounts proportionally as necessary for different final volumes. Use reagents that have been certified low in mercury.
- 3.4.3 Magnesium perchlorate drying tubes - Loosely fill magnesium perchlorate between two glass wool plugs in 3/4" OD by 4" long polyethylene drying tubes. Do not pack too tightly to allow gas flow through the drying tubes.

4.0 Documentation

- 4.1 The CVAA summary logbook is filled out during the run. Any event or observation or action that is worth noting should be recorded in the appropriate hardbound logbook and on the raw data. When the analytical day is complete, a data package for review consists of all raw data, and copies of all related logbook pages. A diskette containing a text file generated during the run, the name of which is based on the date of analysis, should be included for use in the data loading process.

5.0 Inhouse Modifications to Referenced Method

- 5.1 Method 7470 Section 7.2 states that a 10 ppb calibration standard is to be run for the calibration curve. ARI does not run a 10 ppb calibration standard as our instrument is not linear past 5 ppb. Section 8.2 states that only three standards and a blank are needed for a calibration curve, and ARI uses four.
- 5.2 Method 7470 Section 8.2 states that calibration should be done every hour. ARI calibrates at the start of every run and as needed during the day if a CCV is outside of acceptance criteria.

- 5.3 Method 7470 Section 7.5 & Section 8.7 state that certain types of sample be analyzed for by using the MSA. ARI does not analyze samples by the MSA for mercury.
- 5.4 Method 7470 Section 8.6 states that one MSD should be run every 10 samples. ARI normally analyzes duplicates, not a MSD. ARI can analyze a MSD instead of a duplicate per client request.
- 5.5 Method 7471 Section 7.3 states that a 10 ppb calibration standard is to be run for the calibration curve. ARI does not run a 10 ppb calibration standard as the instrument is not linear past 5 ppb. Section 8.2 states that only three standards and a blank are needed for a calibration curve, and ARI uses four.
- 5.6 Method 7471 Section 8.2 states that calibration should be done every hour. ARI calibrates at the start of every run and as needed during the day if a CCV is outside of acceptance criteria.
- 5.7 Method 7471 Section 7.6 and Section 8.7 states that certain types of sample be analyzed for by using the MSA. ARI does not analyze samples by the MSA for mercury.
- 5.8 Method 7471 Section 8.6 states that one MSD should be run every 10 samples. ARI normally analyzes duplicates, not a MSD. ARI can analyze a MSD instead of a duplicate per client request.

6.0 Procedures

6.1 Method Description:

Cold vapor atomic absorption spectroscopy (CVAAS) is a method based on the absorption of radiation at 253.7 nm by atomic mercury vapor. The mercury present in the sample is reduced to the elemental state and aerated from the solution by a carrier gas. The mercury vapor passes through a cell positioned in the light path of a mercury emission source. The absorbance of the mercury specific wavelength is measured to relate light absorbance to the mercury concentration present in the sample.

6.2 Instrument and sample setup:

- 6.2.1 Turn on the Buck mercury analyzer first to allow a 1 hour minimum warm-up.

- 6.2.2 Install a new drying tube and two new pieces of silicon tubing. Both pieces are 15" long and are 3/8" OD and 1/4" ID. One piece connects the lower aerator connection to the drying tube and the other piece connects the drying tube to the absorption cell in the mercury analyzer. Make sure that the drying tube is level.
- 6.2.3 Insert the aerator into a BOD bottle containing about 200 mL of fresh deionized water. This will be called the "wash bottle" throughout the remainder of this document.
- 6.2.4 After the initial warm-up time, set the nitrogen flow through the aerator to 51 units on the flowmeter scale (silver ball). The nitrogen tank regulator should be set to 20 psi. The nitrogen tank should be replaced when the tank pressure reaches 300 psi.
- 6.2.5 Turn on the hood exhaust fan.
- 6.2.6 Check the window on either end of the cell and clean if necessary. Optimize the cell position by setting the %T to midscale on the meter. Adjust the cell position to maximize %T.
- 6.2.7 Block the mercury lamp with the built in swivel shield. Set the 0% transmittance to 0.0 on the %T scale using the zero knob.
- 6.2.8 Remove the shield and set the 100% transmittance to 98.0 on the %T scale using the 100% knob.
- 6.2.9 Recheck the 0% and 98% transmittance settings after adjusting either setting until no further adjustment is necessary.
- 6.2.10 Prepare the samples and standards for analysis. Remove the glass stopper from the sample or standard and add 5 mL of hydroxylamine hydrochloride/sodium chloride solution. Swirl the bottle intermittently. The KMnO_4 will be reduced first to MnO_2 , a brown solid, then will dissolve into solution. The sample is ready for analysis when all the MnO_2 has been dissolved. Make sure no KMnO_4 is left on the stopper or stem of the BOD bottle.
- 6.3 Preparing the computer:
 - 6.3.1 Insert the GWBASIC Mercury Software disk into the "A" drive of the computer (the top drive). Insert a mercury data disk into the "B" drive of the computer (the bottom drive).

- 6.3.2 Turn on the printer, the monitor, and then the computer. The computer will automatically load and start the software.
- 6.3.3 Enter the date and time as directed on the screen. Enter your initials when they are requested.
- 6.3.4 The computer will prompt whether the run is a CLP run or not. If it is not a CLP run, the computer will prompt for a filename to call the data file to store the analytical results to. The format for the name of the disk file is "B:HGYMMDD.TXT" where B: is the disk drive destination of the file, HG stands for mercury, YY is the year, MM is the month, DD is the day, and TXT designates a text file.
- 6.3.5 If the run is a CLP run, there will be two files created on the data disk. The first file is used for the WARD CLP software package. The format for the name of the CLP data file is the same as the normal data file, except for the extension on the filename is .CLP instead of .TXT. The second is the normal file named as above for normal data processing.

6.4 Condition the instrument:

Several standards must be run through the instrument in order to condition the new tubing and drying tube.

- 6.4.1 The computer will prompt you whether you would like to run a conditioning sample. If yes, press the "Y" key, followed by the (Enter) key. (This will be abbreviated as "Y(Enter)" throughout the remainder of this document.) Pressing any other key will cause the computer to go directly into the calibration sequence.
- 6.4.2 Run the conditioning samples, which are the previous mercury run's leftover calibration standards, starting with standard 4 and working back to standard 0.
- 6.4.3 Insert the aerator into each standard, wait about 15 seconds to purge the headspace of the bottle, and then press any key on the computer keyboard to start taking baseline readings.
- 6.4.4 While the 10 baseline readings are taken, fill a 5-mL pipette with stannous chloride solution. When the computer "beeps", quickly withdraw the aerator, pipet the 5 mL of stannous chloride directly into the sample, and replace the aerator tightly.

- 6.4.5 After the computer has taken all of the data readings (about 30 seconds), remove the aerator and insert it into the wash bottle. Press any key to continue.
- 6.4.6 The result of the analysis will be displayed and printed. The average of the 10 baseline readings, the raw peak, and the peak height (raw peak - baseline) will be displayed. Press any key on the computer keyboard to move on to the next step.
- 6.4.7 The computer will return to step 6.4.1 of this section until you do not want to run any more conditioning samples. The computer will continue on to the calibration step when you are through running conditioning standards.

6.5 Calibration:

The computer will prompt if you want to calibrate the instrument from a disk file containing a previously saved calibration curve, from keyboard (manually typing in calibration standards results), or from analyzing calibration standards on the instrument. The instrument is normally calibrated by running calibration standards. The instrument might be calibrated from a saved disk file curve because a computer problem may cause the program to halt (losing the calibration curve) and the mercury run is not completed. This is normally the only time calibrating from a file would be used. Calibrating from the keyboard is used in the case that the calibration was not saved to a disk file and the calibration needs to be recovered.

6.5.1 Disk Calibration:

If you want to calibrate the instrument from a previously saved calibration curve, select "F" (for (F)ile). The computer will prompt for the name of the file containing the calibration curve data. Type in the name of the file and the computer will load and calculate the curve. Proceed to step 6.5.3.11.

6.5.2 Keyboard Calibration:

If you want to calibrate the instrument from the keyboard, select "K" (for (K)eyboard). The computer will prompt you for the concentration of each standard and the blank (in ppb), and the peak height for that standard or blank. When the last standard has been typed in, the computer will calculate the curve. Proceed to step 6.5.3.11.

6.5.3 Standard Calibration:

If you want to calibrate the instrument by running calibration standards, select "I" (for (I)nstrument). This is the normal method of calibration.

6.5.3.1 The first step in the calibration routine is to analyze a calibration blank. Insert the aerator into a calibration blank, and follow the analysis procedure as previously described above.

6.5.3.2 The computer will prompt if the blank is acceptable (see range below). An answer of "Y(Enter)" will accept the result and move on to the next step. Any other answer will cause the computer to repeat the calibration blank analysis.

6.5.3.3 After the calibration blank has been analyzed, the computer will prompt for the concentration (in ppb) of the four calibration standards. Normally these concentrations are 0.5, 1.0, 2.0 and 5.0 ppb.

6.5.3.4 When all four concentrations are entered, the computer will display the four concentrations and prompt for verification of the values. Entering "Y(Enter)" will accept the values and move on to the next step. Any other answer will repeat step 6.5.3.3 of this section.

6.5.3.5 The computer will request the analysis of each of the four calibration standards, starting with the lowest concentration first. Follow steps 6.5.3.6 through 6.5.3.8 for each of the four standards.

6.5.3.6 Insert the aerator into the appropriate calibration standard, and follow the analysis procedure as previously described above.

6.5.3.7 Check the peak height result with the normal result for each standard and the blank. The actual result should fall close to the normal range. The ranges are:

	<u>ppb</u>	<u>Peak Height</u>
Standard 0	0.0	0-10
Standard 1	0.5	70-95
Standard 2	1.0	140-190
Standard 3	2.0	300-400
Standard 4	5.0	650-850

- 6.5.3.8 The computer will prompt if the standard is acceptable. Enter "Y(Enter)" to accept the result and move on to the next step. Any other answer will cause the computer to return to step 6.5.3.6 of this section in order to reanalyze a calibration standard of the same concentration.
- 6.5.3.9 After accepting the results of the standard, the computer will repeat steps 6.5.3.6 to 6.5.3.8 for the next standard.
- 6.5.3.10 After standard 4 has been accepted, the computer will calculate a second order least squares best fit for the standard curve and will then display the "apparent concentrations" of the calibration standards. All the standards' apparent concentrations except for the lowest standard must be within 5% of their true value. The lowest standard should be within 10% of its true value. The calibration blank should be within 0.1 ppb of zero. See the acceptable ranges below. Press any key on the computer keyboard to move on to the next step.

Acceptable apparent concentration - ppb

Standard 0	-0.1 to 0.1
Standard 1	0.45 to 0.55
Standard 2	0.95 to 1.05
Standard 3	1.90 to 2.10
Standard 4	4.75 to 5.25

- 6.5.3.11 The computer will graphically display the calibration standards and the fitted curve.
- 6.5.3.12 If the calibration curve is not acceptable, do not save the curve. The computer will prompt whether to continue or start over. Select the start over option, and recalibration is possible.
- 6.5.3.13 If the curve is acceptable, save the curve to a disk file. Saving the curve to a file will allow you to recall from the disk the calibration curve if a computer error occurs and the Basic program crashes during the run. The format for the name of the standard curve file

is the same as the normal data file, except the extension on the filename is .CUV instead of .TXT. Select continue when prompted to proceed to analyzing samples.

6.6 Analysis:

- 6.6.1 Press any key to begin the sample analysis routine. Follow steps 6.4.3 to 6.4.6 for each sample that is analyzed. Begin filling out mercury analysis summary logbook. Refer to the Mercury QA/QC section (below) as needed for analysis run quality control requirements. The typical run sequence is as follows: ICV, ICB, 10 samples, CCV, CCB, 10 samples, CCV, CCB, etc.
- 6.6.2 Enter the ARI sample designation of the sample. The designation for client samples must be of the format "C368 A SCM" (Job, one space, sample, one space, precode) to be read properly during the mercury data file data processing. The sample designation for calibration check standards and blank standards is not important for the data processing. The computer file is editable to correct sample designation mistakes during the data processing step. Make a note of sample designation corrections on the raw data and in the logbook.
- 6.6.3 Insert the aerator into the sample, and follow the analysis procedure as previously described in the running conditioning standards section.
- 6.6.4 The result of the analysis will be displayed and printed. The average of the 10 baseline readings, the raw peak, and the peak height (raw peak - baseline) will be displayed. The concentration of the sample (in ppb) calculated from the calibration curve rounded to two places past the decimal will be displayed. If the sample is below the instrument detection limit (0.1 ppb), a U will also be displayed after the concentration.
- 6.6.5 When finished reviewing the sample result, press any key to continue.
- 6.6.6 The computer will prompt you to enter the next sample designation. Type in the next sample designation and repeat the analysis procedure.
- 6.6.7 Every 20-30 analyses replace the drying tube with a fresh one. This is to be done after a CV/CB pair and before another CV/CB pair to verify the instrument performance before and after the drying tube change. Turn off the nitrogen gas flow while replacing the drying tube.

- 6.6.8 To exit the program and end the run, type "END" instead of a sample designation. The computer will exit the program. The mercury run is then finished, go to the shutdown procedures.
- 6.7 Shutdown procedures:
- 6.7.1 Take the disks out the computer disk drives, and turn off the computer and printer.
 - 6.7.2 Turn off the nitrogen gas flow, the exhaust fan, and the mercury analyzer.
 - 6.7.3 Keep one set of leftover calibration standards near the instrument for use as conditioning samples for the next run.
 - 6.7.4 Copy the pages from the mercury sample logbook for the analysis run, and place the assembled raw data, prep sheets, logbook pages and disk in the data review bin.
 - 6.7.5 Neutralize analyzed samples and standards with NaOH in the hood and pour down the drain. Any sample with greater than 200 ppb concentration of mercury in solution should be poured in the hazardous waste container.
- 6.8 Detection Limit:
- 6.8.1 Instrument Detection Limit (IDL); The instrument detection limit (IDL) is determined quarterly for each element as described by CLP protocols. An IDL solution is prepared at 3 times the IDL, and analyzed as a sample seven times each day on three non-consecutive days. The standard deviation of the seven samples is calculated on each day, and the sum of the three days' standard deviations is the IDL. In actuality, the IDL determination result for mercury is below our stated IDL of 0.1 ppb.
- 6.9 Maintenance
- 6.9.1 All maintenance should be noted in the mercury maintenance logbook. A CV/CB pair should be run before and after any maintenance done during an analytic run. If this can not be done the instrument must be recalibrated before any additional samples can be analyzed.
 - 6.9.2 If the cell has any deposits in it from drying tube magnesium perchlorate dust, it should be cleaned. Take the cell out of the analyzer and sonicate it for 15 minutes in a weak detergent solution. Rinse the cell well with DI

water and dry thoroughly, using a drying oven if needed, before reinstalling in the analyzer.

- 6.9.3 If the baseline starts changing during the run, or the absorbance intensity readings for the calibration standards start changing, the light source is probably failing and needs to be replaced. Replace the light source with a new one.

7.0 Review

The CVA data is reviewed by the analyst during the sample analysis run. For each sample, the instrument operating software displays graphically the peak and prints out peak baseline, raw peak height, net peak height, and concentration results. The analyst reviews the data for high samples, baseline changes, QC samples in or out of control limits, and method blank contamination.

7.1 Raw data review

Note on the raw data and/or an Analyst Notes Sheet any comments on instrument problems, delays, unusual occurrences, etc. Check for any potential problems and especially check the instrument QC checks, matrix duplicates RPD, matrix spike %R, and reference recoveries, as described in section 8.0.

7.2 CVAA sample logbook review

Copy the appropriate CVA sample logbook pages which correspond with the raw data. Check every sample label (job number, sample letter, prepcode) and dilution factor. Highlight the client sample edits and sample analysis deletions so they are not missed during the data loading process.

8.0 Quality Control

- 8.1 Calibration Verification Standard (CV)- At the beginning of the mercury run, after every 10 samples, and at the end of the run, a CV standard must be run. The true concentration of the CV standard is 3.0 ppb. The result of the analysis must be within 20% of the true value (between 2.4-3.6 ppb). If a CV is outside of these limits, the previous samples run since the last good CV should be reprepmed and rerun. The instrument should be recalibrated after any potential problems have been corrected if another mercury run is to be attempted.

- 8.2 Calibration Blank Standard (CB) - Immediately after every CV standard, a CB standard must be run. The result of the analysis should be between 0.1 and -0.1 ppb (1 IDL). If a CB is outside of these limits, the previous samples run since the last good CB should be reprepmed and rerun. The instrument should be recalibrated after any potential problems have been corrected if another mercury run is to be attempted.
- 8.3 If a break longer than one half hour occurs in the middle of a mercury run, a CV/CB should be run before the break and first thing after the break.
- 8.4 Spike recovery (%R) - The spike amount for mercury in the digests is equal to 1.0 ppb. To calculate the spike recovery, subtract the background sample result from the spiked sample result, divide by the spike added, and multiply by 100:

$$\%R = \frac{(\text{spiked sample result} - \text{background sample result}) \times 100}{\text{spike added}}$$

EXAMPLE: ZXXX ASPK TMM has a result of 1.67 ppb. ZXXX A TMM has a result of 0.85 ppb. The spike amount is 1.0 ppb. The formula to calculate the %R is:

$$\%R = \frac{(1.67 \text{ ppb} - 0.85 \text{ ppb}) \times 100}{1 \text{ ppb}} = 82.0\%$$

If the background sample result is 4X greater than the spike added, the %R result does not matter for quality control, otherwise the %R should be between 75-125%.

- 8.5 Duplicates (RPD-Relative Percent Difference) - The RPD between a background sample and its duplicate should be no greater than 20%, provided the analysis result is above 0.4 ppb. The formula to calculate the RPD of a background sample and its duplicate is:

$$RPD = \frac{|(\text{background result} - \text{duplicate result})| \times 100}{(\text{background result} + \text{duplicate result})/2}$$

EXAMPLE: ZXXX A TMM has a result of 0.86 ppb. ZXXX ADUP TMM has a result of 0.99 ppb. The RPD is:

$$\text{RPD} = \frac{|0.86 \text{ ppb} - 0.99 \text{ ppb}|}{(0.86 \text{ ppb} + 0.99 \text{ ppb})/2} \times 100 = 14.1\%$$

If the background sample result is 1.0 ppb, then the difference between the background sample result and the duplicate result should be no greater than 0.1 ppb, and the RPD is not used for quality control.

- 8.6 If a duplicate or spike is out of control, the samples should be reprepared, possibly at a dilution if a water sample, and reanalyzed. Fill out a yellow corrective action form. If the problem persists in the rerun, the sample may not be homogeneous. Reprep and reanalysis may not be possible due to limited sample volume and/or short turn-around time requested by the client.
- 8.7 If a sample is very high in mercury, an instrument dilution may be necessary. Water samples will normally be diluted during the preparation of the sample, but sometimes they might be diluted at the instrument also. To perform an instrument dilution an extra blank(s) is necessary. The appropriate amount of solution is removed from a blank, and the same volume of sample is added to the blank to make the dilution. Consult the following table to determine the proper amount of blank and sample for each prep type and dilution factor.

Dilution	SCM Digest	Water or SWM Digest
1/2	72.75 mls	67.75 mls
1/3	48.50	45.17
1/5	29.10	27.10
1/10	14.55	13.55
1/20	7.28	6.78
1/50	2.91	2.71
1/100	1.46	1.36
1/200	0.73	0.68

- 8.8 After a sample containing a very high concentration of mercury, it is a good idea to let the instrument purge with nitrogen for about five minutes. Running a blank will test the instrument's condition; whether the whole tubing/glass pieces etc. are contaminated with mercury. It has happened that a very high sample required the whole instrument to be broken down and cleaned out.

9.0 Corrective Actions

- 9.1 Calibration. If the calibration does not meet the criteria in sections 6.5.3.7 and 6.5.3.10, then corrective action may need to be taken before proceeding with re-standardization. The variable nature of CVAAS (which is why CV limits are 20% instead of 10%) may cause calibration curves to fail to meet criteria without an instrument problem. In these cases all that is required is to recalibrate the instrument again. Instrument problems that require corrective action before recalibration could include gas flow leaks, drying tube material being packed too tightly to allow gas flow, light source failure, cell misalignment, or incorrect calibration standards preparation.
- 9.2 QC solutions. If a QC solution result is out of control limits, then corrective action should be taken before proceeding with analysis. This could involve re-preparation of calibration standards and recalibration, or other corrective action as described in section 9.1
- 9.3 Instrument malfunctions. When instrument malfunctions occur, consult with other experienced CVAA operators or the supervisor for guidance. The maintenance logbook and the service manual could be helpful for troubleshooting.
- 9.4 CVAA inhouse software crashes. The mercury controlling software is written in GWBASIC. GWBASIC is prone to 'crashing', for instance, if the printer runs out of paper and goes offline the program will crash when it tries to print next instead of alerting the analyst to the "out of paper" situation. The mercury program therefore allows the analyst to save the calibration results to a computer text file and recall the calibration curve from that file in the event of a program crash.

10.0 Miscellaneous Notes and Precautions

- 10.1 The mercury samples and reagents contain strong oxidizing and reducing compounds. The mercury reagents are made in excess, that is, the

concentration of the reagents is very high to drive the reaction equilibrium equation to one side or the other. Therefore, the solutions must be handled with care and proper safety equipment must be worn at all times. Gloves, safety goggles, and a labcoat for protection are a must.

- 10.2 The work area must be kept clean to eliminate the possibility of contamination, and also as a safety issue to protect the analyst from the hazards of the reagents, as described in section 10.1.
- 10.3 Care must be taken in the analysis procedure, as mercury is a 'one-shot' analysis. If an analysis is invalid for whatever reason, the sample must be redigested to be reanalyzed.

11.0 Method References

- 11.1 USEPA, Test Methods for Evaluating Solid Waste, SW-846, Volume IA, Method 7470, November 1992.
- 11.2 USEPA, Test Methods for Evaluating Solid Waste, SW-846, Volume IA, Method 7471, November 1992.

12.0 Appendices

N/A



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Standard Operating Procedure

Pesticides/PCBs
Water Extraction
Method 3510

311S

Revision 4

6/28/94

PROPRIETARY

Prepared By:

James M. Hawk-Thomson

Approvals:

LA

Section Manager

Ben D. Becker

Laboratory Manager

Michelle J. Turner

Quality Assurance Manager

Mark Van

Laboratory Director

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Standard Operating Procedure

Water Extraction

Chlorinated Pesticides/Polychlorinated Biphenyls (PEST/PCB)

1.0 Scope and Application

- 1.1 This method details the extraction of water samples in preparation for organochlorine pesticides and polychlorinated biphenyls analysis.

2.0 Definitions

- 2.1 Surrogates - known quantities of compounds added to all samples and blanks to evaluate extraction efficiency.
- 2.2 Matrix Spike - known quantities of selected analytes added to a sample to evaluate the effect of sample matrix on analyte recovery.
- 2.3 LCS (Laboratory Control Sample) - a blank fortified with known quantities of selected analytes to monitor extraction efficiency.

3.0 Equipment

- 3.1 200 mL Erlenmeyer flask with ground glass stopper and PTFE stopcock.
- 3.2 250 mL Erlenmeyer flask.
- 3.3 Kuderna-Danish concentrating apparatus (10 mL concentrator tube, 500 mL concentrator flask and 3 ball Snyder column).
- 3.4 25 x 340 mm drying column.
- 3.5 1000 mL graduated cylinder.
- 3.6 10 x 298 mm micro column.
- 3.7 Glass wool, prepared by baking in kiln at 300° C for 4 hours.
- 3.8 Methylene Chloride, high purity.
- 3.9 Hexane, pesticide grade.
- 3.10 Anhydrous sodium sulfate, prepared by baking in kiln at 400° C for 8 hours.
- 3.11 10 N sodium hydroxide solution and 1:1 sulfuric acid solution.



3.12 Surrogate and matrix spike solutions.

3.12.1 Surrogate and spike solutions composed as follows:

	<u>Component</u>	<u>Concentration</u>
Surrogate	Decachlorobiphenyl(DCBP)	2 µg/mL
	Tetrachloro-m-xylene (TCMX)	2 µg/mL
Pest Spike	Gamma BHC	5 µg/mL
	Heptachlor	5 µg/mL
	Aldrin	5 µg/mL
	Dieldrin	10 µg/mL
	Endrin	10 µg/mL
	DDT	10 µg/mL
	Delta BHC	5 µg/mL
	4,4'-DDE	10 µg/mL
	4,4'-DDD	10 µg/mL
PCB Spike	Aroclor 1260	80 µg/mL

3.13 Deionized water (Barnstead E-pure, 4 Module D4641)

3.14 Broad range pH paper.

3.15 Florisil. (See Florisil cleanup SOP).

3.16 Boiling chips - Teflon (Chemware)

3.17 Scintillation vials: 20 mL w/Aluminum-lined caps

3.18 Water bath set at 80° C - 85° C (capable of temperature control $\pm 5^\circ$ C)

3.19 N-Evap - Analytical Nitrogen Evaporator.

3.20 Yellow label tape.

3.21 Vials: 2 mL clear w/ crimp top for GC autosampler.

3.22 100 µL, 1 mL, and 10.0 mL gastight Hamilton syringes

3.23 Personal protective wear(gloves, goggles, lab coat)

4.0 Documentation

4.1 Pest/PCB bench sheet.

5.0 In-house Modifications to Referenced Methods

5.1 Section 1.1: ARI does not use method-referenced concentration techniques 4.3.4 and 4.3.5, and 4.9 has been revised.



- 5.2 10.0 mL, 1.0 mL, and 100 μ L syringes are used. See method 35108 for more information.
- 5.3 Section 6.13 (method section 7.10.3): The exchange procedure has been revised.
- 5.4 Section 6.15 (method 7.11.2): No water is used with the nitrogen evaporator.

6.0 Procedures

- 6.1 Review special analytical requirement's sheet prior to extracting samples to determine if special procedures are required. See Section 7.2.
- 6.2 Fill out bench sheet for job. See attached example. Label each separatory funnel with a piece of yellow label tape with the following information: job number, sample identification letter, matrix ID, type of extraction, and for the blanks, the date.
- 6.3 Warm samples to room temperature, and use graduated cylinder to measure 1 liter of sample and quantitatively transfer it to a separatory funnel labeled with the sample ID. Repeat for each sample. Prepare one separatory funnel with organic free water for use as a method blank and one for use as the Laboratory Control Sample (LCS).
 - 6.2.1 When labeling, use "PEST" for Pest/PCB extraction's and "PCB" for PCB.
- 6.4 Use broad range pH paper and 10 N sodium hydroxide solution or 1:1 sulfuric acid solution to adjust the pH of each sample (and both blanks) to a range of 5 to 9. Record pH on bench sheet.
- 6.5 Add sufficient surrogate solution (100 μ L) to each sample (and both blanks) to result in a final concentration of 0.2 μ g/mL. As per Section 8.4, to verify that surrogates are accurate, surrogates will be witnessed by another lab technician.
- 6.6 Add sufficient matrix spike solution (100 μ L for pesticides)(125 μ L for PCB's) to the LCS, and, if a matrix spike and/or matrix spike duplicate are required, to any QC samples to result in a final concentration of 0.5 and 1.0 μ g/mL for Pest. analytes and 10.0 μ g/mL for PCB. As per Section 8.4, to verify that matrix spiking is accurate, spiking will be witnessed by another lab technician.
- 6.7 Add 60 mL of methylene chloride to each sample bottle, then pour rinsate into each corresponding separatory funnel.
- 6.8 Seal and shake the separatory funnels vigorously for 2 minutes, using periodic venting to release excess pressure.



- 6.9 Allow the organic and aqueous layers to separate. Drain the entire organic layer (including any emulsion) into an Erlenmeyer flask labeled with the sample ID. Check Sample ID.
- 6.10 Repeat steps 6.6 through 6.8 two more times. If emulsion is present, it must be broken up by whatever mechanical means necessary until all non organic material (water, silt, etc.) is removed from the extract. (See Corrective Actions, section 9.0) Drain organic layer and add to the corresponding Erlenmeyer flask. Transfer the sample ID label to the flask.
- 6.11 Assemble a Kuderna-Danish (K-D) concentrator by attaching a rinsed 10 mL concentrator tube with methylene chloride to a rinsed with methylene chloride 500 mL evaporation flask. Prepare a drying column by putting a glass wool plug inside at the narrow end and filling the column with anhydrous sodium sulfate to a bed height of approximately 10 cm. Rinse the prepared column with 30 mL methylene chloride once.
- 6.12 Transfer the sample ID label to the K-D. Dry the extract by passing it through the drying column and collecting it in the K-D concentrator. Rinse the Erlenmeyer flask three times with methylene chloride and add this to the column as well. Once the entire extract has passed through the drying column, rinse the column with 15 mL methylene chloride. Check sample I.D.
- 6.13 Remove drying column, add 2 or 3 clean boiling chips to the concentrator flask, attach a three ball Snyder column, and put entire apparatus on a water bath set at approximately 80° C. Wet the inside of the Snyder column with 1 to 2 mL of methylene chloride before boiling starts.
- 6.14 Once the extract reaches 4 to 6 mL, the solvent is exchanged to hexane by flushing the Snyder column with about 10 mL of hexane. Once the extract again reaches 4 to 6 mL, remove the apparatus from the water bath. Place the K-D in the rack and allow to cool for at least 10 minutes.
- 6.15 Remove Snyder column, remove all water from the joint between the flask and the concentrator tube with a kimwipe, and disassemble the tube and flask. Rinse the lower joint of the flask into the tube with hexane. Do not over fill the tube. Transfer the sample ID label to the tube.



- 6.16 Mount the tube on a nitrogen evaporator and adjust the flow of gas such that with the needle 1 to 2 cm above the surface of the extract a small indentation can be seen in the surface of the extract. If there is bubbling or splashing the flow is too high. If there is no indentation visible the flow is too low. Concentrate to less than 10mL and take 1 mL of 10 mL through Florisil.
- 6.17 Proceed with Florisil cleanup. See Florisil standard procedure.
- 6.18 After clean-up, bring the extract to 1.0 mL final volume by Nitrogen concentration or by adding hexane, and place the extract into a clear, crimp cap auto sampler vial (labeled w/sample ID) for analysis.

7.0 Review

- 7.1 The Organic Extraction's Supervisor will review all bench work and bench sheets before distribution.
- 7.2 Review project documentation (special analytical requirements, etc.) prior to extracting samples to determine if special procedures are required.

8.0 Quality Control

- 8.1 One method blank will be extracted for each batch of 20 or fewer samples.
- 8.2 One LCS (spike blank) will be extracted for each batch of 20 or fewer samples.
- 8.3 One MS/MSD will be extracted for each parameter after every 20 samples of similar matrix and level (sample volume permitting).
- 8.4 To verify that surrogate and matrix spiking is accurate, spiking will be witnessed by another technician.

9.0 Corrective Actions

- 9.1 See Corrective Action Charts, section 12.1..

10.0 Miscellaneous Notes and Precautions

- 10.1 Constant attention must be given when watching K.D.'s on water baths, when extract are below the surface of the water bath so they do not boil dry.
- 10.2 When blowing down extracts on the N-Evap a time should be used to remind the analyst of the volumes so extracts will not blow dry.
- 10.3 The spring that goes around the N-Evap must be stretched out when placing on or taking off concentrator tubes to avoid snapping off the bottom halves of the concentrator tube which could result in loss of extract.



11.0 Method References

- 11.1 U.S. EPA, "Separatory Funnel Liquid-Liquid Extraction", (SW-846), Method 3510,
Revision 1, July, 1992.

12.0 Appendices

- 12.1 Corrective Action Charts.



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EXTRACTION - PEST/PCB - WATER

ARI Job No: Fill in ARI Job #

Client Name: Fill in Client Name

Client Project: Fill in Client Project

Extraction Requirements		Volume Extracted	GPC Aliquot	Florisil Aliquot	Total Final Vol.	Aliquot to Lab	Comments: Any special instructions or comments
<u>Transfer Pink sheet info here</u>							
MB: MB I.D. + DATE		1.0L	/	(1.0mL) 1:10	1.0mL	1:1	Black linked to Jobs: <u>subsequent jobs Batched to</u>
SB: SB I.D. + DATE		↓	/	↓	↓	↓	
ARI Lab ID	Client ID	Volume Extracted	GPC Aliquot	Florisil Aliquot	Total Final Vol.	Aliquot to Lab	Comments
F123 A	Take from batch 1	1.0L	/	(1.0mL) 1:10	1.0mL	1:1	Any pertinent information relating to samples
↓ B	2	↓	/	↓	↓	↓	
↓ C	3	↓	/	↓	↓	↓	↓
			1/2	1.5	1.0mL	1:1	
* Unused portion of Benchsheet must be tied out							
Date/Analyst:		Who extracted + date	Who GPC + date	Who Florisil + date	Who vialled + date		

Florisil Lot # current lot # in use

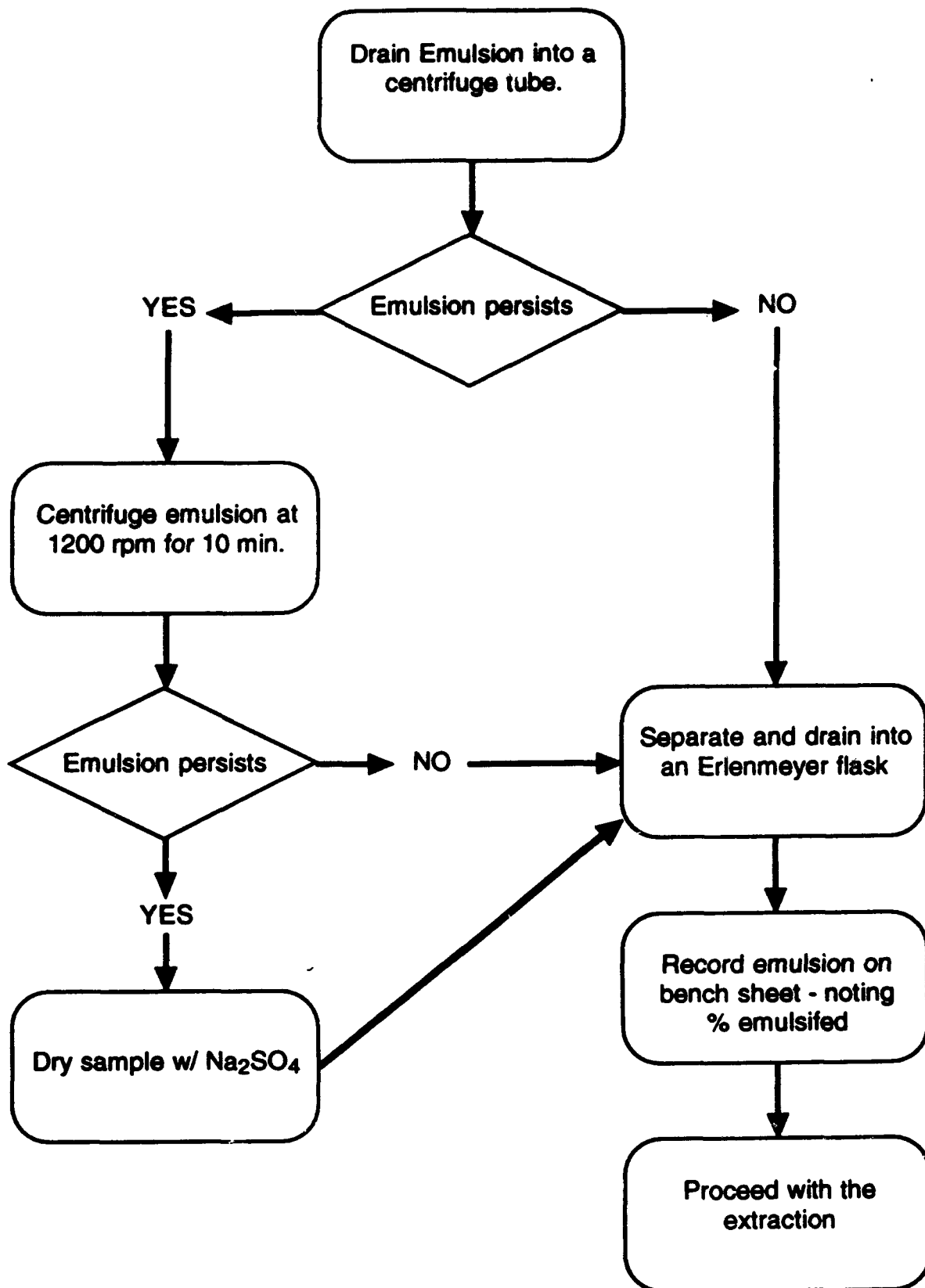
Surrogate Amount: <u>100uL</u>	Added By: <u>who added surrogate/Spk Witness</u>
Concentration: <u>2ug/mL</u>	ID: <u>260-1</u>
Spike Amount: <u>100uL</u>	Added By: <u>who added spike/Spk Witness</u>
Concentration: <u>5/10ug/mL</u>	ID: <u>262-1</u>

Date: Fill in date

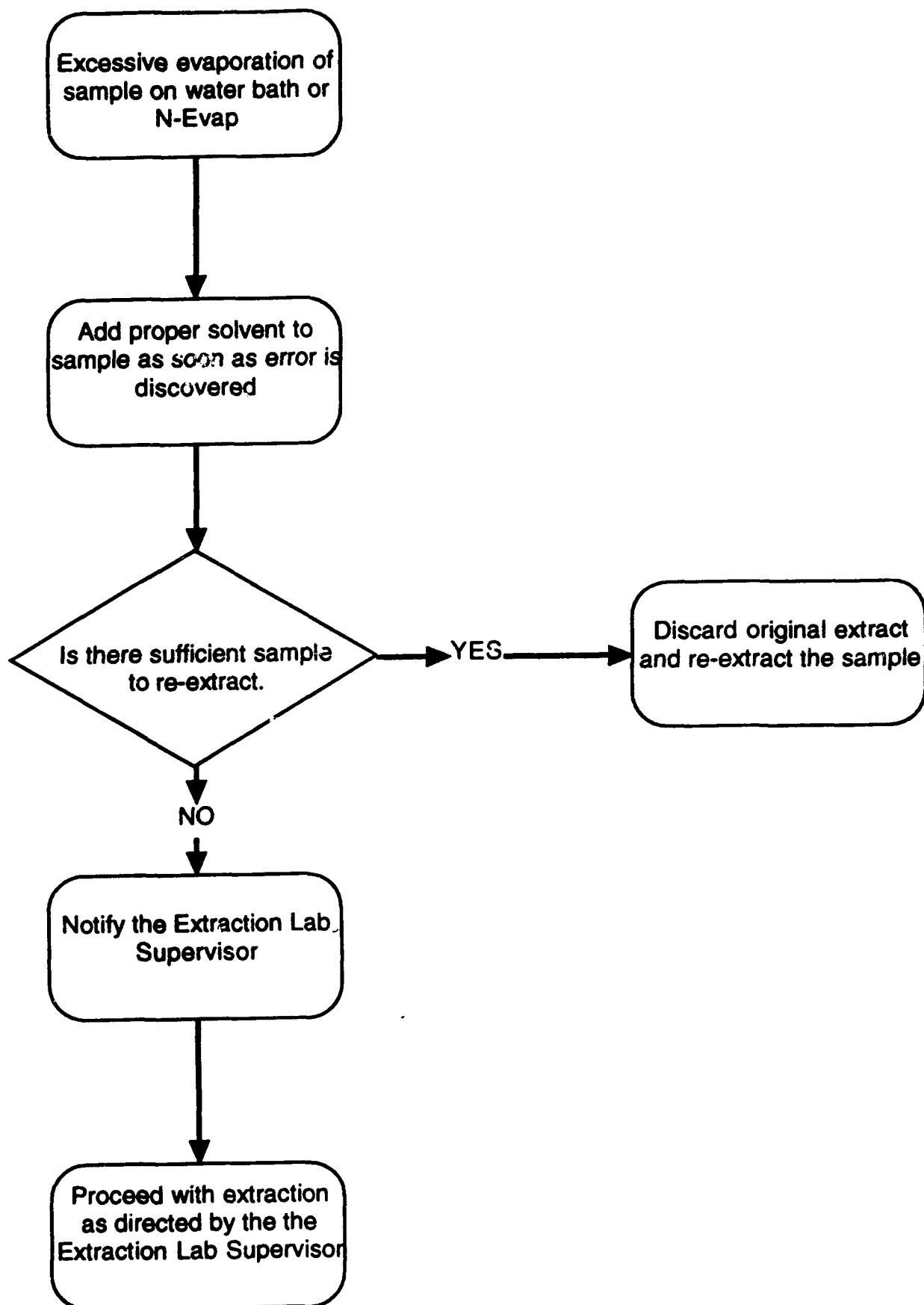
Extraction Storage Location: GC Ref.

* Any errors made must have a single line through the error with initials + date

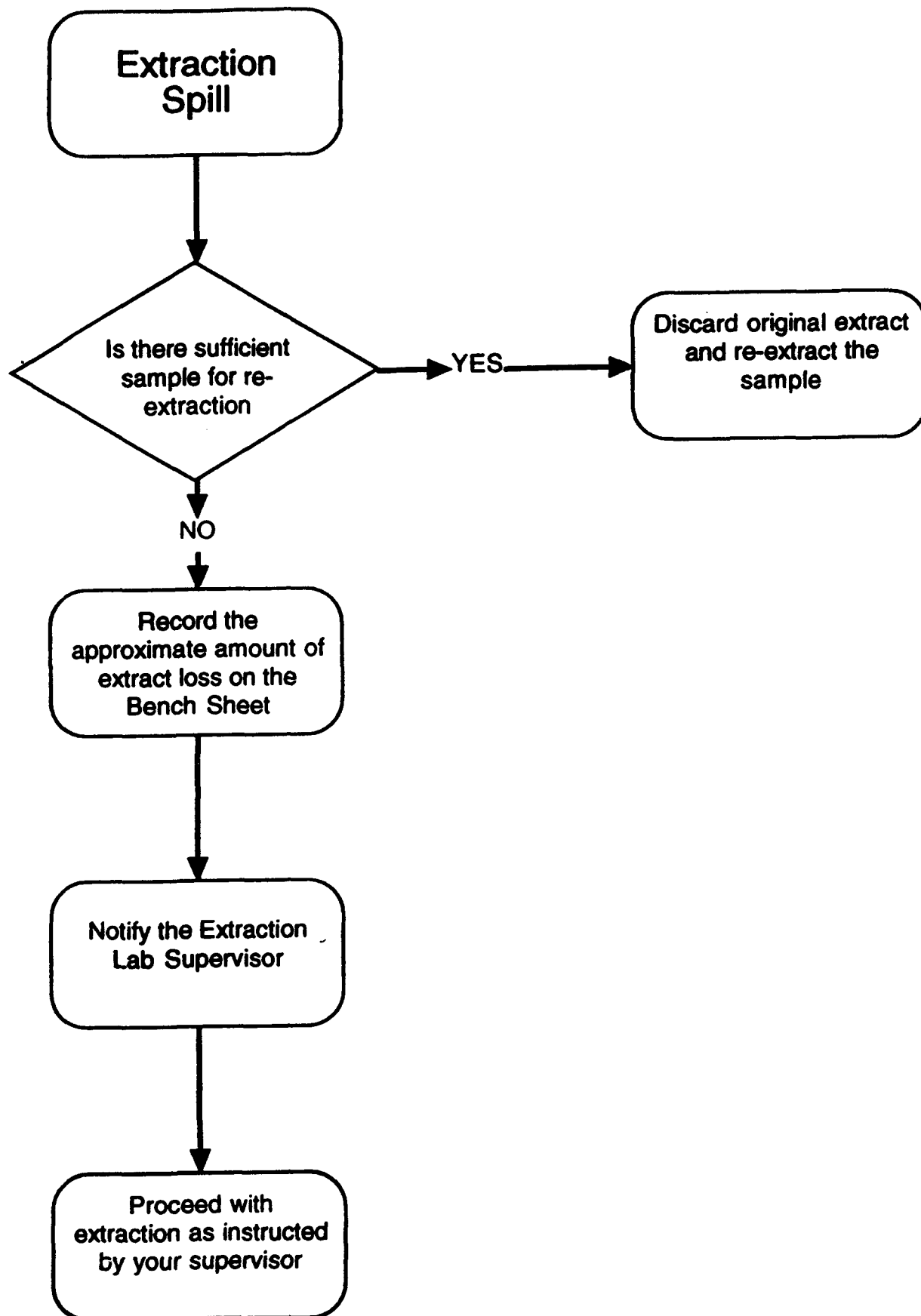
CORRECTIVE ACTION FOR EMULSIONS



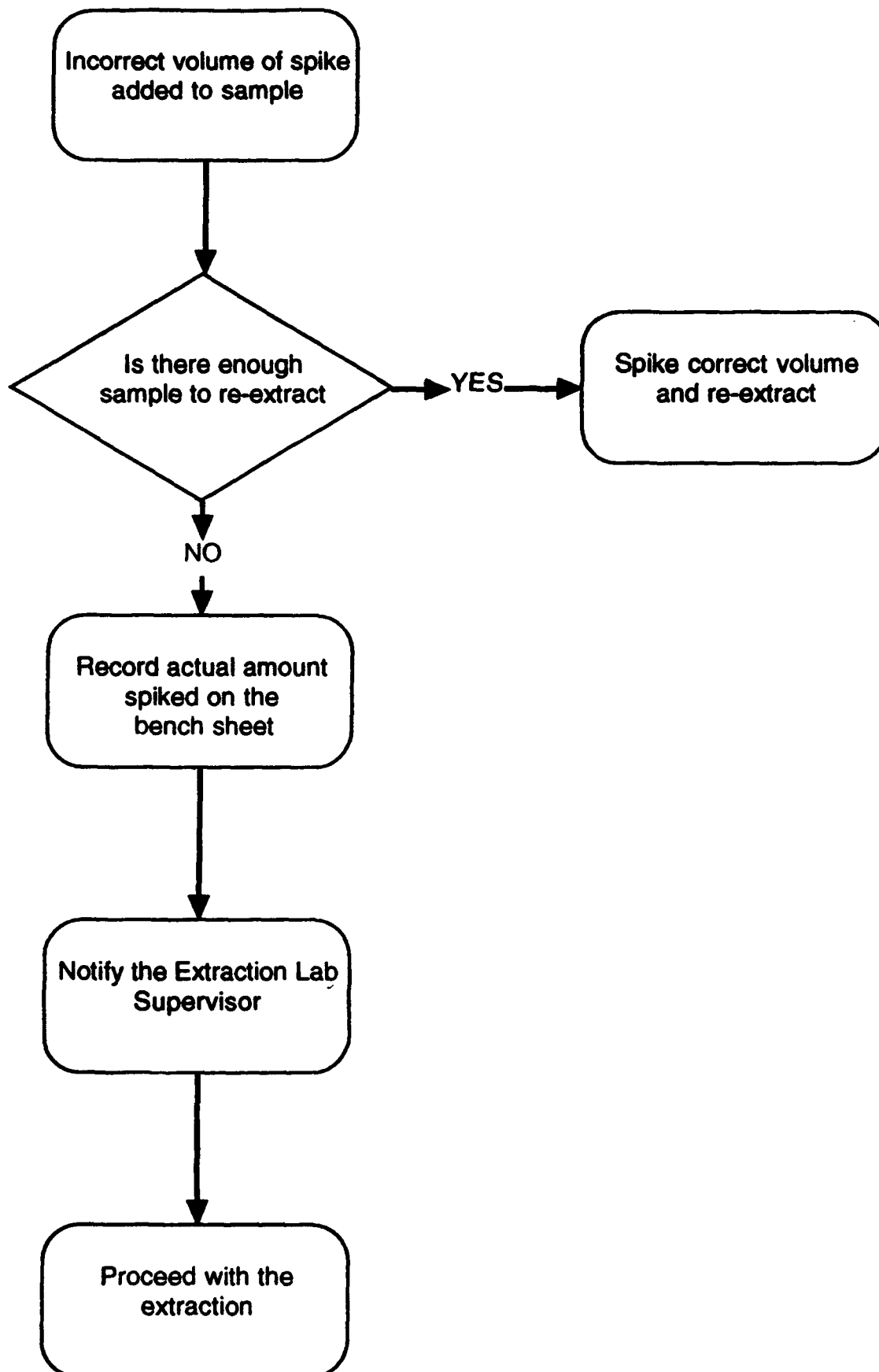
Corrective Action for Loss of Sample on Water Bath or N-Evap



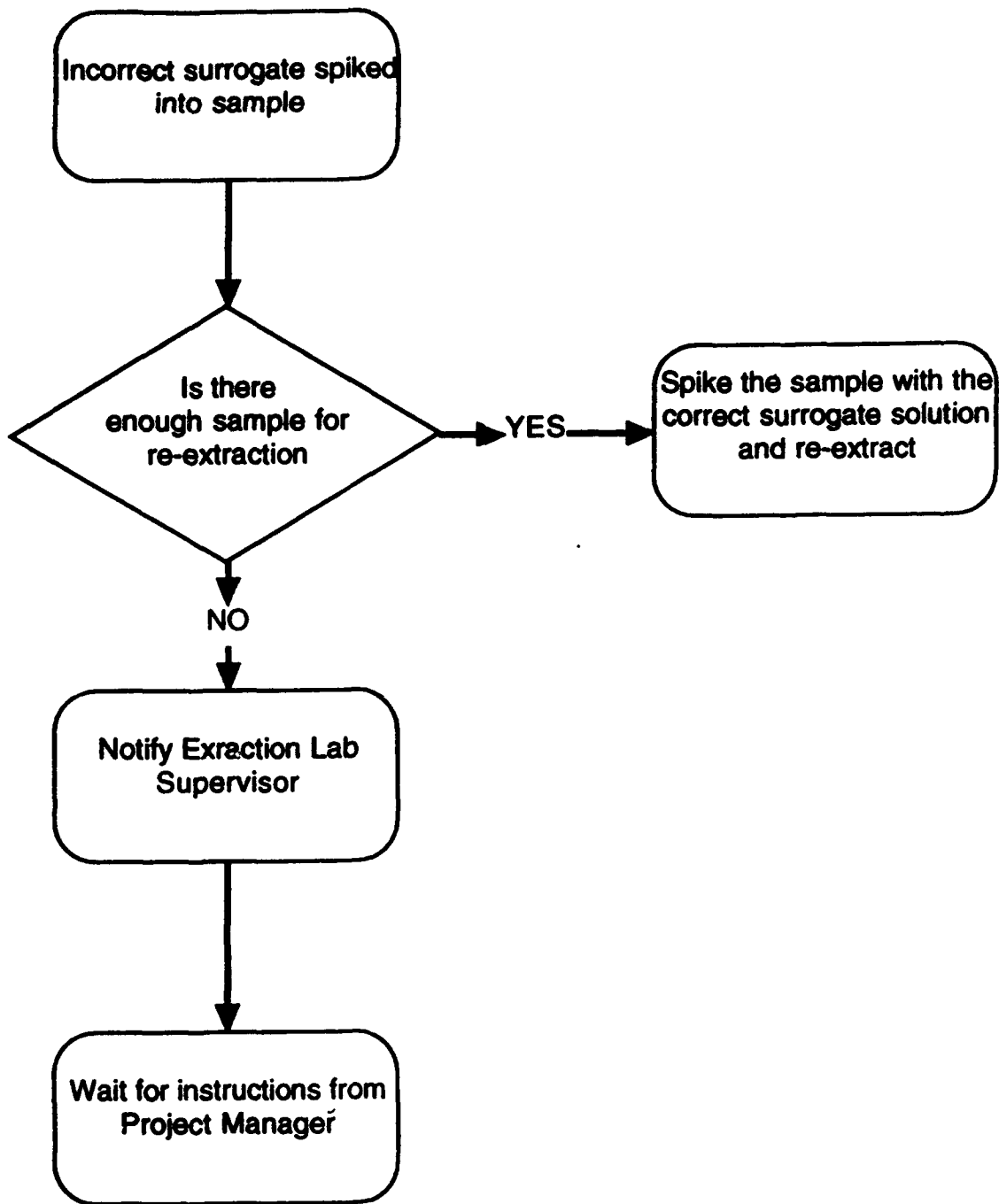
Corrective Action for Extract Spillage



Corrective Action for Incorrect Spike Volume



Corrective Action for Incorrect Surrogate Addition





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Standard Operating Procedure

Pesticides/PCBs
Soil Extraction
Method 3550

312S

Revision 5

6/29/94

PROPRIETARY

Prepared By:

Jayna M. Hawk - Thomas

Approvals:

NA

Section Manager

Don N. Scher
Laboratory Manager

Michelle J. Turner
Quality Assurance Manager

Mark Van
Laboratory Director

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Standard Operating Procedure

Soil Extraction

Chlorinated Pesticides/Polychlorinated Biphenyls (Pest/PCB) (8081)

1.0 Scope and Application

- 1.1 This method details the extraction of soil samples for organochlorine pesticides and polychlorinated biphenyls.

2.0 Definitions

- 2.1 Surrogates - known quantities of compounds added to all samples and blanks to evaluate extraction efficiency.
- 2.2 Matrix Spike - known quantities of selected analytes added to a sample to evaluate the effect of sample matrix on analyte recovery.
- 2.3 LCS (Laboratory Control Sample) - a blank fortified with known quantities of selected analytes to monitor extraction efficiency.

3.0 Equipment

- 3.1 400 mL heavy glass beaker.
- 3.2 100 mm glass funnel.
- 3.3 500 mL Erlenmeyer flask.
- 3.4 Kuderna-Danish concentrating apparatus (10 mL concentrator tube, 500 mL concentrator flask and 3 ball Snyder column).
- 3.5 25 x 340 mm drying column.
- 3.6 10 x 293 mm micro column.
- 3.7 100 mL glass beaker.
- 3.8 Aluminum weighing dish.
- 3.9 Glass wool, prepared by baking in kiln at 300° C for 4 hours.
- 3.10 Hexane, pesticide grade ; Acetone, high purity ; (1:1 mixture).
- 3.11 Disposable 5 3/4" pipet with rubber bulb.
- 3.12 Anhydrous sodium sulfate, prepared by baking in kiln at 400° C for 8 hours.
- 3.13 Florisil (See Florisil cleanup SOP).



3.14 Surrogate and matrix spike solutions.

3.14.1 Surrogate and spike solutions composed as follows:

	<u>Component</u>	<u>Concentration</u>
Surrogate	Decachlorobiphenyl (DCBP)	2 µg/mL
	Tetrachloro-m-xylene (TCMX)	2 µg/mL
Pesticide/ PCB Spike	Gamma BHC	5 µg/mL
	Heptachlor	5 µg/mL
	Aldrin	5 µg/mL
	Dieldrin	10 µg/mL
	Endrin	10 µg/mL
	4,4'-DDT	10 µg/mL
	Delta BHC	5 µg/mL
	4,4'-DDE	10 µg/mL
	4,4'-DDD	10 µg/mL
PCB Spike	Aroclor 1260	80 µg/mL

3.15 Deionized water (Barnstead E-Pure, 4 module D4641).

3.16 Analytical balance (top-loading): accurate to 0.02 g.

3.17 Sonicators: Branson 450 with 3/4" Titanium tip.

3.18 GPC: Models ABC 1002A/1002B.

3.19 N-Evap-Analytical Nitrogen Evaporator (organomation).

3.20 Water bath: set at 80° C-85° C and capable of temperature control $\pm 5^\circ$ C.

3.21 Drying oven (VWR BIOE) set at 105° C.

3.22 Boiling chips (Chemware/Teflon)

3.23 Scintillation Vial - 20 mL with Aluminum lined caps

3.24 Vials (2 mL clear) with crimp tops for GC Autosampler.

3.25 Stainless steel spatula.

3.26 Green & yellow label tape

3.27 2.5 mL amber vial with Teflon lined cap.

3.28 Personal protective gear (gloves, goggles, lab coat)

3.29 100 µL, 1.0 mL, 5.0 mL gastight Hamilton syringes.

3.30 Disposable 5 3/4" pipet with rubber bulb.

3.31 S/P vortex mixer.



- 3.32 0.45 μ m Whatman Puradisc filter.
- 3.33 40 mL vials with Teflon lined caps.
- 4.0 Documentation**
- 4.1 Pest/PCB Benchsheet.
- 5.0 In-house Modifications to Referenced Method**
- 5.1 Section 1.1: ARI does not use method-referenced concentration techniques 4.3.4 and 4.3.5, and 4.9 has been revised.
- 5.2 5.0 mL, 1.0 mL and 100 μ L syringes are used. See method 3510B for more information.
- 5.3 Section 6.12 (method section 7.3.9) Solvent exchange is done through the snyder column during K-D concentration with 8-10 mL of hexane.
- 5.4 Section 6.2 (method section 7.3.1) Surrogate/spike solution is added to extract after the solvent is added.
- 5.5 Section 6.6 (method section 7.3.4) Extracts are decanted and filtered through a 100 mm funnel with a glass wool plug, not through filter paper.
- 5.6 Section 6.13 (method section 7.10.3): The exchange has been revised.
- 5.7 Section 6.12 (method section 7.3.8) The extract is removed from the water bath at an apparent volume of 4-6 mL, not 1 mL.
- 5.8 Section 6.14 (method section 7.3.11.2) A water bath is not used for the nitrogen blow down technique. The internal wall of tube is not rinsed with solvent until the extract is vialled.
- 5.9 Section 6.15: Before GPC or Florisil clean-ups, samples are filtered with a 0.45 μ m Puradisc filter to remove gross particulate matter.
- 5.10 Section 6.22 (Method section 2.2) A 1-8 g sample size is extracted.
- 5.11 Section 6.25 (method section 2.2) a vortex mixer rather than a sonicator is used in the extraction process.
- 6.0 Procedures**
- 6.1 Samples are pre-screened on ECD for either low level or medium/high concentrations (refer to ECD screening SOP).
 - 6.1.1 For those samples that are low; review special analytical requirements sheet prior to extracting samples to determine if special procedures are required.
 - 6.1.2 For medium level concentrations, refer to section 6.21.



- 6.2 Fill out bench sheet for job. See attached example. Label each 400 mL beaker with a piece of green label tape containing the following information: job number, sample ID, matrix ID, type of extraction (Pest/PCB or PCB), method number and, for the blanks, the date.
- 6.3 Warm samples to room temperature, homogenize sample well, and use the top loading balance to measure 5-30 g of sample (the amount depending on the sample screening results) into the 400 mL beaker (labeled with sample ID); also, measure 20 g into a 100 mL beaker labeled with sample ID. Add approximately 30 g sodium sulfate to each sample in the 400 mL beaker and mix well; it should have a sandy consistency. Repeat for each sample. Prepare one 400 mL beaker with 30 g sodium sulfate for use as a method blank and one 400 mL beaker with 30 g sodium sulfate for an LCS. Add 20 mL of deionized water to each 100 mL beaker, stir thoroughly and allow to stand for at least an hour. Take a pH reading on this aliquot and record on soil prep sheet. Weigh out approximately 10 g of sample into a tared weighing dish (labeled with sample ID) for determination of percent moisture. Pour approximately 100 mL of acetone/hexane mixture (half and half) over each sample. Mix well.
- 6.3.1 For determination of % moisture, weigh out approximately 10g of sample into a tared Aluminum weighing dish, which has been labeled with sample ID. (use a permanent marker). Place in a drying oven set at 105° overnight. Take out in the morning and let cool for 15 minutes. Re-weigh samples and record on total solids benchsheet.
- 6.4 Add sufficient surrogate solution (100 μ L of a 2 μ g/mL solution) to each sample, the method blank, and the LCS. As per section 8.4, to verify surrogate is accurate, surrogates will be witnessed by another lab technician.
- 6.5 Add sufficient matrix spike solution (100 μ L of a 5 μ g/mL and 10 μ g/mL solution for pesticides, 125 μ L of an 80 μ g/mL solution for PCB's) to the LCS and, if a matrix spike and/or matrix spike duplicate are required, to any QC samples. As per section 8.4, to verify matrix spike is accurate, spike will be witnessed by another lab technician.
- 6.6 Sonicate the sample as follows: Place the sonic probe into the sample beaker with the tip below the surface of the solvent and above the sediment layer. Set



- the timer for 3 minutes with the mode on pulse, the power output to 10, and the duty cycle to 50%.
- 6.7 Once the timer shuts off, remove the beaker and pour the extraction solvent through the 100 mm funnel, with a glass wool plug in it, into the labeled (with sample ID) 500 mL Erlenmeyer flask.
 - 6.8 Repeat steps 6.5 and 6.6 two more times, using 1:1 hexane/acetone.
 - 6.9 After the last sonication, the sample is transferred to the funnel and the beaker is rinsed with 1:1 hexane/acetone. This rinsate is poured through the funnel, and then the funnel and extracted sample are also rinsed with 1:1 hexane/acetone. All rinsates are collected in the flask. Check Sample ID.
 - 6.10 Assemble a Kuderna-Danish (K-D) concentrator by attaching a rinsed 10 mL concentrator tube to a rinsed 500 mL evaporation flask. Prepare a drying column by putting a glass wool plug inside at the narrow end and filling the column with anhydrous sodium sulfate to a bed height of approximately 10 cm. Rinse the prepared column 30 mL with hexane. Check Sample ID.
 - 6.11 Transfer the sample ID label to the corresponding K-D. Dry the extract by passing it through the drying column and collecting it in the K-D concentrator. Rinse the Erlenmeyer flask three times with hexane and add this to the column as well. Once the entire extract has passed through the drying column, rinse the column with hexane.
 - 6.12 Remove the drying column, add 2 or 3 clean boiling chips to the concentrator flask, attach a three ball Snyder column, and put the entire apparatus on the water bath set at approximately 80° C. Wet the inside of the Snyder column with 1 to 2 mL of methylene chloride before boiling starts.
 - 6.13 Once the extract has concentrated to about 4 to 6 mL, remove the apparatus from the water bath. Place apparatus in rack and allow to stand for about 10 minutes.
 - 6.14 Remove the Snyder column, remove all water from the joint between the flask and the concentrator tube with a kimwipe, and disassemble the tube and flask. Rinse the lower joint of the flask into the tube with methylene chloride. Do not overfill the tube. Transfer the sample ID label to the tube.
 - 6.15 Mount the tube on a nitrogen evaporator and adjust the flow of gas so that, with the needle 1 to 2 cm above the surface of the extract, a small indentation can



- be seen in the surface of the extract. If there is bubbling or splashing, the flow is too high. If there is no indentation visible, the flow is too low.
- 6.16 When the volume reaches 1 to 2 mL remove the tube from the evaporator and proceed with clean up by gel permeation chromatography (GPC). See appropriate SOP for details. If GPC is not required, proceed with Florisil cleanup according to instructions in the Florisil Cleanup SOP.
- 6.17 After GPC clean up the extract is once again concentrated using a K-D apparatus on a water bath. Once the extract reaches 4 to 6 mL the solvent is exchanged to hexane by flushing the Snyder column with 10 mL of hexane. Once the extract again reaches 4 to 6 mL remove the apparatus from the water bath and rinse the column with 1 to 2 mL of hexane. Put the K-D in the rack and allow to stand for at least 10 minutes.
- 6.18 Remove Snyder column, remove all water from the joint between the flask and the concentrator tube with a kimwipe, and disassemble the tube and flask. Rinse the lower joint of the flask into the tube with hexane. Do not overfill the tube. Transfer the sample ID label to the tube.
- 6.19 Proceed with Florisil cleanup. (See appropriate standard procedure.)
- 6.20 If necessary, the extract is returned to the nitrogen evaporator. Once the extract reaches 10 mL (or specified final volume), an aliquot is transferred to a 2 mL clear auto sampler vial (labeled with the sample ID) for analysis.
- 6.21 If samples screen medium/high, review special analytical requirements sheet prior to extracting samples to determine if special procedures are required. See section 10.4.
- 6.22 Fill out bench sheet for job. See attached example. Warm samples to room temperature, decant and discard any water layer on a sediment sample. Homogenize sample well. Label each 20 or 40 mL vial with a piece of green label tape containing the following information: job number, sample ID, Matrix, type of extraction (Pest/PCB or PCB), method number, and (for the blanks only) date. Use the top loading balance to measure 1-8 g (to 0.1 g) of sample into appropriate vial (labeled with the sample ID); also measure 20 g into 100 mL beaker labeled with the sample ID for pH determination. Add approximately equal weight of anhydrous sodium sulfate to each sample vial and mix well. Sample should have a sandy consistency. Repeat for each sample. Prepare



one extraction vial with 1-8 g anhydrous sodium sulfate for use as a method blank and one vial with anhydrous sodium sulfate for an LCS. Pour 9.9 mL of Hexane/Acetone (1:1) over each sample and method blank; 9.7 mL for LCS or matrix spike samples.

- 6.23 Add sufficient surrogate solution (100 μ L of a 2 μ g/mL solution) to each sample, the method blank, and the LCS. As per section 8.4, to verify surrogate is accurate, surrogates will be witnessed by another lab technician.
- 6.24 Add sufficient matrix spike solution (100 μ L of a 5 μ g/mL and 10 μ g/mL solution for pesticides, 125 μ L of an 80 μ g/mL solution for PCB's) to the LCS and, if a matrix spike and/or matrix spike duplicate are required, to any QC samples. As per section 8.4, to verify matrix spike is accurate, spike will be witnessed by another lab technician.
- 6.25 Vortex the sample 1-2 minutes with periodic shaking of the vial. Let stand, or centrifuge if necessary.
- 6.26 Florisil cleanup is mandatory (usually 1 of 10 mL extract is cleaned by the florisil technique). See Florisil cleanup SOP. Other cleanups and filtrations, such as GPC, are optional.
- 6.27 After florisil cleanup the sample is concentrated on the nitrogen evaporator to a specified final volume. Mount the tube on a nitrogen evaporator and adjust the flow of gas so that, with the needle 1 to 2 cm above the surface of the extract, a small indentation can be seen in the surface of the extract. If there is bubbling or splashing, the flow is too high. If there is no indentation visible, the flow is too low. Transfer the extract to a 2 mL clear autosampler vial (labeled with the sample ID) for analysis.

7.0 Review

- 7.1 The Organic Extraction's Supervisor will review all bench work and bench sheets before distribution.
- 7.2 Review project documentation (special analytical requirements, etc.) prior to extracting samples to determine if special procedures are required.

8.0 Quality Control

- 8.1 One method blank will be extracted for each batch of 20 or fewer samples.
- 8.2 One LCS (spike blank) will be extracted for each batch of 20 or fewer samples.



- 8.3 One MS/MSD will be extracted for each parameter after every 20 samples of similar matrix and level (sample volume permitting).
- 8.4 To verify that surrogate and matrix spiking is accurate, spiking will be witnessed by another technician.
- 9.0 Corrective Actions**
- 9.1 See Corrective Action Charts, section 12.1.
- 10.0 Miscellaneous Notes and Precautions**
- 10.1 Constant attention must be given when watching K-Ds on water baths when extracts are below the surface of the water bath so they do not boil dry.
- 10.2 When boiling down extracts on the N-Evap a time should be used to remind the analyst of the volumes so extract will not be blown dry.
- 10.3 The spring that goes around the N-Evap must be stretched out when placing on or taking off concentrator tubes to avoid snapping off the bottom halves of the concentrator tube which could result in loss of extract.
- 10.4 Modified extraction levels may be required as the GC Supervisor or Extractions Supervisor deems necessary. Such decisions will be based on GC/ECD screen data or the analysis of the initial Pest/PCB extract. The particular extraction procedure will be determined on a case by case basis, but in general will involve the medium/high extraction of 1-8 g of sample in 10 mL of 1:1 Hexane/Acetone in a 20 mL scintillation vial. Appropriate amounts of sodium sulfate, surrogate spike, and matrix spike should be added (based on the anticipated final effective volume). The vial should be vortexed for at least 1 minute. Florisil cleanup is required, and all other relevant cleanups (as well as centrifuging and filtration) should be considered. The final effective volume of the extract should be between 10-100 mL based on the recommendation of the GC analyst and/or the supervisor.
- 11.0 Method References**
- 11.1 U.S. EPA, "Sonication Extraction". (SW-846), Method 3550, Revision 0, September, 1986.
- 12.0 Appendices**
- 12.1 Corrective Action Charts.



ANALYTICAL
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Standard Operating Procedure

Base, Acid, Neutral (BAN)
Water Extraction
Method 3510

305S

Revision 4

6/28/94

PROPRIETARY

Prepared By:

Jana M. Hawk-Thomas

Approvals:

NA
Section Manager

Ben N. Decker
Laboratory Manager

Michael J. Turner
Quality Assurance Manager

M. J. H. H. H.
Laboratory Director

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Standard Operating Procedure

Water Extraction

Base, Acid, Neutral (BAN) - 8270

1.0 Scope and Application

- 1.1 This method details the procedure for extracting the extraction of water samples in preparation for Semivolatile analysis.

2.0 Definitions

- 2.1 Surrogates - known quantities of compounds added to all samples and blanks to evaluate extraction efficiency.
- 2.2 Matrix Spike - known quantities of selected analytes added to a sample to evaluate the effect of sample matrix on analyte recovery.
- 2.3 LCS (Laboratory Control Sample) - a blank fortified with known quantities of selected analytes to monitor extraction efficiency.

3.0 Equipment

- 3.1 Water Bath set at 80° C - 85° C (with temperature control of +5° C)
- 3.2 N-Evap - Analytical nitrogen evaporator.
- 3.3 250 µL, 500 µL Hamilton Gastight syringe.
- 3.4 Boiling chips - Teflon (Chemware).
- 3.5 2000 mL separatory funnel with ground glass stopper and PTFE stopcock.
- 3.6 500 mL Erlenmeyer flask.
- 3.7 Kuderna-Danish concentrating apparatus (10 mL concentrator tube, 500 mL concentrator flask and 3 ball Snyder column).
- 3.8 25 x 240 mm drying column.
- 3.9 1000 mL graduated cylinder.
- 3.10 Glass wool, prepared by baking in kiln at 300° C for 4 hours.
- 3.11 Methylene Chloride, high purity.
- 3.12 Anhydrous sodium sulfate, prepared by baking in kiln at 400° C for 8 hours.
- 3.13 10 N sodium hydroxide solution and 1:1 sulfuric acid solution.



3.14 Surrogate and matrix spike solutions:

	<u>Component</u>	<u>Concentration</u>
3.14.1 Surrogate	2-chlorophenol-d4	150 µg/mL
	Phenol 2,3,4,5,6-d5	150 µg/mL
	2-Fluorophenol	150 µg/mL
	2,4,6-Tribromophenol	150 µg/mL
	p-Terphenyl-d14	100 µg/mL
	Nitrobenzene-d5	100 µg/mL
	2-Fluorobiphenyl	100 µg/mL
	1,2-Dichlorobenzene-d4	100 µg/mL
3.14.2 Spike	Phenol	150 µg/mL
	2-Chlorophenol	150 µg/mL
	4-Chloro-3-Methylphenol	150 µg/mL
	4-Nitrophenol	150 µg/mL
	Pentachlorophenol	150 µg/mL
	Pyrene	100 µg/mL
	1,4-Dichlorobenzene	100 µg/mL
	1,2,4-Trichlorobenzene	100 µg/mL
	2,4-Dinitrotoluene	100 µg/mL
	Acenaphthene	100 µg/mL
	n-Nitroso-Di-n-propylamine	100 µg/mL
	2-Methylnaphthalene	100 µg/mL

3.15 Deionized water (Barnstead E-Pure, 4-Module D4641)

3.16 Broad range pH paper.

3.17 Blue label tape.

3.18 2.5 mL Amber vial with Teflon lined cap.

3.19 Personal protective wear (gloves, goggles, lab coat).

4.0 Documentation

4.1 BAN bench sheet.

5.0 In-house Modifications to Referenced Method

5.1 Section 1.1: ARI does not use method-referenced concentration techniques 4.3.4 and 4.3.5. Also, technique 4.9 has been adapted.

5.2 Section 3.8: Anhydrous sodium sulfate is baked for 8 hours rather than 4 hours.

5.3 Section 6.17 (method section 7.11.2): No warm water is used with the nitrogen evaporator.



5.4 1.0 mL and 250 μ L syringes are used.

6.0 Procedures

- 6.1 Review special analytical requirements sheet prior to extracting samples to determine if special procedures are required. See Section 7.2.
- 6.2 Fill out bench sheet for job. See attached example.
- 6.3 Warm the samples to room temperature. Label each separatory funnel with a piece of blue label tape with the following information: job number, sample identification letter, matrix ID, type of extraction (BAN). For the blanks, include the date. Use a graduated cylinder to measure 1 liter of sample and quantitatively transfer it to the separatory funnel. Repeat for each sample. Prepare two separatory funnels with organic-free water for use as a method blank and an LCS.
- 6.4 Add sufficient surrogate solution (250 μ L) to each sample (and both blanks) to result in a final concentration of 25 μ g/mL for each base/neutral analyte and 37.5 μ g/mL for each acid analyte. See method 3510B, 8270 for syringe selection and use. As per Section 8.4 to verify that surrogate is accurate, surrogates will be witnessed by another lab technician.
- 6.5 Add sufficient matrix spike solution (250 μ L) to the LCS, and, if a matrix spike and/or matrix spike duplicate are required, to any QC samples to result in a final concentration of 25 μ g/mL for each base/neutral analyte and 37.5 μ g/mL for each acid analyte. As per Section 8.4 to verify that matrix spiking is accurate, spiking will be witnessed by another lab technician.
- 6.6 Use broad range pH paper and 10N sodium hydroxide solution to adjust the pH of each sample (and both blanks) to 9 or greater.
- 6.7 Add 60 mL of methylene chloride to sample bottle, then add rinsate to each corresponding separatory funnel.
- 6.8 Seal and shake the separatory funnels vigorously for 2 minutes, using periodic venting to release excess pressure.
- 6.9 Allow organic and aqueous layers to separate. Drain entire organic layer (including any emulsion) into a 500 mL Erlenmeyer flask which has been labeled with the sample ID (written with a sharpie pen).



- 6.10 Repeat steps 6.6 through 6.8 two more times. If emulsion is present, it must be broken up by whatever mechanical means necessary until all non organic material (water, silt, etc.) is returned to the separatory funnel. Drain the organic layer into the corresponding Erlenmeyer flask.
- 6.11 Use pH paper and 1:1 sulfuric acid solution to adjust the pH of all samples (and both blanks) to 2 or lower.
- 6.12 Repeat the procedures outlined in step 6.6 through 6.9.
- 6.13 Assemble a Kuderna-Danish (K-D) concentrator by attaching a Methylene Chloride rinsed 10 mL concentrator tube to a rinsed 500 mL evaporation flask. Prepare a drying column by putting a glass wool plug inside at the narrow end and filling the column with anhydrous sodium sulfate to a bed height of approximately 10 cm. Rinse the prepared column with 30 mL methylene chloride.
- 6.14 Dry the extract by passing it through the drying column and collecting it in the K-D concentrator. Rinse the Erlenmeyer flask three times with methylene chloride and add this to the column as well. Once the entire extract has passed through the drying column, rinse the column with 15 mL methylene chloride. Transfer the sample ID label to the K-D. Check sample I.D.
- 6.15 Remove the drying column, add 2 or 3 clean boiling chips to the concentrator flask, attach a three ball Snyder column, and put the entire apparatus on a water bath set at approximately 80°C. Wet the inside of the Snyder column with 1 to 2 mL of methylene chloride before boiling starts.
- 6.16 Once the extract has concentrated to about 4 to 6 mL remove the apparatus from the water bath and rinse the column with about 1 to 2 mL of methylene chloride. Put the apparatus in a rack and allow to stand for about 10 minutes.
- 6.17 Remove Snyder column, remove all water from the joint between the flask and the concentrator tube with a kimwipe, and disassemble the tube and flask. Rinse the lower joint of the flask into the tube with methylene chloride. Do not over fill the tube. Transfer the label to the tube.
- 6.18 Mount the tube on a nitrogen evaporator and adjust the flow of gas so that, with the needle 1 to 2 cm above the surface of the extract, a small indentation can be seen in the surface of the extract. If there is bubbling or splashing, the flow is too high. If there is no indentation visible, the flow is too low.



- 6.19 Once the extract reaches 1 mL (or specified final volume) it is transferred to a 2 mL amber, PTFE lined, screw cap vial for analysis. Transfer sample I.D. to the vial.

7.0 Review

- 7.1 The Organic Extractions Supervisor will review all bench work and bench sheets before distribution.
- 7.2 Review project documentation (special analytical requirements, etc.) prior to extracting samples to determine if special procedures are required.

8.0 Quality Control

- 8.1 One method blank will be extracted for each batch of 20 or fewer samples.
- 8.2 One LCS (spike blank) will be extracted for each batch of 20 or fewer samples.
- 8.3 One MS/MSD will be extracted for each parameter after every 20 samples of similar matrix and level (sample volume permitting).
- 8.4 To verify that surrogate and matrix spiking is accurate, spiking will be witnessed by another technician.

9.0 Corrective Actions

- 9.1 See Corrective Action Charts, section 12.1.

10.0 Miscellaneous Notes and Precautions

- 10.1 Constant attention must be given when watching K.D.s on water baths. When extracts are below the surface of the water bath so they do not blow dry.
- 10.2 When blowing down extracts on the N-Evap a time should be used to remind the analyst of the volumes so extract will not be blown dry.
- 10.3 The spring that goes around the N-Evap must be stretched out when placing or taken off the concentrator tubes to avoid snapping off the bottom halves of the concentrator tube which could result in loss of extract.

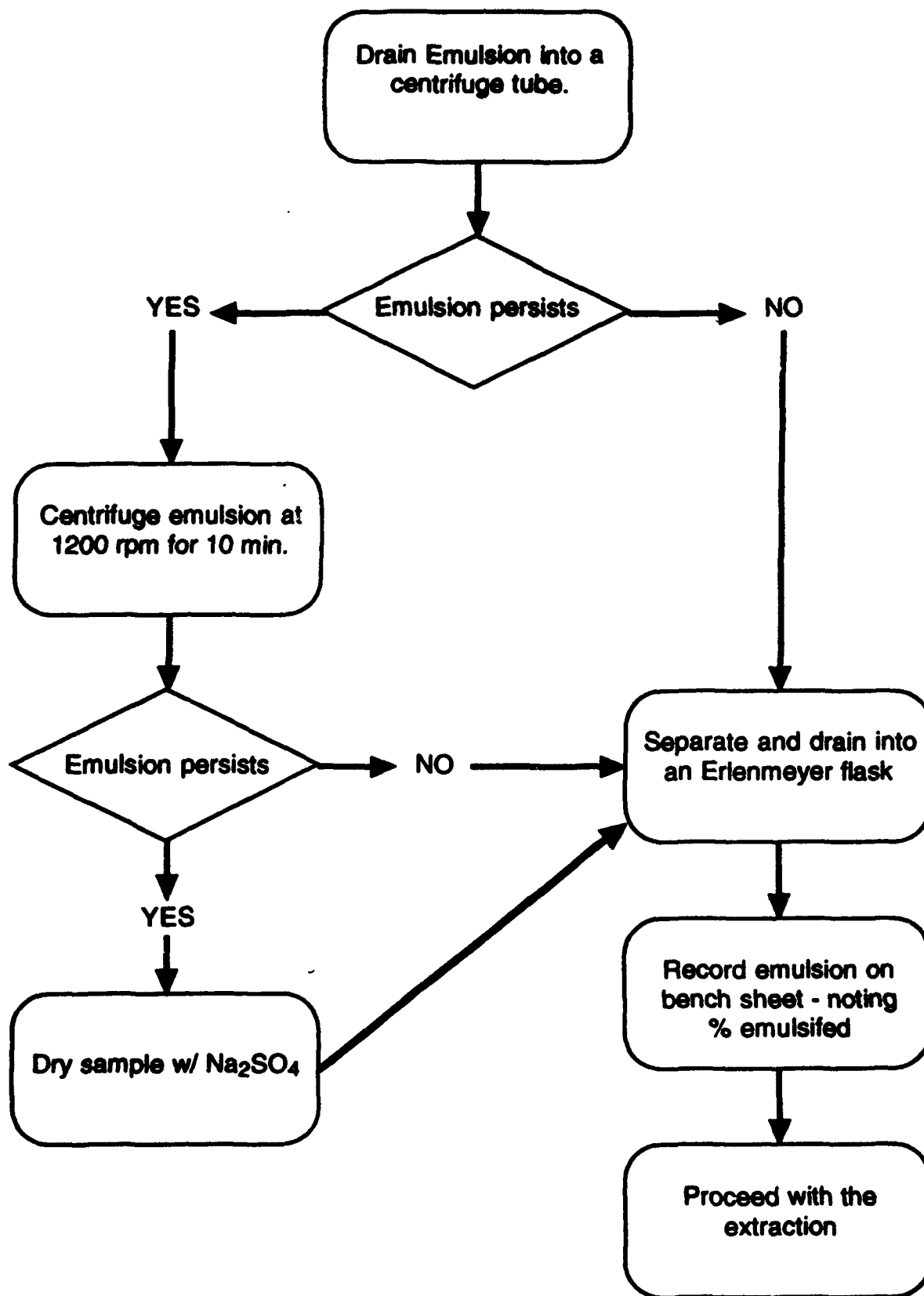
11.0 Method References

- 11.1 U.S. EPA, "Separatory Funnel Liquid-Liquid Extraction", (SW-846), method 3510B, Revision 2, November, 1992.

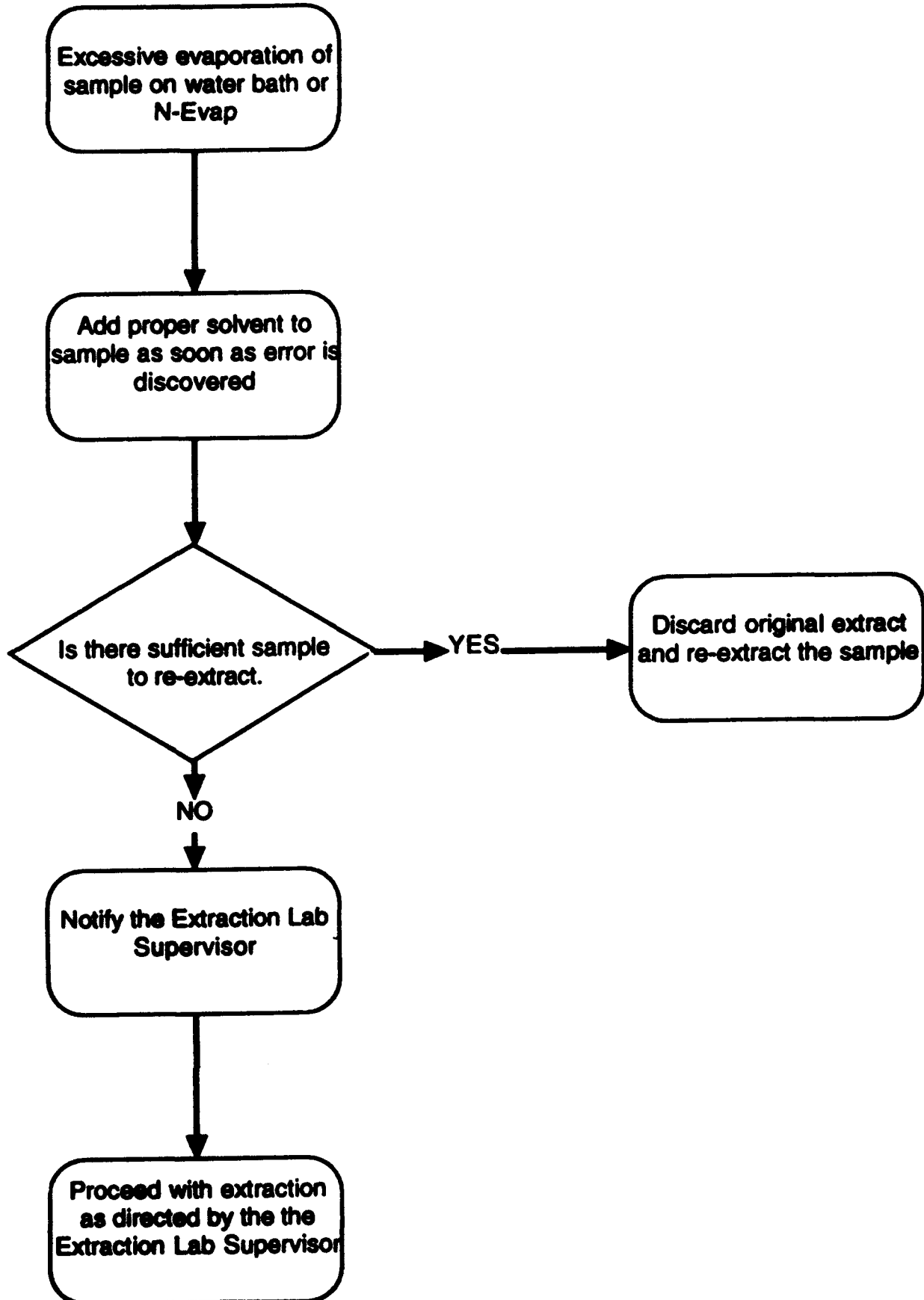
12.0 Appendices

- 12.1 Corrective Action Charts for H₂O.

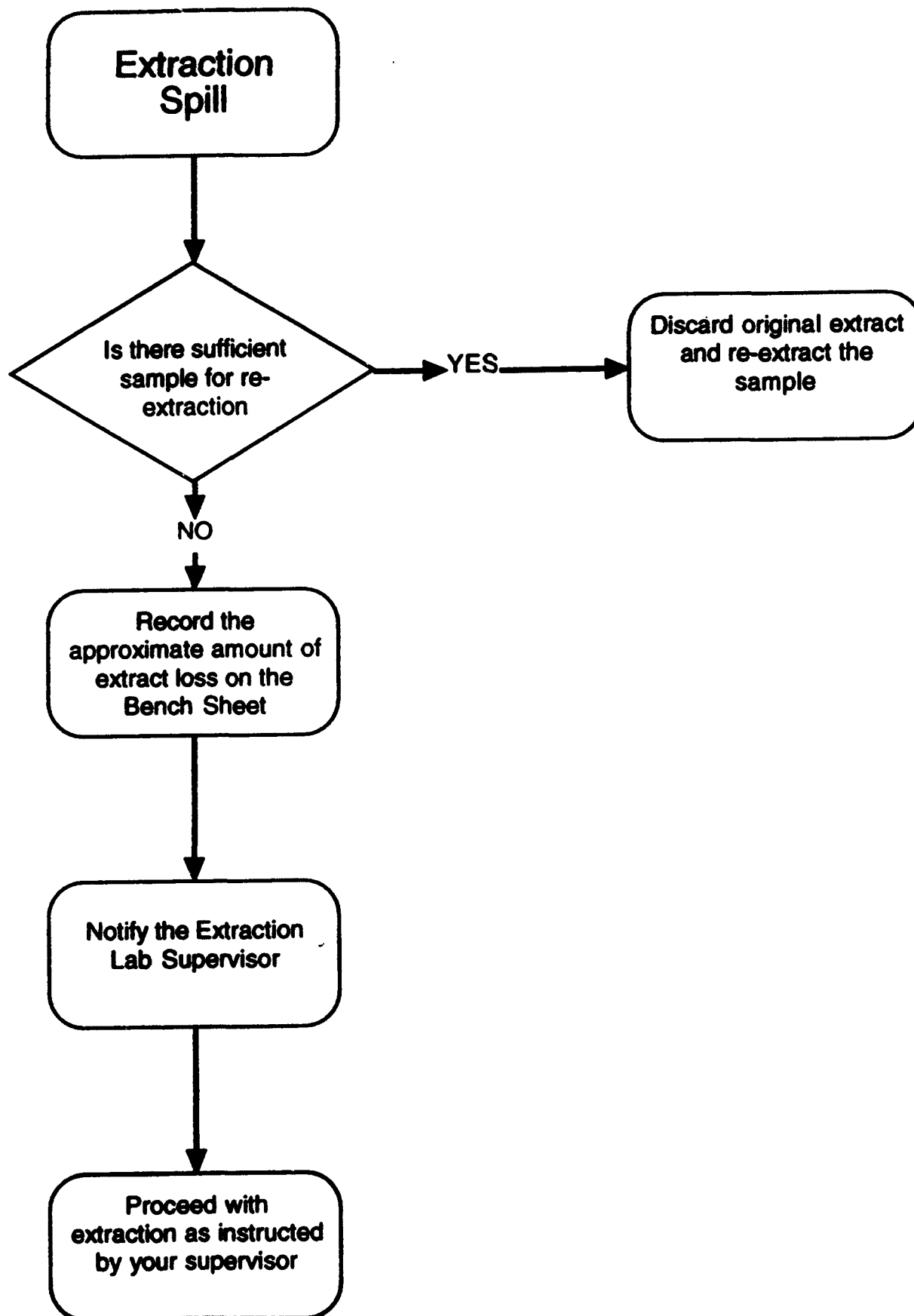
CORRECTIVE ACTION FOR EMULSIONS



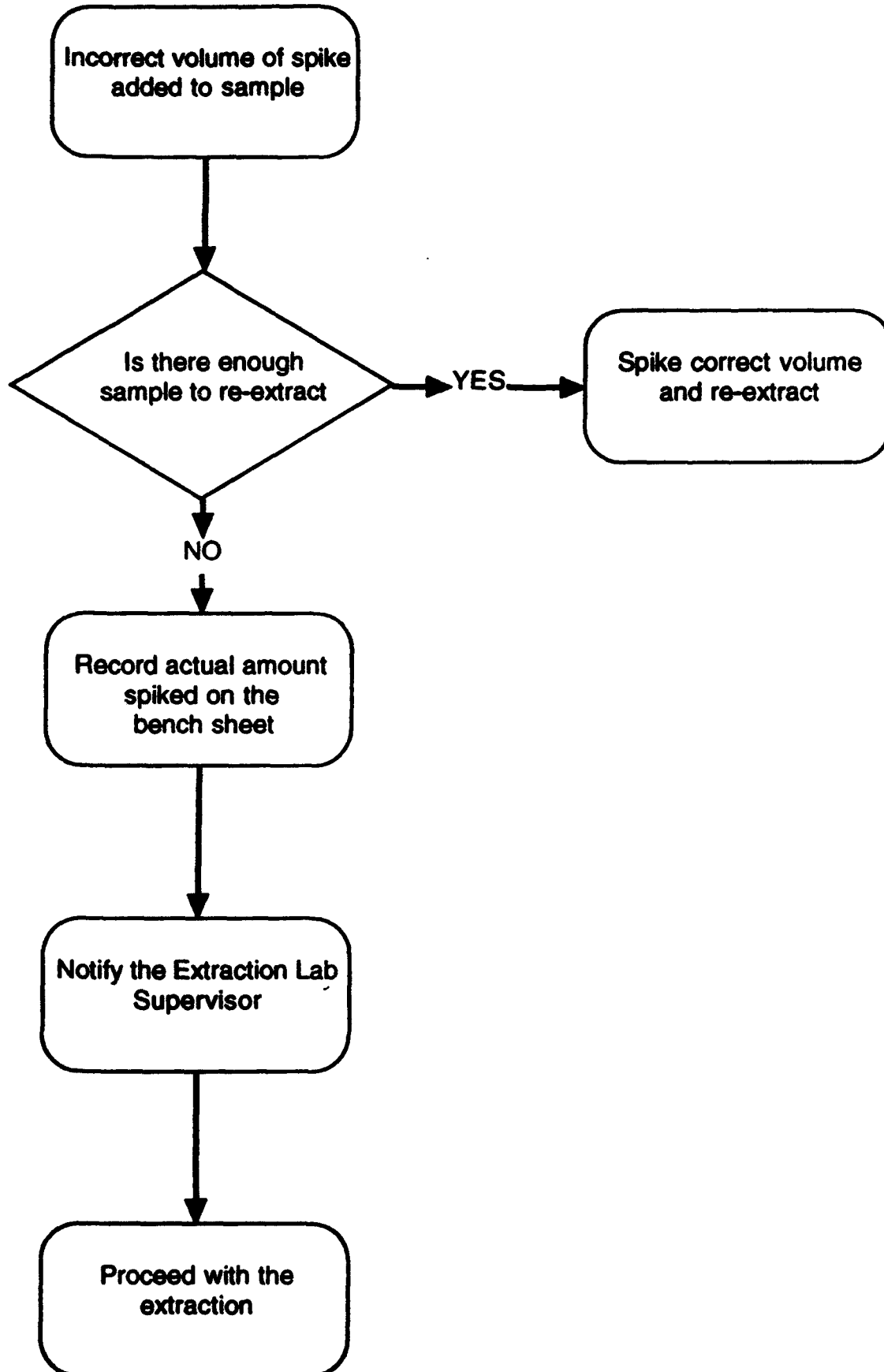
Corrective Action for Loss of Sample on Water Bath or N-Evap



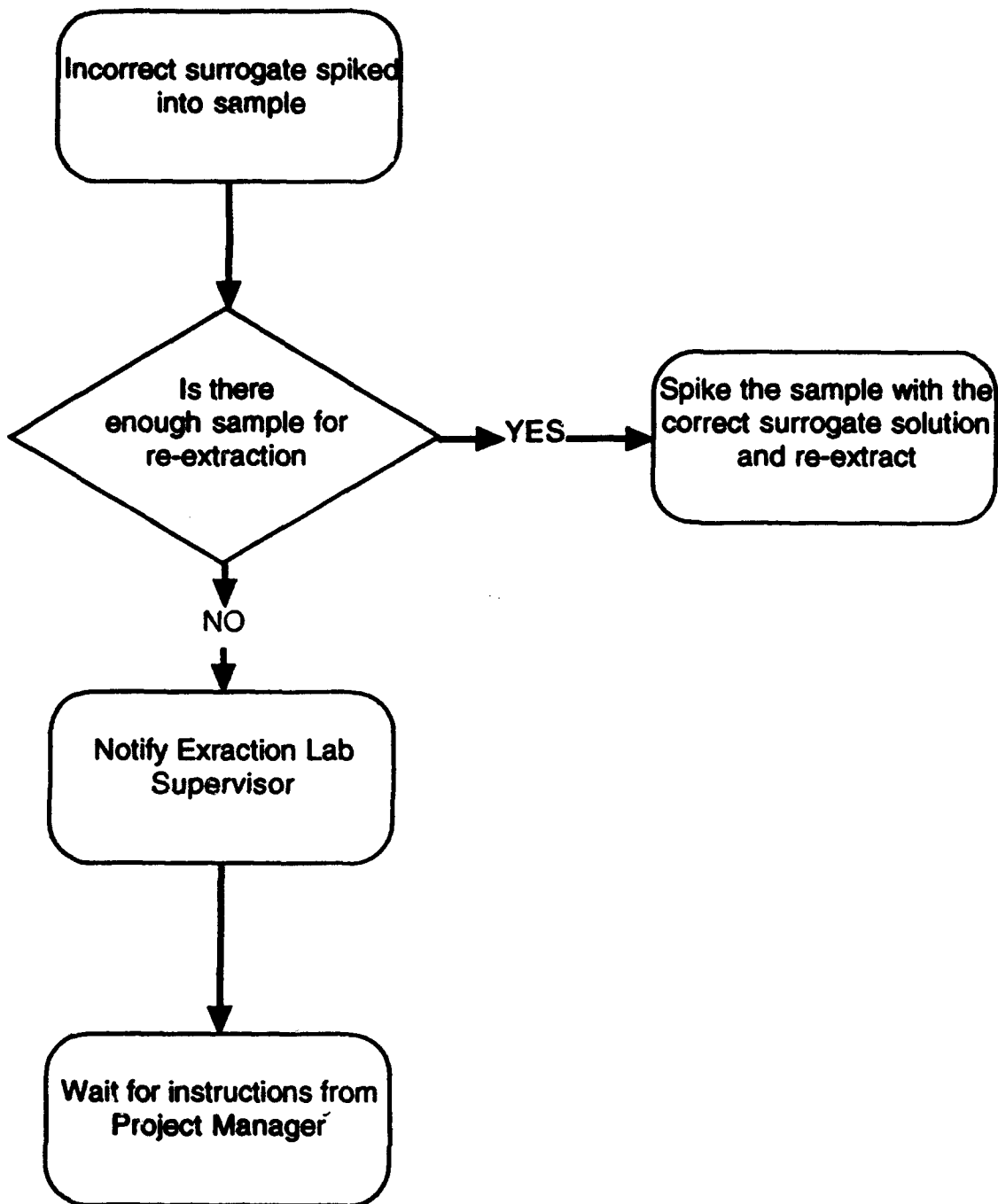
Corrective Action for Extract Spillage



Corrective Action for Incorrect Spike Volume



Corrective Action for Incorrect Surrogate Addition





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Standard Operating Procedure

Base, Acid, Neutral (BAN)
Soil Extraction
Method 3550

310S

Revision 4

6/28/94

PROPRIETARY

Prepared By:

Jane M. Hawk-Thomas

Approvals:

LA
Section Manager

Bruce M. Baker
Laboratory Manager

Michelle J. Turner
Quality Assurance Manager

Mark W. ...
Laboratory Director

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Standard Operating Procedure

Soil Extraction

Base, Acid, Neutral (BAN)

1.0 Scope and Application

- 1.1 This method details the procedure for the extraction of soil samples for Semivolatile analysis.

2.0 Definitions

- 2.1 Surrogates - known quantities of compounds added to all samples and blanks to evaluate extraction efficiency.
- 2.2 Matrix Spike - known quantities of selected analytes added to a sample to evaluate the effect of sample matrix on analyte recovery.
- 2.3 LCS (Laboratory Control Sample) - a blank fortified with known quantities of selected analytes to monitor extraction efficiency.

3.0 Equipment

- 3.1 240 mm heavy duty shaker.
- 3.2 100 mm glass funnel.
- 3.3 500 mL Erlenmeyer flask.
- 3.4 Kuderna-Danish concentrating apparatus (10 mL concentrator tube, 500 mL concentrator flask and 3-ball Snyder column).
- 3.5 25 x 340 mm drying column.
- 3.6 100 mL glass beaker.
- 3.7 Aluminum weighing dish.
- 3.8 Glass wool, prepared by baking in kiln at 300° C for 4 hours.
- 3.9 Methylene chloride, high purity.
- 3.10 1:1 mixture of acetone and methylene chloride (high purity).
- 3.11 Anhydrous sodium sulfate, prepared by baking in kiln at 400° C for 8 hours.
- 3.12 Surrogate and matrix spike solutions.



3.12.1 Surrogate and spike solutions composed as follows:

	<u>Component</u>	<u>Concentration</u>
Surrogate	2-Chlorophenol-d4	150 µg/mL
	Phenol 2,3,4,5,6-d5	150 µg/mL
	2-Fluorophenol	150 µg/mL
	2,4,6-Tribromophenol	150 µg/mL
	p-Terphenyl-d14	100 µg/mL
	Nitrobenzene-d5	100 µg/mL
	2-Fluorobiphenyl	100 µg/mL
	1,2-Dichlorobenzene-d4	100 µg/mL
Spike	Phenol	150 µg/mL
	2-Chlorophenol	150 µg/mL
	4-Chloro-3-Methylphenol	150 µg/mL
	4-Nitrophenol	150 µg/mL
	Pentachlorophenol	150 µg/mL
	Pyrene	100 µg/mL
	1,4-Dichlorobenzene	100 µg/mL
	1,2,4-Trichlorobenzene	100 µg/mL
	2,4-Dinitrotoluene	100 µg/mL
	Acenaphthene	100 µg/mL
	n-Nitroso-Di-n-propylamine	100 µg/mL
	2-Methylnaphthalene	100 µg/mL

- 3.13 Deionized water (Barnstead E-Pure, 4 Module D4641)
- 3.14 Top Loading Balance accurate to 0.02g
- 3.15 Sonicator - Branson 450 with 3/4" tip.
- 3.16 N-Evap - Analytical nitrogen evaporation.
- 3.17 Water bath - Set at 80° C - 85° C (with temperature control +5° C).
- 3.18 GPC - ABC 1002A/1002B.
- 3.19 Boiling chips - Teflon (Chemware).
- 3.20 250 µL, 500 µL, and 1.0 mL syringe gastight Hamilton syringe.
- 3.21 Green and orange label tape.
- 3.22 2.5 mL amber vial with Teflon lined screw cap
- 3.23 Stainless steel spatula.
- 3.24 Personal protective gear(gloves, goggles, lab coat)
- 3.25 S/P Vortex Mixer



- 3.26 40 mL vials with Teflon lined caps
- 3.27 Scintillation vial - 20 mL with aluminum caps
- 3.28 0.45 μ m Whatman Puradisc filter

4.0 Documentation

- 4.1 ABN bench sheet.

5.0 In-house Modifications to Reference Method

- 5.1 Section 6.5 (method section 7.3.1): Surrogate/spike added to extract after solvent is added.
- 5.2 Section 6.8 (method section 7.3.4): Extracts are decanted and filtered through a 100 mm funnel with a glass wool plug, not through filter paper.
- 5.3 Section 6.14 (method 7.3.8): The extract is removed from the water bath at a volume of 4 - 6 mL, not 1 mL.
- 5.4 Section 6.16 (method section 7.3.11.2): A water bath is not used for the nitrogen blow down technique. The internal wall of the tube is not rinsed with solvent.
- 5.5 Section 6.26: Samples are filtered with 0.45 μ m Puradisc filter to remove gross particulate matter.
- 5.6 Section 6.21 (method section 2.2): A 1-8 g. sample size is extracted.
- 5.7 Section 6.26 (method section 2.2): Samples are extracted using a vortex mixer, not sonication.

6.0 Procedures

- 6.1 Review special analytical requirement sheet prior to extracting samples to determine if special procedures are required. See Section 7.2.
- 6.2 Prior to extraction, samples are screened on FID to determine if samples are low level or medium/high level. See Sample Screening SOP.
 - 6.2.1 If samples screen low, see section 6.3.
 - 6.2.2 If samples screen medium/high, see section 6.20.
- 6.3 Low level - Prepare a bench sheet for the job. See attached example (section 4.1.).
- 6.4 Warm samples to room temperature. Label each 400 mL beaker with a piece of green label tape with the following information: job number, sample identification letter, type of extraction (BAN), and for the blanks, the date. Based on screening results, use the top loading balance to measure 5-30 g of sample into the 400 mL



beaker and 20 g into the 100 mL beaker labeled with the sample I.D. Add approximately 30 g sodium sulfate to each sample in the 400 mL beaker; mix well. It should have a sandy consistency. Repeat for each sample. Prepare one 400 mL beaker with 30 g sodium sulfate for use as a method blank and one for use as an LCS. Add 20 mL of organic free water to each 100 mL beaker, stir thoroughly, and allow to stand for at least an hour. Take a pH reading on this portion. Weigh out approximately 10 g of sample into a tared and sample ID labeled weighing dish for determination of percent moisture. Pour approximately 100 mL of acetone/methylene chloride mixture (1:1) over each sample.

- 6.4.1 For percent moisture determination, weigh out approximately 10g of sample into a tared aluminum weighing dish which has been labeled with sample I.D. using a permanent marker, and place in a the drying oven set at 105°C overnight. Take out in the morning and let cool 15 minutes. Re-weigh samples and record on the total solids benchsheet.
- 6.5 Add sufficient surrogate solution (500 μ L) to each sample, method blank and LCS to result in a final concentration of 25 μ g/mL for each base/neutral analyte and 37.5 μ g/mL for each acid analyte. As per Section 8.4, to verify that surrogate is accurate, surrogates will be witnessed by another lab technician.
- 6.6 Add sufficient matrix spike solution (500 μ L) to LCS, and if a matrix spike and/or matrix spike duplicate are required, to any QC samples to result in a final concentration of 25 μ g/mL for each base/neutral analyte and 37.5 μ g/mL for each acid analyte. As per Section 8.4, to verify that matrix spiking is accurate, spikes will be witnessed by another lab technician.
- 6.7 Sonicate the sample as follows: Place the sonic probe into the sample beaker with the tip below the surface of the solvent and above the sediment layer. Set the timer for 3 minutes with mode set on pulse, the power output to 10, and the duty cycle to 50%.
- 6.8 Once the timer shuts off, remove the beaker and pour the extraction solvent through the 100 mm funnel, with a glass wool plug in it, into the 500 mL Erlenmeyer flask labeled with the sample ID. Check the sample IDs.
- 6.9 Repeat steps 6.7 and 6.8 two more times. Once using the acetone and methylene chloride mixture, and once using methylene chloride.



- 6.10 After the last sonication, the sample is transferred to the funnel and the beaker is rinsed with methylene chloride. This rinse is poured through the funnel. The funnel and extracted sample are also rinsed with methylene chloride. All rinses are collected in the Erlenmeyer flask labeled with the sample ID.
- 6.11 Assemble a Kuderna-Danish (K-D) concentrator by attaching a methylene chloride rinsed 10 mL concentrator tube to a rinsed 500 mL evaporation flask and label the flask with the sample ID. Prepare a drying column by putting a glass wool plug inside at the narrow end and filling the column with anhydrous sodium sulfate to a bed height of approximately 10 cm. Rinse the prepared column once with methylene chloride.
- 6.12 Dry the extract by passing it through the drying column and collecting it in the K-D concentrator. Rinse the Erlenmeyer flask three times with methylene chloride and add this to the column as well. Once the entire extract has passed through the drying column, rinse the column with 15 mL methylene chloride. Transfer the sample ID label to the K-D. Check sample I.D.
- 6.13 Remove the drying column, add 2 or 3 clean boiling chips to the concentrator flask, attach a three ball Snyder column, and put the entire apparatus on a water bath set at approximately 80° C. Wet the inside of the Snyder column with 1 to 2 mL of methylene chloride before boiling starts.
- 6.14 Once the extract has concentrated to about 4 to 6 mL remove the apparatus from the water bath. Place apparatus in a rack and allow to stand for about 10 minutes.
- 6.15 Detach the Snyder column, remove all water from the joint between the flask and the concentrator tube with a kimwipe, and disassemble the tube and flask. Rinse the lower joint of the flask into the tube with methylene chloride. Do not overfill the tube. Transfer the sample ID label to the concentrator.
- 6.16 Mount the tube on a nitrogen evaporator and adjust the flow of gas such that with the needle 1 to 2 cm above the surface of the extract a small indentation can be seen in the surface of the extract. If there is bubbling or splashing the flow is too high. If there is no indentation visible, the flow is too low.
- 6.17 When the volume reaches 1 to 2 mL, remove the tube from the evaporator and, if needed, proceed with clean up by gel permeation chromatography (GPC). See appropriate SOP for details.



- 6.18 After GPC clean up, transfer the sample ID label to the K-D. The extract is once again concentrated using a methylene chloride K-D apparatus on a water bath and then a nitrogen evaporator.
- 6.19 Once the extract reaches 1 mL (or specified final volume), it is transferred to a PTFE lined, 2 mL amber screw cap vial for analysis which has been labeled with the sample ID (orange if there was a GPC, green if no GPC was performed).
- 6.20 Medium/high level - Prepare a bench sheet for the job. See attached example (section 4.1).
- 6.21 Decant and discard any water layer on the sediment samples. Label each 20 mL or 40 mL vial with a piece of green label tape with the following information: job number, sample identification letter, extraction type (BAN), and, for the blanks, the date. Use the top loading balance to measure 1-8 g (to 0.1 g.) of homogenized sample into an appropriate, labeled vial. Add an approximately equal weight of anhydrous sodium sulfate to the sample and mix well; the mixture should have a sandy consistency. Prepare two extraction vials with an equivalent sample weight of anhydrous sodium sulfate: one for use as the method blank and one for use as the LCS. Pour 9.5 mL of acetone/methylene chloride (1:1) over each sample and method blank; pour 9.0 mL of the mixture over the LCS and matrix spike samples.
- 6.22 For soil pH, weigh 20 g. into a labeled 100 mL beaker and add 20 mL of organic-free water. Stir thoroughly and allow to stand for at least one hour. Take a pH reading on this portion. Record the reading on the benchsheet.
- 6.23 See section 6.4.1 for percent moisture determination.
- 6.24 Add sufficient surrogate solution (500 μ L) to each sample, method blank and LCS to result in a final concentration of 25 μ g/mL for each base/neutral analyte and 37.5 μ g/mL for each acid analyte. As per Section 8.4, to verify that surrogate is accurate, surrogates will be witnessed by another lab technician.
- 6.25 Add sufficient matrix spike solution (500 μ L) to LCS, and if a matrix spike and/or matrix spike duplicate are required, to any QC samples to result in a final concentration of 25 μ g/mL for each base/neutral analyte and 37.5 μ g/mL for each acid analyte. As per Section 8.4, to verify that matrix spiking is accurate, spikes will be witnessed by another lab technician.



- 6.26 Vortex the sample 1-2 minutes, periodically shaking the sample vial. Filter 5 mL of the 10 mL extract through a 0.45 μ m Whatman Puradisc filter into a 10 mL concentrator tube.
- 6.27 Mount the tube on a nitrogen evaporator and adjust the flow of gas such that with the needle 1 to 2 cm above the surface of the extract a small indentation can be seen in the surface of the extract. If there is bubbling or splashing the flow is too high. If there is no indentation visible, the flow is too low.
- 6.28 When the volume reaches approximately 1 mL, remove the tube from the evaporator. If necessary, proceed with GPC cleanup. Use only GPC 1002A. See GPC Cleanup SOP.
- 6.29 After GPC clean up, transfer the sample ID label to the K-D. The extract is once again concentrated using a methylene chloride K-D apparatus on a water bath and then a nitrogen evaporator.
- 6.30 Once the extract reaches 1 mL (or specified final volume), it is transferred to a PTFE lined, 2 mL amber screw cap vial for analysis which has been labeled with the sample ID (orange if there was GPC, green if no GPC was performed).

7.0 Review

- 7.1 The Organic Extractions Supervisor will review all bench work and bench sheets before distribution.
- 7.2 Review project documentation (special analytical requirements, etc.) prior to extracting samples to determine if special procedures are required. See Section 6.0.

8.0 Quality Control

- 8.1 One method blank will be extracted for each batch of 20 or fewer samples.
- 8.2 One LCS (spike blank) will be extracted for each batch of 20 or fewer samples.
- 8.3 One MS/MSD will be extracted for each parameter after every 20 samples of similar matrix and level (sample volume permitting).
- 8.4 To verify that surrogate and matrix spiking is accurate, spiking will be witnessed by another technician.

9.0 Corrective Actions

- 9.1 See Corrective Action Charts, section 12.1.



10.0 Miscellaneous Notes and Precautions

- 10.1 Constant attention must be given when watching K.D.'s on water baths, when extracts are below the surface of the water bath so they do not blow dry.
- 10.2 When blowing down extracts on the N-Evap a time should be used to remind the analyst of the volumes so extracts will not be blown dry.
- 10.3 The spring that goes around the N-Evap must be stretched out when placing or taking of concentrator tubes to avoid snapping off the bottom halves of the concentrator tube which could result in loss of extract.

11.0 Method References

- 11.1 U.S. EPA, "Sonication Extraction", (SW-846), Method 3550, Revision 0, September, 1986.

12.0 Appendices

- 12.1 Corrective Action Charts.



EXTRACTION - BAN - SOIL

ARI Job No.: Fill in ARI Job #

Client Name: Fill in Client Name

Client Project: Fill in Client Project

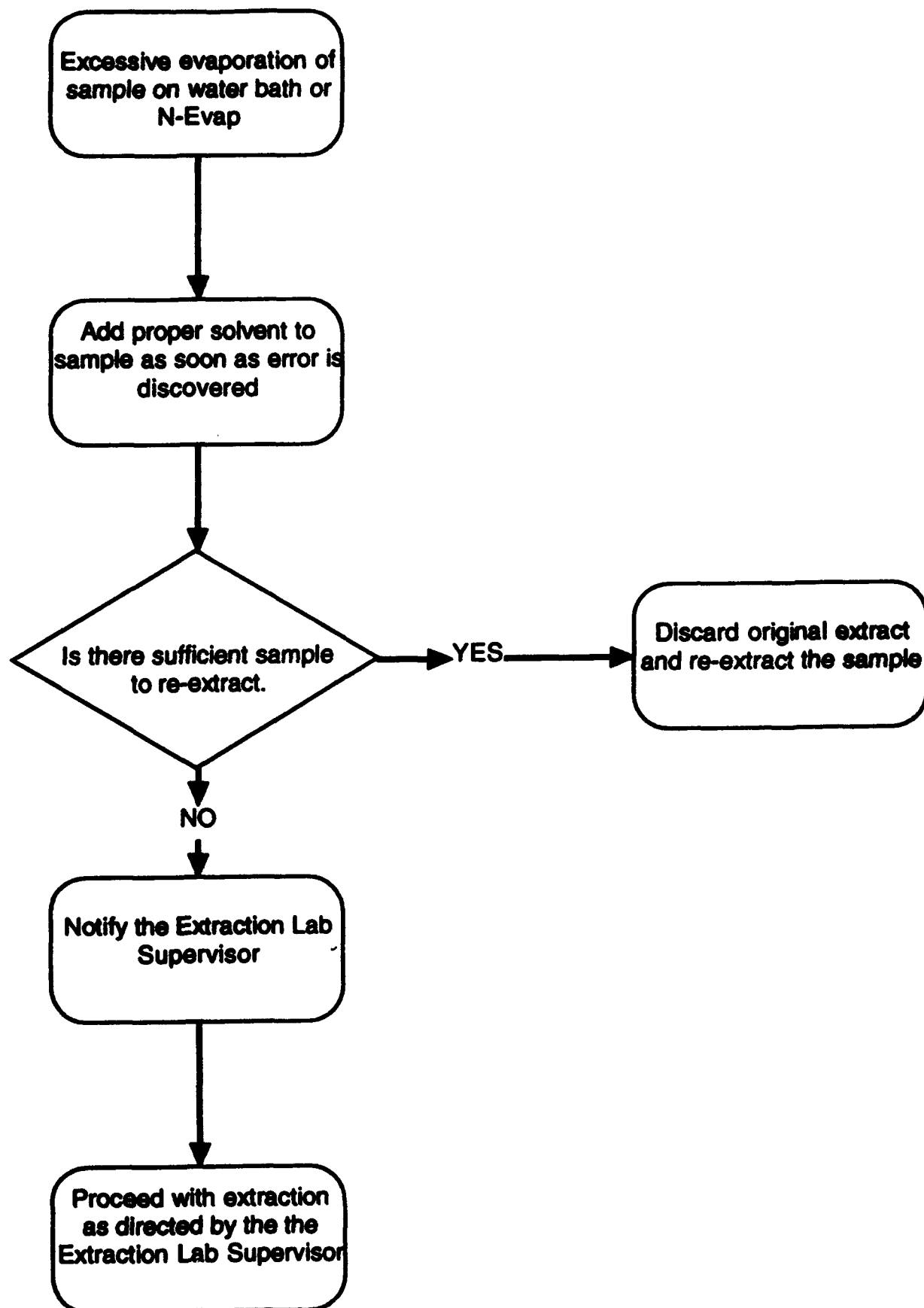
Extraction Requirements		Amount Extracted	GPC Allquot	Final Vol. BAN	Allquot to Lab	Comments:
Transfer Print Sheet info here						What job # is this job Batched too? Any important information or part of the ordinary
MB: MB I.D. + DATE		30g	1:2	1.0ml	1:1	Blank linked to Jobs: what job # is this job Batched too?
SB: SB I.D. + DATE		↓	↓	↓	↓	
ARI Lab ID	Client ID	Amount Extracted	GPC Allquot	Final Vol. BAN	Allquot to Lab	Comments:
F123 A	Read from sample 1	30.00g	1:2	1.0ml	1:1	Any pertinent information relating to samples
↓ B	2	30.00g	↓	↓	↓	↓
↓ C	3	30.00g	↓	↓	↓	↓
			IF THIS IS NOT USED CROSS-OUT			
* Unused portion of bench sheet must be lined out.						
Date/Analyst:		Who Extracted + date	Who GPC + date	Who Vialled + date		

Surr. Amt.: <u>500ul</u>	Added By: <u>who surrogate</u>	/Spk Witness
Conc.: <u>60/150ug/ml</u>	ID: <u>264-Y</u>	
Spike Amt.: <u>500ul</u>	Added By: <u>who spiked</u>	/Spk Witness
Conc.: <u>100/150ug/ml</u>	ID: <u>268-Y</u>	

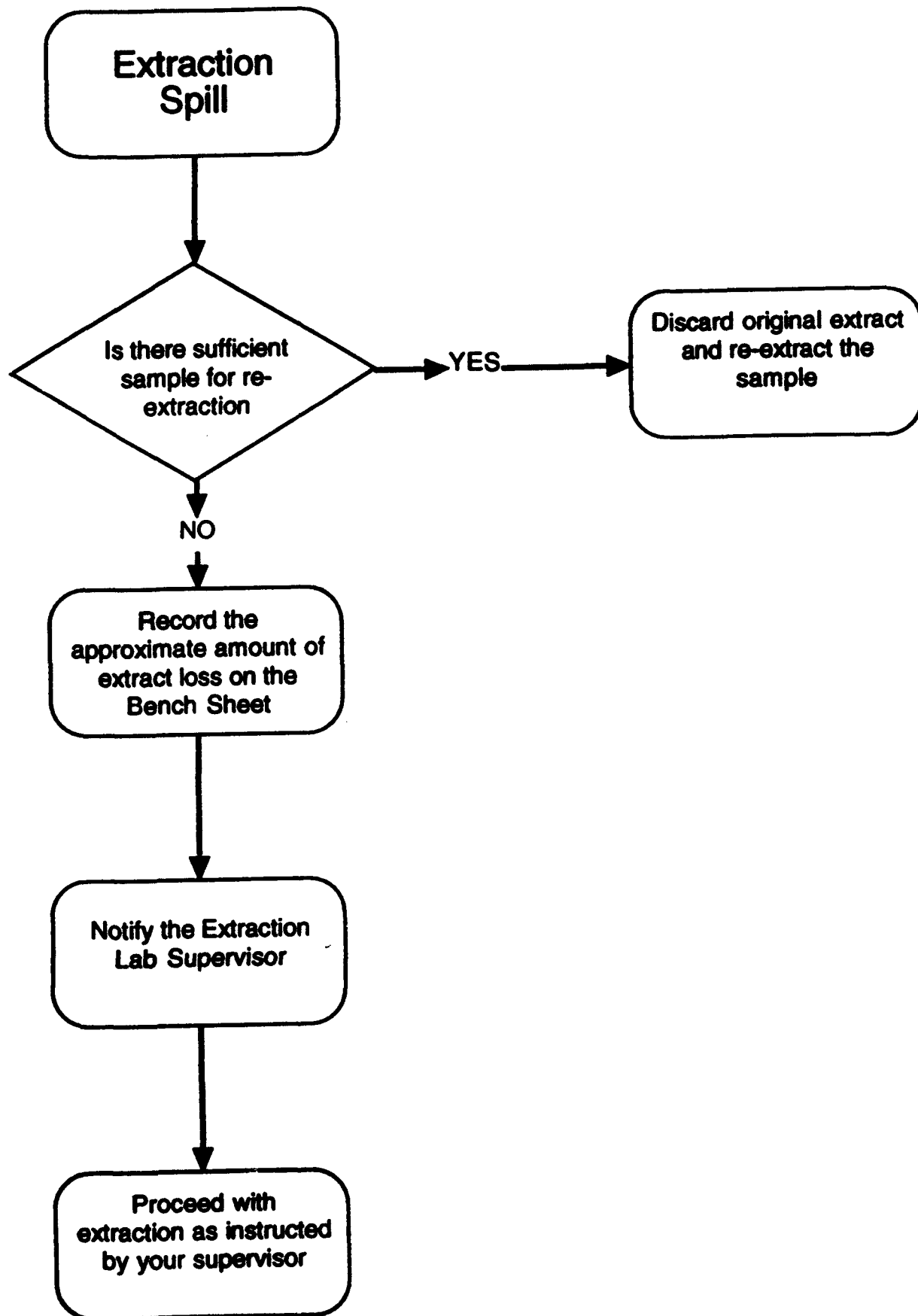
Date: _____

Ext. Storage
Location: _____

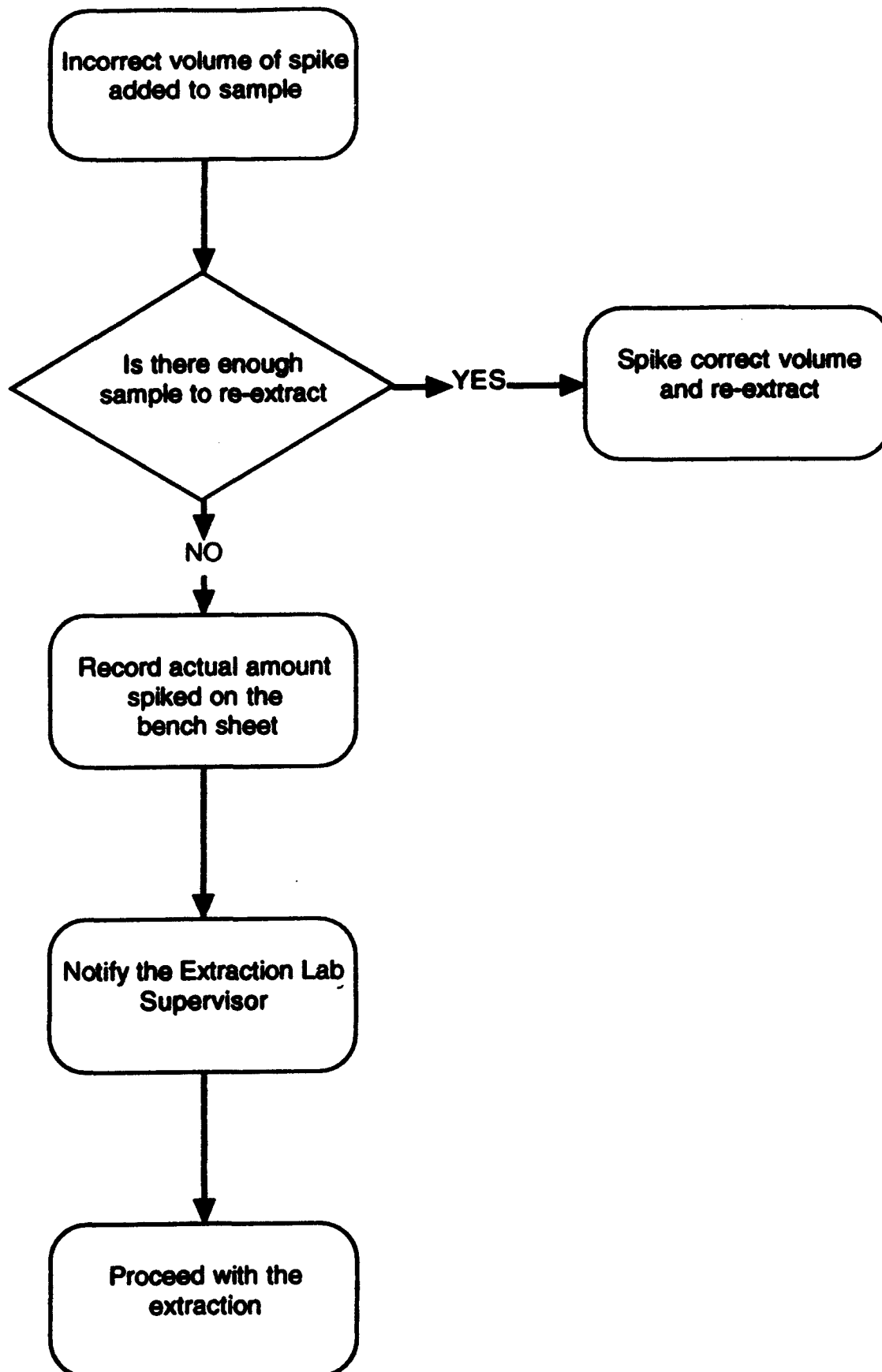
Corrective Action for Loss of Sample on Water Bath or N-Evap



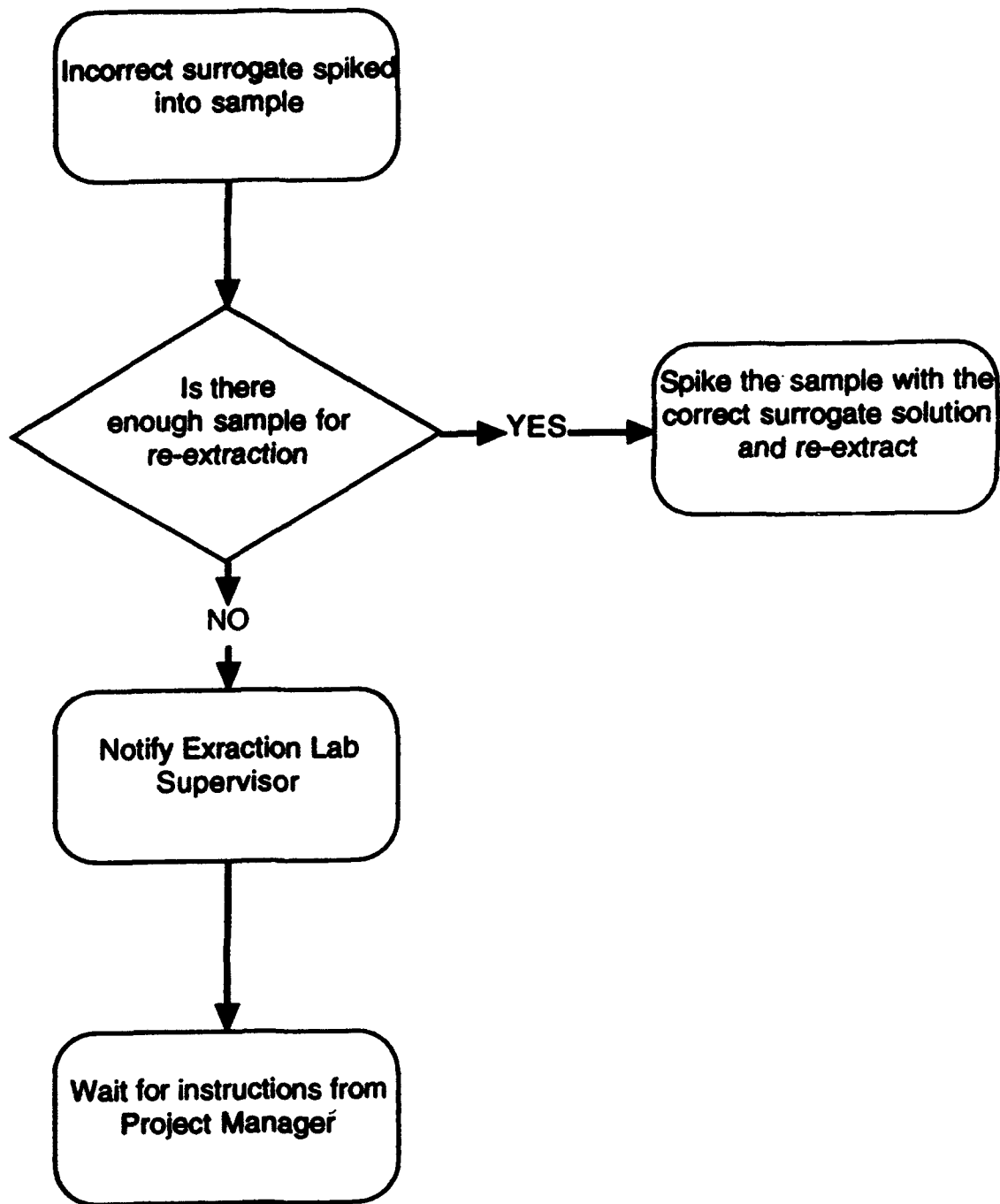
Corrective Action for Extract Spillage



Corrective Action for Incorrect Spike Volume



Corrective Action for Incorrect Surrogate Addition





ANALYTICAL
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Standard Operating Procedure

Medium Level TPH
Soil Extraction
Method 3550

306S

Revision 4

6/28/94

PROPRIETARY

Prepared By:

Jarvis M. Hawk-Thomson

Approvals:

NH
Section Manager

Ben N. Baker
Laboratory Manager

Michelle J. Turner
Quality Assurance Manager

Mark L. Turner
Laboratory Director

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Standard Operating Procedure

Soil Extraction

Total Petroleum Hydrocarbon (Medium Level)

1.0 Scope and Application

- 1.1 This method details the procedure for extracting medium level soil samples for petroleum hydrocarbons.

2.0 Definitions

- 2.1 Surrogates - known quantities of compounds added to all samples and blanks to evaluate extraction efficiency.
- 2.2 Matrix Spike - known quantities of selected analytes added to a sample to evaluate the effect of sample matrix on analyte recovery.
- 2.3 LCS (Laboratory Control Sample) - a blank fortified with known quantities of selected analytes to monitor extraction efficiency.

3.0 Equipment

- 3.1 2 mL sample vials or 10 mL VOA vial.
- 3.2 Anhydrous sodium sulfate. Prepared by baking in kiln at 400° C for 8 hours.
- 3.3 5 3/4" Pasteur pipets.
- 3.4 Aluminum weighing dishes.
- 3.6 Methylene chloride, high purity.
- 3.7 Surrogate and matrix spike solutions.

3.7.1 Surrogate and spike solutions composed as follows:

	<u>Component</u>	<u>Concentration</u>
Surrogate	Methyl arachidate	1500 µg/mL
Spike	Gasoline or Diesel	5000 µg/mL

- 3.8 Top loading balance accurate to 0.02 g.
- 3.9 Vortexer (Genie 2) output to 10 with touch control.
- 3.10 Stainless steel spatula
- 3.11 Water Bath set at 80° C (±5° C)
- 3.12 N-Evap - Analytical Nitrogen Evaporator
- 3.13 GPC - ABC Model 1002A/1002B
- 3.14 1.0 mL, syringe



- 3.15 100 μ L, 500 μ L syringe gastight Hamilton syringe.
- 3.16 2.5 mL clear GC autosampler vial.
- 3.17 Personal protective gear (gloves, goggles, lab coat)

4.0 Documentation

- 4.1 TPH/HCID bench sheet (LIMS)

5.0 In-house Modifications to Referenced Method

- 5.1 Section 6.1.3 (method section 7.5.3): Surrogate/spike solution is added to extract after solvent is added.
- 5.2 Section 6.1.3 (method section 7.5.4): Samples are not sonicated. Extract by vortexing samples for approximately 1 minute.
- 5.3 Section 6.1.4 (method section 7.5.5). Samples are filtered with a 0.45 μ m Puradisc filter to remove gross particulates.

6.0 Procedures

- 6.1 Review special analytical requirements' sheet prior to extracting samples to determine if special procedures are required. See Section 7.2.

6.2 Soil Extraction

- 6.2.1 Prepare a bench sheet for the job.
- 6.2.2 Warm samples to room temperature. Mix sample to ensure a homogeneous and representative portion from the sample matrix, mark a cap with job number, sample identification letter, matrix ID, and type of analysis. Next, use a top loading balance to weigh out 10 g of sample (to 0.02g) into a tared scintillation vial labeled with the sample ID (use a permanent marker to write on the cap). Weigh out an additional 10 g of sample into a tared weighing dish labeled with the sample ID (use a permanent marker to write on the dish) for dry weight determination. Add enough sodium sulfate to the vial to dry the sample. Cap sample and set aside. Repeat for all samples.
 - 6.2.2.1 To determine dry weight, weigh approximately 10 g of sample into a tared aluminum weighing dish which has been labeled with sample I.D. (use a permanent marker) and set in the drying oven set at 105°C overnight. Take out in morning and let cool for 15 minutes. Re-weigh samples and record on total solids benchsheet.



- 6.2.3 Prepare a method blank and LCS by weighing out 10 g of sodium sulfate into a scintillation vial. Mark cap with "mb's" or "sb's" and date. Cap and set aside.
- 6.2.4 Uncap each vial. Add 10 mL methylene chloride and sufficient surrogate solution (100ul) for a final concentration of 15 µg/Kg. As per Section 8.4, to verify that surrogate is accurate, surrogates will be witnessed by another technician.
- 6.2.5 Add matrix spiking solution (1000µL) to LCS, matrix spike, and matrix spike duplicate to result in a final concentration of 500 µg/Kg. To keep final volume consistent, adjust the amount of solvent added to those samples receiving spiking solution. Recap vial and use vortexer to shake for about 1 min. As per Section 8.4, to verify that matrix spike is accurate, spike will be witnessed by another technician.
- 6.2.6 Centrifuge sample if necessary. Filter sample to remove gross particulates, using a 0.45 µm Puradisc filter.
- 6.2.7 Pipet approximately 1 mL of the extraction solvent with a Pasteur pipet to a clear glass auto sampler vial which has been labeled with the sample ID (using a permanent marker) for analysis.

7.0 Review

- 7.1 The Organic Extractions Supervisor will review all bench work and bench sheets before distribution.
- 7.2 Review project documentation (special analytical requirements, etc.) prior to extracting samples to determine if special procedures are required. See Section 6.0.

8.0 Quality Control

- 8.1 One method blank will be extracted for each batch of 20 or fewer samples.
- 8.2 One LCS (spike blank) will be extracted for each batch of 20 or fewer samples.
- 8.3 One MS/MSD will be extracted for each parameter after every 20 samples of similar matrix and level (sample volume permitting).
- 8.4 To verify that surrogate and matrix spiking is accurate, spiking will be witnessed by another technician.

9.0 Corrective Actions

- 9.1 See Corrective Action Charts, section 12.1.



10.0 Miscellaneous Notes and Precautions

- 10.1 If extracting sediments or soils that are extremely wet, you must use a 40 mL VOA vial to weigh out 10g of sample. It is easier to vortex the sample in a 40mL VOA vial rather than the 20 mL scintillation vial due to the space provided to mix sample. Low recoveries will occur in a 20 mL scintillation vial because sample cannot mix adequately.

11.0 Method References

- 11.1 U.S. EPA, "Ultrasonic Extraction", (SW-846), Method 3550B, Revision 2, November, 1990.

12.0 Appendices

- 12.1 Corrective Action Charts.

TPH 8015d - HCID Gas - HCID Diesel - SOIL

ARI Job No: Fill in ARI JOB #

Client Name: Ful in client Name

Client Project: Fill in client project

ARI Lab ID	Client Sample ID	Amount Extracted	Vol. Solv. Added	Final Total Vol.	Allquot Vol. for Analysis	Comments
Method Blank I.d. + date		10.00 g	9.9 ml	10.0 ml	1.10	(Batched QC) what job # is this job attached to?
Spike Blank I.d. + date			9.9 ml			
F123 A	1		9.9 ml			Any pertinent information relating to samples.
B	2					
C	3					
Unused portion of benchsheet must be lined out.						
Analyst/ Date:		who Extracted + date	who vialled + date			

Surr. Armt: 1002 L Added By: who surrogated / Spk Witness
Conc.: 1500 µg/ml ID: 257-4
Spike Armt: 1002 L Added By: who spmed / Spk Witness
Conc.: 5000 µg/ml ID: 266-5

Ext. Storage Location:

* Any errors made must have a single line drawn through error w/ initials + date

HCID QA Extraction
hcidqa.wlf printed 3/31/94

Worklist Number 947

Data Analyst: Susan D. Dunnihoo
Data Reported: 3/31/94
Comments:

Analyzed by: SDRD
Date Analyzed:

Sample Number	Client ID	Amt Ext (gm or ml)	Vol Solv Added	Final Total Vol
Extraction Requirements:				
94-1886	1. Method Blank AAA7			Adjusted Sample Amt:
	Spike Blank			
94-1886	AAA7 A Matrix Spike			Adjusted MS Amt:
94-1886	AAA7 A MS Duplicate			Adjusted MSD Amt:
94-1886	AAA7 A Duplicate			Adjusted Dupl Amt:

Surr Added By: SDRD
ID#:

Surr Conc: _____
Surr Amt: _____

Spike ID#: _____
Spike Conc: _____
Spike Added: _____

Analyst Signature _____ Extract Stored/Given to _____

HCID Extraction
hcidext.wlf printed 3/31/94

Worklist Number 948

Data Analyst: Susan D. Dunnihoo
Data Reported: 3/31/94
Comments:

Analyzed by: SDRD
Date Analyzed:

Sample Number	Client ID	Amt Ext (gm or ml)	Vol Solv Added	Final Total Vol	Sample Final Amt

Extraction Requirements:

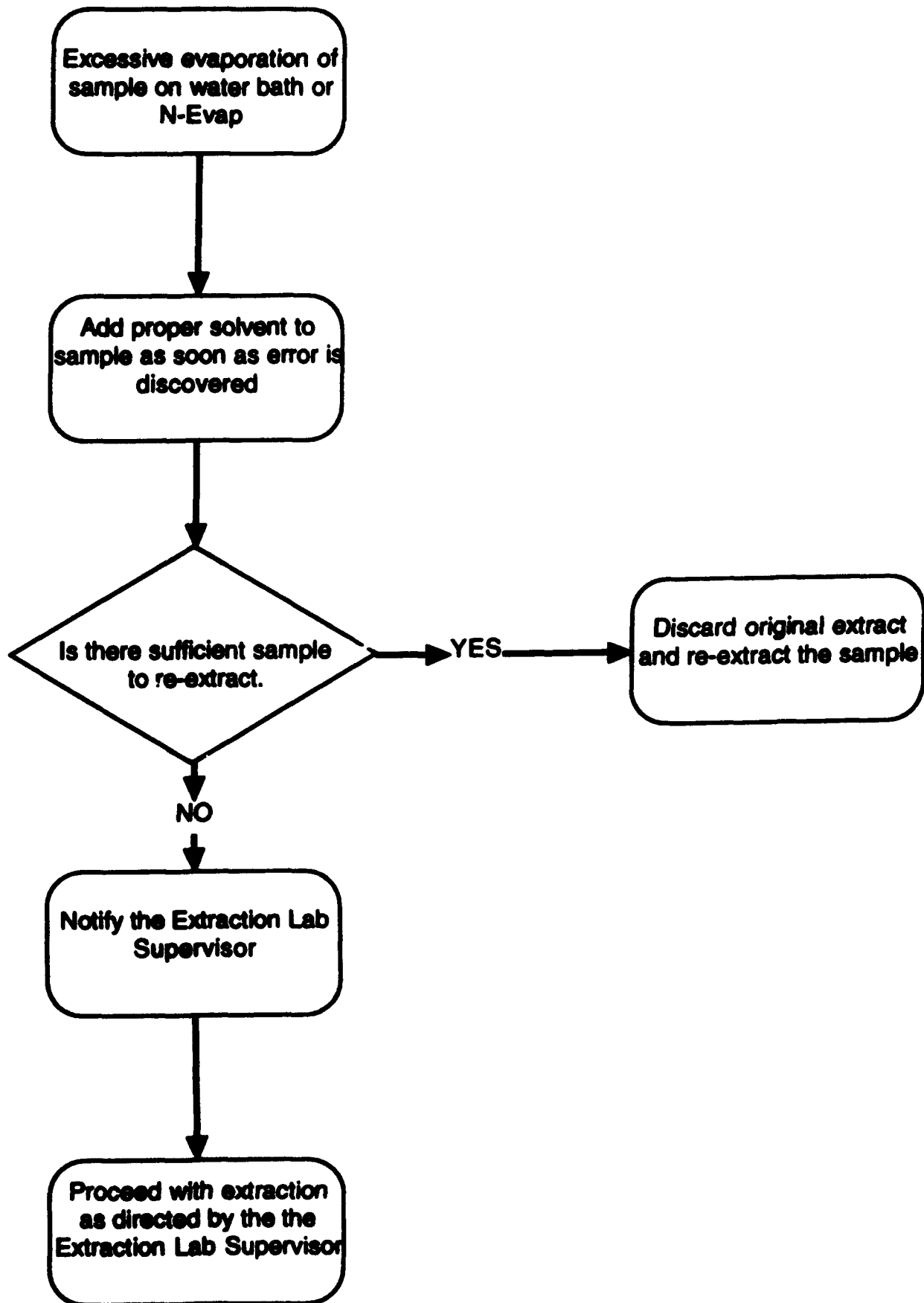
1. AAA7 A
94-1886 TEST SAMPLE 1994

Surr Added By: SDRD
ID#:

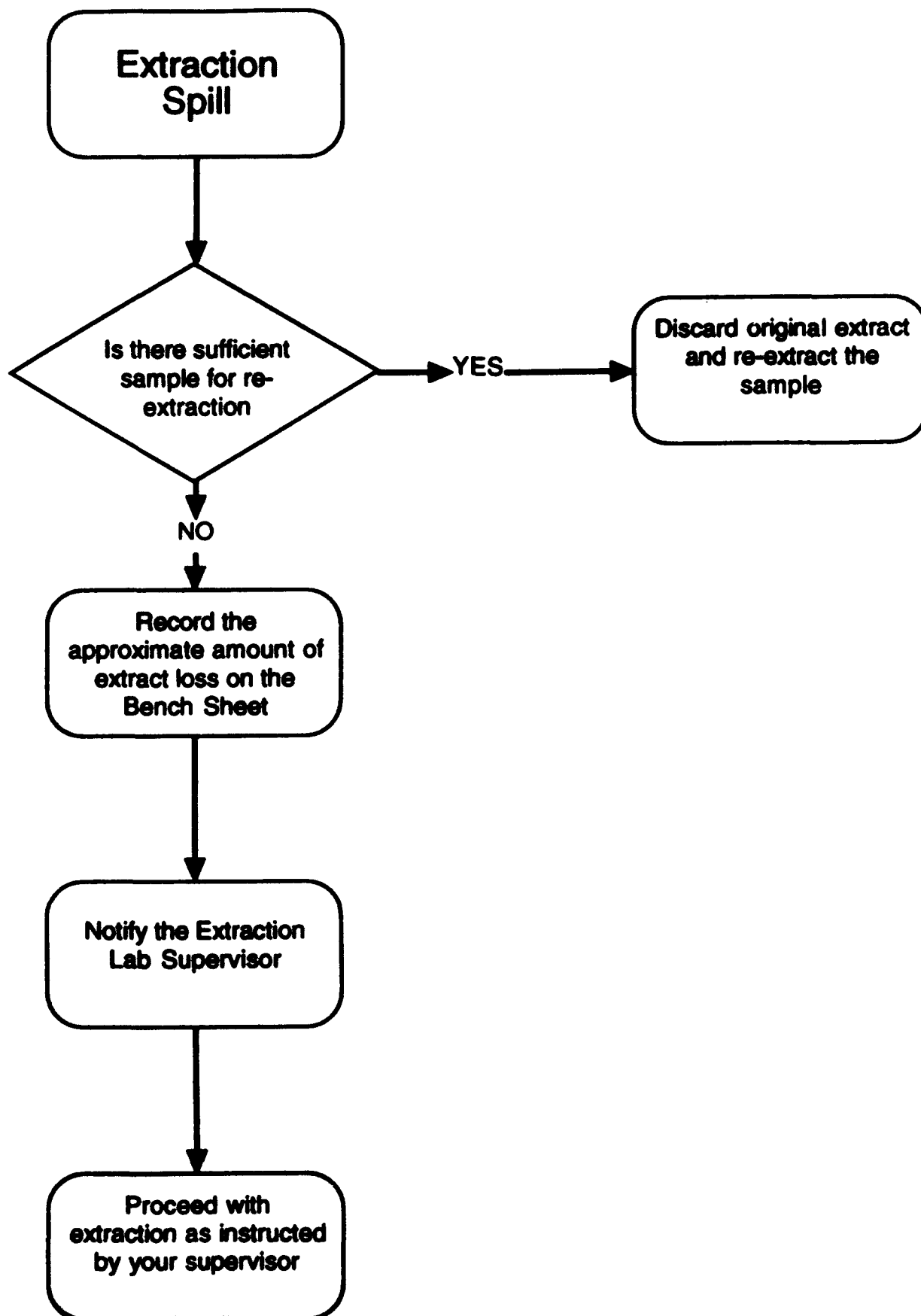
Surr Conc: _____
Surr Amt: _____

Analyst Signature _____ Extract Stored/Given to _____

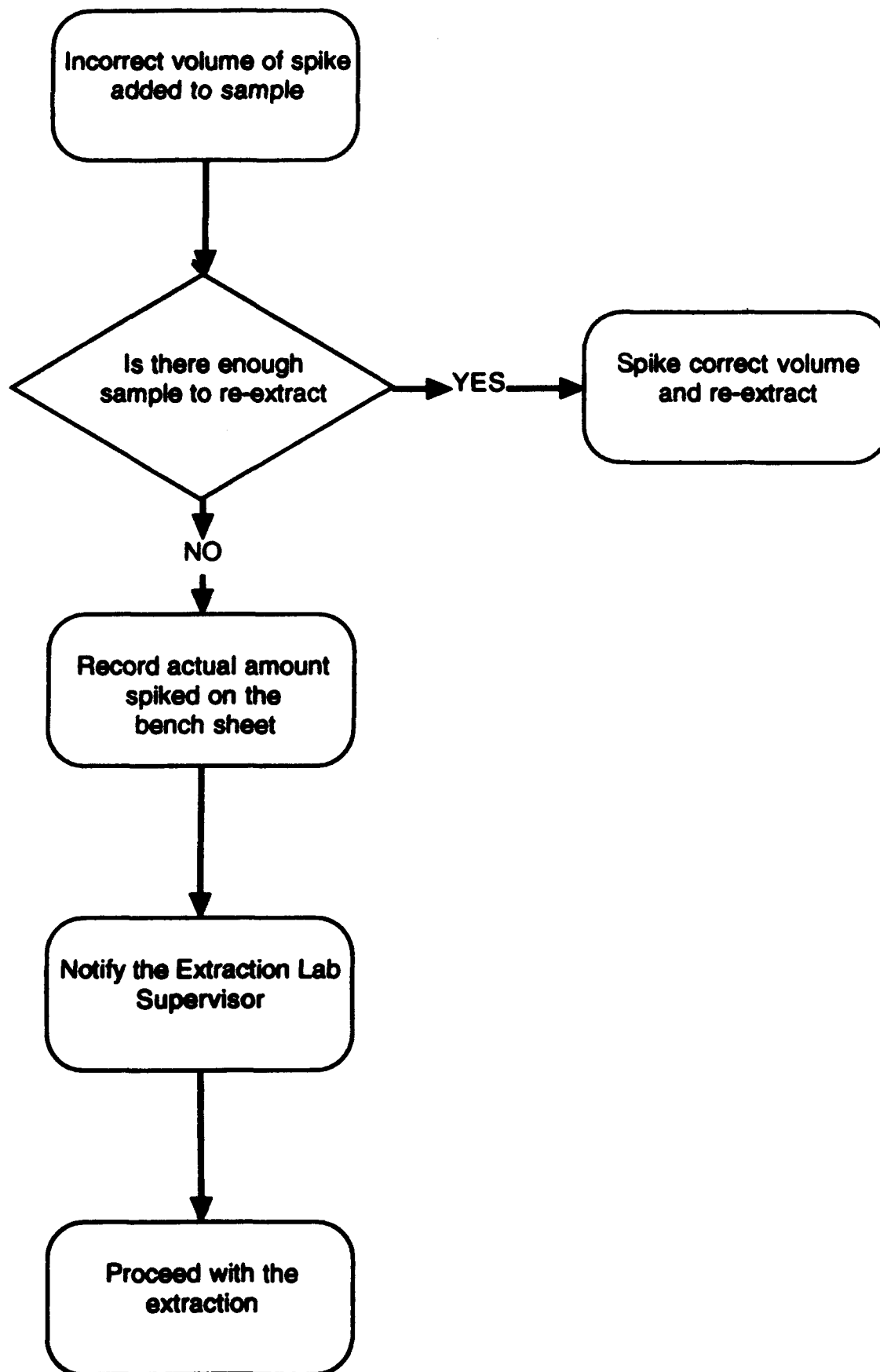
Corrective Action for Loss of Sample on Water Bath or N-Evap



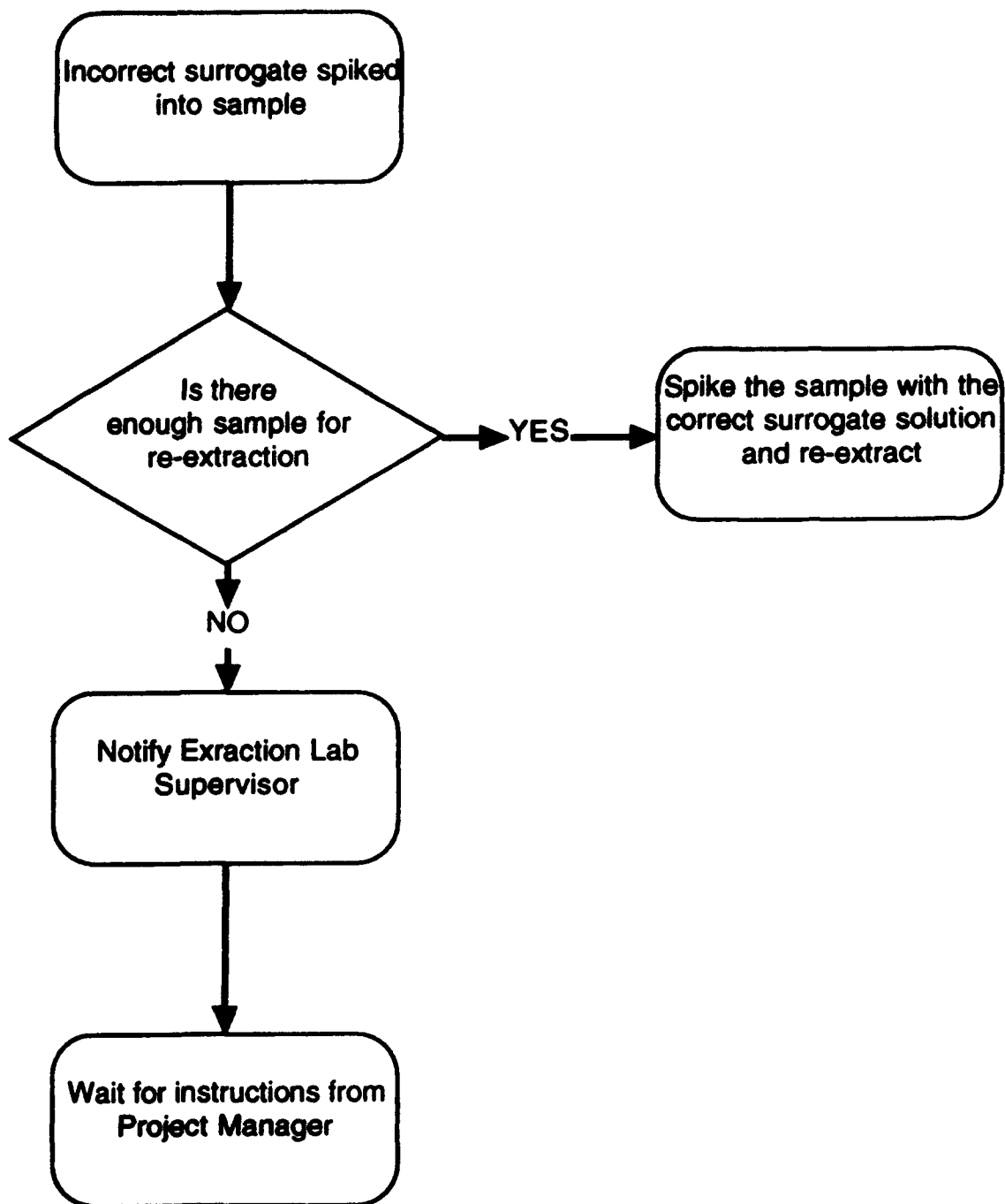
Corrective Action for Extract Spillage



Corrective Action for Incorrect Spike Volume



Corrective Action for Incorrect Surrogate Addition





ANALYTICAL
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Standard Operating Procedure

Low Level TPH
Water Extraction
Method 3510B

308S

Revision 4

6/28/94

PROPRIETARY

Prepared By:

Jane M. Hawk-Thorn

Approvals:

NA
Section Manager

John H. Baker
Laboratory Manager

Michelle G. Turner
Quality Assurance Manager

W. J. W.
Laboratory Director

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Standard Operating Procedure

Water Extraction

Low Level Total Petroleum Hydrocarbon (TPH)

1.0 Scope and Application

This method details the procedure for extracting water samples for petroleum hydrocarbons analysis.

2.0 Definitions

- 2.1 Surrogates - known quantities of compounds added to all samples and blanks to evaluate extraction efficiency.
- 2.2 Matrix Spike - known quantities of selected analytes added to a sample to evaluate the effect of sample matrix on analyte recovery.
- 2.3 LCS (Laboratory Control Sample) - a blank fortified with known quantities of selected analytes to monitor extraction efficiency.

3.1 200 mL separatory funnel with ground glass stopper and PTFE stopcock.

3.2 500 mL Erlenmeyer flask.

3.3 Kuderna-Danish concentrating apparatus (10 mL concentrator tube, 500 mL concentrator flask and 3 ball Snyder column).

3.4 25 x 340 mm drying column.

3.5 1000 mL graduated cylinder.

3.6 Glass wool, prepared by baking in kiln at 300° C for 4 hours.

3.7 Methylene Chloride, high purity.

3.8 Anhydrous sodium sulfate, prepared by baking in kiln at 400° C for 8 hours.

3.9 Surrogate and matrix spike solutions.

	<u>Component</u>	<u>Concentration</u>
Surrogate	Methyl arachidate	1500 µg/mL
Spike	Diesel #2	5000 µg/mL

3.10 Deionized water (Barnstead E-Pure, 4-Module D4641)

3.11 Water bath set at 80° C - 85° C (with temperature control +5° C).

3.12 N-Evap - Analytical nitrogen evaporator.



- 3.13 Scintillation vials (20 mL) with aluminum lined cap.
- 3.14 50 μ L, 500 μ L, and 5.0 mL gastight Hamilton syringe.
- 3.15 Boiling chips - Teflon (Chemware).
- 3.16 Grey label tape
- 3.17 2.5 mL clear GC autosampler vial
- 3.18 5 3/4" disposable pipet
- 3.19 Personal protective gear(gloves, goggles, lab coat)

4.0 Documentation

- 4.1 WTPH (low level) bench sheet.

5.0 In-house Modifications to Referenced Method

- 5.1 Section 6.2 (WDOE Appendix L): Extract 1.0 L instead of 400 mL.
- 5.2 Section 6.10: Flask is rinsed with 60 mL rather than 30 mL of MeCl_2 .
- 5.3 Section 6.14 (method section 7.11.2): No warm water is used with the nitrogen evaporator.
- 5.4 Section 6.15 (WDOE Appendix L): Extract to 5.0 mL final volume instead of 2 mL.
- 5.5 Concentration Techniques 4.3.4 (Snyder column, two-ball micro) and 4.3.5 (1/2 in. springs) are not in use at ARI. Technique 4.9 (5.0 mL syringe) is different.
- 5.6 ARI uses 5.0 mL, 500 μ L, and 50 μ L syringes.
- 5.7 Section 3.8: Anhydrous sodium sulfate is baked for 8 hours rather than 4.

6.0 Procedures

- 6.1 Review special analytical requirements' sheet prior to extracting samples to determine if special procedures are required. See Section 7.2.
- 6.2 Fill out bench sheet for job. See attached example.
- 6.3 Warm samples to room temperature, and mix samples to ensure a homogeneous portion. Label each separatory funnel with a piece of gray label tape with the following information: job number, sample identification letter, matrix ID, type of extraction and, for the blanks, the date.

(Note: Duplicate of one sample required per 10 samples.)

Use graduated cylinder to measure 1 liter of sample, and transfer it to the separatory funnel. Repeat for each sample. Prepare two separatory funnels with organic-free water for use as method blank and LCS.



- 6.4 Add sufficient surrogate solution (30 μ L) to each sample, method blank and LCS to result in a final concentration of 75 μ g/mL. As per Section 8.4 to verify that surrogate is accurate, surrogates will be witnessed by another lab technician.
- 6.5 Add sufficient matrix spike solution (300 μ L) to the LCS, and, if a matrix spike and/or matrix spike duplicate are required, to any QC samples to result in a final concentration of 1500 μ g/mL. As per Section 8.4 to verify that matrix spiking is accurate, surrogates will be witnessed by another lab technician.
- 6.6 Add 60 mL of methylene chloride to each sample bottle, then pour into the corresponding separatory funnel.
- 6.7 Seal and shake the separatory funnels vigorously for 1 to 2 minutes with periodic venting to release excess pressure.
- 6.8 Allow organic and aqueous layers to separate. Drain entire organic layer (including any emulsion) into an Erlenmeyer flask labeled with the sample ID (use a permanent marker).
- 6.9 Repeat steps 6 through 8 two more times. If emulsion is present it must be broken up by whatever mechanical means necessary and all non organic material (water, silt, etc.) is returned to the separatory funnel. Drain the organic layer.
- 6.10 Assemble a Kuderna-Danish (K-D) concentrator by attaching a methylene chloride rinsed 10 mL concentrator tube to a rinsed with methylene chloride 500 mL evaporation flask. Prepare a drying column by putting a glass wool plug inside at the narrow end and filling the column with anhydrous sodium sulfate to a bed height of approximately 10 cm. Rinse the prepared column once with 30 mL methylene chloride.
- 6.11 Dry the extract by passing it through the drying column and collecting it in the K-D concentrator. Rinse the Erlenmeyer flask three times with 15 mL methylene chloride and add this to the column as well. Once the entire extract has passed through the drying column, rinse the column with 15 mL methylene chloride. Transfer the label which has been labeled with the sample ID to the K-D. Check sample I.D.
- 6.12 Remove drying column, add 2 or 3 clean boiling chips to the concentrator flask, attach a three ball Snyder column, and put entire apparatus on a water bath set at approximately 80°C. Wet the inside of the Snyder column with 1 to 2 mL of methylene chloride before boiling starts.



- 6.13 Once the extract has concentrated to about 4 to 6 mL, remove the apparatus from the water bath. Put apparatus in rack and allow to stand for about 10 minutes.
- 6.14 Remove Snyder column, remove all water from the joint between the flask and the concentrator tube with a kimwipe, and disassemble the tube and flask. Rinse the lower joint of the flask into the tube with methylene chloride. Do not over fill the tube. Transfer the label with the sample ID to the tube.
- 6.15 Mount the tube on a nitrogen evaporator and adjust the flow of gas so that, with the needle 1 to 2 cm above the surface of the extract, a small indentation can be seen in the surface of the extract. If there is bubbling or splashing, the flow is too high. If there is no indentation visible, the flow is too low.
- 6.16 Once the extract reaches 3 mL (or specified final volume), an aliquot is transferred via disposal pipet to a 2 mL clear GC auto sampler vial (which has been labeled in permanent marker with the sample ID) for analysis.

7.0 Review

- 7.1 The Organic Extractions Supervisor will review all bench work and bench sheets before distribution.
- 7.2 Review project documentation (special analytical requirements, etc.) prior to extracting samples to determine if special procedures are required. See Section 6.0.

8.0 Quality Control

- 8.1 One method blank will be extracted for each batch of 20 or fewer samples.
- 8.2 One LCS (spike blank) will be extracted for each batch of 20 or fewer samples.
- 8.3 One MS/MSD will be extracted for each parameter after every 20 samples of similar matrix and level (sample volume permitting).
- 8.4 To verify that surrogate and matrix spiking is accurate, spiking will be witnessed by another technician.

9.0 Corrective Action

- 9.1 See Corrective Action Charts, section 12.1.

10.0 Miscellaneous Notes and Precautions

- 10.1 If sample will not blow to final volume (5.0 mL), take a 1.0 mL aliquot of its existing volume (e.g. 10 mL), note the volume on the bench sheet, and send sample to the appropriate laboratory for analysis.



- 10.2 Constant attention must be given when watching K.D.'s on the water baths, when extracts are below the surface of the water bath so they do not blow dry.
- 10.3 When blowing down extracts on the N-Evap a time should be used to remind the analyst of the volumes so extracts will not be blown dry.
- 10.4 The spring that goes around the N-Evap must be stretched out when placing or taking of concentrator tubes to avoid snapping off the bottom halves of the concentrator tube which could result in loss of extract.

11.0 Method References

- 11.1 U.S. EPA. "Separatory Funnel Liquid-Liquid Extraction", (SW-846), Methods 3510B, Revision 2, November, 1992.
- 11.2 Washington Department of Ecology, Appendix L, April 1992.

12.0 Appendices

- 12.1 Corrective Action Charts.

TPH-d Extraction
tphdext.wlf printed 3/31/94

Worklist Number 945

Data Analyst: Susan D. Dunnihoo
Data Reported: 3/31/94
Comments:

Analyzed by: SDRD
Date Analyzed:

Sample Number	Client ID	Amt Ext (gm or ml)	Final Total Vol	Sample Final Amt

Extraction Requirements: _____

1. AAA7 A
94-1886 TEST SAMPLE 1994

Surr Added By: SDRD
ID#: _____ Surr Conc: _____
Surr Amt: _____

Analyst Signature _____ Extract Stored/Given to _____

TPHd QA Extraction
tphdqa.wlf printed 3/31/94

Worklist Number 946

Data Analyst: Susan D. Dunnihoo
Data Reported: 3/31/94
Comments:

Analyzed by: SDRD
Date Analyzed:

Sample Number	Client ID	Amt Ext (gm or ml)	Final Total Vol	Sample Adj Amt

Extraction Requirements:

1.	Method Blank			
94-1886	AAA7			
	Spike Blank			
	AAA7 A			
94-1886	Matrix Spike			
	AAA7 A			
94-1886	MS Duplicate			
1.	AAA7 A			
94-1886	Duplicate			

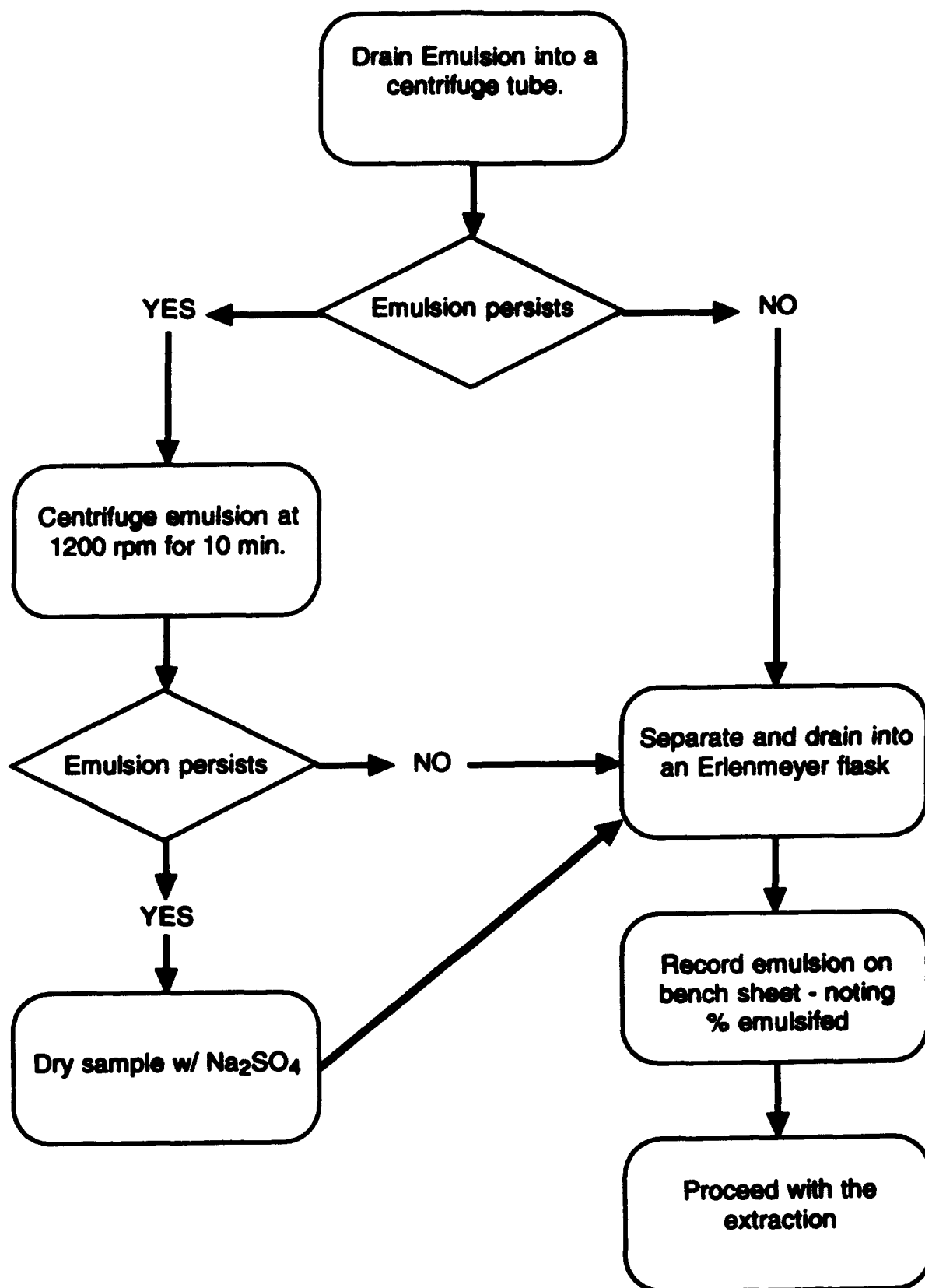
Surr Added By: SDRD
ID#: _____

Surr Conc: _____
Surr Amt: _____

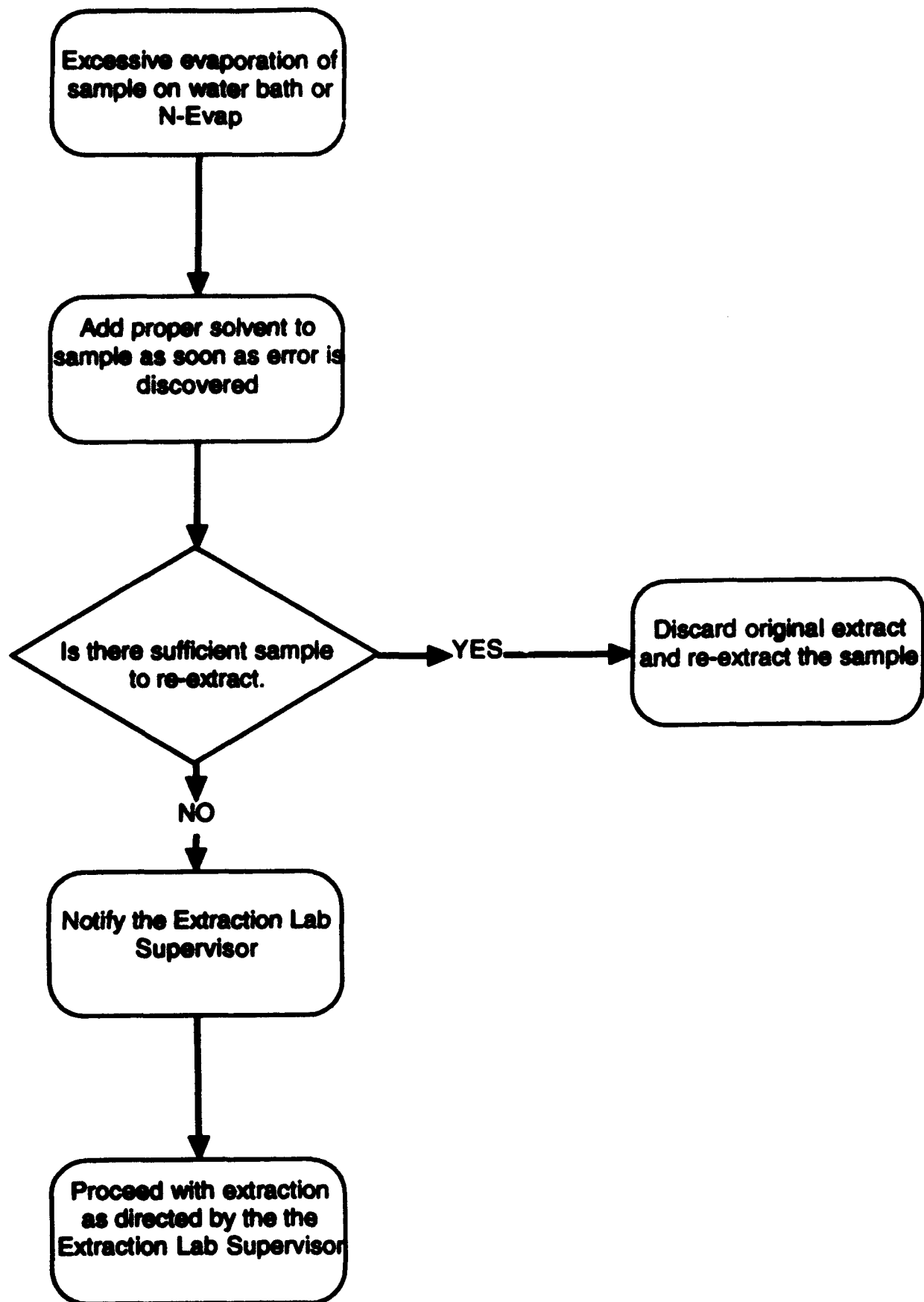
Spike ID#: _____
Spike Conc: _____
Spike Added: _____

Analyst Signature _____ Extract Stored/Given to _____

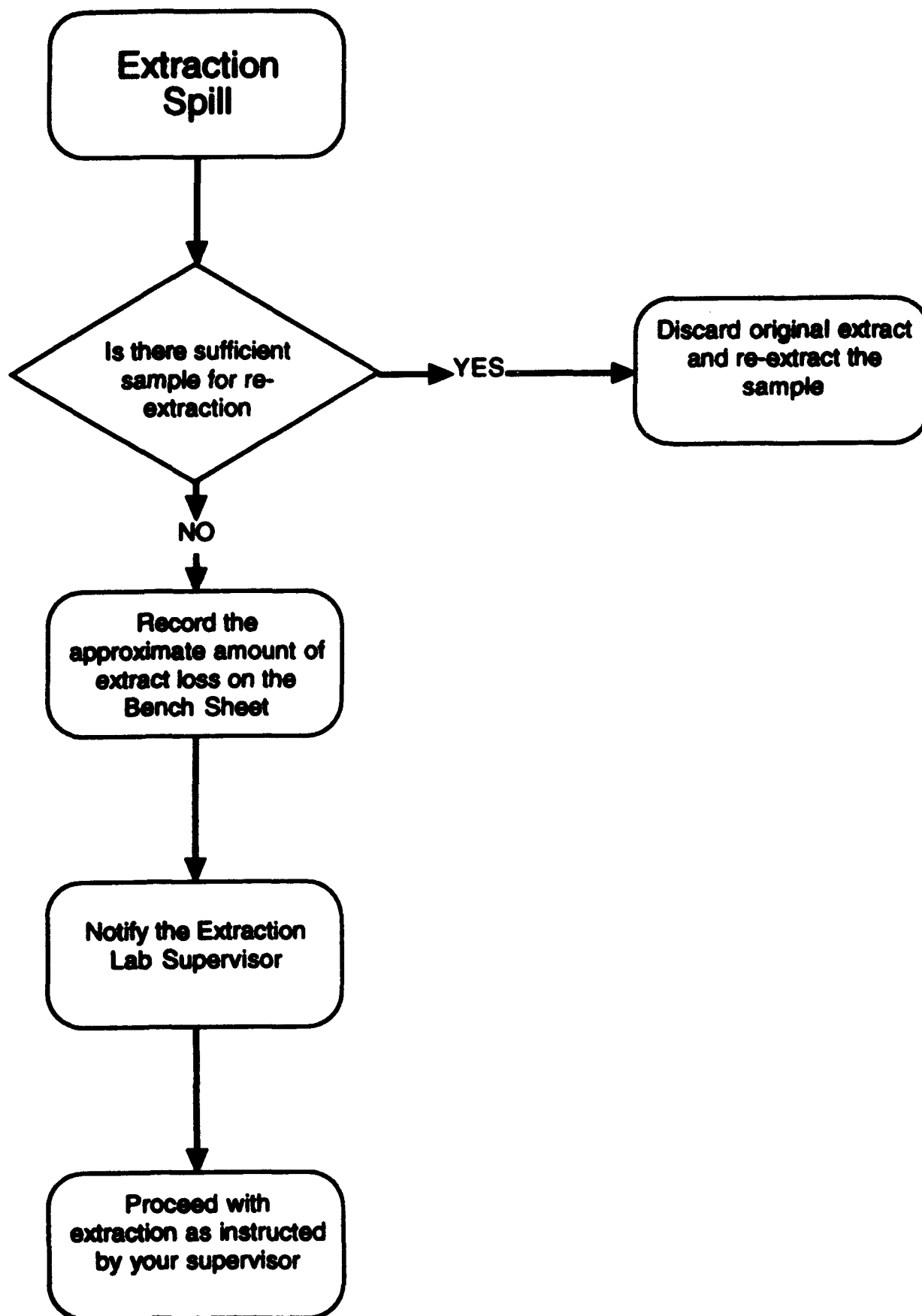
CORRECTIVE ACTION FOR EMULSIONS



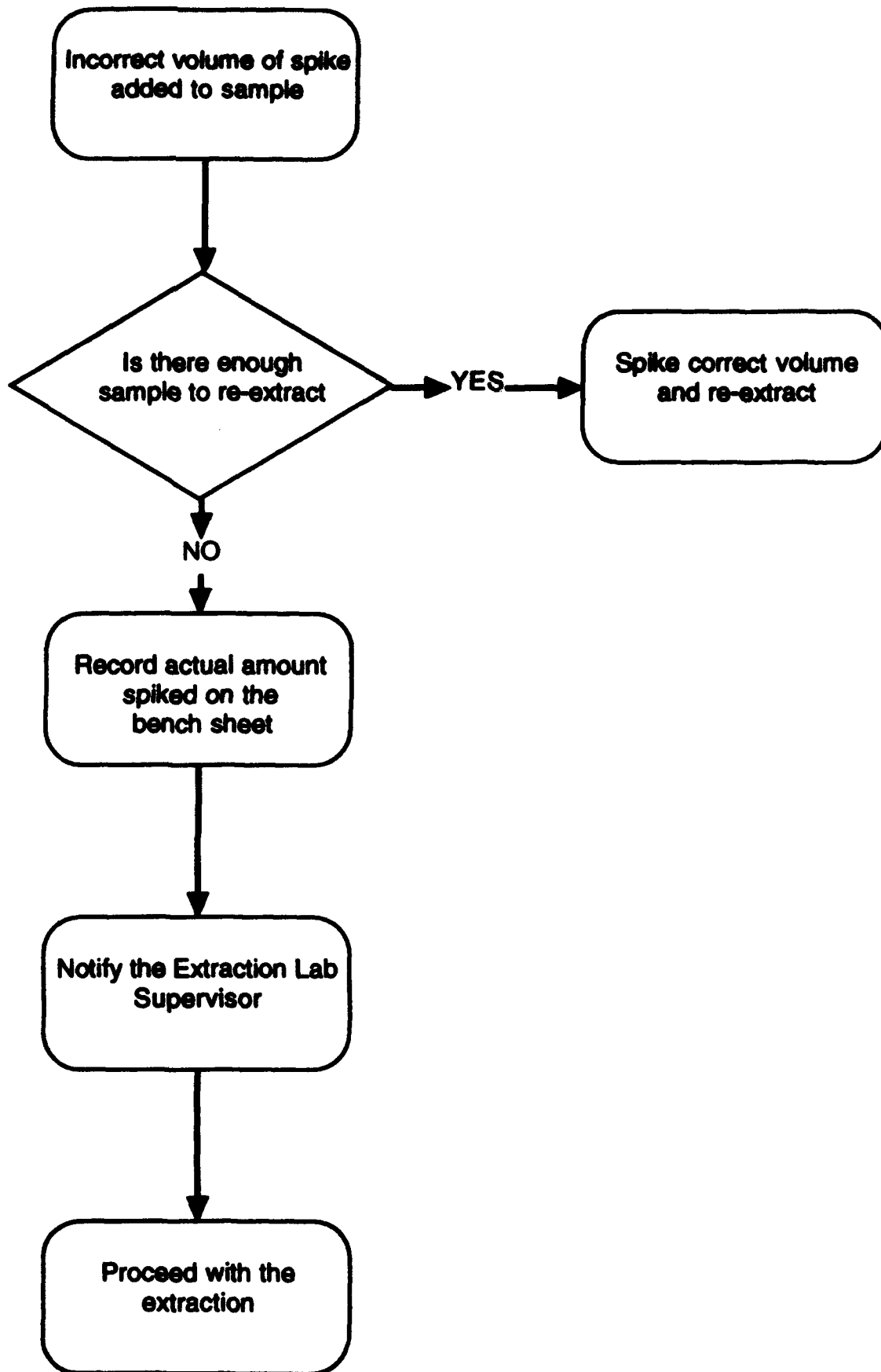
Corrective Action for Loss of Sample on Water Bath or N-Evap



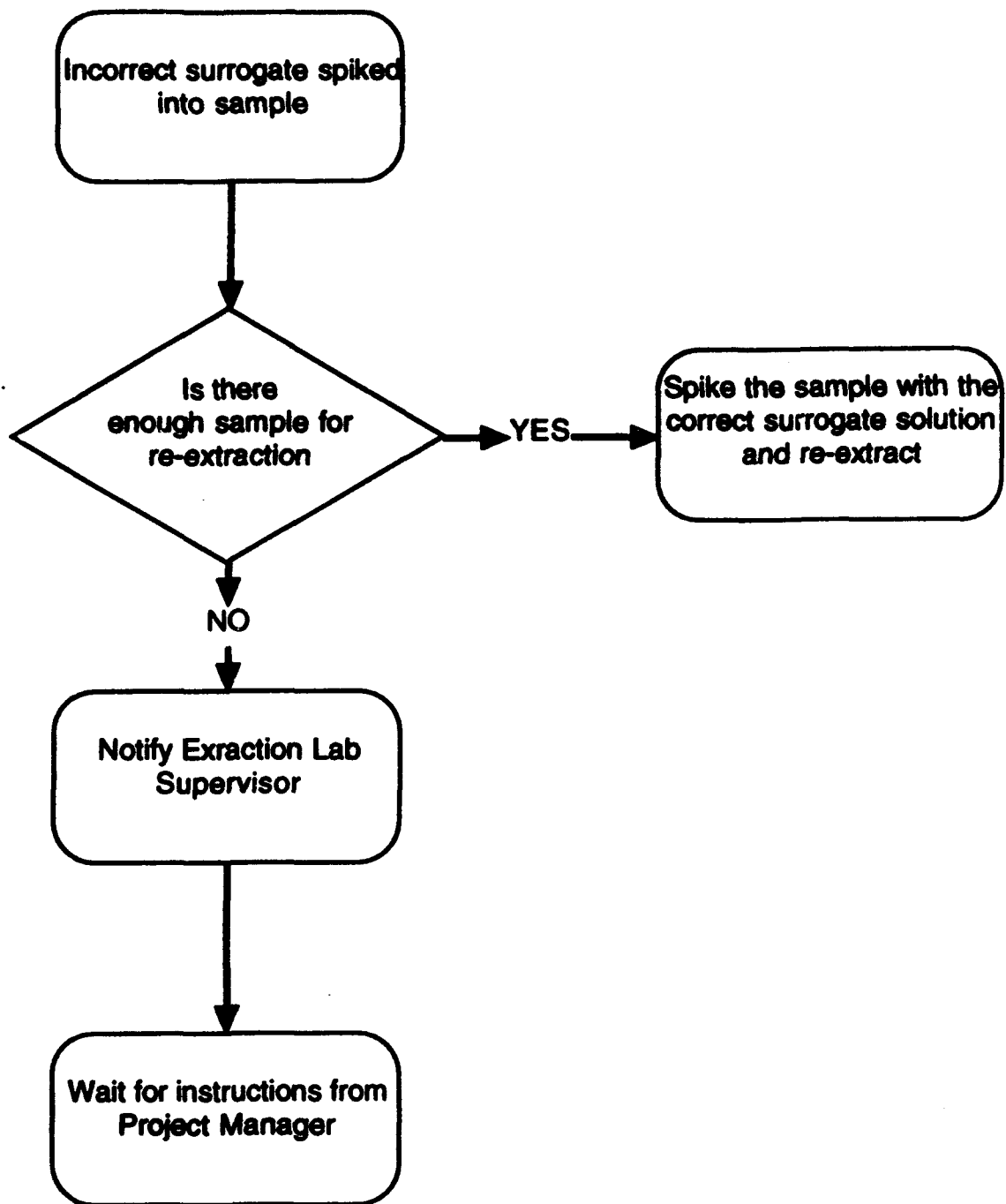
Corrective Action for Extract Spillage



Corrective Action for Incorrect Spike Volume



Corrective Action for Incorrect Surrogate Addition





ANALYTICAL
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Standard Operating Procedure

Volatile Organics by GC/MS
8260 (Air Force)

701S

Revision 2

7/13/94

Prepared By:

Jean P. Chancer

Approvals:

NA
Section Manager

Don T. Loh
Laboratory Manager

Michelle J. Turner
Quality Assurance Manager

Mark Van
Laboratory Director

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**Standard Operating Procedure - Volatiles Analysis (Method 8260)
(United States Air Force)**

**Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)
Capillary Column Technique**

1.0 Scope and Application

- 1.1 ARI 8260 is used to determine the concentration of volatile organic compounds in a variety of solid waste matrices, soils, and ground water. See Section 12.5, Table 5 for the compounds that can be determined by this method.
- 1.2 This method is applicable to nearly all types of samples, regardless of water content, including ground water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments.
- 1.3 ARI 8260 can be used to quantitate most volatile organic compounds that have boiling points below 200°C and that are insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique. However, for the more soluble compounds, quantitation limits are approximately ten times higher because of poor purging efficiency. Such compounds include ketones, nitriles, acetates, acrylates, ethers, and sulfides. See Tables 2 and 5 for lists of analytes and their characteristic ions that have been evaluated on a purge and-trap GC/MS system.
- 1.4 The estimated detection limit (DL) of Method 8260 for an individual compound is approximately 5 µg/kg (wet weight) for soil/sediment samples, and 5 µg/L for groundwater. DLs will be proportionately higher for sample extracts and for samples that require dilution or reduced sample size to avoid saturation of the system. Method detection limit (MDL) studies are performed for each matrix.
- 1.5 ARI 8260 is based upon a purge-and-trap, gas chromatographic/mass spectrometric (GC/MS) procedure. This method is restricted to use by, or under the supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.
- 1.6 This document summarizes the laboratory procedures for GC/MS analysis for Volatile organics. Text has been taken from SW-846 Method 8260, Revision 0, July 1992. Modifications to these methods have been incorporated into the document text and are identified in section 5.0.

2.0 Definitions

N/A



3.0 Equipment

3.1 Gas chromatograph/mass spectrometer system

- 3.1.1 Gas chromatograph: Varian 3400 and Hewlett-Packard 5790 are temperature-programmable, and suitable for purge-and-trap systems.
- 3.1.2 Column: 105 m x 0.53 mm ID capillary column, Megabore, 3.0m film thickness silicone coated fused silica capillary column.(Restek Rtx502.2 or Mtx502.2)
- 3.1.3 Mass spectrometer: Finnigan Incos 50 and Finnigan 4500 are capable of scanning from 35 to 300 amu every 1 second or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for Bromofluorobenzene (BFB) which meets all of the criteria in Table 1 when 50 ng of the GC/MS tuning standard (BFB) is purged onto the column.
- 3.1.4 Purge-and-trap system
 - 3.1.4.1 Dynatech PTA-30 Autosampler: In the soil mode, samples are purged at the autosampler; in the water mode, an aliquot of sample is delivered to the LSC. (See Autosampler SOP)
 - 3.1.4.2 Trap: Supelco trap K (VOCARB) or equivalent.
 - 3.1.4.3 Tekmar LSC 2000 with MCM 3000: capable of rapidly heating the trap to 250°C during desorption. The trap bake-out temperature should not exceed 260°C, or 270°C for conditioning of trap (may be fitted with "Turbo Cool").

3.2 GC/MS Interface: A Glass Jet Separator.

3.3 Data system: A computer system interfaced to the mass spectrometer. The system must allow continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer has software that can search any GC/MS data file for ions of a specified mass and can plot such ion abundance versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that can integrate the abundance in any EICP between specified time or scan-number limits. The Finnigan Incos 50 system uses Revision 11.0, and the Finnigan 4500 uses Revision 8.0 with the Nova 4x data system.

3.4 Microsyringes: 10, 25, 100, 250, 500, and 1,000 μ l.

3.5 Syringe valve: Two-way, with Luer ends (three each), if applicable to the purging device.



- 3.6 Syringes: 5, 10, or 25 mL, gas-tight with shutoff valve.
- 3.7 Balances: Analytical, 0.0001g, and top loading, 0.01g.
- 3.8 Glass scintillation vials: 20 mL, with Teflon lined screw-caps.
- 3.9 40 mL sample vial with Teflon septa (precleaned or baked at 105°C for 1 hour)
- 3.10 Disposable pipets: Pasteur.
- 3.11 Volumetric flasks, Class A: 5mL, 10 mL, 25 mL, 50 mL, and 100 mL, with ground glass stoppers.
- 3.12 Spatula: Stainless steel.
- 3.13 Reagents
- 3.13.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. There grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.
- 3.13.2 Organic-free water -- All references to water in this method refer to organic-free reagent water.
- 3.13.2.1 The organic-free water system is a Barnstead E-PURE with an insta-pure prefilter R40, using Barnstead/Thermolyne cartridges.
1. DO803 high capacity cartridge
 2. DO809 ultrapure DI cartridge
 3. DO813 organic removal cartridge
- 3.13.2.2 Filters are changed every three to six months, or when chloroform or methylene chloride levels exceed 0.2 ppb.
- 3.13.3 Methanol, CH₃OH: Purge and Trap quality, demonstrated to be free of analytes. Store apart from other solvents.
- 3.13.4 Hydrochloric acid (1:1 v/v), HCl: Carefully add a measured volume of concentrated HCl to an equal volume of organic-free water.
- 3.13.5 Stock standard solutions (1000 µg/ml, 2000 µg/ml) -- Standards are purchased as certified solutions.



4.0 Documentation

- 4.1 GC/MS logbook
- 4.2 Standard Preparation logbook
- 4.3 Maintenance logbook

5.0 In-house Modifications to Referenced Method

The Laboratory employs the following modifications to SW-846 Method 8260, Revision 0, July 1992.

- 5.1 Sections 6.6.3.1, 6.6.4, 6.6.5 (method section 3.2) Screening is accomplished using a portable Organic Vapor Meter (OVM) with a photo ionization detector (PID).
- 5.2 Section 3.1.2 (method section 4.3.2) Columns used are Restex Rtx502.2, 105 meter, 0.53 id, 3 micron and Restex Mtx502.2, 105 meter, 0.53 id, 3 micron.
- 5.3 Section 6.3.2 (method section 4.3.4) 50 ng total BFB equivalent is purge onto the system.
- 5.4 Section 6.2.3 (method section 5.7) Purchased certified stock solutions expiration dates are used, or if solutions are held under proper storage conditions in sealed ampules for 5 years.
- 5.5 Section 6.2.5 (method section 5.9) α -1,2-dichlorobenzene is an additional surrogate standard.
- 5.6 Method section 7.1 has been omitted. Direct injection of samples is not performed.
- 5.7 Section 6.3.1 (method section 7.2) operating conditions have been modified to reflect instrument conditions.
- 5.8 Section 6.3.3: A table of purge-and-trap condition recommendations has been added.
- 5.9 Section 6.4.1 (method section 7.5) water and soil autosamplers are in use. See related SOP.
- 5.10 Method section 7.5.1.14 has been omitted. Narrow bore capillary columns are not in use.
- 5.11 Section 6.6.6.1 (method section 7.5.3.2.1) 2g wet weight of sample and 5mL purge-and-trap grade methanol are used.
- 5.12 Sections 6.6.6.1.1, 6.6.6.1.7 (method section 7.5.3.2.2) 50 μ L surrogate spiking solution at 250 μ g/mL



- 5.13 Section 6.6.1 Addition of EICP area responses and RRT shift allowance in the daily analysis.
- 5.14 Section 6.6.6.1.7 (method section 7.5.3.2.9) 50 μ L matrix spiking solution at 250 μ g/mL. 50 μ L surrogate spiking solution is added to 2g/5mL purge-and-trap grade methanol.
- 5.15 Section 7.1.1.1 (method section 7.6.1.1) Standard reference mass spectra are checked daily against the fit in the diagnostic report having to meet the 700 fit criteria for non-coeluting compounds and 550 fit criteria for coeluting compounds.
- 5.16 Section 8.3: Method section 8.5 has been omitted. Method detection limit (MDL) studies have been performed of this analysis as per 40 CFR, part 136.
- 5.17 Addition of Analysis records procedures in section 7.2
- 5.18 Addition of Analyst review of data in section 7.3
- 5.19 Addition of Holding times in section 8.6
- 5.20 Section 9.2.1.3 (method section 8.8.5) "Estimated concentration" is changed to "matrix effect." (NO FLAG)
- 5.21 Section 6.5.4: The range of internal standard response limits from the initial calibration have been added to the method.

6.0 Procedure

6.1 Summary of Method

- 6.1.1 The volatile compounds are introduced into the gas chromatograph by the purge-and-trap method. Purged sample components are trapped in a tube containing suitable sorbent materials. When purging is complete, the sorbent tube is heated and back flushed with helium to desorb trapped sample components. The analytes are desorbed directly to a megabore capillary column. The column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) interfaced to the gas chromatograph through a jet separator.
- 6.1.2 If the above sample introduction techniques are not applicable (as with highly contaminated or product samples), a methanol extract of the sample is combined with organic-free reagent water in the purge chamber. It is then analyzed by purge-and-trap GC/MS following the normal water method.



- 6.1.3 Qualitative identifications are confirmed by analyzing standards under the same conditions used for samples and comparing resultant mass spectra and GC retention times. Each identified component is quantitated by relating the MS response for each compound to the MS response for a specific internal standard, using specific quantitation masses.

6.2 Standards

- 6.2.1 Stock standards are used if they are certified by the manufacturer or by an independent source. If certified standards are not available, prepare stock solutions by accurately weighing about 0.0200 g of pure material. Dissolve the material in purge-and-trap methanol and dilute to volume in a 10mL volumetric flask. Other volumes can be used at the discretion of the analyst. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard.

- 6.2.1.1 Standards are prepared by measuring a calculated amount of stock standards into a volumetric flask containing a small amount of purge-and-trap grade methanol. Bring up to volume and invert several times to mix.

$$\text{Calculated standard amt.} = \frac{(FV)(VWS)}{SS}$$

where:

- FV = Final Volume of working standard
VWS = Desired concentration of volatile working standard
SS = Certified stock standards

- 6.2.2 Transfer the stock standard solutions into vials with Teflon-lined screw-caps. Store at -15 to -20°C and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.
- 6.2.3 Stock standards solutions must be replaced after 1 year if prepared from neat, or sooner if comparison with quality control check samples indicates a problem. Purchased certified stock standards must be replaced at or before the expiration date provided by the supplier. Store at -15 to -20°C when not being used.
- 6.2.4 Prepare fresh working standards if comparison with check standards indicates a problem. Both gas and liquid standards must be monitored closely by comparison to the initial calibration curve and by comparison to QC check standards. It may be necessary to replace the standards more frequently if either check exceeds 25% difference. Store at -15 to -20°C when not being used.



- 6.2.5 Surrogate standards: The surrogates recommended are toluene-d8, 4-bromofluorobenzene, 1,2-dichlorobenzene-d4, 1,2-dichloroethane-d4, and dibromofluoromethane. Other compounds may be used as surrogates, depending upon the analysis requirements. A surrogate standard spiking solution should be prepared from the stock at a concentration of 25-250 $\mu\text{g/mL}$ in methanol. Store at -15 to -20°C when not being used.
- 6.2.6 Internal standards: Internal standards used are chlorobenzene-d5, 1,4-difluorobenzene, 1,4-dichlorobenzene-d4, and pentafluorobenzene. Other compounds may be used as internal standards as long as they have retention times similar to the compounds being detected by GC/MS. It is recommended that the secondary dilution standard should be prepared at a concentration of 25 $\mu\text{g/mL}$ of each internal standard compound. Addition of 10 μL of this standard to 5.0 mL of sample or calibration standard would be the equivalent of 50 ng/mL. Store at -15 to -20°C when not being used.
- 6.2.7 4-Bromofluorobenzene (BFB) standard: A standard solution containing 25 $\mu\text{g/mL}$ of BFB in methanol should be prepared. Store at -15 to -20°C when not being used.
- 6.2.8 Document Standard preparation according to instructions in the VOA Standard Preparation SOP.
- 6.2.9 Calibration standards: Calibration standards at a minimum of five concentrations are prepared from the secondary dilution of stock standards. ARI uses final concentrations of 5, 10, 20, 50, 100, and 200 ng/mL. Prepare these solutions in organic-free reagent water. One of the concentrations is near but above the method detection limit. The remaining concentrations correspond to the expected range of concentrations found in real samples but should not exceed the working range of the GC/MS system. Each standard contains each analyte for detection by this method (e.g. some or all of the compounds listed in Table 2 may be included). Calibration standards must be prepared on the day of use.
- 6.2.10 Matrix spiking standards: Matrix spiking standards are prepared from volatile organic compounds which will be representative of the compounds being investigated. At a minimum, the matrix spike will include 1,1 dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene. Occasionally, a project may require the spiking of specific compounds of interest, especially if they are polar and would not be represented by the above listed compounds. The standard should be prepared in a client sample, with each compound present at a concentration of 50ng/mL.



6.3 Operating Parameters:

6.3.1 GC/MS

Required GC/MS operating conditions:

Mass range:	35-300 amu
Scan time:	1 sec./scan or less
Electron volts:	70 volts (nominal)

Recommended conditions:

Initial temperature:	35°C 2 min
Temperature program:	35-175°C at 9°C/min, 50°C/min. to 250°C
Final temperature:	250°C, hold 4 min.
Source temperature:	According to manufacturer's specs. 150-250°C
Transfer nozzle/line:	200-300°C
Carrier Gas:	Hellum at 30-60mL/min.

6.3.2 Purge & Trap

Recommended conditions:

Purge	11 minutes
Dry purge	2 minutes
MCM desorb	10-20°C
Desorb preheat	250°C
Desorb	6 minutes at 250°C
Bake	4 minutes at 260°C
Valve temperature	50-110°C
Mount temperature	30-110°C
Line	50-200°C
MCM Bake	60-90°C

- 6.3.3 The purge-and-trap is assembled to manufacturer's specifications. It should be capable of rapidly heating the trap to 250°C during desorption. The trap bake-out temperature should not exceed 260°C. A sample heater should be capable of maintaining the purging chamber to within 1°C over the temperature range of ambient to 100°C.

6.4 Initial calibration:

- 6.4.1 The GC/MS system must be hardware tuned to meet the criteria in section 12.1, Table 1 for a 50 ng total purge of BFB. Analysis cannot begin until all these criteria have been met.
- 6.4.2 A set of at least five calibration standards containing the method analyte is needed. One calibration standard should contain each analyte at a concentration approaching but greater than the method detection limit for that compound. The other calibration standards



should contain analytes at concentrations that define the range of the method. ARI uses final concentrations of 5, 10, 20, 50, 100, and 200 ng/mL (ng/g for soils). The purging efficiency for 5 mL of water is greater than that for 25 mL; therefore, develop the standard curve from the specific volume of sample that will be analyzed. To prepare a calibration standard, add an appropriate volume of a secondary dilution standard solution to an aliquot of organic-free reagent water in a volumetric flask. Transfer the contents to a purging device.

- 6.4.3 Analyze each calibration standard and tabulate the area response of the quantitation ions against concentration for each compound and each internal standard (see Table 2). Calculate response factors (RF) for each compound relative to its internal standard. The internal standard selected for the calculation of the RF for a compound should be the internal standard that has a retention time closest to the compound being measured. Calculate response factors (RF) for each compound as follows.

$RF = (Ax/Cis)/(Ais/Cx)$, where:

- Ax = Area of the characteristic ion for the compound being measured.
- Ais = Area of the characteristic ion for the specific internal standard.
- Cis = Concentration of the specific internal standard.
- Cx = Concentration of the compound being measured.

- 6.4.4 The average RF should be calculated for each compound. The percent relative standard deviation (%RSD = $100(SD/RF)$) should also be calculated for each compound. The relative retention times of each compound in each calibration run should agree within 0.06 relative retention time units of each other.
- 6.4.5 System Performance Check Compounds (SPCC): Five compounds are checked for a minimum average response factor. These compounds are chloromethane; 1,1-dichloroethane; bromoform; 1,1,2,2-tetrachloroethane; and chlorobenzene. The minimum acceptable average RF for these compounds should be 0.300 (0.250 for bromoform, 0.100 for chloromethane). These compounds typically have RFs of 0.4 - 0.6; they are used to check compound instability and to check for degradation caused by contaminated lines or active sites in the system.



- 6.4.6 Calibration Check Compounds (CCC): After the system performance check is met, CCCs are used to check the validity of the initial calibration. Calculate the percent relative standard deviation as follows:

$$\%RSD = \frac{SD}{x} \times 100$$

where:

RSD = Relative standard deviation
x = Mean of 5 initial RFs for a compound
SD = Standard deviation of average RFs for a compound.

$$SD = \frac{\text{Sq.Rt} \{N \sum (x_i - x)^2 / N - 1\}}{\sum_{i=1}^N}$$

- 6.4.7 The %RSD for each individual CCC must be less than 30 percent. This criterion must be met for the individual calibration to be valid. The CCCs are:

1,1-Dichloroethene
Chloroform
1,2-Dichloropropane
Toluene
Ethylbenzene
Vinyl chloride.

6.5 Daily GC/MS Calibration

- 6.5.1 Prior to the analysis of samples, the GC/MS tuning standard must be met. Purge 50 ng of the 4-bromofluorobenzene standard. The resulting mass spectra must meet all of the criteria given in Section 12.1, Table 1 before sample analysis begins. A spectrum is obtained by summing three scans (the peak apex scan and a scan immediately preceding and following the apex) and subtracting a single scan not more than 20 scans prior to the elution of BFB. These criteria must be demonstrated each 12-hour shift.
- 6.5.2 A calibration standard at mid-concentration (50 ppb), containing each compound of interest, including all required surrogates, must be performed every 12 hours during analysis. Compare the response factor data of the standard every 12 hours against the average response factor from the initial calibration for a specific instrument as per the SPCC and CCC criteria.



6.5.3 System Performance Check Compounds (SPCC) and Calibration Check Compounds (CCC).

6.5.3.1 System Performance Check Compounds (SPCCs): A system performance check must be made during every 12 hour shift. If the SPCC criteria are met, a comparison of response factors is made for all compounds. This is the same check that is applied during the initial calibration. If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Some possible problems are standard mixture degradation, contamination at the front end of the analytical column, and active sites in the column or purge-and-trap system.

6.5.3.2 After the system performance check is met, CCC's listed in Section 6.4.7 are used to check the validity of the initial calibration.

Calculate the percent difference using:

$$\% \text{Difference} = \frac{\text{RFI} - \text{RFc}}{\text{RFI}} \times 100$$

RFI = Average response factor from initial calibration.

RFc = Response factor from current verification standard.

If the percent difference for any compound is greater than 20, this is considered a warning limit. If the percent difference for CCCs is less than 25%, the initial calibration is assumed to be valid. If the criterion is not met (>25% difference) for any one CCC, corrective action must be taken. Problems similar to those listed under SPCC's could affect this criterion. If no source of the problem can be determined after corrective action has been taken, a new calibration must be generated. This criterion must be met before sample analysis begins.

6.5.4 The internal standard responses and retention times in the continuing calibration standard must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the last daily calibration, the chromatographic system must be inspected for malfunctions and corrections must be made, as required. If the EICP area for any of the internal standards changes by -25% to +50% from the initial calibration standard, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. Areas are documented in the daily run log (Section 4.0).



6.6 GC/MS analysis

6.6.1 Internal standard area criteria in the samples must be evaluated for retention time shift and EICP areas. If the EICP area for any internal standard changes by a factor of 2 (-50% to +100%) from the continuing calibration standard, the sample must be reanalyzed. Retention time shift is the same as continuing calibration criteria (section 6.5.4).

6.6.2 Method Blank/LCS

6.6.2.1 A laboratory control sample (LCS) must be run after the daily standard before analyzing a method blank and samples. Refer to advisory limits before continuing analysis.

1. Prepare a water LCS by adding an alternate source standard to 5 mL organic-free water, to a final concentration equivalent to 50 ng/ μ L.
2. Prepare a soil LCS by adding 5 g of blank soil to 5 mL organic-free water, to a final concentration equivalent to 50 ng/gr.

6.6.2.2 A method blank is run after the daily LCS to demonstrate system cleanliness (no analytes greater than reporting limits with the exception acetone, methylene chloride and 2-butanone at ≤ 5 times the reporting limit). Surrogates are to be within the established control limits.

6.6.2.3 A blank must be rerun if contamination is greater than the reporting limits. If the rerun blank still shows analytes greater than the reporting limits, the purge-and-trap system must be cleaned. Analyze another method blank to demonstrate that the system is back in control.

1. Methylene Chloride, Acetone, and 2-Butanone must be ≤ 5 times the reporting limit.
2. Prepare a water method blank by adding an IS/SS standard to 5 mL organic-free water to a final concentration equivalent to 50 ng/ μ L.
3. Prepare a soil method blank by adding 5 g of blank soil to 5 mL organic-free water, to a final concentration equivalent to 50 ng/ μ L.



6.6.3 Screening

6.6.3.1 Screening of the sample prior to purge-and-trap analysis will provide guidance on whether sample dilution is necessary, and will prevent contamination of the purge-and-trap system. An OVM (PID) is used. (See manufacturer's operation manual and Table 6 for dilution versus OVM reading.)

1. For screening soils, sludge, oils, and solid materials, place 5 g of sample into a scintillation vial with 5 mL water and vortex until well mixed. Place the vial at the sample port of the OVM and measure the organic vapors. The OVM indicates which dilution is needed. (See 12.6)
2. For screening waters, place 5 mL of sample into a scintillation vial. Shake vial, place it at the sample port of the OVM, and measure the organic vapors. The OVM indicates which dilution is needed. Note: If the water samples have been preserved, an accurate OVM reading may not be possible. (See 12.6)

6.6.4 Water samples

6.6.4.1 All samples and standard solutions must be allowed to warm to ambient temperature before analysis.

6.6.4.2 Set up the GC/MS system as outlined in Sections 6.3.

6.6.4.3 BFB tuning criteria and daily GC/MS calibration criteria must be met (Table 1) before analyzing samples.

6.6.4.4 Adjust the purge gas (helium) flow rate to 30-60 mL/min. on the purge-and-trap device. Optimize the flow rate to provide the best response for chloromethane and bromoform.

6.6.4.5 Manual Sample Preparation: Remove the plunger from a 5 mL syringe and attach a closed syringe valve. If lower detection limits are required, use a 25 mL syringe. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel just short of overflowing. Replace syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. Transfer remaining sample to a 20 mL VOA vial with a teflon-sealed cap, or fill a second syringe at this time to protect sample integrity.



6.6.4.6 The following techniques are appropriate for diluting samples.

1. Dilutions may be made in volumetric flasks (10 to 100 mL). Select the volumetric flask that allows the necessary dilution. Intermediate Dilutions may be necessary for extremely large dilutions.
2. Calculate the volume of organic-free water to add to the volumetric flask and add slightly less. Inject the aliquot of sample with a syringe. Dilute the sample to the mark with organic free water. Invert and shake the volumetric 3 times and transfer to a gas tight syringe.
3. Dilution can be made in a 5mL gastight syringe. Fill the syringe with the appropriate amount of organic free water and add sample aliquot. i.e. 500 μ L sample to 4.5mL water = 1:10 dilution.

6.6.4.7 Compositing samples prior to GC/MS analysis

1. The samples must be cooled at 4°C during this step to minimize volatilization losses. Combine an equal amount of each sample to be composited in a volumetric flask. Invert and shake 3 times and transfer to a sample vial or a 5mL mL gas tight syringe.

6.6.4.8 Add 10 μ L of surrogate/internal standard spiking solution through the valve bore of the syringe. The surrogate and internal standards may be mixed and added as a single spiking solution. The addition of the surrogate and internal standard spiking solution to 5 mL of sample is equivalent to a concentration of 50 μ g/L of each standard in the sample.

6.6.4.9 Deliver prepared sample to the purging chamber and seal. Purge sample for the designated time. Trap should be at ambient temperature.

6.6.4.10 Sample desorption: After purging, desorb the sample, initiate the temperature program of the gas chromatograph, and start data acquisition. Introduce the trapped materials to the GC column by rapidly heating the trap to 250°C while back flushing the trap.

1. After desorbing the sample, condition the trap by baking it. Consult manufacturer's specifications for temperature and time. ARI uses 260°C/4 minutes.



- 6.6.4.11 If the analysis shows the sample to have a concentration of analytes that exceed the highest standard, the sample must be rerun at a dilution. Analyst considerations for chromatographic "system overload" are analytes that are above the linear range, saturation of the mass spectrometer, chromatography overload, or analyte/interference carryover. Professional judgement and experience must be used by the analyst as to the modification of the analytical sequence. If system contamination is present, an organic-free water blank must be analyzed. If the blank analysis is not free of analytes/interferences, the system should undergo maintenance, such as baking the trap or purging with methanol to decontaminate the system. If a blank is not run, as with autosamplers, the following sample must be checked for carryover and rerun if it contains the same compounds which were at high levels. Sample analysis may not resume until the system is free of interferences (less than 3 the reporting limit).
- 6.6.4.12 Secondary ion quantitation is allowed only if there are sample matrix interferences with the primary ion.
- 6.6.4.13 For matrix spike and LCS analysis, add 10 μL of the matrix spike solution to the 5 mL of sample to be purged. Disregarding any dilutions, this is equivalent to a concentration of 50 $\mu\text{g/L}$ of each matrix spike standard in the final sample concentration.
- 6.6.4.14 All dilution efforts should try to keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve. To determine the dilution factor, compare a minor ion in the saturated analyte against the daily standard.
- 6.6.5 Water-miscible liquids: It is highly recommended that all samples of this type be screened prior to analysis using the OVM.
- 6.6.5.1 Water-miscible liquids are analyzed as water samples after first diluting them at least 50 fold with organic-free reagent water.
- 6.6.5.2 Initial and serial dilutions can be made in a 100 mL volumetric flask with organic-free reagent water.
- 6.6.5.3 Alternatively, prepare dilutions directly in a 5mL syringe filled with organic-free reagent water by adding at least 20 μL , but not more than 100 μL of liquid sample. The sample is ready for addition of internal and surrogate standards.



6.6.6 Sediment/soil and waste samples: It is highly recommended that all samples of this type be screened prior to analysis using the OVM.

6.6.6.1 Low-concentration method. This is designed for samples containing individual purgeable compounds of < 1 mg/kg. The low-concentration method is based on purging a heated sediment/soil sample mixed with organic-free reagent water containing the surrogate and internal standards. Analyze all blanks and standards under the same conditions as the samples.

6.6.6.2 Use a 5g sample if the expected concentration is < 0.1 mg/kg or a 1g sample for expected concentrations between 0.1 and 1 mg/kg.

1. The GC/MS system should be set up as in section 6.3. This should be done prior to the preparation of the sample to avoid loss of volatiles from standards and samples. A heated purge calibration curve must be prepared and used for the quantitation of all samples analyzed with the low-concentration method. Follow the initial and daily calibration instructions, with the addition of a 40°C purge temperature.
2. Remove the plunger from a 5 mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 5.0 mL. Add 10 μ L each of surrogate spiking solution (Section 5.9) and internal standard solution (Section 5.10) to the syringe through the valve. (ARI's surrogate spiking solution and internal standard solution are mixed together.) The addition of 10 μ L of the surrogate spiking solution to 5g of sediment/soil is equivalent to 50 μ g/kg of each surrogate standard in the final sample concentration.
3. The sample consists of the entire contents of the sample container. Do not discard any supernatant liquids. If sample has free liquid, vortex unopened for 1 min or mix the contents with a small metal spatula. If there is no free liquid present remove the top layer to expose sample that has not been compromised. Weigh the sample into a tared purge device and record the actual weight to the nearest 0.1g.
4. Determine the percent dry weight of the soil/sediment sample. Other wastes should be reported on a wet-weight basis.



- a. Weigh 5-10g of the sample into a tared weighing dish. Determine the %dry weight of the sample by drying overnight at 105°C. Allow to cool. Concentrations of individual analytes are reported relative to the dry weight of sample.

$$\% \text{ dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

- b. All weights are recorded on the Total Solids sheet.
5. Add the spiked organic-free reagent water with surrogate and internal standard to the weighed amount of sample.
6. Heat and purge the sample. Be sure the trap is cool (<35°C)
7. Proceed with the analysis as outlined in Section 6.3. Use 5 mL of the same organic-free reagent water as in the blank. If saturated peaks occurred or would occur if a 1g sample were analyzed, the high concentration method (Medium Level soil method) must be followed.
8. For matrix spike analysis of low concentration sediment/soils, add 10 µL of the matrix spike solution to the 5 mL of organic-free reagent water. The concentration for a 5 g sample would be equivalent to 50 µg/kg of each matrix spike standard.

6.6.7 High-concentration method (Medium Level soils): The method is based on extracting the sediment/soil with methanol. A waste sample is either extracted or diluted, depending on its solubility in methanol.

6.6.7.1 The sample consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. Weigh 2 g (wet weight) of sample into a tared 20 mL vial. Use a top-loading balance. Note and record in the run log the actual weight to 0.1 gram and also determine the percent dry weight of the sample (Section 6.6.3.2.4.a). Measure 5 mL of solvent into the vial.

1. For sediment/soil or solid waste, add 5 mL of purge-and-trap grade methanol then add 50 µL of 250 µg/mL surrogate spiking solution to the vial. Cap and shake for 2 minutes.



2. Pipet a portion of the extract to a baked and cooled amber teflon sealed vial for storage (limiting headspace). The remainder may be disposed. Store the extracts at 4°C in the dark, prior to analysis.
3. Measure 100 μL of the extract into a 20 mL scintillation vial containing 5ml organic free water and after mixing measure the headspace on the OVM. Make appropriate dilutions if needed to assure concentration of the analytes are in the linear range of the initial calibration.
4. Table 6 can be used to determine the volume of solvent extract to add to the 5 mL of organic-free reagent water for analysis. Otherwise, estimate the concentration range of the sample from the low-concentration analysis to determine the appropriate volume. If the sample was submitted as a high-concentration sample, start with 100 μL . All dilutions must keep the response of the major constituents in the upper half of the linear range of the curve. Analyst must consider background matrix and chromatography overloading.
5. Remove the plunger from a 5.0 mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 4.9 mL. Pull the plunger back to 5.0 mL to allow volume for the addition of the sample extract and of standards. Add to the syringe 100 μL of solvent extract (or the amount as determined in section 6.6.3.2.4) plus additional MEOW to equal 100 μL . Add 10 μL of 25 $\mu\text{g/mL}$ internal standard solution.
6. Proceed with the analysis as outlined in Sections 6.6.1-6.6.1.14. Analyze all blanks on the same instrument as that used for the samples. The standards and blanks should also contain 100 μL of the purge-and-trap grade MeOH to simulate the sample conditions.
7. For a matrix spike in the medium level samples, add to 2g of sample and 5 mL of purge-and-trap grade methanol, 50 μL of surrogate spike solution (250 $\mu\text{g/mL}$), and 50 μL of matrix spike solution (250 $\mu\text{g/mL}$). Add a 100 μL aliquot of this extract to 5 mL of organic-free water for purging. Add the 10 μL of 25 $\mu\text{g/mL}$ internal standard. Purge and start analysis of the sample.



6.7 Calculations

6.7.1 When a compound has been identified, the quantitation target compounds will be based on the integrated abundance from the EICP of the quantitation mass. Quantitation will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of that of a given analyte.

6.7.2 Finnigan program calculations can be checked using the following formula:

Water and Water-Miscible Waste:

$$\text{concentration } (\mu\text{g/L}) = \frac{(A_x)(I_s)}{(A_{Is})(RF)(VO)}$$

where:

A_x = Area of characteristic ion for compound being measured.
 I_s = Amount of internal standard injected (ng).
 A_{Is} = Area of characteristic ion for the internal standard.
 RF = Response factor for compound being measured
 VO = Volume of water purged (mL), taking into consideration any dilutions made.

Sediment/Soil, Sludge, and Waste:

High-concentration:

$$\text{concentration } (\mu\text{g/kg}) = \frac{(A_x)(I_s)(V_t)}{(A_{Is})(RF)(V_i)(W_s)}$$

Low-concentration:

$$\text{concentration } (\mu\text{g/kg}) = \frac{(A_x)(I_s)}{(A_{Is})(RF)(W_s)}$$

where:

A_x , I_s , A_{Is} , RF = Same as in water and water-miscible waste above.

V_t = Volume of total extract (L) (use 10,000 μL or a factor of this when dilutions are made).

V_i = Volume of extract added (L) for purging.

W_s = Weight of sample extracted or purged (g). The wet weight or dry weight may be used depending upon the specific applications of the data.



- 6.7.3 Sediment/soil samples are generally reported on a dry weight basis, while sludges and wastes are reported on a wet weight basis. In either instance, the percent dry weight of the sample should be reported along with the data.
- 6.7.4 Where applicable, an estimate of concentration for non calibrated components in the sample should be made. The formula given above should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1. The concentration obtained should be reported, with indication (1) that the value is an estimate and (2) which internal standard was used to determine concentration. Use the nearest interference-free internal standard.

7.0 Review

7.1 Qualitative analysis

- 7.1.1 An analyte is identified by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference should be obtained on the user's GC/MS. These standard reference spectra may be obtained through analysis of the calibration standards. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC relative retention time (RRT) as those of the standard component; and (2) correspondence of the sample component and the standard component mass spectrum.
- 7.1.1.1 Standard reference mass spectra are checked daily against the fit in the diagnostic report having to meet the 700 fit criteria for non-eluting compounds and 500 fit for co-eluting compounds.
- 7.1.1.2 If secondary ion quantitation is necessary due to interference, then a short quantitation report is generated. This quantitation contains the integrated areas of the affected compounds, based on the secondary ion(s) for that compound, and of the relevant internal standards. Identical reports must be generated for the sample with interference and for the relevant continuing calibration. The report for the continuing calibration is used to generate a response factor for the affected compound based on its secondary ion. This response factor is then used in the calculations for that compound in the affected sample.



- 7.1.2 The sample component RRT must compare within ± 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run within the same 12 hours as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.
- 7.1.3 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100% must be present in the sample spectrum).
- 7.1.4 The relative intensities of ions specified in 7.1.3 must agree within $\pm 20\%$ between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 30 and 70 percent.)
- 7.1.5 Tentatively Identified Compounds
- 7.1.5.1 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. For example, the RCRA permit or waste delisting requirements may require the reporting of nontarget analytes. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:
1. Relative intensities of major ions in the reference spectrum (ions $> 10\%$ of the most abundant ion) should be present in the sample spectrum. If not, the compound may be flagged with "M" if the analyst feels the identification is correct (this favors false positives).
 2. The relative intensities of the major ions should agree within $\pm 20\%$. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).
 3. Molecular ions present in the reference spectrum should be present in the sample spectrum.
 4. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.



5. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

7.2 Analysis records

- 7.2.1 Each analytical run will be recorded in the instrument run log, including all information for each run. This log book serves as a observation/comment and the chain-of-custody for analyzed samples, therefore any change of operator must be included in the notations.
- 7.2.2 Fill in the date, your name, and tune file (including analysis start time) in the run log. For each standard and analytical run, fill in the file name, client sample number, sample amount, ARI sample number, and any necessary comments.
- 7.2.3 On instruments without autosamplers, fill out the internal standard scan/response time information for each run as it is completed, to assure the analysis falls within QA limits for internal standards. (See section 6.6.1) Insurments with autosamplers should have scan/response times filled out as soon as possible to identify any problems quickly.
- 7.2.4 Any maintenance performed during the day shall be recorded in the appropriate log. Also log any standard or quality control which was performed to reconcile out-of-control events.

7.3 Data Review

- 7.3.1 It is the analyst's responsibility to confirm all chromatographic peaks in the RIC, with automated assistance (TCA) by the Incos data system. Use retention time, spectral data, and the operator's expertise to determine whether analytes found by the system are in fact real hits.
- 7.3.2 The operator will manually check off those hits that are correct and cross off any false positives found by the system, and will include any appropriate qualifiers that may be needed.
- 7.3.3 Blank and sample data (library comparison) submitted shall include enhanced mass spectra at the minimum. For coelutions and bad matrix backgrounds, chromatographic window with unique compound ions should be provided to confirm analytes and qualifiers. Those samples requiring full deliverable packages shall include both enhanced, unenhanced mass spectra, and TICs.



8.0 Quality Control

- 8.1 Refer to the specific analytical method and the laboratory Quality Assurance Plan for quality control procedures. Specific quality control requirements are specified in the Quality Assurance Project Plan (QAPP).
- 8.2 Specific quality control procedures are specified in section 6.0, Analytical Procedures Review in section 7.0, and in section 9.0, Corrective Actions.
- 8.3 Method Detection Limits (MDL) are performed on each instrument to provide recovery and precision for the method.
- 8.4 One method blank is analyzed every 12 hour shift, following the BFB tuning standard and the daily calibration standard.
- 8.5 One set of matrix spikes is analyzed for each 20 samples/matrix/instrument at 50 ng/mL.
- 8.6 Water samples are to be stored at 4°C plus or minus 2°C and analyzed within 7 days of sampling if not preserved with 1:1 HCL, and if preserved are to be analyzed within 14 days. Soil samples are to be stored at 4°C plus or minus 2°C are to be analyzed within 14 days of sampling.
- 8.7 One laboratory control sample (LCS) will be performed each 12 hour shift.

9.0 Corrective Actions

- 9.1 If the instrument is out of control at any point up to running the method blank (6.6.1), the entire procedure must be restarted with the mass tune (6.5.1) once the appropriate corrective action has been taken. If the instrument goes out of control during sample processing, all sample data not affected by the out-of-control event are considered valid, and any samples which were affected must be rerun in a new QC period that meets QC acceptance criteria. Reestablishment of control must be verified before sample analysis can resume. In this way, proper recovery from an out-of-control condition is assured.
- 9.2 For aqueous and soil matrices, surrogate recovery values should fall within the surrogate control limits specified in the project QAPP.
 - 9.2.1 If surrogate recovery is not within limits, the following procedures are required.
 - 9.2.1.1 Check calculations, surrogate solutions, and internal standards. If errors are found, recalculate the data accordingly.
 - 9.2.1.2 Check instrument performance. If instrument performance is suspect, correct the problem and re-analyze the sample.



9.2.1.3 If, upon re-analysis, the recovery is again not within limits, flag the data "matrix effect."

9.2.1.4 At a minimum the laboratory should update surrogate, MS/MSD, and LCS control limits annually on a matrix-by-matrix basis.

9.2.1.5 A corrective action form is used to document the out-of-control event.

9.3 See section 6.0, Analytical Procedures, section 7.0, Review, and section 8.0, Quality Control for additional guidance on appropriate actions.

9.4 The analyst must provide a narrative of the volatile analysis in the Analyst Notes and Corrective Action form. Quality control and other sample-specific information must be included.

10.0 Miscellaneous Notes and Precautions

10.1 Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed sequentially. To reduce carryover, the sample syringe must be rinsed with organic-free water and baked until dry. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of a method blank.

10.2 Contamination can occur by diffusion of volatiles through the septa into the sample during shipment and storage. Analysis of a trip blank prepared from organic-free water and carried through the sampling and handling protocol can serve as a check on such contamination.

10.3 For transfer of data to Formsmaster, or LIMS, test files shall be generated from quan lists by transferring to .91 files. (See Finnigan Manuals and LIMS Standard Procedure. Also refer to the SOP for Automated Data Transfer.)

10.3.1 Files for transfer to FormsMaster shall be named in such a way as to be traceable and unique; i.e. data run on Finn1 on 12/05/93 may be named F11205da.91. A list of .91 files shall be part of the hardcopy submission to the data section.

11.0 Method References

11.1 Methods for the Determination of Organic Compounds in Finished Drinking Water and Raw Source Water Method 524.2; U.S. Environmental Protection Agency. Office of Research Development. Environmental Monitoring and Support Laboratory; Cincinnati, OH 1986.

11.2 U.S.EPA Contract Laboratory Program, Statement of Work for Organic Analysis, July 1985, Revision.



11.3 USEPA SW-846, Method 8260. Revision 0.

12.0 Appendices

12.1 Table 1: BFB Mass-Intensity Specification (4-Bromofluorobenzene).

12.2 Table 2: Characteristic Masses (M/Z) for Purgeable Organic Compounds.

12.3 Table 3: Volatile Internal Standards with Corresponding Analytes assigned for Quantitation.

12.4 Table 4: Control Limits for Water and Soil/Sediment Samples.

12.5 Table 5: Compounds that can be determined by Method 8260.

12.6 Table 6: Screening by Organic Vapor Meter (OVM).

Job/Case: _____

Date: _____

**ANALYTICAL
RESOURCES
INCORPORATED**

**GC/MS VOLATILE ORGANICS LOGBOOK
FINN HI**

Column No.: _____

Type: _____

Program: _____

EM Voltage: _____

Tune: _____

Calibration File: _____

Mass Tuning File: _____

Time: _____

Analyst: _____

Run	Time	File	Scan	Area	Scan	Area	Scan	Area
1	:							
2	:							
3	:							
4	:							
5	:							
6	:							
7	:							
8	:							
9	:							
10	:							
11	:							
12	:							
13	:							
14	:							
15	:							
16	:							
17	:							
18	:							
19	:							
20	:							
21	:							
22	:							
23	:							
24	:							
25	:							

Job/Case: _____



ANALYTICAL
RESOURCES
INCORPORATED

GC/MS VOLATILE ORGANICS LOGBOOK
FINN III

Maintenance: _____

Fill out all information completely.

Z-out all entry spaces not used at end of day/QC period.

Start new page for each new EPA case or QC period.

Run	Scan	Area	Sample Description / Comments	AS	Type
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					
21					
22					
23					
24					
25					

[illegible]

Preparation Date:

1

Expiration Date:

FINN 1

FINN 3

FINN 5

FINN 7

Internal Standard/Surrogate

Spike



ANALYTICAL
RESOURCES
INCORPORATED

Year: _____

PREVENTATIVE MAINTENANCE LOG
INCOS 50 - FINN 3

	JAN	FEB	MAR	APRIL	MAY	JUNE	JULY	AUG	SEPT	OCT	NOV	DEC
MS Fans clean verify operation three (3) months												
Mechanical Pump (verify oil level) six (6) months												
Turbomolecular Pump (flush with new oil) six (6) months												
Mechanical Pump Oil (change) one (1) year												

Supervisor

Review



Year: _____

PREVENTATIVE MAINTENANCE LOG
4500 - FINN 1

ANALYTICAL
RESOURCES
INCORPORATED

	JAN	FEB	MAR	APRIL	MAY	JUNE	JULY	AUG	SEPT	OCT	NOV	DEC
Winchester Disk Drive Fans clean verify operation three (3) months												
QEM Filters/Fan (clean/verify operation) one (1) month												
Power Controller Filters/Fans (clean/verify operation) one (1) month												
2010 Interface Filter/Fans (clean/verify operation) one (1) month												
Nova 4X Fans (4) (verify operation, change as needed) three (3) months												
Mechanical Pump Oil (verify level) six (6) months												
Mechanical Pump Oil (change) one (1) calendar year												
Water Filter for Diffusion (dump supply/check and change as needed) three (3) months												
Water Flow Diffusion Pumps (check/adjust) one (1) month												
Supervisor Review												



12.1 TABLE 1

BFB MASS - INTENSITY SPECIFICATIONS (4-BROMOFLUOROBENZENE)

<u>Mass</u>	<u>Intensity Required (relative abundance)</u>
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	greater than 95% but less than 101% of mass 174
177	5 to 9% of mass 176



12.2 TABLE 2.

CHARACTERISTIC MASSES (M/Z) FOR PURGEABLE ORGANIC COMPOUNDS

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Acetone	43	58
Acrolein	56	55, 58
Acrylonitrile	53	52, 51
Benzene	78	52, 77
Bromobenzene	156	77, 158
Bromochloromethane	128	49, 130
Bromodichloromethane	83	85
Bromoethane	108	
Bromoform	173	175, 254
Bromomethane	94	96
2-Butanone	43	57, 43
n-Butylbenzene	91	92, 134
sec-Butylbenzene	105	134
tert-Butylbenzene	119	91, 134
Carbon disulfide	76	78
Carbon tetrachloride	117	119
Chlorobenzene	112	77, 114
Chloroethane	64	66
2-Chloroethyl vinyl ether	63	65, 106
Chloroform	83	85
Chloromethane	50	52
2-Chlorotoluene	91	126
4-Chlorotoluene	91	126
1,2-Dibromo-3-chloropropane	75	155, 157
Dibromochloromethane	129	127
1,2-Dibromoethane	107	109, 188
Dibromomethane	93	95, 174
1,2-Dichlorobenzene	146	111, 148
1,3-Dichlorobenzene	146	111, 148
1,4-Dichlorobenzene	146	111, 148
1,4-Dichloro-2-butene	75	53, 89
*Dichlorodifluoromethane	85	87
1,1-Dichloroethane	63	65, 83
1,2-Dichloroethane	62	98
1,1-Dichloroethene	96	61, 63
cis-1,2-Dichloroethene	96	61, 98
trans-1,2-Dichloroethene	96	61, 98
1,2-Dichloropropane	63	112
1,3-Dichloropropane	76	78
2,2-Dichloropropane	77	97
1,1-Dichloropropene	75	110, 77



12.2 TABLE 2.
CHARACTERISTIC MASSES (M/Z) FOR PURGEABLE ORGANIC COMPOUNDS (cont'd)

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion(s)
*Ethylbenzene	91	106
Hexachlorobutadiene	225	223, 227
Iodomethane	142	
2-Hexanone	43	58, 57, 100
Isopropylbenzene	105	120
p-Isopropyltoluene	119	134, 91
Methylene chloride	84	86, 49
4-Methyl-2-Pentanone	58	43, 100
Naphthalene	128	
n-Propylbenzene	91	120
Styrene	104	78
1,1,1,2-Tetrachloroethane	131	133, 119
1,1,2,2-Tetrachloroethane	83	131, 85
Tetrachloroethene	166	168, 129
Toluene	92	91
1,2,3-Trichlorobenzene	180	182, 145
1,2,4-Trichlorobenzene	180	97, 85
1,1,1-Trichloroethane	97	
1,1,2-Trichloroethane	97	
Trichloroethene	95	130, 132
Trichlorofluoromethane	101	103
1,1,2-trichloro- 1,2,2-trifluoromethane	101	151
1,2,3-Trichloropropane	75	77
1,2,4-Trimethylbenzene	105	120
1,3,5-Trimethylbenzene	105	120
Vinyl chloride	62	64
o-Xylene	106	91
m-Xylene	106	91
p-Xylene	106	91
Vinyl acetate	43	86
*trans-1,3-Dichloropropene	75	77
*cis-1,3-Dichloropropene	75	77

* = not a standard analyte

INTERNAL STANDARDS/SURROGATES

4-Bromofluorobenzene	95	174, 176
1,2-Dichloroethane-d4	65	
Toluene-d8	98	
Pentafluorobenzene	168	
1,4-Difluorobenzene	114	
Chlorobenzene-d5	117	
1,4-Dichlorobenzene-d4	152	
1,2-dichlorobenzene-d4	152	



12.3 TABLE 3.

VOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR
QUANTITATION

Pentafluorobenzene

Acetone
Acrolein
Acrylonitrile
Bromochloromethane
Bromomethane
2-Butanone
Carbon disulfide
Chloroethane
Chloroform
Chloromethane
Dichlorodifluoromethane
1,1-Dichloroethane
1,1-Dichloroethene
cis-1,2-Dichloroethene
trans-1,2-Dichloroethene
2,2-Dichloropropane
Iodomethane
Methylene chloride
1,1,1-Trichloroethane
Trichlorofluoromethane
Vinyl acetate
Vinyl chloride

Chlorobenzene-d5

Bromoform
Chlorodibromomethane
Chlorobenzene
1,3-Dichloropropane
Ethylbenzene
2-Hexanone
Styrene
1,1,1,2-Tetrachloroethane
Tetrachloroethene
Xylene

1,4-Difluorobenzene

Benzene
Bromodichloromethane
Bromofluorobenzene (surrogate)
Carbon tetrachloride
2-Chloroethyl vinyl ether
1,2-Dibromoethane
Dibromomethane
1,2-Dichloroethane
1,2-Dichloroethane-d4 (surrogate)
1,2-Dichloropropane
1,1-Dichloropropene
cis-1,3-Dichloropropene
trans-1,3-Dichloropropene
4-Methyl-2-pentanone
Toluene
Toluene-d8 (surrogate)
Trichloroethene
1,1,2-Trichloroethane

1,4-Dichlorobenzene-d4

Bromobenzene
n-Butylbenzene
d4-1,2-Dichlorobenzene(surrogate)
sec-Butylbenzene
tert-Butylbenzene
2-Chlorotoluene
4-Chlorotoluene
1,2-Dibromo-3-chloropropane
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
Hexachlorobutadiene
Isopropyl benzene
p-Isopropyltoluene
Naphthalene
n-Propylbenzene
1,1,2,2-Tetrachloroethane
1,2,3-Trichlorobenzene
1,2,4-Trichlorobenzene
1,2,3-Trichloropropane
1,2,4-Trimethylbenzene
1,3,5-Trimethylbenzene



12.4 TABLE 4.

CONTROL LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

<u>Laboratory Control Sample</u>	<u>Water</u>	<u>Soil</u>
1,1-Dichloroethene	71-147	71-147
Trichloroethene	82-138	82-138
Benzene	79-147	79-147
Toluene	87-140	87-140
Chlorobenzene	87-145	87-145
Chlorobromomethane	60-125	60-125
1,1,2-Trichlorofluoromethane	60-125	60-125
Ethylbenzene	60-125	60-125
Xylene (Total)	60-125	60-125
Surrogate:		
Toluene-d8	66-138	87-113
Bromofluorobenzene	63-131	72-121
1,2-Dichloroethane-d4	62-139	86-136
<u>Matrix Spike/Matrix Spike Duplicate</u>		
1,1-Dichloroethene	37-117	32-144
Trichloroethene	60-125	76-117
Benzene	60-115	72-128
Toluene	62-125	79-120
Chlorobenzene	59-126	78-122
Chlorobromomethane	60-125	60-125
1,1,2-Trichlorofluoroethane	60-125	60-125
Ethylbenzene	60-125	60-125
Xylene (Total)	60-125	60-125
<u>Surrogate (MS/MSD and Sample)</u>		
Toluene-d8	94-109	87-112
Bromofluorobenzene	88-119	47-130
1,2-Dichloroethane-d4	92-121	88-126

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12.5 TABLE 5

COMPOUNDS THAT CAN BE DETERMINED BY 8260

<u>Analyte</u>	<u>CAS No.^b</u>	<u>Technique</u>
<u>Purge-and-Trap</u>		
Acetone	67-64-1	pp
Acetonitrile	75-06-9	pp
Acrolein	107-02-8	pp
Acrylonitrile	107-13-1	pp
Allyl alcohol	107-18-6	ht
allyl chloride	107-05-1	a
Benzene	71-43-2	a
Benzyl chloride	100-44-7	a
Bromoacetone	598-31-2	pp
Bromobenzene	108-86-1	a
Bromochloromethane	74-97-5	a
Bromodichloromethane	75-27-4	a
Bromoforn	75-25-2	a
Bromomethane	74-83-9	a
n-Butanol	71-36-3	ht
2-Butanone	78-93-3	pp
n-Butylbenzene	104-61-8	a
sec-Butylbenzene	135-98-8	a
tert-Butylbenzene	98-06-6	a
Carbon disulfide	75-15-0	pp
Carbon tetrachloride	56-23-5	a
Chloral hydrate	302-17-0	pp
Chlorobenzene	108-90-7	a
2-Chloro-1,3-butadiene	126-99-8	a
Chlorodibromomethane	124-48-1	a
Chloroethane	75-00-3	a
2-Chloroethanol	107-03-3	pp
bis-(2-Chloroethyl) sulfide	505-60-2	pp
2-Chloroethyl vinyl ether	110-75-2	pp
Chloroform	67-66-3	a
Chloromethane	74-87-3	a
Chloroprene	126-99-8	pc
3-Chloropropene	107-05-1	a
3-Chloropropionitrile	542-76-7	i
2-Chlorotoluene	95-49-8	a
4-Chlorotoluene	106-43-4	a
1,2-Dibromo-3-chloropropane	96-12-8	pp
1,2-Dibromoethane	106-93-4	a
Dibromomethane	74-95-3	a
1,2-Dichlorobenzene	95-50-1	a
1,3-Dichlorobenzene	541-73-1	a
1,4-Dichlorobenzene	106-46-7	a
Dichlorodifluoromethane	75-71-8	a
1,1-Dichloroethane	75-34-3	a
1,2-Dichloroethane	107-06-2	a



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COMPOUNDS THAT CAN BE DETERMINED BY 8260 (cont'd)

<u>Analyte</u>	<u>CAS No.</u> ^b	<u>Technique</u>
<u>Purge-and-Trap</u>		
1,1-Dichloroethene	75-35-4	a
cis-1,4-Dichloro-2-butene	1476-11-5	a
trans-1,4-Dichloro-2-butene	110-57-6	pp
Dichlorofluoromethane	75-71-8	a
cis-1,2-Dichloroethene	156-59-2	a
trans-1,2-Dichloroethene	156-60-5	a
1,2-Dichloropropane	78-87-5	a
1,3-Dichloropropane	142-28-9	a
2,2-Dichloropropane	594-20-7	a
1,3-Dichloro-2-propanol	96-23-1	pp
1,1-Dichloropropene	563-58-6	a
cis-1,3-Dichloropropene	10061-01-5	a
trans-1,3-Dichloropropene	1006	pp
Iodomethane	74-88-4	a
Isobutyl alcohol	78-83-1	pp
Isopropylbenzene	98-82-8	a
p-Isopropyltoluene	99-87-6	a
Malononitrile	109-77-3	pp
Methacrylonitrile	126-98-7	pp
Methylene chloride	75-09-2	a
Methyl iodide	74-09-2	a
Methyl methacrylate	80-62-6	a
4-Methyl-2-Pentanone	108-10-1	pp
Naphthalene	91-20-3	a
Nitrobenzene	98-95-3	a
2-Nitropropane	79-46-9	a
2-Picoline	109-06-8	pp
Propargyl alcohol	107-19-7	pp
Propiolactone	57-57-8	pp
Propionitrile (ethyl cyanide)	107-12-0	ht
n-Propylamine	107-10-8	a
n-Propylbenzene	103-65-1	a
Styrene	100-42-5	a
1,1,1,2-Tetrachloroethane	630-20-6	a
1,1,2,2-Tetrachloroethane	79-34-5	a
Tetrachloroethene	127-18-4	a
Toluene	108-88-3	a



12.5 TABLE 5

COMPOUNDS THAT CAN BE DETERMINED BY 8260 (cont'd)

<u>Analyte</u>		<u>Technique</u>
<u>Purge-and-Trap</u>	<u>CAS No.^b</u>	
1,2,3-Trichlorobenzene	87-61-6	a
1,2,4-Trichlorobenzene	120-82-1	a
1,1,1-Trichloroethane	71-55-6	a
1,1,2-Trichloroethane	79-00-5	a
Trichloroethene	79-01-6	a
Trichlorofluoromethane	75-69-4	a
1,2,3-Trichloropropane	96-18-4	a
1,2,4-Trimethylbenzene	95-63-6	a
1,3,5-Trimethylbenzene	108-67-8	a
Vinyl Acetate	108-05-4	a
Vinyl chloride	75-01-4	a
o-Xylene	95-47-6	a
m-Xylene	108-38-3	a
p-Xylene	106-42-3	a

- a Adequate response by this technique.
b Chemical Abstract Services Registry Number.
pp Poor purging efficiency resulting in high EQLs.
ht Method analyte only when purged at 80°C



12.6 TABLE 6

SCREENING BY ORGANIC VAPOR METER (OVM)
Dilution vs meter reading

<u>PID Reading</u>	<u>Dilution</u>
0-10	1 / 1
10-15	1 / 5
15-25	1 / 10
25-35	1 / 20
35-45	1 / 40
45-50	1 / 50
50-75	1 / 100
75-100	1 / 300
100-200	1 / 500



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Standard Operating Procedure

Organochlorine Pesticides/PCBs
by GC/ECD
Method 8081 (Air Force)

417S

Revision 1

7/5/94

PROPRIETARY

Prepared By:

[Signature]

Approvals:

Section Manager

Burn N. Baker
Laboratory Manager

Michelle L. Turner
Quality Assurance Manager

[Signature]
Laboratory Director

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Standard Operating Procedure

Organochlorine Pesticides and PCBs by GC/ECD - (Method 8081)

(United States Air Force)

1.0 Scope and Application

- 1.1 Method 8081 is used to determine the concentrations of various organochlorine pesticides and polychlorinated biphenyls (PCBs) as Aroclors, in extracts from solid and liquid matrices. Open-tubular, capillary columns with electron capture detectors (ECD) are required. When compared to packed columns, these fused-silica, open-tubular columns offer improved resolution, better selectivity, increased sensitivity, and faster analysis. Below is a list of normal analytes.

Compound Name	CAS No.
Aldrin	309-00-2
Aroclor-1016	12674-11-2
Aroclor-1221	1104-28-2
Aroclor-1232	11141-16-5
Aroclor-1242	53469-21-9
Aroclor-1248	12672-29-6
Aroclor-1254	11097-69-1
Aroclor-1260	11096-82-5
alpha-BHC	319-84-6
beta-BHC	319-85-7
delta-BHC	319-86-8
gamma-BHC (Lindane)	58-89-9
4,4-DDD	72-54-8
4,4-DDE	72-55-9
~~4,4-DDT~~	50-29-3
alpha-Chlordane	5103-71-9
gamma-Chlordane	5103-74-2
Dieldrin	60-57-1
Endosulfan I	959-98-8
Endosulfan II	33213-65-9
Endosulfan sulfate	1031-07-8
Endrin	72-20-8
Endrin aldehyde	7421-93-4
Endrin ketone	53494-70-5
Heptachlor	76-44-8
Heptachlor epoxide	1024-57-3
Methoxychlor	72-43-5
Toxaphene	8001-35-2



- 1.2 Several multi-component mixtures are listed as target compounds. When samples contain more than one multi-component analyte, a higher level of analyst expertise is required to attain acceptable levels of qualitative and quantitative analysis. The same is true of multi-component analytes that have been subjected to environmental degradation or degradation by treatment technologies. These result in "weathered" Aroclors (or any other multi-component mixtures) that may have significant differences in peak patterns than those of standards. In these cases, individual congener analyses may be preferred over total mixture analyses.
- 1.3 Compound identification based on single column analysis must be confirmed on a second column, or must be supported by at least one other qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm the measurements made with the primary column. GC/MS Method 8270 is also recommended as a confirmation technique if sensitivity permits (8270, section 8).
- 1.4 This method describes a dual column option. The option allows a hardware configuration of two analytical columns joined to a single injection port. The option allows one injection to be used for dual column analysis.
- 1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph (GC) and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 Definitions

N/A

3.0 Equipment

- 3.1 Gas Chromatograph (GC): An analytical system suitable for split/splitless injection, all required accessories including syringes, analytical columns, gases, electron capture detectors (ECD), and data system are required.



3.2 Columns (megabore)

- 3.2.1 Column 1: 30 m x 0.53 mm ID fused silica capillary column, chemically bonded with 35% phenyl methylpolysiloxane (DB 608, SPB 608, RTx-35, or equivalent), 0.83 μ m film thickness.
- 3.2.2 Column 2: 30 m x 0.53 mm ID fused silica capillary column, chemically bonded with 50% phenyl methylpolysiloxane (DB 1701 or equivalent), 1.0 μ m film thickness.
- 3.2.3 Column 3: 30 m x 0.53 mm ID fused silica capillary column, chemically bonded with SE-54 (DB 5, SPB 5, RTx5, or equivalent), 1.5 μ m film thickness.
- 3.2.4 Megabore columns should be installed in 1/4 inch injectors, with deactivated liners designed specifically for use with these columns.

3.3 Columns (dual column analysis)

3.3.1 Column pair:

- 3.3.1.1 J & W Scientific press-fit Y-shaped glass 3-way union splitter (J & W Scientific, Catalog no. 705-0733), or equivalent.
- 3.3.1.2 30 m x 0.53 mm ID DB-5 (J & W Scientific), 1.5 μ m film thickness or equivalent.
- 3.3.1.3 30 m x 0.53 mm ID DB-608 (J & W Scientific), 0.83 μ m film thickness or equivalent.

3.4 Glassware (see Methods 3510, 3520, 3540, 3541, 3550, 3630, 3640, 3660, and 3665 for specifications).

3.5 Kuderna-Danish (K-D) apparatus. See extraction methods for specifics.

3.6 REAGENTS

3.6.1 Reagent or pesticide grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

3.6.1.1 Store the standard solutions (stock, composite, calibration, internal, and surrogate) at 4°C in Teflon-sealed containers in the dark. When a lot of standards is prepared, store aliquots of the lot



In individual small vials. All working standard solutions must be replaced after six months, or sooner if routine quality control (See 10.0) suggests a problem.

- 3.6.2 Use solvents and reagents appropriate for Method 3510, 3520, 3540, 3541, 3550, 3630, 3640, 3660, or 3665: n-hexane, diethyl ether, methylene chloride, acetone, ethyl acetate, and isooctane (2,2,4-trimethylpentane). All solvents should be pesticide quality or equivalent, and each lot of solvent should be determined to be phthalate free. Extracts must be exchanged to hexane or isooctane prior to analysis.
- 3.6.3 Organic-free reagent water: All references to water in this method refer to organic-free reagent water.
- 3.6.4 Calibration and linearity standards should be prepared at five concentrations by dilution of the composite stock standard with isooctane. The concentrations should correspond to the expected range of concentrations found in real samples and should bracket the linear range of the detector. Stock standards are purchased as certified solutions. (See section 6 for details on curve and calibration procedures)
- 3.6.4.1 Although all single component analytes can be resolved on a new 35% phenyl methyl silicone (e.g. DB-608), two calibration mixtures should be prepared for the single component analytes of this method.
- 3.6.4.2 This requirement is established to 1) minimize potential resolution and quantitation problems on confirmation columns or on older 35% phenyl methyl silicone (e.g. DB-608) columns, and to 2) allow determination of Endrin and DDT breakdown for method quality control. (See 10.0)
- 3.6.4.3 Separate calibration standards are required for each multi-component target analyte, with the exception of Aroclors 1016 and 1260 which can be run as a mixture.
- 3.6.5 Surrogate standards: The performance of the method is monitored using surrogate compounds. From the certified stock solution containing tetrachloro-m-xylene and decachlorobiphenyl, make a working solution at 2.0 µg/mL in Acetone. Spike 100 µL in both aqueous and solid samples



and in all blanks. 200 μ L is required if an extract is to go through GPC cleanup. Corrective action is required when both surrogates are outside of recovery limits.

4.0 Documentation

- 4.1 Pesticide/PCB worksheet.

5.0 In-house Modifications to Referenced Method

- 5.1 Section 1.1: The compound list for this method is the same as for Method 8080. No analytes are added.
- 5.2 Section 3.6.5: The surrogates for dual-column analysis (tetrachloro-m-xylene and decachlorobiphenyl) are listed in the Method for single-column analysis.
- 5.3 Section 8.3: Only select single-component pesticides will be in the LCS spike solution. Per section 9.3, aroclors and toxaphene will be spiked only when those compounds are the only analytes of interest, unless otherwise requested.
- 5.4 Section 6.3.4: RT windows will be $\pm 3 \times$ SD over 72 hours or 0.08 minutes, whichever is greater.
- 5.5 Section 6.6: All multi-component compounds will be quantitated with 3 - 5 peaks. The Method lists 5 for Toxaphene.
- 5.6 Section 6.4.3: Delta BHC, Endosulfan sulfate, and endrin ketone will sometimes be allowed QC limits for continuing calibrations of + 30% to -15% instead of $\pm 15\%$.
- 5.7 Section 6.6.4: Chlordane will always be quantitated as alpha- and gamma-chlordane, respectively, unless otherwise requested. Method 8081 allows some discretion.
- 5.8 Section 8.1: Both surrogates will be quantitated and reported. Method 8081 requires quantitation of only decachlorobiphenyl unless there is interference.

6.0 Procedures

- 6.1 Summary of Method: A measured volume or weight of sample (approximately 1 L for liquids, 2 - 30 g for solids) is extracted using the appropriate sample extraction technique. (See Extractions SOPs) Liquid samples are extracted at neutral pH with methylene chloride, using a separatory funnel (Method 3510). Solid samples are extracted with hexane-acetone (1:1), using the Ultrasonic Extraction procedure



(Method 3550). A variety of cleanup steps may be applied to the extract, depending on 1) the nature of the coextracted matrix interferences and 2) the target analytes. After cleanup, the extract is analyzed by injecting a 1 - 2 μ L sample into a gas chromatograph equipped with dual mega-bore, fused-silica capillary columns and two electron capture detectors (GC/ECD). The final effective volume (FEV) for all extracts will be 10 mL, unless GPC cleanup is performed (FEV = 20 mL).

6.1.1 Hexane/acetone (1:1) is a more effective extraction solvent for organochlorine pesticides and PCBs in environmental and waste matrices than is methylene chloride. Use of hexane/acetone generally reduces the amount of co-extracted interferences and improves signal/noise ratios.

6.1.2 Method Detection Limit (MDL) Studies are used to verify the applicability of the chosen extraction technique to each new sample type. See Method 8000 for guidance on the determination of method reporting limits.

6.2 Cleanup/Fractionation

6.2.1 Cleanup procedures may not be necessary for a relatively clean sample matrix, but most extracts from environmental and waste samples will require additional preparation before analysis. The specific cleanup procedure used will depend on the nature of the sample to be analyzed and the data quality objectives for the measurements. General guidance for sample extract cleanup is provided in this section and in Method 3600.

6.2.1.1 If a sample is of biological origin, or contains high molecular weight materials, the use of the GPC cleanup option (Method 3640) is recommended. All soil samples should go through GPC cleanup, unless they are obviously clean. Frequently, one of the adsorption chromatographic cleanups may also be required following the GPC cleanup.

6.2.1.2 If only PCBs are to be measured in a sample, the sulfuric acid cleanup (Method 3665) is recommended.



6.2.1.3 All samples except those that have been acid-cleaned should go through Florisil cleanup (Method 3620).

6.2.1.4 Elemental sulfur, which may appear in certain sediments and industrial wastes, interferes with the electron capture gas chromatography of certain pesticides and aroclors. Sulfur should be removed by the technique described in Method 3660, Sulfur cleanup.

6.3 Analysis Preparation

6.3.1 The dual-column/dual-detector approach involves the use of two 30 m x 0.53 mm ID fused-silica open-tubular columns of different polarities and, thus, different selectivities towards the target compounds. The columns are connected to a single injector via a glass "Y" splitter and a precolumn. Operating conditions for a DB-5/DB-608 pair are listed in Section 12.1, Table 1.

6.3.2 Prepare calibration and linearity standards using the procedures in Section 6.4. External standard calibration is used with Method 8081 because of the sensitivity on the electron capture detector and the probability of the internal standard being affected by interferences. Because several of the pesticides may co-elute on any single column, analysts should use two calibration mixtures (Section 12.2).

6.3.2.1 Method 8081 has many multi-component target analytes. For this reason, the target analytes chosen for calibration should be limited to those specified in the project plan. Sites may require analysis only for the organochlorine pesticides or the PCBs. Toxaphene and/or technical Chlordane may also not be specified at certain sites. In addition, where PCBs are specified in the project plan, a mixture of Aroclors 1016 and 1260 will suffice for the initial calibration of all Aroclors, since they include all congeners present in the various regulated Aroclors. A midpoint calibration standard of all Aroclors must be included with the initial calibration, so that the analyst is familiar with each Aroclor pattern and with retention times on each column.



6.3.2.2 For calibration curve verification, all target analytes required in the project plan must be injected with the following exception for the Aroclors. For sites that require PCB analysis, include only the Aroclors that are expected to be found at the site. If PCBs are required, but it is unknown which Aroclors may be present, only the midpoint concentration Aroclors 1016/1260 mixture may be injected. However, if specific Aroclors are found during sample analysis, it is recommended that the relevant aroclor standard(s) be injected within 24 hours of the aroclor-containing samples.

6.3.3 Because of the low concentration of pesticide standards injected on a GC/ECD, column adsorption may be a problem when the GC has not been used for a day or more. Therefore, the GC column should be primed or deactivated by injecting a pesticide standard mixture at least 4 times more concentrated than the mid-concentration standard. Inject this standard mixture prior to beginning the initial calibration or calibration verification.

CAUTION: Several analytes, including Aldrin, may be observed in the injection just following this system priming. Always run an acceptable blank prior to running any standards or samples.

6.3.4 Retention time windows

6.3.4.1 Before establishing the retention time windows, make sure the gas chromatographic system is within optimum operating conditions. The width of the retention time window should be based upon actual retention times of standards measured over the course of 72 hours.

6.3.4.2 Retention time windows shall be defined as plus or minus three times the standard deviation of the absolute retention times for each standard, or 0.08 minutes, whichever is greater. However, the experience of the analyst should weigh heavily in the



interpretation of the chromatograms. For multi-component analytes (e.g. PCBs), the analyst should consider the retention time window, but should rely primarily on pattern recognition and relative retention times.

6.4 Calibration

6.4.1 Establish gas chromatographic operating parameters equivalent to those indicated in Section 12.1, Table 1. Calibrate the chromatographic system using the external standard technique.

6.4.2 External standard calibration procedure

6.4.2.1 For each analyte of interest, prepare calibration standards at a minimum of five concentrations by adding volumes of one or more certified stock standards to a volumetric flask and diluting to volume with isooctane. Pesticides are curved as follows: Low concentration analytes - 0.005, 0.01, 0.02, 0.04, 0.08 ($\mu\text{g/mL}$). Aroclor 1016/1260 is calibrated at 0.25, 0.5, 1.0, 2.5, and 5.0 ($\mu\text{g/mL}$). Toxaphene is calibrated at 0.5, 2.5, 5.0, 10 and 25 ($\mu\text{g/mL}$).

6.4.2.2 Inject each calibration standard using the technique that will be used to introduce the actual samples into the gas chromatograph (e.g. 1-2 μL injections). Tabulate peak height responses against the mass injected. The results are used to prepare a calibration curve for each analyte. If the percent relative standard deviation (%RSD) of the calibration factor is less than 20% over the working range, linearity through the origin can be assumed, and the average calibration factor can be used in place of a calibration curve. If the calibration curve is used for quantitation, the upper limit for % RSD is 30%.

$$\text{Calibration Factor} = \frac{\text{Total Area of Peak}^*}{\text{Mass Injected (In nanograms)}}$$

* For multi-response pesticides/PCBs, use the 3-5 major peaks. The % RSD of the average of the 3-5 peaks must be $\leq 20\%$ in order to use the average calibration factor.



6.4.2.3 The working calculation curve must be verified at the beginning of each new run. The verification standards are Pesticide Mix A, Pesticide Mix B, and 1016/1260, each at midpoint concentrations. If the response for any analyte varies from the predicted response by more than $\pm 15\%$, a new calibration curve must be prepared for that analyte.

$$\text{Percent Difference} = \frac{R_1 - R_2}{R_1} \times 100$$

where:

R_1 = Calibration Factor from first analysis.

R_2 = Calibration Factor from succeeding analyses.

6.4.2.4 Initial Calibration Sequence

1. Instrument Blank
- 2-6. Toxaphene Curve
- 7-11. 1016/1260 Curve
- 12-17. Aroclor standards
- 18-27. Pesticide curves (A & B mixes)
28. Rinse
29. Breakdown standard

6.4.3 Continuing Calibration

6.4.3.1 At least one calibration standard and the breakdown standard must be run after every 10 extracts.

6.4.3.2 Rotation of the calibration mixes should be as follows:

First 10 samples
Pesticide B/breakdown standard (BS)
Second 10 samples
Pesticide A/BS
Third 10 samples
Aroclor/BS
Repeat

6.4.3.3 The calculated amounts for all continuing calibration analytes must be within $\pm 15\%$ of the true amount, with the following exceptions:

1. Several years of pesticide analyses involving various difficult matrices have documented that select pesticides are more susceptible than others to matrix effects. Delta BHC,



endosulfan sulfate, and endrin ketone tend to have elevated responses when run in sequences with particularly contaminated samples. For this reason, these analytes will be allowed a wider continuing calibration range when none of the 3 analytes have been identified in the relevant run bracket.

2. Delta BHC, endosulfan sulfate, and endrin ketone will be allowed +30% to -15% as long as they have not been identified (and confirmed) in any extracts run within the relevant sequence bracket.

6.4.3.4 For calculating %D for multi-component analytes, the average calculated amount (for 3-5 peaks) must be within $\pm 15\%$ of the true value.

6.4.3.5 The breakdown mix is run after every 10 extracts. DDT and endrin must each have breakdown $\leq 15\%$.

1. Breakdown is calculated as follows:

$$\text{DDT \% Breakdown} = \frac{\text{DDE Ht} + \text{DDD Ht}}{\text{DDT Ht} + \text{DDE Ht} + \text{DDD Ht}} \times 100$$

2. Endrin breakdown is calculated similarly, using Endrin Aldehyde and Endrin ketone.

6.4.3.6 Because second column confirmation is required only when an analyte has been identified on the primary column, all continuing calibration QC limits apply only to the primary column until an analyte is identified on the primary column. If the analyte is also identified on the confirmation column, the confirmation column must also meet QC limits for that analyte(s).

6.4.3.7 Either column may be the primary column for a given run sequence. Within a single run, the primary column designation may not be switched.

6.5. Sample Analysis

6.5.1 Set up the GC system using the conditions described in Table 1. (See 12.1)

6.5.1.1 Establish calibration by injecting calibration standards prior to conducting any analyses. (Section 6.4.1.2) A continuing



calibration standard also must be injected at intervals of not less than once every ten samples and at the end of the analysis sequence.

6.5.1.2 Sample injection may continue for as long as the continuing calibration standards meet instrument QC requirements. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded.

1. Each sample analysis must be bracketed with acceptable continuing calibration standards. All samples that were injected after the standard that last met the QC criteria must be reinjected.

6.5.1.3 The continuing calibration standards run after each sequence bracket should be one calibration mix and the DDT/Endrin breakdown standard. The particular calibration mix chosen should be rotated between pesticide mix A, mix B, and the aroclor standards. (See section 6.4.3.2)

6.5.2 Establish absolute retention time windows for each analyte. The midpoint for each analyte's RT window is updated approximately every 24 hours, based on the continuing calibrations. (See Method 8000) The retention time window equals the midpoint $\pm$ three times the standard deviation or 0.08 minutes, whichever is greater. The window midpoint may change according to the retention time of the relevant standard.

6.5.2.1 Tentative identification of an analyte occurs when a peak falls within the daily retention time window, and when its relative retention time is consistent with the bracketing standards for that 10 sample sequence.

6.5.2.2 Validation of gas chromatographic system qualitative performance: Use the calibration standards analyzed during the sequence to evaluate retention time stability. If any of the standards fall outside their daily retention time windows, the system is out of control. Determine the cause of the problem and correct it. (See Section 9 and Method 8000 for details)



- 6.5.3 Record the volume injected to the nearest 0.5 μ L and the resulting peak size in height units. Using the external calibration procedure (Method 8000), determine the identity and the quantity of each component peak in the sample chromatogram.
- 6.5.3.1 If the response of any analyte of interest exceeds the calibration range of the system, dilute the extract and reanalyze. Peak height measurements are recommended over peak area integration, especially where overlapping or coeluting peaks are involved.
- 6.5.3.2 If partially overlapping or coeluting peaks are found on one column, use the confirmation column to quantitate the respective analytes and flag the value as "unable to confirm."
- 6.5.3.3 If the peak response is less than the reporting limit, no hit is reported.
- 6.5.4 Quantitation of the target compounds is based on: 1) a reproducible response of the ECD within the calibration range, and 2) a direct proportionality between the magnitude of response of the detector to peaks in the sample extract and the calibration standards. Proper quantitation requires the appropriate selection of a baseline from which the height of the characteristic peak(s) can be determined.
- 6.5.4.1 If compound identification or quantitation are precluded due to interference (e.g. broad, rounded peaks or ill-defined baselines are present), additional cleanup of the extract or replacement of the capillary column or detector may be warranted. Refer to Method 3600 for sample cleanup procedures. Analyst experience must be relied upon in such cases.
- 6.6 Quantitation of Multiple Component Analytes: Multi-component analytes present problems in measurement. Suggestions are offered in the following sections for handling Toxaphene, Chlordane, PCB, DDT, and BHC.
- 6.6.1 Toxaphene: Toxaphene is manufactured by the chlorination of camphenes, whereas Strobane results from the chlorination of a mixture of camphenes and pinenes. Quantitative calculation of toxaphene is



difficult, but reasonable accuracy can be obtained. To calculate toxaphene on GC/ECD: (a) adjust the sample size so that the major toxaphene peaks are within the linear range of the detector, and (b) quantitate using the 3 to 5 major peaks of the toxaphene pattern.

- 6.6.2 Chlordane is a technical mixture of at least 11 major components and 30 or more minor components. Trans- and cis-chlordane (alpha and gamma), respectively, are the two major components of technical chlordane. However, the exact percentage of each in the technical material is not completely defined, and is not consistent from batch to batch.
- 6.6.3 The GC pattern of a chlordane residue may differ considerably from that of the technical standard. Depending on the sample substrate and its history, residues of chlordane can consist of almost any combination of constituents from the technical chlordane, plant and/or animal metabolites, and products of degradation caused by exposure to environmental factors such as water and sunlight.
- 6.6.4 Unless otherwise requested, Chlordane should always be quantitated as alpha-Chlordane and gamma-Chlordane.
- 6.6.5 If requested, the analyst may quantitate technical chlordane residues using 3 to 5 major peaks from a technical chlordane calibration standard.
- 6.7 Polychlorinated Biphenyls (PCBs): Quantitation of residues of PCB involves problems similar to those encountered in the quantitation of toxaphene and chlordane. In each case, the chemical is made up of numerous compounds which generate multi-peak chromatograms. Also, in each case, the chromatogram of the residue may not match that of the standard.
- 6.7.1 Mixtures of PCBs of various chlorine contents were sold for many years in the U.S. by the Monsanto Co. under the trade name Aroclor (1200 series and 1016). Although these Aroclors are no longer marketed, the PCBs remain in the environment and are sometimes found as residues in foods, especially fish. The Aroclors most commonly found in the environment are 1242, 1254, and 1260.
- 6.7.2 PCB residues are generally quantitated by comparison to the most similar Aroclor standard. A choice must be made as to which Aroclor or mixture



of Aroclors will produce a chromatogram most similar to that of the residue, and whether that standard is truly representative of the PCBs in the sample.

- 6.7.3 PCB Quantitation: Quantitate the PCB residues by comparing the responses of 3 to 5 major peaks in the appropriate Aroclor standard(s) with the corresponding peaks in the sample extract. The amount of Aroclor is calculated by averaging the calculated amounts of these peaks. Major peaks are defined as those peaks in the Aroclor standards that are at least 30% of the height of the largest Aroclor peak. Late-eluting Aroclor peaks are generally the most stable in the environment.
- 6.7.4 When samples appear to contain weathered PCBs, treated PCBs, or mixtures or Aroclors, use of Aroclor standards may not be straightforward (or technically appropriate). In such cases, the analyst must decide what aroclor or aroclors most closely represent the range of PCBs present and must attempt to quantitate total PCBs by quantitating and averaging both weathered and unweathered congeners. This may require more than 3 - 5 peaks. Weathered patterns and difficult mixtures should be noted in the Analyst Notes report.
- 6.8 Hexachlorocyclohexane (BHC, from the former name benzene hexachloride): Technical grade BHC is a cream-colored amorphous solid with a very characteristic musty odor; it consists of a mixture of six chemically distinct isomers and one or more heptachlorocyclohexanes and octachlorocyclohexanes. Commercial BHC preparations may show a wide variance in the percentage of individual isomers present. Quantitate each isomer (alpha, beta, gamma, and delta) separately against a standard of the respective pure isomer.
- 6.9 DDT: Technical DDT consists primarily of a mixture of 4,4'-DDT (approximately 75%) and 2,4'-DDT (approximately 25%). As DDT weathers, 4,4'-DDE, 2,4'-DDE, 4,4'-DDD, and 2,4'-DDD are formed. Since the 4,4'-isomers of DDT, DDE, and DDD predominate in the environment, these are the isomers normally regulated by US EPA and they should be quantitated against standards of the respective pure isomer.



6.10 Suggested chromatography maintenance: Corrective measures may require any one or more of the following remedial actions.

6.10.1 Splitter connections: For dual columns which are connected using a press-fit Y-shaped glass splitter (J&W Scientific), clean and deactivate the splitter, or replace with a cleaned and deactivated splitter. Break off the first few inches (up to one foot) of the injection port side of the pre-column. If necessary, remove the columns and solvent backflush with methylene chloride and then hexane. If these procedures fail to eliminate the degradation problem, it may be necessary to clean the metal injector body and/or replace the columns.

6.10.1.1 GC injector ports can be of critical concern, especially in the analysis of DDT and Endrin. Injectors that are contaminated, chemically active, or too hot can cause the degradation ("breakdown") of the analytes. Endrin and DDT breakdown to endrin aldehyde, endrin ketone, and DDD and/or DDE, respectively. When degradation of any analyte(s) becomes evident, injector port maintenance is warranted.

6.10.2 Injector Maintenance: Turn off the oven and remove the analytical columns when the oven has cooled. Remove the glass injection port insert. Lower the injection port temperature to room temperature. Inspect the injection port and remove any noticeable foreign material.

6.10.2.1 Place a beaker beneath the injector port inside the oven. Using a wash bottle, serially rinse the entire inside of the injector port with acetone and then hexane. Catch the rinsate in the beaker. In addition, remove the nut at the base of the injector and clean the gold base plate (that serves as the liner seat) with aluminum oxide. Reassemble the injector, including a clean liner with deactivated glass wool. Before reattaching the precolumn, bring the injector temperature to 275°C for at least 30 minutes, and then bring it back to the 200° operating temperature. Clip several inches off the precolumn, remount it, and check all connections for leaks with deionized water.



7.0 Review

- 7.1 Refer to Method 8000 for review and quantitation procedures.

8.0 Quality Control

- 8.1 Two surrogates, tetrachloro-m-xylene and decachlorobiphenyl, are added to each extract. Recoveries of both surrogates should be calculated and should meet limits specified in the QAPP. Corrective action is not required unless both surrogates are outside limits.
- 8.2 A method blank must be extracted and analyzed with each sample batch of up to 20 samples. Surrogate recoveries should meet internal limits, and there should be no confirmed analytes at concentrations above method reporting limits.
- 8.3 A blank spike, or laboratory control sample (LCS), must also be extracted and analyzed with each batch of up to 20 samples. It will be spiked with the matrix spike pesticides, at minimum, at on-column concentrations equal to the calibration standards. If requested, the LCS will be spiked with additional analytes up to and including all of the single-component pesticides.
- 8.3.1 If only PCBs are being analyzed, the LCS should be spiked with an aroclor that is not expected to be found in the samples. This will normally be Aroclor 1260 at a concentration of 10 µg/L.
- 8.4 Matrix spikes and matrix spike duplicates will be extracted upon request. If no jobs within a sample batch request MS/MSD, batch MS/MSD will be analyzed every 20 samples (not restricted to the same batch). Matrix spike compounds are lindane, heptachlor, aldrin, dieldrin, endrin, DDT delta BHC, DDE and DDD.
- 8.5 All spiked analytes in LCS and MS/MSD extracts should meet limits specified in the QAPP. If spike recovery limits are not met, corrective action (possibly including reextraction) may be required. (See section 9.0)

9.0 Corrective Actions

See Method 8000 for general corrective action procedures. Specific additions/exceptions to 8000 are as follows:



- 9.1 If a continuing calibration standard does not meet the $\pm 15\%$ D QC limits, one or more of the following corrective actions may be required.
- 9.1.1 Closely examine the offending peak on the data system. It is possible that the baseline was incorrectly drawn due to coelution/interference. If so, correct the baseline and determine if the new peak height will bring the calculated amount within limits.
- 9.1.2 If baseline correction is not possible, but it appears that matrix effects have caused a change in instrument response, it may be possible to clean the system and restore proper detector response.
- 9.1.2.1 First try baking the oven (275°C), injector (275°C), and detectors (400°C) for at least one hour. After returning the temperatures to normal, run several hexane rinses. If the chromatography appears normal, rerun the offending standard to see if it now meets QC limits.
- 9.1.2.2 If the above procedures do not solve the problem, proceed to injector/column maintenance outlined in Section 6.10 and in Method 8000. When done, rerun the offending standard to determine if QC limits have been met.
- 9.2 If all of the above measures prove ineffective, the general requirement is that all samples analyzed after the continuing calibration standard that last met the QC limits must be reanalyzed with a new initial linearity/calibration sequence. This requirement is subject to the following exception:
- 9.2.1 In particular circumstances, the project manager for the affected samples may decide that meeting QC limits may be of relatively little significance when considered against other project issues, such as turn-around-time. Such a decision is particularly likely when continuing calibration responses are too high but there are no analytes identified in the samples. QC criteria specified in the QAPP will be considered by the project manager.
- 9.3 The samples need not be rerun if the project manager so instructs the analyst. The analyst should have the project manager initial all such decisions. It is preferable that the client be consulted, but that decision is made by the project manager. (See Project Management SOP)



- 9.4 All QC limit issues (including continuing calibration limits and all recovery limits) may be decided by the project manager, QA officer, and GC Supervisor, preferably after consultation with the client.

10.0 Miscellaneous Notes and Precautions

- 10.1 Refer to Methods 3500 (Section 3, in particular), 3600, and 8000.
- 10.2 Sources of interference in this method can be grouped into three broad categories: contaminated solvents, reagents or sample processing hardware; contaminated GC carrier gas, parts, column surfaces or detector surfaces; and the presence of coeluting compounds in the sample matrix to which the ECD will respond. Interferences coextracted from the sample, will vary considerably from waste to waste. While general cleanup techniques are referenced or provided as part of this method, unique samples may require additional cleanup approaches to achieve desired degrees of discrimination and quantitation.
- 10.3 Interferences by phthalate esters introduced during sample preparation can pose a major problem in pesticide determinations. These materials can pose a major problem to analysis using Gel Permeation Cleanup, pesticide option (Method 3640), or as Fraction III of the silica gel cleanup procedure (Method 3630). Common flexible plastics contain varying amounts of phthalate esters which are easily extracted or leached from such materials during laboratory operations. Cross-contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalate esters can best be minimized by avoiding contact with any plastic materials and by checking all solvents and reagents for phthalate contamination.
- 10.4 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing with hot water, and rinses with tap water and organic-free reagent water. Drain the glassware and dry it in an oven at 130°C for several hours, or rinse with methanol and drain. Store dry glassware in a clean environment.



- 10.5 The presence of elemental sulfur will result in broad peaks that interfere with the detection of early-eluting organochlorine pesticides. Sulfur contamination should be expected with sediment samples; therefore, all soils should go through GPC cleanup whenever possible.
- 10.6 In addition to sulfur, waxes, lipids, and other high molecular weight co-extractables can be removed by Gel-Permeation Cleanup (Method 3640).
- 10.7 It may be difficult to quantitate Aroclor patterns and single component pesticides together. Some pesticides can be removed by sulfuric acid/permanganate cleanup (Method 3665) and silica fractionation (Method 3630). Guidance on the identification of PCBs is given in Section 7.
- 10.8 Other halogenated pesticides or industrial chemicals may interfere with the analysis of pesticides. Certain co-eluting organophosphorus pesticides are eliminated by the Gel Permeation Chromatography cleanup, pesticide option (Method 3640). Co-eluting chlorophenols are eliminated by Silica gel (Method 3630), Florisil (Method 3620), or Alumina (Method 3610) cleanup.
- 10.9 If contaminants (including target and non-target compounds) continue to cause significant interference, even after all relevant cleanups have been performed, the sample should be reextracted at a level appropriate to the amount of contamination. The particular reextraction level should be based on the initial analysis or pre-analysis GC/ECD screen. The experience and discretion of the analyst and section supervisor will be relied upon for reextraction decisions. The project manager will be notified if reextraction at a different level is required.

11.0 Method References

- 11.1 U.S. EPA, Test Methods for Evaluating Solid Waste (SW-846), Method 8081, Organochlorine Pesticides, Halowaxes and PCBs as Aroclors by Gas Chromatography: Capillary Column Technique, Revision 0, November, 1992.

12.0 Appendices

- 12.1 Table 1 Operating Conditions
- 12.2 Table 2 Pesticide Mix A and B Analytes



Appendix

12.1 TABLE 1:

Operating Conditions for DB-5/DB-608 Dual Columns

Instrument:	HP 5890 GC with Autosampler
Injector Type:	split/splitless
Detectors:	electron capture (2)
Injector Temp:	200°C
Detector Temps:	310°C (DB-5) 275°C (DB-608)
Carrier Flow (He):	5 mL/min.
Makeup Flow (P-5):	45 mL/min.
Oven Program:	160°C for 1 min. 4°/min. to 275°C Hold 275° for 18-20 min.

12.2 TABLE 2:

Pesticide Mix A and B Analytes

<u>Mix A</u>	<u>Mix B</u>
alpha-BHC	beta-BHC
Heptachlor	delta-BHC
gamma-BHC	Aldrin
Endosulfan I	Heptachlor epoxide
Dieldrin	alpha-Chlordane
Endrin	gamma-Chlordane
p,p'-DDD	p,p'-DDE
p,p'-DDT	Endosulfan sulfate
Methoxychlor	Endrin aldehyde
TCMX (Surr.)	Endrin ketone
DCB (Surr.)	Endosulfan II
	TCMX (Surr.)
	DCB (Surr.)



12.3 TABLE 3: Control Limits

<u>Laboratory Control Sample</u>	<u>Water</u>	<u>Soil</u>
Lindane	39-144	37-142
Heptachlor	35-109	43-124
Aldrin	39-109	40-120
Dieldrin	53-145	44-133
Endrin	45-136	38-139
DDT	55-142	47-135
Delta-BHC	35-120	35-120
DDE	55-142	49-135
DDD	55-142	49-135
Aroclor 1260	55-142	49-135
Surrogate:		
TCX	30-102	37-114
DCBP	30-135	40-127
<u>Matrix Spike/Matrix Spike Dup./RPD</u>		
Lindane	40-140/27	37-142/37
Heptachlor	35-110/47	43-124/29
Aldrin	35-110/65	40-120/41
Dieldrin	53-145/23	44-133/34
Endrin	45-136/31	38-139/58
DDT	55-142/34	49-135/33
Delta-BHC	35-120/49	35-120/43
DDE	55-142/34	49-135/33
DDD	55-142/34	49-135/33
Aroclor 1260	55-142/34	49-135/33
Surrogate:		
TCX	41-121	46-131
DCBP	45-139	54-138



ANALYTICAL
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Standard Operating Procedure

Gas Chromatography Analysis
Method 8000 - (United States Air Force)

401S

Revision 0

3/30/94

PROPRIETARY

Prepared By:

[Signature]

Approvals:

NA
Section Manager

[Signature]
Laboratory Manager

Michelle J. Turner
Quality Assurance Manager

[Signature]
Laboratory Director

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Standard Procedure

Gas Chromatography (GC) Analysis - Method 8000AF

1.0 Scope and Application

- 1.1 Gas chromatography is a quantitative analytical technique useful for organic compounds capable of being volatilized without being decomposed or chemically rearranged. Gas chromatography (GC), also known as vapor phase chromatography (VPC), has two subcategories: gas-solid chromatography (GSC), and gas-liquid chromatography (GLC) or gas-liquid partition chromatography (GLPC). This last group is the most commonly used, and is distinguished by type of column adsorbent or packing.
- 1.2 The chromatographic methods are recommended for use only by, or under the close supervision of, experienced residue analysts.
- 1.3 This document summarizes the laboratory procedure for GC analysis. Most text has been taken directly from SW-846 Method 8000A, Revision 1, July, 1992. Laboratory deviations from the referenced method have been incorporated into the document text and also identified in section 5.0.
- 1.4 NOTE: Method 8081 incorporates many procedures and limits that supersede the relevant sections of this method. See Method 8081 for details.

2.0 Definitions

N/A

3.0 Equipment

- 3.1 Gas chromatograph: Analytical system complete with gas chromatograph suitable for split/splitless injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak height and/or peak areas is required.
- 3.2 Gas chromatographic columns: See the specific determinative method. Other packed or capillary (open-tubular) columns may be used if the requirements of Section 8.4 are met.
- 3.3 Reagents: See the specific determinative method for the reagents needed.

4.0 Documentation

N/A



5.0 Inhouse Modifications to Referenced Method

The laboratory employs the following modifications to SW-846 Method 8000A, Revision 1, November, 1990:

- 5.1 Section 6.2.4.2.2 (method section 7.4.2.2) - Multiresponse pesticides/PCBs are quantitated using 3 to 5 major peaks (per Method 8081), not the total area of all peaks as indicated in Method 8000.
- 5.2 Section 6.2.5 (method section 7.5) - The procedure as indicated in the method has been deleted and rewritten as it appears in section 6.2.5.
- 5.3 Section 6.2.6.8 (method section 7.6.9) - See the determinative method of interest for retention time window information.
- 5.4 Section 8.4.1 (method section 8.4.1) - A spike blank (LCS) will be analyzed as the quality control check sample. The compounds analyzed will be, at minimum, those compounds included in the matrix spike solution, and may not include all analytes of interest as indicated in the method, unless specifically requested by the Client.
- 5.5 Section 8.4.2 (method section 8.4.3) - The spike blank will be analyzed as specified, not four replicate aliquots of QC check sample as indicated in the method.
- 5.6 Section 8.4.3 (method section 8.4.4) - The recovery is calculated for each compound in the spike blank, not four replicate QC check samples as indicated in the method.
- 5.7 Section 8.5.1.1 (method section 8.5.1.2) - The sample spike concentration will be at or near the same concentration as the calibration standard.
- 5.8 Section 8.5.3 (method section 8.5.3) - The QC acceptance criteria specified in the analytical methods will be followed only until internal QC limits for matrix spikes have been established.
- 5.9 Section 8.6.1 (method section 8.7.1) - Control limits used for surrogate recovery evaluation will be as specified in the analytical methods.
- 5.10 Section 6.3.2 (method section 9.2) - MDLs are determined as indicated in this section of the procedure.

6.0 Procedures

6.1 Summary of Method

Each organic analytical method that follows provides a recommended technique for extraction, cleanup, and, occasionally, derivatization of the samples to be analyzed. Before the prepared sample is introduced into the GC, a procedure for standardization must be followed to determine the recovery and the limits of detection for the analytes



of interest. Following sample introduction into the GC, analysis proceeds with a comparison of sample chromatograms with standard chromatograms. Quantitative analysis is achieved through integration of peak area or peak height.

6.2 Analytical Procedure

6.2.1 Extraction - Adhere to those procedures specified in the referring determinative method.

6.2.2 Cleanup and separation - Adhere to those procedures specified in the referring determinative method.

6.2.3 The recommended gas chromatographic columns and operating conditions for the instrument are specified in the referring determinative method.

6.2.4 Calibration

6.2.4.1 Establish gas chromatographic operating parameters which conform to the QC requirements indicated in the method of interest. Prepare calibration standards using the procedures indicated in the determinative method of interest. Calibrate the chromatographic system using either the external standard technique (Section 6.2.4.2) or the internal standard technique (Section 6.2.4.3).

6.2.4.2 External standard calibration procedure and linearity check

1. For each analyte of interest, prepare linearity standards at a minimum of five concentrations by diluting one or more certified stock standards. One of the standards should be at a concentration near, but above, the method reporting limit. The other concentrations should correspond to the expected range of concentrations found in real samples, or should define the working range of the detector.
2. Inject each calibration standard using the technique that will be used to introduce the actual samples into the gas chromatograph (e.g. 1 - 5 μ L injections, purge-and-trap, etc.). Tabulate peak height or area responses against the mass injected. The results can be used to prepare a linearity curve for each analyte. Alternatively, for samples that are introduced into the gas chromatograph using a syringe, the ratio of the response to the amount injected, defined as the response factor (RF), can be calculated for each analyte at



each standard concentration. If the percent relative standard deviation (%RSD) of the response factor is less than 20% over the working range, the average calibration factor may be used in place of the calibration curve. The curve must be used if the %RSD is greater than 20%.

$$\text{Calibration factor} = \frac{\text{Total Area/Height of Peak}}{\text{Mass injected (in nanograms)}}$$

* For multi-response pesticides/PCBs, use 3 to 5 major peaks for quantitation.

3. The working calibration curve must be verified at the beginning of each new run by the injection of one or more calibration standards. If the response varies from the predicted response by more than $\pm 15\%$, a new curve must be run. Continuing calibration mixes must be run at a minimum frequency of every ten (10) samples. Continuing calibrations must have a percent difference of $\pm 15\%$ from the predicted value, or the instrument is considered out of compliance. The run may continue as long as continuing calibration mixes meet the $\pm 15\%$ difference limit. If this limit is exceeded, and the instrument cannot be brought back within limits through corrective action, a new linearity curve and calibration standard must be run.

$$\text{Percent Difference} = \frac{R1 - R2}{R1} \times 100$$

where:

R1 = Calibration Factor from midpoint curve standard.

R2 = Calibration Factor from calibration standard.

6.2.4.3 Internal standard calibration procedure (for Methods 8010 and 8141)

1. To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Due to these limitations, no internal standard applicable to all samples can be suggested.



2. Prepare calibration standards at a minimum of five concentrations for each analyte of interest by adding volumes of one or more stock standards to a volumetric flask. To each curve standard, add a known constant amount of one or more internal standards and dilute to volume with an appropriate solvent. One of the standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.
3. Inject each linearity standard using the sample introduction technique that will be applied to the actual samples (e.g. 2 to 5 μL injection, purge-and-trap, etc.). Tabulate the peak height or area responses against the concentration of each compound and internal standard. Calculate calibration factors (CF) for each compound as follows (this calculation is performed by the data system):

$$\text{CF} = (\text{AsCis})/(\text{AisCs})$$

As = Response for the analyte to be measured.

Ais= Response for the internal standard.

Cis= Concentration of the internal standard, $\mu\text{g/L}$.

Cs = Concentration of the analyte to be measured, $\mu\text{g/L}$.

If the CF value over the working range is $\leq 20\%$ RSD, the average calibration factor may be used instead of the curve. If the %RSD is greater than 20%, quantitation must be off the curve.

4. The working calibration curve must be verified at the start of each new run by the injection of one or more calibration standards. If the response varies from the predicted response by more than $\pm 15\%$, a new curve must be run. Continuing calibration mixes must be run at a minimum frequency of every ten (10) samples. Continuing calibrations must have a percent difference of $\pm 15\%$ from the predicted value, or the instrument is considered out of compliance. The run may continue as long as continuing calibration mixes meet



the $\pm 15\%$ difference limit. If this limit is exceeded, and the instrument cannot be brought back within limits through corrective action, a new linearity curve and calibration standard must be run.

6.2.5 Retention time windows

6.2.5.1 Retention time windows are generally ± 0.10 minutes for most methods and analytes. Method 8081 has RT windows of no more than ± 0.08 minutes.

6.2.6 Gas chromatographic analysis

6.2.6.1 Introduction of organic compounds into the gas chromatograph varies depending on the volatility of the compound. Volatile organics are introduced by purge-and-trap (Method 5030). Semivolatile organics are introduced by splitless injection.

6.2.6.2 The appropriate detector(s) is named in the specific method.

6.2.6.3 Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration followed by sample extracts interspersed with multi-concentration calibration standards. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded.

6.2.6.4 Injection: Inject 1 - 5 μL of the sample extract using the splitless injection mode. Record the volume injected.

6.2.6.5 If the responses exceed the linear range of the system, dilute the extract and reanalyze. Extracts must be diluted so that all potential hits are on scale. Overlapping peaks are not always evident when peaks are off scale. Computer reproduction of chromatograms, manipulated to ensure all peaks are on scale over a 100-fold range, are acceptable if linearity is demonstrated. Peak height measurements are recommended over peak area integration, especially when overlapping peaks cause errors in area integration.

6.2.6.6 If peak detection is prevented by the presence of interferences, further cleanup is required, where appropriate.

6.2.6.7 Examples of chromatograms for the compounds of interest are available in the calibration file.



6.2.6.8 Calibrate the system immediately prior to conducting any analyses (see Section 6.2.4). A mid-concentration standard must also be injected at intervals specified in the method and at the end of the analysis sequence. The calibration factor for each analyte must not exceed a 15% difference when compared to the initial calibration of the analysis sequence. When this criteria is exceeded, inspect the GC system to determine the cause, and perform whatever maintenance is necessary (see Section 9.1) before recalibrating and proceeding with sample analysis. All samples that were injected after the last standard meeting the criteria must be reinjected.

6.2.6.9 Establish daily retention time windows for each analyte. Use the absolute retention time for each analyte from Section 6.2.6.8 as the midpoint of the window for that day. When using autosamplers and extending runs beyond 24 hours, the standard injected closest to 24 hours from the injection of the initial calibration will be used to update the daily RT window midpoint. The maximum shift for daily RT updates from the initial calibration RT is ± 3 times the analyte RT window. The daily retention time window equals the midpoint ± 0.10 minutes except where specifically noted.

1. Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention time window and the relative retention time is consistent with bracketing continuing calibration mixes. Normally, confirmation is required on a second GC column, by GC/MS if concentration permits, or by other recognized confirmation techniques. Confirmation may not be necessary if the composition of the sample matrix is well established by prior analyses.
2. Validation of GC system qualitative performance: Use the mid-concentration standards interspersed throughout the analysis sequence (Section 6.2.6.8) to evaluate this criterion. If any of the standards fall outside their daily retention time window, the system is out of control. Determine the cause of the problem and correct it (see Section 9.1).



6.3 Method Performance

6.3.1 The ARI reporting limit (RL) will be equal to the analyte Practical Quantitation Limit (PQL). PQL is defined as 10 times the standard deviation between seven replicate LCS samples containing the analytes of interest at 1-5 times the estimated Method Detection Limit (MDL).

6.4 Second Column Confirmation

6.4.1 Most GC/ECD methods require second column confirmation. Only when an analyte is identified on both columns, and the solution concentrations on each column are relatively consistent, is that analyte reported as a positive identification. If the analyte is confirmed on both columns, the lower of the two column values will be reported. If an analyte is positively identified on both columns, but the percent difference between the two values indicates the probability of matrix interference on one column, the analyte will be reported as an elevated detection limit based on the lower of the two values.

7.0 Review

7.1 Calculations

7.1.1 External standard calibration - The concentration of a positively identified analyte is calculated as follows:

Aqueous samples

$$\text{Concentration } (\mu\text{g/L}) = S \times \text{FV}/V \times 1000 \times \text{DF}$$

S = Solution concentration ($\mu\text{g/mL}$), calculated by data system

FV = Sample extract effective final volume

V = Volume of sample extracted (mL)

DF = Dilution factor

Note: Calculation assumes the amount purged or injected is the same for all standards, samples, blanks, and QC samples.

Nonaqueous samples

$$\text{Concentration } (\mu\text{g/Kg}) = S \times \text{FV}/\text{DW} \times 1000 \times \text{DF}$$

where:

DW = Dry weight of sample extracted (g)



S, FV, and DF have the same definition as for aqueous samples.

- 7.1.2 Internal standard calibration - For each analyte of interest, the concentration of that analyte in the sample is calculated the same way as with the external calibration technique. The internal standard correction factor for each run is already factored into the solution concentration(s) calculated by the data system.

8.0 Quality Control

- 8.1 Refer to the specific analytical method and the laboratory Quality Assurance Plan for quality control procedures.

- 8.2 The experience of the analyst in performing gas chromatography is invaluable to the success of the methods.

8.2.1 All continuing calibration standards should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still good, the injector is leaking, the injector septum needs replacing, etc. If any major changes are made to the system (e.g. column changed), recalibration of the system must take place.

8.2.2 The performance of the entire analytical system should be checked daily, using data gathered from analyses of blanks, standards, and QC samples. Any abnormalities must be corrected.

8.2.3 The precision between replicate analyses should be evaluated. A properly operating system should perform with an average percent difference between replicates of less than 10%. Poor precision is generally traceable to pneumatic leaks, especially at the injection port.

8.3 Required Instrument Quality Control

8.3.1 Section 6.2.5 requires the establishment of retention time windows.

8.3.2 Section 6.2.6.8 sets a limit of $\pm 15\%$ difference when comparing the response of a given analyte in the initial calibration versus any continuing calibration standards analyzed during an analysis sequence.



- 8.3.3 Section 6.2.6.8.2 requires that all succeeding standards in an analysis sequence must fall within the daily retention time window.
- 8.4 To establish the ability to generate data of acceptable quality, the analyst must perform the following operations:
- 8.4.1 A laboratory control sample (LCS) or spike blank is required containing, at a minimum, the matrix spike compounds. The LCS concentrate is prepared from certified solutions.
- 8.4.1.1 The concentration of the LCS concentrate is highly dependent upon the analytes being investigated. Therefore, refer to Method 3500, Section 8.0 for the required concentration of the LCS concentrate.
- 8.4.2 Analyze the LCS by the same procedures used to analyze actual samples (see appropriate section of each of the methods). For volatile organics, the preparation/analysis process is purge-and-trap/gas chromatography. For semivolatile organics, the QC check samples must undergo solvent extraction (see Method 3500) prior to chromatographic analysis.
- 8.4.3 Calculate the recovery for each analyte of interest.
- 8.4.4 For each analyte, compare the recovery with the corresponding limits established by statistical evaluation of historical data within the laboratory. If any individual recovery exceeds the QC limits, system performance is considered to be out of compliance for that analyte.
- 8.4.5 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 8.4.5.1 or 8.4.5.2.
- 8.4.5.1 Locate and correct the source of the problem and repeat the test for all analytes of interest, beginning with Section 8.4.2.
- 8.5 The laboratory must have procedures for documenting the effect of the matrix on method performance, including the analysis of at least one Laboratory Control Sample and one matrix spike/matrix spike duplicate per batch, sample volume permitting.
- 8.5.1 The concentration of the spike in the sample should be at or near the concentration of the calibration standard.
- 8.5.2 Analyze one unspiked and one spiked sample aliquot to determine percent recovery of each of the spiked compounds.
- 8.5.2.1 Volatile organics: Analyze one 5 mL sample aliquot to determine the background concentration of each analyte. Spike a second 5 mL



sample aliquot (LCS) with the matrix spike solution and analyze it to determine the concentration after spiking of each analyte. Calculate each percent recovery (%R) as:

$$\%R = 100 (x_s - x_u) / K,$$

where: x_s = measured value for spiked sample,
 x_u = measured value for unspiked sample, and
 K = known value of the spike in the sample.

8.5.2.2 Semivolatile organics: Analyze one sample aliquot (extract of 1 L sample) to determine the background concentration of each analyte. Spike a second 1 L sample aliquot (LCS) with the matrix spike solution and analyze it to determine the concentration after spiking of each analyte. Calculate each percent recovery according to the calculation in Section 8.5.2.1.

8.5.3 Compare the percent recovery (%R) for each analyte in a water sample with the corresponding limits established by the laboratory. If any analyte recovery is not within QC limits, follow the procedures in Section 8.4.5.

8.6 Procedures for determination of acceptable recoveries.

8.6.1 For aqueous and soil matrices, laboratory surrogate control limits will be generated and will define acceptable recovery.

8.6.2 If recovery is not within limits, the following steps are required.

8.6.2.1 Check to be sure that there are no errors in the calculations, surrogate solutions or internal standards. If errors are found, recalculate the data accordingly.

8.6.2.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and re-analyze the extract.

8.6.2.3 If no problem is found, re-extract and re-analyze the sample.

8.6.2.4 If, upon re-analysis, the recovery is again not within limits, flag the data as "estimated concentration."

8.7 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory, the nature of the samples, and project-specific requirements. Field duplicates may be analyzed to assess the precision of the environmental



measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector, or mass spectrometer must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 Corrective Actions

9.1 Suggested chromatography system maintenance - Corrective measures may require one or more of the following remedial actions. See section 8 (Quality Control) for corrective actions concerning QC limits.

9.1.1 Capillary columns - Replace the deactivated glass wool and/or septum, or replace the liner with a cleaned and deactivated liner. Break off the first few inches, up to one foot, of the injection port end of the column. If necessary, remove the column and solvent backflush according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the column.

9.1.2 Metal Injector body - Turn off the oven and remove the analytical column. Remove the glass injection port liner. Lower the injection port temperature, inspect the injection port, and remove any noticeable foreign material.

9.1.2.1 Place a beaker beneath the injector port inside the GC oven. Using a wash bottle, serially rinse the entire inside of the injector port with acetone and then hexane; catching the rinsate in the beaker. Also remove the 1/4" nut on the bottom of the injection port. Clean the gold HP injector plate (that serves as the seat for the glass liner) with aluminum oxide in water. After cleaning, dip the plate in Sylon CT solution and rinse with methylene chloride, then acetone, then hexane. Reassemble the injector and bake it at 275° for at least one hour before replacing the column. Be sure to lower the temperature before replacing the column.

9.2 Preventive Maintenance: Prior to the analysis of an initial calibration sequence, the following procedures should be followed.

9.2.1 If needed, change the glass wool and, possibly, the injector liner itself.

9.2.2 If needed, change the septum. All ECD instruments use "Merlin" mechanical septa to minimize retention time drift. Merlins should be changed after 2000



injections (approximately), or sooner if drift is noticed and a Merlin leak is verified. Normal GC septa should be replaced at least once per 150 injections. Changing the septum during an analytical sequence should be avoided, if possible. If a septum is changed during a run, immediately run a standard to verify retention times and response factors.

- 9.2.3 Check all column connections and injector/detector fittings.
 - 9.2.4 Refill solvent rinse vials.
 - 9.2.5 Bake the GC oven at 275° - 310°C (depending on the column(s) installed) for at least half an hour.
 - 9.2.6 Other maintenance: Gas cylinder traps should be replaced yearly. ECD detectors are wipe tested every six months for radiation leaks.
- 9.3 See section 6.0, Analytical Procedures, and section 8.0, Quality Control, for additional guidance on appropriate corrective actions.

10.0 Miscellaneous Notes and Precautions

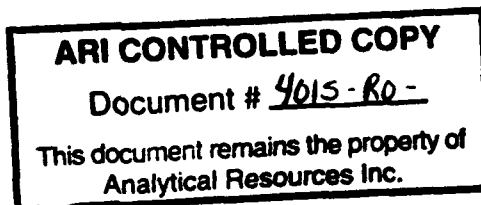
- 10.1 Interferences: Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe or purging device must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a solvent blank to check for cross contamination. For volatile samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high organohalide concentrations, it may be necessary to wash out the syringe or purging device with a detergent solution, rinse it with distilled water, and then dry it in a 105°C oven between analyses.

11.0 Method References

- 11.1 U.S. EPA, "Test Methods for Evaluating Solid Waste" (SW-846), Method 8000A, Revision 1, November, 1990.
- 11.2 U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, July 1985, Revision.

12.0 Appendices

GC Instrument Operations





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Appendix

12.1 GC Instrument Operations/Sample Analysis



12.1 Appendix A

GC Instrument Operations/Sample Analysis

12.1.1 Workflow Tracking and Management

12.1.1.1 After job folders are delivered to the GC laboratory, the job number, client, VTSR, due date, number of samples and sample type are transferred onto sample tags. The sample tags are color-coded by parameter. These sample tags are placed on the tracking board in the laboratory for job monitoring during analysis and data reduction. The tracking board is monitored for sample prioritization and balance of instrument and analyst capacities. The tracking board is primarily monitored and coordinated by the analysts, but the GC Supervisor may intervene to resolve prioritization or workload conflicts.

12.1.1.2 Completed extracts delivered to the GC laboratory are logged into the GC sample refrigerator by the technician delivering the samples. The job number, parameter, number of extracts, and date are recorded on the GC Refrigerator Extract Log. The log will serve as a record to indicate which extracts have been delivered and which are still outstanding.

12.1.1.3 After extracts have been received by the GC laboratory, the color-coded sample tags are moved to the "instrument" section of the tracking board. The scheduled analysis date and instrument will be recorded on the tracking board beside the sample tag.

12.1.1.4 After the samples have been analyzed, the sample tags for all jobs affected are moved to the "analyst" section of the tracking board. On the tracking board beside the sample tag, the analyst responsible for data reduction will be indicated.

12.1.1.5 After data reduction has been completed, data will be forwarded to the reviewers for a second-level review of quantitative and qualitative accuracy. When the job leaves the GC laboratory for review, the sample tag will be removed from the tracking board by the analyst completing the job. Submission of data to the reviewer will be documented on the GC Data Tracking Log. The job number, parameter, analyst, and date submitted for review will be recorded.



12.1.1.6 After GC review has been completed, the reviewer will initial and date the job. The data will then be forwarded to the Project Manager for reporting. Submission of data for reporting will be documented on the GC Data Tracking Log by the reviewer.

12.1.2 Logbook and Worksheet Completion

12.1.2.1 Prior to starting a new analytical sequence, the analyst should draw a single line through any empty spaces on the previous logbook page. The lined-out area should be initialed and dated by the analyst.

12.1.2.2 Information pertinent to the analytical sequence to be analyzed should be included on the new logbook page, including:

Date

Analyst

Data path (e.g., C:/MAX/PEST/081893)

Initial calibration

Sample identifications

Continuing standards

12.1.2.3 Sample vial placement should be verified by the analyst and compared to the logbook entries. To avoid sample mislabeling, save the autosampler trays with vials still in analytical sequence for a short period prior to archiving. Should the instrument data system mislabel data during the analytical sequence (e.g., skipped vial, etc.), the trays can be referenced for correct sample identification.

12.1.2.4 Corrections to logbook entries should be made by drawing a single line through the entry and indicating the correct information. The entry should be initialed and dated by the analyst making the correction. Correction fluid cannot be used on any laboratory documents.

12.1.2.5 Any notes or comments related to the analytical run, such as samples inserted into the analytical sequence, shifts in vial placement, problems encountered during analysis (e.g., computer, instrument failures, standard failure, etc.), and any corrective actions taken during the analytical sequence should be noted in the "comments" section of the logbook page.



- 12.1.2.6 Logbook entries should be periodically reviewed and signed by the GC Supervisor or the GC data reviewer.
- 12.1.3 Instrument Operations
 - 12.1.3.1 Instrument operating procedures can be found in the instrument manufacturer's manuals. The manuals are filed in the GC laboratory for easy reference. Analysts should refer to these manuals for guidance in instrument operations.
 - 12.1.3.2 Instrument operating conditions are detailed in SOPs for each specific analysis.
- 12.1.4 Data Acquisition/System Operation
 - 12.1.4.1 Data is acquired using the Waters Maxima 820 system. Manuals detailing Maxima operations are on file in the GC laboratory. Analysts should refer to these manuals for guidance in data system operations.
 - 12.1.4.2 Develop a method for the analysis to be performed. If possible, modify an existing method rather than create a new method.
 - 12.1.4.3 Save the new method to a selected file name.
 - 12.1.4.4 Verify that sufficient computer memory is available for data acquisition.
 - 12.1.4.5 Develop the sample queue.
 - 12.1.4.6 Delete existing sample identifications using the command (CONTROL) "Y".
 - 12.1.4.7 Change file numbers for previous standards and samples. (If file numbers are not changed, existing files will be overwritten.)
 - 12.1.4.8 Enter the new file numbers to be acquired. File numbers will consist of the month, day and sequence number. (Example: The first file acquired on 8/16/93 would be named "081601.")
 - 12.1.4.9 Save the newly created sample queue.
 - 12.1.4.10 Edit any other method sections needed to meet method criteria (such as peak integration). Reference the data system operations manuals for guidance.
 - 12.1.4.11 Prior to beginning the analytical run, set the data system to acquire data.



- 12.1.4.12 Set up subsequent methods to acquire in sequence for the number of samples to be analyzed.
PEST/081601
PEST/081602, etc.
- 12.1.4.13 Copy the method and change sample queue file numbers as detailed in sections 12.1.4.5 through 12.1.4.9.
- 12.1.4.14 Verify the standard concentrations in the sample queue. If necessary, process quantitation standards against the updated component standards and sample queue concentrations.
- 12.1.4.15 Enter the sample identifications into the sample queue to be printed on raw data and chromatograms.
- 12.1.4.16 Set the data system for processing, including text file (.PRN) generation if needed for transfer to Formaster.
- 12.1.4.17 Print chromatographs and reports. Continue with data reduction and compound identification.
- 12.1.4.18 After the initial calibration has been analyzed, the quantitation standards are verified and, if necessary, the component table is updated. The linearity curve should be evaluated to verify that %RSD values are within the specified guidelines.
- 12.1.4.19 All standards and samples in the sample queue are processed and printed using the Maxima data system. The sample chromatograms and quantitation reports are evaluated to verify acceptable surrogate recoveries, appropriate peak integration, carryover and need for dilution. Standards are evaluated for continuing calibration acceptability and compound breakdown. If it appears that the peak integration procedures were not appropriate for the sample analyzed, the sample is reprocessed and revisions to peak integration, identification, etc. are made.
- 12.1.4.20 When all samples and standards are determined to be acceptable, all data are printed for data review. If CLP forms are to be generated, the results are printed to a text file for transfer to Formaster.
- 12.1.4.21 Any abnormal events that occur during analysis or data acquisition and conditions specifically related to the sample batch are



described on the Analyst Notes form for inclusion in the data package. Any corrective actions taken are detailed on the Corrective Action form, which is also included in the data package. Instrument modifications, repairs or maintenance are recorded in the Instrument Maintenance Logbook. The maintenance logbook notes should contain the nature of the problem, the corrective action performed, and the disposition of the problem.



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Standard Operating Procedure

Semivolatile Organics by GC/MS
8270 (Air Force)

804S

Revision 2

7/13/94

PROPRIETARY

Prepared By:

Eli M. Hudson

Approvals:

NA
Section Manager

Don N. Baker
Laboratory Manager

Michael J. Farnham
Quality Assurance Manager

Michael J. Farnham
Laboratory Director

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**Standard Operating Procedure
Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry
(GC/MS) Capillary Column Technique - SW-846 Method 8270**

1.0 Scope and Application

1.1 Method 8270 is used to determine the concentration of semivolatile organic compounds in extracts prepared from all types of solid waste matrices, soils, and ground water. Direct injection of a sample may be used in limited applications. See Table 1 for the compounds that can be determined by this method.

1.2 Method 8270 can be used to analyze for most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted from a gas-liquid chromatographic system. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols. See Table 1 for a list of compounds and their characteristic ions that have been evaluated on the specified GC/MS system. Air Force list of compounds is found in the QAPP. Other compounds may be analyzed if specifically requested.

1.3 The following compounds may require special treatment when being determined by this method. Benzidine can be subject to oxidative losses during solvent concentration, and its chromatography is poor. Under the alkaline conditions of the extraction step, alpha-BHC, gamma-BHC, endosulfan I and II, and endrin are subject to decomposition. Neutral extraction should be performed if these compounds are expected. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition. N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described. N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine. Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

1.4 The estimated quantitation limit (EQL) of Method 8270 for determining an individual compound is approximately 0.100 mg/Kg (wet weight) for soil/sediment samples, 1-200 mg/Kg for wastes (medium/high level) (dependent on matrix and method of preparation), and 5 µg/L for ground water samples. EQLs will be proportionately higher for sample extracts that require dilution to avoid saturation of the detector and/or chromatographic phase overload.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.



1.6 This document summarizes the laboratory procedures for GC/MS analysis for semivolatile organics. Most text has been taken directly from SW-846 Method 8270A, Revision 1, July, 1992. Laboratory deviations from the referenced method have been incorporated into the document text and also identified in section 5.0.

2.0 Definitions

N/A

3.0 Equipment

3.1 Gas chromatograph/mass spectrometer system

3.1.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.

3.1.2 Column - 30 m x 0.25 mm ID (or 0.32 mm ID) 0.25 - 1 μ m film thickness silicone-coated fused-silica capillary column (J&W Scientific DB-5 or equivalent).

3.1.3 Mass spectrometer - Capable of scanning from 35 to 500 amu every 1 second or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets all of the criteria in Table 3 when 1-2 μ L of the GC/MS tuning standard is injected through the GC (50 ng of DFTPP).

3.1.4 GC/MS interface - Any GC-to-MS interface that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria may be used.

3.1.5 Data system - A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIST Mass Spectral Library should also be available.

3.2 Syringe - 10 μ L, 25 μ L, 50 μ L, 100 μ L, 500 μ L, 1000 μ L

3.3 Volumetric flasks, Class A - 10 mL to 1000 mL.

3.4 Balance - Analytical, 0.0001 g.

3.5 Bottles - glass with Teflon-lined screw caps or crimp tops.



3.6 Reagents

3.6.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

3.6.2 Acetone, hexane, methylene chloride, isooctane, carbon disulfide, toluene, and other appropriate solvents - Pesticide quality or equivalent.

3.6.3 Organic-free reagent water - All references to water in this method refer to organic-free reagent water.

3.6.4 Stock standard solutions (1000 - 10,000 $\mu\text{g/L}$) - Standard solutions can be prepared from pure standard materials or purchased as certified solutions.

4.0 Documentation

4.1 Instrument Run Log

5.0 In-house Modifications to Referenced Method

The laboratory employs the following modifications to SW-846 Method 8270A, Revision 1, July, 1992:

5.1 Section 1.4 (method section 1.4) - EQLs for soil/sediment and water are 0.1 mg/Kg and 5 $\mu\text{g/L}$ respectively.

5.2 Section 3.1.2 (method section 4.1.2) - the film thickness for the column used for analysis is 0.25 - 1 μm .

5.3 Section 6.2.4 (method section 5.4) - The final internal standard concentration is 1000 ng/ μL .

5.4 Section 6.2.4 (method section 5.4) - A 0.5 ml extract is spiked with 10 μL internal standard solution for analysis, resulting in a concentration of 20 ng/ μL of internal standard.

5.5 Section 6.2.5 (method section 5.5) - DFTPP (tuning standard) is added to the continuing calibration standard for analysis. ARI uses a combined DFTPP/Continuing calibration standard.

5.6 Section 6.2.5 (method section 5.5) - The DFTPP standard contains 25 ng/ μL of pentachlorophenol and benzidine. As DDT is not an analysis compound, it is not added to the DFTPP standard.



- 5.7 Section 6.2.6 (method section 5.6) - The aliquot of calibration standard used is 0.5 mL.
- 5.8 Section 6.2.8 (method section 5.8) - Matrix spike analyte concentrations are 25 ng/ μ L for base/neutral compounds and 37.5 ng/ μ L for acid compounds .
- 5.9 Section 6.3.3 (method section 7.3) - operating conditions have been modified to reflect laboratory instrument conditions.
- 5.10 Section 6.3.3.1 (method section 7.3.1) - Changing the injection port liner has been added as a maintenance option if calibration criteria are not met.
- 5.11 Section 6.3.3.3 (method section 7.3.3) - 1-2 μ L of each calibration standard is analyzed.
- 5.12 Section 6.3.3.4 (method section 7.3.4) - Acid compounds in dirty or active samples may exhibit relative retention time shifts, also.
- 5.13 Section 6.3.5.2 (method section 7.5.2) - Internal standard is added to 0.5 ml of the 1 mL extract.
- 5.14 Section 6.3.5.3 (method section 7.5.3) - 0.5 ml of the 1 ml extract is analyzed. Base/neutral and acid surrogate concentrations are 50 ng and 75 ng on column respectively, if a 2 μ L injection is used.
- 5.15 Section 8.3 as written in the published method has been omitted. Laboratory quality control requirements have been specified in section 8.0.
- 5.16 Method section 9.0 has been omitted. Method detection limit (MDL) studies have been performed for this analysis as per CFR 40, part 136.
- 5.17 Section 6.2.6: A four-point initial calibration may be used for the eight compounds listed in section 6.2.6.

6.0 Procedure

6.1 Summary of Method

6.1.1 Prior to using this method, the samples should be prepared for chromatography using the appropriate sample preparation and cleanup methods. This method describes chromatographic conditions that will allow for the separation of the compounds in the extract.

6.2 Standard Preparation

6.2.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in pesticide quality acetone or other suitable solvent and dilute to volume in a 10 mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock



standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

6.2.2 Transfer the stock standard solutions into bottles with Teflon lined screw-caps. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.2.3 Stock standard solutions must be replaced after 1 year or sooner if comparison with quality control check samples indicates a problem.

6.2.4 Internal standard solutions - The internal standards recommended are 1,4-dichlorobenzene-d₄, naphthalene-d₈, acenaphthene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂, and perylene-d₁₂. Other compounds may be used as internal standards as long as the requirements are met. Dissolve 0.200 g of each compound with a small volume of carbon disulfide. Transfer to a 50 mL volumetric flask and dilute to volume with methylene chloride so that the final solvent is approximately 10-20% carbon disulfide. Most of the compounds are also soluble in small volumes of methanol, acetone, or toluene, except for perylene-d₁₂. The resulting solution will contain each standard at a concentration of 1,000 ng/μL. 0.5 mL of each 1 mL sample extract undergoing analysis should be spiked with 10 μL of the internal standard solution, resulting in a concentration of 20 ng/μL of each internal standard. Store at 4°C or less when not being used.

6.2.5 GC/MS tuning standard: 50 ng on column of decafluorotriphenylphosphine (DFTPP) should be added to the daily (12 hour) standard. The standard should also contain 25 ng/μL each of pentachlorophenol, and benzidine to verify injection port inertness and GC column performance. Store at 4°C or less when not being used.

6.2.6 Calibration standards - A minimum of five calibration standards should be prepared. Eight compounds, 2,4-Dinitrophenol, 2,4,5-Trichlorophenol, 2-Nitroaniline, 3-Nitroaniline, 4-Nitroaniline, 4-Nitrophenol, 4,6-Dinitro-2-methylphenol, and Pentachlorophenol will require only a four-point initial calibration since detection at less than 20 ng per injection is difficult. One of the calibration standards should be at a concentration near, but above, the method detection limit; the others should correspond to the range of concentrations found in real samples but should not exceed the working range of the GC/MS system. Each standard should contain each analyte for detection by this method (e.g. some or all of the compounds listed in Table 1 may be included). Each 0.5 mL aliquot of calibration standard should be spiked with 10 μL of the internal standard solution prior to analysis. All standards should be stored at 4°C and should be freshly prepared once a year, or sooner if check standards indicate a problem. The daily calibration standard should be prepared weekly and stored at 4°C.

6.2.7 Surrogate standards - The recommended surrogate standards are phenol-d₆, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d₅, 2-fluorobiphenyl, 2-chlorophenol-d₄, 1,2 dichlorobenzene-d₄, and p-terphenyl-d₁₄. See Method 3500 for the instructions on preparing the surrogate standards. Determine what concentration should be in the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery of surrogate standards



in all blanks, spikes, and sample extracts. Take into account all dilutions of sample extracts.

6.2.8 Matrix spike standards - See Method 3500 for instructions on preparing the matrix spike standard. Determine what concentration should be in the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery of surrogate standards in all matrix spikes. Take into account all dilutions of sample extracts.

6.2.8.1 Matrix spike compound concentrations in the final extract are at 25 ng/ μ L for base/neutral compounds and 37.5 ng/ μ L in acid compounds.

6.3 Procedure

6.3.1 Sample preparation - Samples must be prepared by one of the following methods prior to GC/MS analysis.

<u>Matrix</u>	<u>Methods</u>
Water	3510, 3520
Soil/sediment	3540, 3550
Waste	3540, 3550, 3580

6.3.1.1 Direct injection - In very limited applications direct injection of the sample into the GC/MS system with a 10 μ L syringe may be appropriate. The detection limit is very high (approximately 10,000 μ g/L); therefore, it is only permitted where concentrations in excess of 10,000 μ g/L are expected. The system must be calibrated by direct injection.

6.3.2 Extract cleanup - Extracts may be cleaned up by any of the following methods prior to GC/MS analysis.

<u>Compounds</u>	<u>Methods</u>
Phenols	3630, 3640, 8040a
Phthalate esters	3610, 3620, 3640
Nitroamines	3610, 3620, 3640
Organochlorine pesticides & PCBs	3620, 3660
Nitroaromatics and cyclic ketones	3620, 3640
Polynuclear aromatic hydrocarbons	3611, 3630, 3640
Haloethers	3620, 3640
Chlorinated hydrocarbons	3620, 3640
Organophosphorus pesticides	3620
Petroleum waste	3611, 3650
All priority pollutant base, neutral, and acids	3640

a - Method 8040 includes a derivatization technique followed by GC/ECD analysis, if interferences are encountered on GC/FID.



6.3.3 Initial calibration - The recommended GC/MS operating conditions:

Mass range:	35-500 amu
Scan time:	1 sec/scan
Initial temperature:	40°C, hold for 4 minutes
Temperature program:	40-300°C at 8°C/min, 20°C/min to 320°C
Final temperature:	320°C, hold until benzo(g,h,i)perylene has eluted
Injector temperature:	250-300°C
Transfer line temperature:	250-300°C
Source temperature:	According to manufacturer's specifications 190°C - 205°C for IncoS 50
Injector:	Grob-type, splitless/split
Sample volume:	1-2 µL
Carrier gas:	Helium at 30 cm/sec

6.3.3.1 Each GC/MS system must be hardware-tuned to meet the criteria in Table 3 for a 50 ng injection of DFTPP. Analyses should not begin until all these criteria are met. Background subtraction should be straightforward and designed only to eliminate column bleed or instrument background ions. The GC/MS tuning standard should also be used to assess GC column performance and injection port inertness. Benzidine and pentachlorophenol should be present at their normal responses, and no peak tailing should be visible. If degradation is excessive and/or poor chromatography is noted, the injection port may require cleaning. It may also be necessary to break off the first 6-12 in. of the capillary column or change the liner.

6.3.3.2 The internal standards selected should permit most of the components of interest in a chromatogram to have retention times of 0.80-1.20 relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Table 1). If interferences are noted, use the next most intense ion as the quantitation ion (i.e. for 1,4-dichlorobenzene-d4 use m/z 152 for quantitation).

6.3.3.3 Analyze 1 or 2 µL of each calibration standard (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each compound (as indicated in Table 1). Figure 1 shows a chromatogram of a calibration standard containing base/neutral and acid analytes. Calculate response factors (RFs) for each compound as follows:

$$RF = (Ax/Cs)/(Als/Cx)$$

where:

- Ax - Area of the characteristic ion for the compound being measured.
- Als - Area of the characteristic ion for the specific internal standard.
- Cs - Concentration of the specific internal standard (ng/µL).
- Cx - Concentration of the compound being measured (ng/µL).



6.3.3.4 The average RF should be calculated for each compound. The percent relative standard deviation ($\% \text{RSD} = 100(\text{SD}/\text{RF})$) should also be calculated for each compound. The $\% \text{RSD}$ should be less than 30% for each compound. The $\% \text{RSD}$ for each CCC (Table 4) must be less than 30%. The relative retention times of each compound in each calibration run should agree within 0.06 relative retention time units. Late-eluting compounds usually have much better agreement. Many acid compounds can show relative retention time shifts in dirty or active samples. The analyst should be aware of and watch for this situation.

6.3.3.5 A system performance check must be performed to ensure that minimum average RFs are met before the calibration curve is used. For semivolatiles, the System Performance Check Compounds (SPCCs) are: N-nitroso-di-n-propylamine; hexachlorocyclopentadiene; 2,4-dinitrophenol; and 4-nitrophenol. The minimum acceptable average RF for these compounds SPCCs is 0.050. These SPCCs typically have very low RFs (0.1-0.2) and tend to decrease in response as the chromatographic system begins to deteriorate or the standard material begins to deteriorate. They are usually the first to show poor performance. Therefore, they must meet the minimum requirement when the system is calibrated.

6.3.4 Daily GC/MS calibration

6.3.4.1 Prior to analysis of samples, the GC/MS tuning standard must be analyzed. A 50 ng injection of DFTPP must result in a mass spectrum for DFTPP which meets the specified criteria (Table 3). These criteria must be demonstrated during each 12 hour shift.

6.3.4.2 A calibration standard(s) at mid-concentration, containing each compound of interest, including all required surrogates, must be performed every 12 hours during analysis. Compare the response factor data from the standards every 12 hours with the average response factor from the initial calibration for a specific instrument as per the SPCC and CCC criteria.

6.3.4.3 System Performance Check Compounds (SPCCs): A system performance check must be made during every 12 hour shift. If the SPCC criteria are met, a comparison of response factors is made for all compounds. This is the same check that is applied during the initial calibration. If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. If the minimum RFs are not met, the system must be evaluated, and corrective action must be taken before sample analysis can begin. The minimum RF for semivolatile SPCCs is 0.050. Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before analysis begins.

6.3.4.4 Calibration Check Compounds (CCCs): After the system performance check is met, CCCs listed in Table 4 are used to check the validity of the initial calibration.



Calculate the percent difference using:

$$\% \text{ Difference} = \frac{RF_i - RF_c}{RF_i} \times 100$$

where:

RF_i = Average response factor from initial calibration.

RF_c = Response factor from current verification check standard.

If the percent difference for any compound is greater than 20, this is considered a warning limit. If the percent difference for CCC is less than 30%, the initial calibration is assumed to be valid. If the criterion is not met ($\geq 30\%$ difference) for any one CCC, corrective action must be taken. Problems similar to those listed under SPCCs could affect this criterion. If no source of the problem can be determined after corrective action has been taken, a new five-point calibration must be generated. This criterion must be met before sample analysis begins.

6.3.4.5 The internal standard responses and retention times in the calibration check standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the last check calibration (12 hours), the chromatographic system must be inspected for malfunctions and corrections must be made, as required. If the EICP area for any of the internal standards changes by a factor of two (-50% to $+100\%$) from the last daily calibration standard check, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate.

6.3.5 GC/MS analysis

6.3.5.1 It is highly recommended that the extract be screened on a GC/FID or GC/PID using the same type of capillary column. This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds and may show high background samples that should be analyzed using a medium/high level extraction.

6.3.5.2 Spike 0.5 ml of the 1 ml extract obtained from sample preparation with 10 μL of the internal standard solution just prior to analysis. This is the equivalent internal standard concentration of 20 ng/ μL of each standard in the sample.

6.3.5.3 Analyze the 0.5 ml extract by GC/MS using a 30 m x 0.25 mm (or 0.32 mm) silicone-coated fused-silica capillary column. The volume to be injected should ideally contain 25 ng/ μL of base/neutral and 37.5 ng/ μL of acid surrogates. The recommended GC/MS operating conditions to be used are specified in Section 6.3.3.



6.3.5.4 If the response for any quantitation ion exceeds the initial calibration curve range of the GC/MS system, extract dilution must take place. Additional internal standard must be added to the diluted extract to maintain the required 20 ng/ μ l of each internal standard in the extracted volume. The diluted extract must be reanalyzed.

6.3.5.5 Perform all qualitative and quantitative measurements as described in Section 7. Store the extracts at 4°C, protected from light in screw-cap vials equipped with unperced Teflon lined septa.

7.0 Review

7.1 Qualitative analysis

7.1.1 An analyte is identified by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference should be obtained or verified on the user's GC/MS within the same 12 hours as the sample analysis. These standard reference spectra may be obtained through analysis of the calibration standards. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC relative retention time (RRT) as the standard component; and (2) correspondence of the sample component and the standard component mass spectrum.

7.1.2 The sample component RRT must compare within ± 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run within the same 12 hours as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted, ion-current profiles for ions unique to the component of interest.

7.1.3 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.

7.1.4 The relative intensities of ions specified in Section 7.1.3 must agree within plus or minus 20% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample abundance must be between 30 and 70 percent.) If not, the compound may be flagged with an "m" if the analyst determines that the identification is real (favors false positive).

7.1.4.1 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important. Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the



identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

7.1.5 Tentatively Identified Compounds

7.1.5.1 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. For example, the RCRA permit or waste delisting requirements may require the reporting of nontarget analytes. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions >10 % of the most abundant ion) should be present in the sample spectrum. If not, the compound may be flagged with an "m" if the analyst determines that the identification is real (this favors false positives).

(2) The relative intensities of the major ions should agree within $\pm 20\%$.

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

7.2 Quantitative analysis

7.2.1 When a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantitation will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of a given analyte. If secondary ion quantitation is necessary due to interference, then a short quantitation report list is generated. This quantitation contains the integrated areas of the affected compounds, based on the secondary ion(s) for that compound, and of the relevant internal standards. Identical reports must be generated for the sample with interference and for the relevant continuing calibration. The report for the continuing calibration is used to generate a response factor for the affected compound based on its secondary ion. This response factor is then used in the calculations for that compound in the affected sample.



7.2.2 Calculate the concentration of each identified analyte in the sample as follows:

Water

$$\text{concentration } (\mu\text{g/L}) = \frac{(A_x)(I_s)(V_t)}{(A_{I_s})(RF)(V_o)(V_i)}$$

A_x= Area of characteristic ion for compound being measured.

I_s= Amount of internal standard injected(ng).

V_t= Volume of total extract, taking into account dilutions (i.e. a 1 to 10 dilution of a 1 ml extract volume will mean V_t = 10,000 μ L.)

A_{I_s}= Area of characteristic ion for the internal standard.

RF= Response factor for compound being measured (section 6.3.3.3)

V_o= Volume of water extracted (ml)

V_i= Volume of extract injected (μ L)

Sediment/Soil/Sludge(on a dry weight basis) and Waste(normally on a wet weight basis)

$$\text{concentration } (\mu\text{g/Kg}) = \frac{(A_x)(I_s)(V_t)}{(A_{I_s})(RF)(V_i)(W_s)(D)}$$

where:

A_x, I_s, V_t, A_{I_s}, RF, V_i = Same as for water

W_s = Weight of sample extracted or diluted in grams.

D = % dry weight of sample/100, or 1 for a wet-weight basis.

7.2.3 Where applicable, an estimate of concentration for noncalibrated components in the sample should be made. The formula given above should be used with the following modifications: The area A_x and A_{I_s} should be from the total ion chromatograms and the RF for the compound should be assumed to be 1. The concentration obtained should be reported indicating (1) that the value is an estimate and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

7.2.4 Quantitation of multicomponent compounds (e.g. Aroclors) is beyond the scope of this method. Normally, quantitation is performed using a GC/ECD by Method 8080 of 8081.

8.0 Quality Control

8.1 Refer to the laboratory Quality Assurance Plan for quality control procedures.



8.2 Specific quality control procedures are specified in section 6.0 Analytical Procedures; section 7.0 Review ; and section 9.0 Corrective Actions.

8.3 One method blank is prepared and analyzed with each sample batch. Sample batch size cannot exceed 20 samples.

8.4 One blank spike (LCS) is prepared and analyzed with each sample batch. Sample batch size cannot exceed 20 samples. Refer to Quality Assurance Project Plan (QAPP) for QC limits.

8.5 A matrix spike is prepared and analyzed in duplicate at a minimum 5% frequency. If additional sample aliquots are not available for matrix spike analysis, a duplicate blank spike analysis may be performed. See QAPP for QC limits.

9.0 Corrective Actions

9.1 Surrogate Recovery

For aqueous and soil matrices, surrogate recovery values should fall within the specified surrogate control limits. Refer to the QAPP for QC limits.

One acid and one base/neutral surrogate may be out , but not less than 10%.

9.1.1 If recovery is not within limits, the following procedures are required.

9.1.1.1 Check calculations, surrogate solutions or internal standards. If errors are found, recalculate the data accordingly.

9.1.1.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and re-analyze the extract.

9.1.1.2.1 If it is determined that sample background contamination (eg."humptogram") is causing QC/instrument/chromatography problems, then it maybe advisable to do a medium/high level extraction for re-analysis.

9.1.1.3 If re-analysis produces the same out of limits results, re-extract and re-analyze the sample.

9.1.1.4 If, upon re-analysis, the recovery is again not within limits, flag the data as "estimated concentration".

9.1.1.5 At a minimum, surrogate recovery limits should be updated on a matrix-by-matrix basis, annually.

9.2 If the LCS recovery is not within QC limits, proceed with corrective actions specified in section 9.1.1.

9.3 See section 6.0, Analytical Procedures, section 7.0, Review and section 8.0, Quality Control for additional guidance on appropriate corrective actions.



10.0 Miscellaneous Notes and Precautions

10.1 Interferences: Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.

10.2 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

11.0 Method References

11.1 U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, 1/91.

11.2 U.S. EPA Test Methods for Evaluating Solid Waste (SW-846), Method 8270A, Revision 1, July, 1992.

12.0 Appendices

12.1 Table 1: Characteristic Ions for Semivolatile Compounds

12.2 Table 2: Estimated Quantitation Limits for Semivolatile Organics

12.3 Table 3: Table of Key Ions and Ion Abundance Criteria

12.4 Table 4: Calibration Check Compounds

12.5 Table 5: Semivolatile Internal Standards with Corresponding Analytes Assigned for Quantitation

12.6 Table 6: Laboratory Control Sample Recovery Limits

12.7 Table 7: Matrix Spike/Matrix Spike Duplicate Recovery Limits

12.8 Table 8: Surrogate Recovery Limits

Job/Case: _____

Date: _____

**ANALYTICAL
RESOURCES
INCORPORATED**

**GC/MS SEMIVOLATILE ORGANICS LOGBOOK
FINN VI**

Column No.: _____

Type: _____

GC Program: _____

EM Voltage: _____

Tune: _____

Calibration File: _____

Mass Tuning File: _____

Time: _____

Analyst: _____

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GC/MS SEMIVOLATILE ORGANICS LOGBOOK
FINN VI

Maintenance: _____

Fill out all information completely.
Z-out all entry spaces not used at end of day/QC period.
Start new page for each new EPA case or QC period.

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TABLE 1.
CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS

Compound	Retention Time (min.)	Primary Ion	Secondary Ion(s)
2-Picoline	3.75a	93	66,92
Aniline	5.68	93	66,65
Phenol	5.77	94	65,66
Bis(2-chloroethyl) ether	5.82	93	63,95
2-Chlorophenol	5.97	128	64,130
1,3-Dichlorobenzene	6.27	146	148,111
1,4-Dichlorobenzene-d4 (I.S.)	6.35	152	150,115
1,4-Dichlorobenzene	6.40	146	148,111
Benzyl alcohol	6.78	108	79,77
1,2-Dichlorobenzene	6.85	146	148,111
N-Nitrosomethylethylamine	6.97	88	42,88,43,56
Bis(2-chloroisopropyl) ether	7.22	45	77,121
Ethyl carbamate	7.27	62	62,44,45,74
Thiophenol (Benzenethiol)	7.42	110	110,66,109,84
Methyl methanesulfonate	7.48	80	80,79,65,95
N-Nitrosodi-n-propylamine	7.55	70	42,101,130
Hexachloroethane	7.65	117	201,199
Maleic anhydride	7.65	54	54,98,53,44
Nitrobenzene	7.87	77	123,65
Isophorone	8.53	82	95,138
N-Nitrosodilethylamine	8.70	102	102,42,57,44,56
2-Nitrophenol	8.75	139	109,65
2,4-Dimethylphenol	9.03	122	107,121
p-Benzoquinone	9.13	108	54,108,82,80
Bis(2-chloroethoxy)methane	9.23	93	95,123
Benzoic acid	9.38	122	105,77
2,4-Dichlorophenol	9.48	162	164,98
Trimethyl phosphate	9.53	110	110,79,95,109,140
Ethyl methanesulfonate	9.62	79	79,109,97,45,65
1,2,4-Trichlorobenzene	9.67	180	182,145
Naphthalene-d8 (I.S.)	9.75	136	68
Naphthalene	9.82	128	129,127
Hexachlorobutadiene	10.43	225	223,227
Tetraethyl pyrophosphate	11.07	99	99,155,127,81,109
Diethyl sulfate	11.37	139	139,45,59,99,111,125
4-Chloro-3-methylphenol	11.68	107	144,142
2-Methylnaphthalene	11.87	142	141
2-Methylphenol	12.40	107	107,108,77,79,90
Hexachloropropene	12.45	213	213,211,215,117,106,141
Hexachlorocyclopentadiene	12.60	237	235,272



TABLE 1.
(Continued)

Compound	Retention Time (min.)	Primary Ion	Secondary Ion(s)
N-Nitrosopyrrolidine	12.65	100	100,41,42,68,69
Acetophenone	12.67	105	71,105,51,120
4-Methylphenol	12.82	107	107,108,77,79,90
2,4,6-Trichlorophenol	12.85	196	198,200
o-Toluidine	12.87	106	106,107,77,51,79
3-Methylphenol	12.93	107	107,108,77,79,90
2-Chloronaphthalene	13.30	162	127,164
N-Nitrosopiperidine	13.55	114	42,114,55,56,41
1,4-Phenylenediamine	13.62	108	108,80,53,54,52
1-Chloronaphthalene	13.65a	162	127,164
2-Nitroaniline	13.75	65	92,138
5-Chloro-2-methylaniline	14.28	106	106,141,140,77,89
Dimethyl phthalate	14.48	163	194,164
Acenaphthylene	14.57	152	151,153
2,6-Dinitrotoluene	14.62	165	63,89
Phthalic anhydride	14.62	104	104,76,50,148
o-Anisidine	15.00	108	80,108,123,52
3-Nitroaniline	15.02	138	108,92
Acenaphthene-d10 (I.S.)	15.05	164	162,160
Acenaphthene	15.13	154	153,152
2,4-Dinitrophenol	15.35	184	63,154
2,6-Dinitrophenol	15.47	162	162,164,126,98,63
4-Chloroaniline	15.50	127	127,129,65,92
Isosafrole	15.60	162	162,131,104,77,51
Dibenzofuran	15.63	168	139
2,4-Diaminotoluene	15.78	121	121,122,94,77,104
2,4-Dinitrotoluene	15.80	165	63,89
4-Nitrophenol	15.80	139	109,65
2-Naphthylamine	16.00a	143	115,116
1,4-Naphthoquinone	16.23	158	158,104,102,76,50,130
p-Cresidine	16.45	122	122,94,137,77,93
Dichlorovos	16.48	109	109,185,79,145
Diethyl phthalate	16.70	149	177,150
Fluorene	16.70	166	165,167
2,4,5-Trimethylaniline	16.70	120	120,135,134,91,77
N-Nitrosodibutylamine	16.73	84	84,57,41,116,158
4-Chlorophenyl phenyl ether	16.78	204	206,141
Hydroquinone	16.93	110	110,81,53,55
4,6-Dinitro-2-methylphenol	17.05	198	51,105
Resorcinol	17.13	110	110,81,82,53,69
N-Nitrosodiphenylamine	17.17	169	168,167
Safrole	17.23	162	162,162,104,77,103,135

TABLE 1.
(Continued)

Compound	Retention Time (min.)	Primary Ion	Secondary Ion(s)
Hexamethyl phosphoramide	17.33	135	135,44,179,92,42
3-(Chloromethyl)pyridine hydrochl.	17.50	92	92,127,129,65,39
Diphenylamine	17.54a	169	168,167
1,2,4,5-Tetrachlorobenzene	17.97	216	216,214,179,108,143,218
1-Naphthylamine	18.20	143	143,115,89,63
1-Acetyl-2-thiourea	18.22	118	43,118,42,76
4-Bromophenyl phenyl ether	18.27	248	250,141
Toluene diisocyanate	18.42	174	174,145,173,146,132,91
2,4,5-Trichlorophenol	18.47	196	196,198,97,132,99
Hexachlorobenzene	18.65	284	142,249
Nicotine	18.70	84	84,133,161,162
Pentachlorophenol	19.25	266	264,268
5-Nitro-o-toluidine	19.27	152	77,152,79,106,94
Thionazine	19.35	107	96,107,97,143,79,68
4-Nitroaniline	19.37	138	138,65,108,79,80,39
Phenanthrene-d10(I.S.)	19.55	188	94,80
Phenanthrene	19.62	178	179,176
Anthracene	19.77	178	176,179
1,4-Dinitrobenzene	19.83	168	168,75,50,76,92,122
Mevinphos	19.90	127	127,192,109,67,164
Naled	20.03	109	109,145,147,301,79,189
1,3-Dinitrobenzene	20.18	168	168,76,50,75,92,122
Diallate (cis or trans)	20.57	86	86,234,43,70
1,2-Dinitrobenzene	20.58	168	168,50,63,74
Diallate (trans or cis)	20.78	86	86,234,43,70
Pentachlorobenzene	21.35	250	250,252,108,248,215,254
5-Nitro-o-anisidine	21.50	168	168,79,52,138,153,77
Pentachloronitrobenzene	21.72	237	237,142,214,249,295,265
4-Nitroquinoline-1-oxide	21.73	174	174,101,128,75,116
Di-n-butyl phthalate	21.78	149	150,104
2,3,4,6-Tetrachlorophenol	21.88	232	232,131,230,166,234,168
Demeton-O	22.72	88	88,89,60,61,115,171
Fluoranthene	23.33	202	101,203
1,3,5-Trinitrobenzene	23.68	75	75,74,213,120,91,63
Dicrotophos	23.82	127	127,67,72,109,193,237
Benzidine	23.87	184	92,185
Trifluralin	23.88	306	306,43,264,41,290
Bromoxynil	23.90	277	277,279,88,275,168
Pyrene	24.02	202	200,203
Monocrotophos	24.08	127	127,192,67,97,109
Phorate	24.10	75	75,121,97,93,260
Sulfalate	24.23	188	188,88,72,60,44

TABLE 1.
(Continued)

Compound	Retention Time (min.)	Primary Ion	Secondary Ion(s)
Demeton-S	24.30	88	88,60,81,89,114,115
Phenacetin	24.33	108	180,179,109,137,80
Dimethoate	24.70	87	87,93,125,143,229
Phenobarbital	24.70	204	204,117,232,146,161
Carbofuran	24.90	164	164,149,131,122
Octamethyl pyrophosphoramidate	24.95	135	135,44,199,286,153,243
4-Aminobiphenyl	25.08	169	169,168,170,115
Terbufos	25.35	231	231,57,97,153,103
α,α -Dimethylphenylamine	25.43	58	58,91,65,134,42
Pronamide	25.48	173	173,175,145,109,147
Aminoazobenzene	25.72	197	92,197,120,65,77
Dichloro	25.77	191	191,163,226,228,135,193
Dinoseb	25.83	211	211,163,147,117,240
Disulfoton	25.83	88	88,97,89,142,186
Fluchloralin	25.88	306	306,63,326,328,264,65
Mexacarbate	26.02	165	165,150,134,164,222
4,4'-Oxydianiline	26.08	200	200,108,171,80565
Butyl benzyl phthalate	26.43	149	91,206
4-Nitrobiphenyl	26.55	199	199,152,141,169,151
Phosphamidon	26.85	127	127,264,72,109,138
2-Cyclohexyl-4,6-Dinitrophenol	26.87	231	231,185,41,193,266
Methyl parathion	27.03	109	109,125,263,79,93
Carbaryl	27.17	144	144,115,116,201
Dimethylaminoazobenzene	27.50	225	225,120,77,105,148,42
Propylthiouracil	27.68	170	170,142,114,83
Benz(a)anthracene	27.83	228	229,226
Chrysene-d12 (I.S.)	27.88	240	120,236
3,3'-Dichlorobenzidine	27.88	252	254,126
Chrysene	27.97	228	226,229
Malathion	28.08	173	173,125,127,93,158
Kepone	28.18	272	272,274,237,178,143,270
Fenthion	28.37	278	278,125,109,169,153
Parathion	28.40	109	109,97,291,139,155
Anilazine	28.47	239	239,241,143,178,89
Bis(2-ethylhexyl) phthalate	28.47	149	167,279
3,3'-Dimethylbenzidine	28.55	212	212,106,196,180
Carbophenothion	28.58	157	157,97,121,342,159,199
5-Nitroacenaphthene	28.73	199	199,152,169,141,115
Methapyrilene	28.77	97	97,50,191,71
Isodrin	28.95	193	193,66,195,263,265,147
Captan	29.47	79	79,149,77,119,117
Chlorfenvinphos	29.53	267	267,269,323,325,295



TABLE 1.
(Continued)

Compound	Retention Time (min.)	Primary Ion	Secondary Ion(s)
Crotoxypfos	29.73	127	127,105,193,166
Phosmet	30.03	160	160,77,93,317,76
EPN	30.11	157	157,169,185,141,323
Tetrachlorvinphos	30.27	329	109,329,331,79,333
Di-n-octyl phthalate	30.48	149	167,43
2-Aminoanthraquinone	30.63	223	223,167,195
Barban	30.83	222	222,51,87,224,257,153
Aramite	30.92	185	185,191,319,334,197,321
Benzo(b)fluoranthene	31.45	252	253,125
Nitrofen	31.48	283	283,285,202,139,253
Benzo(k)fluoranthene	31.55	252	253,125
Chlorobenzilate	31.77	251	251,139,253,111,141
Fensulfothion	31.87	293	293,97,308,125,292
Ethion	32.08	231	231,97,153,125,121
Diethylstilbestrol	32.15	268	268,145,107,239,121,159
Famphur	32.67	218	218,125,93,109,217
Tri-p-tolyl phosphateb	32.75	368	368,367,107,165,198
Benzo(a)pyrene	32.80	252	253,125
Perylene-d12 (I.S.)	33.05	264	260,265
7,12-Dimethylbenz(a)anthracene	33.25	256	256,241,239,120
5,5-Diphenylhydantoin	33.40	180	180,104,252,223,209
Captafol	33.47	79	79,77,80,107
Dinocap	33.47	69	69,41,39
Methoxychlor	33.55	227	227,228,152,114,274,212
2-Acetylaminofluorene	33.58	181	181,180,223,152
4,4'-Methylenebis(2-chloroaniline)	34.38	231	231,266,268,140,195
3,3'-Dimethoxybenzidine	34.47	244	244,201,229
3-Methylcholanthrene	35.07	268	268,252,253,126,134,113
Phosalone	35.23	182	182,184,367,121,379
Azinphos-methyl	35.25	160	160,132,93,104,105
Leptophos	35.28	171	171,377,375,77,155,379
Mirex	35.43	272	272,237,274,270,239,235
Tris(2,3-dibromopropyl) phosphate	35.68	201	137,201,119,217,219,199
Dibenz(a,h)acridine	36.40	279	279,280,277,250
Mestrand	36.48	277	277,310,174,147,242
Coumaphos	37.08	362	362,226,210,364,97,109
Indeno(1,2,3-cd)pyrene	39.52	276	138,227
Dibenz(a,h)anthracene	39.82	278	139,279
Benzo(g,h,i)perylene	41.43	276	138,277
1,2,4,5-Dibenzopyrene	41.60	302	302,151,150,300
Strychnine	45.15	334	334,335,333
Piperonyl sulfoxide	46.43	162	162,135,105,77



TABLE 1.
(Continued)

Compound	Retention Time (min.)	Primary ion	Secondary ion(s)
Hexachlorophene	47.98	196	196, 198, 209, 211, 406, 408
Aldrin	-	66	263, 220
Aroclor-1016	-	222	260, 292
Aroclor-1221	-	190	224, 260
Aroclor-1232	-	190	224, 260
Aroclor-1242	-	222	256, 292
Aroclor-1248	-	292	362, 326
Aroclor-1254	-	292	362, 326
Aroclor-1260	-	360	362, 394
Alpha-BHC	-	183	181, 109
Beta-BHC	-	181	183, 109
Delta-BHC	-	183	181, 109
γ-BHC (Lindane)	-	183	181, 109
4,4'-DDD	-	235	237, 165
4,4'-DDE	-	246	248, 176
4,4'-DDT	-	235	237, 165
Dieldrin	-	79	263, 279
1,2-Diphenylhydrazine	-	77	105, 182
Endosulfan I	-	195	339, 341
Endosulfan II	-	337	339, 341
Endosulfan sulfate	-	272	387, 422
Endrin	-	263	82, 81
Endrin aldehyde	-	67	345, 250
Endrin ketone	-	317	67, 319
2-Fluorobiphenyl (surr.)	-	172	171
2-Fluorophenol (surr.)	-	112	64
Heptachlor	-	100	272, 274
Heptachlor epoxide	-	353	355, 351
Nitrobenzene-d5(surr.)	-	82	128, 54
N-Nitrosodimethylamine	-	42	74, 44
Phenol-d6 (surr.)	-	99	42, 71
Terphenyl-d14 (surr.)	-	244	122, 212
2,4,6-Tribromophenol (surr.)	-	330	332, 141
Toxaphene	-	159	231, 233

I.S. = internal standard.

surr. = surrogate.

a = Estimated retention times.

b = Substitute for the non-specific mixture, tricresyl phosphate.



TABLE 2.
ESTIMATED QUANTITATION LIMITS (EQLs) FOR SEMIVOLATILE ORGANICS

	Estimated Quantitation Limits	
	Ground water $\mu\text{g/L}$	Low Soil/Sediment $\mu\text{g/Kg}$
<u>Semivolatiles</u>		
Acenaphthene	10	660
Acenaphthylene	10	660
Acetophenone	10	ND
2-Acetylaminofluorene	20	ND
1-Acetyl-2-thiourea	1000	ND
2-Aminoanthraquinone	20	ND
Aminoazobenzene	10	ND
4-Aminobiphenyl	20	ND
Anilazine	100	ND
o-Anisidine	10	ND
Anthracene	10	660
Aramite	20	ND
Azinphos-methyl	100	ND
Barban	200	ND
Benz(a)anthracene	10	660
Benzo(b)fluoranthene	10	660
Benzo(k)fluoranthene	10	660
Benzoic acid	50	3300
Benzo(g,h,i)perylene	10	660
Benzo(a)pyrene	10	660
p-Benzoquinone	10	ND
Benzyl alcohol	20	1300
Bis(2-chloroethoxy)methane	10	660
Bis(2-chloroethyl) ether	10	660
Bis(2-chloroisopropyl) ether	10	660
4-bromophenyl phenyl ether	10	660
Bromoxynil	10	ND
Butyl benzyl phthalate	10	660
Captafol	20	ND
Captan	50	ND
Carbaryl	10	ND
Carbo	10	ND
Carbophenothion	10	ND
Chlorfenvinphos	20	ND
4-Chloroaniline	20	1300



TABLE 2 (cont'd)
ESTIMATED QUANTITATION LIMITS (EQLs) FOR SEMIVOLATILE ORGANICS

	Estimated Quantitation Limits	
	Ground water µg/L	Low Soil/Sediment µg/Kg
<u>Semivolatiles</u>		
Chlorobenzilate	10	ND
5-Chloro-2-methylaniline	10	ND
4-Chloro-3-methylphenol	20	1300
3-(Chloromethyl)pyridine hydrochloride	100	ND
2-Chloronaphthalene	10	660
2-Chlorophenol	10	660
4-Chlorophenyl phenyl ether	10	660
Chrysene	10	660
Coumaphos	40	ND
p-Cresdine	10	ND
Crotoxyphos	20	ND
2-Cyclohexyl-4,6-dinitrophenol	100	ND
Demeton-O	10	ND
Demeton-S	10	ND
Diallate (cis or trans)	10	ND
Diallate (trans or cis)	10	ND
2,4-Diaminotoluene	20	ND
Dibenz(a,j)acridine	10	ND
Dibenz(a,h)anthracene	10	660
Dibenzofuran	10	660
Dibenzo(a,e)pyrene	10	ND
Di-n-butyl phthalate	10	ND
Dichlone	NA	ND
1,2-Dichlorobenzene	10	660
1,3-Dichlorobenzene	10	660
1,4-Dichlorobenzene	10	660
3,3'-Dichlorobenzidine	20	1300
2,4-Dichlorophenol	10	660
2,6-Dichlorophenol	10	ND
Dichlorvos	10	ND
Dicrotophos	10	ND
Diethyl phthalate	10	660
Diethylstilbestrol	20	ND
Diethyl sulfate	100	ND
Dimethoate	20	ND
3,3'-Dimethoxybenzidine	100	ND



TABLE 2 (cont'd)
ESTIMATED QUANTITATION LIMITS (EQLs) FOR SEMIVOLATILE ORGANICS

	Estimated Quantitation Limits	
	Ground water µg/L	Low Soil/Sediment µg/Kg
<u>Semivolatiles</u>		
Dimethylaminoazobenzene	10	ND
7,12-Dimethylbenz(a)anthracene	10	ND
3,3'-Dimethylbenzidine	10	ND
α,α-Dimethylphenethylamine	ND	ND
2,4-Dimethylphenol	10	660
Dimethyl phthalate	10	660
1,2-Dinitrobenzene	40	ND
1,3-Dinitrobenzene	20	ND
1,4-Dinitrobenzene	40	ND
4,6-Dinitro-2-methylphenol	50	3300
2,4-Dinitrophenol	50	3300
2,4-Dinitrotoluene	10	660
2,6-Dinitrotoluene	10	660
Dinocap	100	ND
Dinoseb	20	ND
5,5-Diphenylhydantoin	20	ND
Di-n-octyl phthalate	10	660
Disulfoton	10	ND
EPN	10	ND
Ethion	10	ND
Ethyl carbamate	50	ND
Bis(2-ethylhexyl) phthalate	10	660
Ethyl methanesulfonate	20	ND
Famphur	20	ND
Fensulfothion	40	ND
Fenthion	10	ND
Fluchloralin	20	ND
Fluoranthene	10	660
Fluorene	10	660
Hexachlorobenzene	10	660
Hexachlorobutadiene	10	660
Hexachlorocyclopentadiene	10	660
Hexachloroethane	10	660
Hexachlorophene	50	ND
Hexachloropropene	10	ND
Hexamethylphosphoramide	20	ND



TABLE 2.(cont'd)
ESTIMATED QUANTITATION LIMITS (EQLs) FOR SEMIVOLATILE ORGANICS

	Estimated Quantitation Limits	
	Ground water µg/L	Low Soil/Sediment µg/Kg
<u>Semivolatiles</u>		
Hydroquinone	ND	ND
Indeno(1,2,3-cd)pyrene	10	660
Isodrin	20	ND
Isophorone	10	660
Isosafrole	10	ND
Kepon	20	ND
Leptophos	10	ND
Malathion	50	ND
Maleic anhydride	NA	ND
Mestranol	20	ND
Methapyrene	100	ND
Methoxychlor	10	ND
3-Methylcholanthrene	10	ND
4,4'-Methylenbis(2-chloroaniline)	NA	ND
Methyl methanesulfonate	10	ND
2-Methylnaphthalene	10	660
Methyl parathion	10	ND
2-Methylphenol	10	660
3-Methylphenol	10	ND
4-Methylphenol	10	660
Mevinphos	10	ND
Mexacarbate	20	ND
Mirex	10	ND
Monocrotophos	40	ND
Naled	20	ND
Naphthalene	10	660
1,4-Naphthoquinone	10	ND
1-Naphthylamine	10	ND
2-Naphthylamine	10	ND
Nicotine	20	ND
5-Nitroacenaphthene	10	ND
2-Nitroaniline	50	3300
3-Nitroaniline	50	3300
4-Nitroaniline	20	ND
5-Nitro-o-anisidine	10	ND
Nitrobenzene	10	660



TABLE 2.(cont'd)
ESTIMATED QUANTITATION LIMITS (EQLs) FOR SEMIVOLATILE ORGANICS

	Estimated Quantitation Limits	
	Ground water µg/L	Low Soil/Sediment µg/Kg
<u>Semivolatiles</u>		
4-Nitrobiphenyl	10	ND
Nitrofen	20	ND
2-Nitrophenol	10	666
4-Nitrophenol	50	3300
5-Nitro-o-toluidine	10	ND
4-Nitroquinoline-1-oxide	40	ND
N-Nitrosodibutylamine	10	ND
N-Nitrosodiethylamine	20	ND
N-Nitrosodiphenylamine	10	666
N-Nitroso-di-n-propylamine	10	666
N-Nitrosopiperidine	20	ND
N-Nitrosopyrrolidine	40	ND
Octamethyl pyrophosphoramidate	200	ND
4,4'-Oxydianiline	20	ND
Parathion	10	ND
Pentachlorobenzene	10	ND
Pentachloronitrobenzene	20	ND
Pentachlorophenol	50	3300
Phenacetin	20	ND
Phenanthrene	10	666
Phenobarbital	10	ND
Phenol	10	666
1,4-Phenylenediamine	10	ND
Phorate	10	ND
Phosalone	100	ND
Phosmet	40	ND
Phosphamidon	100	ND
Phthalic anhydride	100	ND
2-Picoline	ND	ND
Piperonyl sulfoxide	100	ND
Pronamide	10	ND
Propylthiouracil	100	ND
Pyrene	10	666
Pyridine	ND	ND
Resorcinol	100	ND
Safrole	10	ND



TABLE 2.(cont'd)
ESTIMATED QUANTITATION LIMITS (EQLs) FOR SEMIVOLATILE ORGANICS

	Estimated Quantitation Limits	
	Ground water µg/L	Low Soil/Sediment µg/Kg
<u>Semivolatiles</u>		
Strychnine	40	20
Sulfalate	10	20
Terbufos	20	20
1,2,4,5-Tetrachlorobenzene	10	20
2,3,4,6-Tetrachlorophenol	10	20
Tetrachlorvinphos	20	20
Tetraethyl pyrophosphate	40	20
Thionazine	20	20
Thiophenol (Benzenethiol)	20	20
Toluene diisocyanate	100	20
o-Toluidine	10	20
1,2,4-Trichlorobenzene	10	60
2,4,5-Trichlorophenol	10	60
2,4,6-Trichlorophenol	10	60
Trifluralin	10	20
2,4,5-Trimethylaniline	10	20
Trimethyl phosphate	10	20
1,3,5-Trinitrobenzene	10	20
Tris(2,3-dibromopropyl) phosphate	200	20
Tri-p-tolyl phosphate(h)	10	20
O,O,O-Triethylphosphorothioate	NT	20



TABLE 2.(cont'd)
ESTIMATED QUANTITATION LIMITS (EQLs) FOR SEMIVOLATILE ORGANICS

- a EQLs listed for soil/sediment are based on wet weight. Normally data is reported on a dry weight basis, therefore, EQLs will be higher based on the % dry weight of each sample. This is based on a 30 g sample and gel permeation chromatography cleanup.
- b Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

ND = Not determined.
NA = Not applicable.
NT = Not tested.

Other Matrices

Factor

High-concentration soil and sludges by ultrasonic extractor
Non-water miscible waste

7.5
75

EQL = (EQL for Low Soil/Sediment (Table 2)) X (Factor).



TABLE 3.

TABLE OF KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
51	30-80 % of mass 198
68	< 2 % of mass 69
70	< 2 % of mass 69
127	25-75 % of mass 198
197	< 1 % of mass 198
198	Base peak, 100 % relative abundance
199	5-9 % of mass 198
275	10-30 % of mass 198
365	> 0.75 of mass 198
441	Present but less than mass 443
442	40-110 % of mass 198
443	15-24 % of mass 442

TABLE 4.

CALIBRATION CHECK COMPOUNDS

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Base/Neutral Fraction

Acenaphthene
1,4-Dichlorobenzene
Hexachlorobutadiene
N-Nitrosodiphenylamine
Di-n-octyl phthalate
Fluoranthene
Benzo(a)pyrene

Acid Fraction

4-Chloro-3-methylphenol
2,4-Dichlorophenol
2-Nitrophenol
Phenol
Pentachlorophenol
2,4,6-trichlorophenol



TABLE 5.
SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES
ASSIGNED FOR QUANTITATION

1,4-Dichlorobenzene-d4	Naphthalene-d8	Acenaphthene-d10
Aniline	Acetophenone	Acenaphthene
Benzyl alcohol	Benzoic acid	Acenaphthylene
Bis(2-chloroethyl) ether	Bis(2-chloroethoxy)methane	1-Chloronaphthalene
Bis(2-chloroisopropyl) ether	4-Chloroaniline	2-Chloronaphthalene
2-Chlorophenol	4-Chloro-3-methylphenol	4-Chlorophenyl phenyl ether
1,3-Dichlorobenzene	2,4-Dichlorophenol	Dibenzofuran
1,4-Dichlorobenzene	2,6-Dichlorophenol	Diethyl phthalate
1,2-Dichlorobenzene	α , α -Dimethyl- phenethylamine	Dimethyl phthalate
Ethyl methanesulfonate	2,4-Dimethylphenol	2,4-Dinitrophenol
2-Fluorophenol (surr.)	Hexachlorobutadiene	2,4-Dinitrotoluene
Hexachloroethane	Isophorone	2,6-Dinitrotoluene
Methyl methanesulfonate	2-Methylnaphthalene	Fluorene
2-Methylphenol	Naphthalene	2-Fluorobiphenyl (surr.)
4-Methylphenol	Nitrobenzene	Hexachlorocyclo pentadiene
N-Nitrosodimethylamine	Nitrobenzene-d8 (surr.)	1-Naphthylamine
N-Nitroso-di-n-propylamine	2-Nitrophenol	2-Naphthylamine
Phenol	N-Nitrosodibutylamine	2-Nitroaniline
Phenol-d6 (surr.)	N-Nitrosopiperidine	3-Nitroaniline
2-Picoline	1,2,4-Trichlorobenzene	4-Nitroaniline
		4-Nitrophenol
		Pentachlorobenzene
		1,2,4,5-Tetra chlorobenzene
		2,3,4,6-Tetra chlorophenol
		2,4,6-Tribromo phenol (surr.)
		2,4,6-Trichloro phenol
		2,4,5-Trichloro phenol



TABLE 5.
(Continued)

Phenanthrene-d10

4-Aminobiphenyl
Anthracene
4-Bromophenyl phenyl ether
Di-n-butyl phthalate
4,6-Dinitro-2-methylphenol
Diphenylamine
1,2-Diphenylhydrazine
Fluoranthene
Hexachlorobenzene
N-Nitrosodiphenylamine
Pentachlorophenol
Pentachloronitrobenzene
Phenacetin
Phenanthrene
Pronamide

Chrysene-d-2

Benzidine
Benzo(a)anthracene
Bis(2-ethylhexyl) phthalate
Butyl benzyl phthalate
Chrysene
3,3'-Dichlorobenzidine
p-Dimethylaminoazobenzene
Pyrene
Terphenyl-d14 (surr.)

Perylene-d12

Benzo(b)fluor
anthene
Benzo(k)fluor
anthene
Benzo(g,h,i)
perylene
Benzo(a)pyrene
Dibenz(a,i)acridine
Dibenz(a,h)
anthracene
7,12-Dimethylbenz
(a)anthracene
Di-n-octyl phthalate
Indeno(1,2,3-cd)
pyrene
3-Methylchol
anthrene

(surr.) = surrogate



TABLE 6.
LABORATORY CONTROL SAMPLE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENTS

Surrogate compound	Low/High Soil	Low/High Water
Phenol	37-104	37-104
2-Chlorophenol	45-108	41-107
1,4-Dichlorobenzene	38-105	37-100
n-Nitroso-di-n-propylamine	38-107	41-103
1,2,4-Trichlorobenzene	35-113	10-103
4-Chloro-3-Methylphenol	34-111	41-104
Acenaphthene	41-113	44-107
4-Nitrophenol	11-124	10-100
2,4-Dinitrotoluene	33-106	37-101
Pentachlorophenol	10-128	10-130
Pyrene	39-128	42-130
2-Methylnaphthalene	47-145	47-145

TABLE 7.
MATRIX SPIKE/MATRIX SPIKE DUPLICATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENTS

Surrogate compound	Low/High Soil	Low/High Water
Phenol	5-112	5-112
2-Chlorophenol	23-134	23-134
1,4-Dichlorobenzene	20-124	20-124
n-Nitroso-di-n-propylamine	10-230	10-230
1,2,4-Trichlorobenzene	44-142	44-142
4-Chloro-3-Methylphenol	22-147	22-147
Acenaphthene	47-145	47-145
4-Nitrophenol	10-132	10-132
2,4-Dinitrotoluene	39-139	39-139
Pentachlorophenol	14-176	14-176
Pyrene	52-115	52-115
2-Methylnaphthalene	47-145	47-145



TABLE 8.
SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

Surrogate compound	Low/High Soil	Low/High Water
d4-2-Chlorophenol	43-102	33-102
d4-1,2-Dichlorobenzene	24-112	28-105
Tribromophenol	24-122	16-122
2-Fluorophenol	36-111	21-110
d5-Phenol	40-104	10-100
d5-Nitrobenzene	29-117	35-110
2-Fluorobiphenyl	33-114	43-104
d14-p-Terphenyl	28-133	33-133



ANALYTICAL
RESOURCES
INCORPORATED

Standard Operating Procedure

Determination of Diesel Range Organics (AK102 - 2/92)

421S

Revision 1

7/5/94

PROPRIETARY

Prepared By:

[Signature]

Approvals:

NA
Section Manager

[Signature]
Laboratory Manager

[Signature]
Quality Assurance Manager

[Signature]
Laboratory Director

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Standard Operating Procedure

Determination of Diesel Organics-Alaska Method AK102 (1992)

1.0 Scope and Application

1.1 Objectives

- 1.1.1 This method is designed to measure the concentration of diesel range organics in water and soil. (This corresponds) to an n-alkane range of C₁₀ - C₂₈ and a boiling point range of approximately 170°C to 400°C.
- 1.1.2 This method is primarily designed to measure diesel or other mid-range petroleum products such as fuel oil. Components greater than C₂₈ present in products such as motor oils or lubricating oils are detectable under the conditions of this method. More detailed identification and characterization of mid-range non-petroleum products and heavier petroleum products may be based on comparison against additional referenced materials using pattern recognition techniques. These additional efforts are not contained in this method.

1.2 Quantitation Limits

- 1.2.1 Quantitation limits are based on 100 µg/ml of Diesel 2 in the extract and are 0.2 mg/L for waters and 4.0 mg/kg for soils.

1.3 Dynamic Range

- 1.3.1 Dilutions should be performed as necessary to put the chromatographic envelope within the linear range of the method.

1.4 Experience

- 1.4.1 This method is based on a solvent extraction, gas chromatography (GC) procedure. This method should be used by, or under the supervision of, analysts experienced in the use of solvent extractions and gas chromatographs. The analysts should be skilled in the interpretation of gas chromatograms and should understand their use as a quantitative tool.



1.5 Method Summary

- 1.5.1 One liter of water or 25 grams of soil is spiked with a surrogate compound and extracted with methylene chloride. The extract is dried and concentrated to a volume of 1 to 3 ml. An aliquot of the extract is injected into a capillary column gas chromatograph equipped with a flame ionization detector (FID). Quantitation is performed by comparing the total chromatographic area between C₁₀ and C₂₈, both resolved and unresolved peaks, to the response of the diesel calibration standard.
- 1.5.2 This method is primarily a modification of the API consensus method "Method for the Determination of Diesel Range Organics," Revision 2, 2/5/92. (See section 11.11) It is based in part on USEPA Methods 8000 and 8100, SW-846, "Test Methods for Evaluating Solid Waste," 3rd Edition (11.1), Method OA-2 (11.2), and work by the EPA Total Petroleum Hydrocarbons Method Committee (11.3), and the State of Oregon, "Total Petroleum Hydrocarbon Methods" QAR 340-122-350, dated December 11, 1990.

2.0 Definitions

- 2.1 Diesel Range Organics (DRO): All chromatographic peaks, both resolved and unresolved, eluting between n-decane (C₁₀) and n-octacosane (C₂₈). Quantitation is based on direct comparison of the area within this range to the total area of the diesel standard, as determined from FID response using baseline integration.
- 2.2 Diesel Calibration Standard (DCS): Analytical Resources, Inc. (ARI) uses a certified, commercially prepared standard.
- 2.3 Surrogate Control Standard (SCS): Methyl arachidate is used by ARI.
- 2.4 Laboratory Control Sample: A reagent water or method blank sample spiked with a commercial diesel fuel other than those blended to make the Diesel Standard (2.2). The control sample is used a quality control check. The spike recovery is used to evaluate method control.
- 2.5 Pattern Recognition Standards: Various commercial petroleum products used by the laboratory to identify specific petroleum product types.



- 2.6 N-Alkane Standard (NAS): A mixture of normal alkanes, decane and octacosane (C₁₀ and C₂₈) at a minimum. This standard serves to verify expected boiling point ranges for petroleum products, to provide data on column performance, and to define the retention time window for Diesel Range Organics.
- 2.7 Other terms are as defined in SW-486 (11.1).

3.0 Equipment

- 3.1 Gas Chromatograph: HP 5890 GC with HP 7673A Autosampler and AK required accessories, including a Flame Ionization Detector (FID), column supplies, gases, and syringes. A data system capable of determining peak areas of retention time ranges as well as storing and reintegrating GC data is used.
- 3.2 Columns: 30 mm x .53 mm ID J + W DB-5
- 3.3 Ultrasonic cell disrupter: A horn-type sonicator equipped with a titanium tip should be used. A heat Systems-Ultrasonics, Inc. Model W-385 (475 watt) sonicator or equivalent (power wattage must be a minimum of 375 with pulsing capacity and No. 200 1/2" Tapped Disrupter Horn) plus No. 307 3/4" Tapped Disrupter Horn, and No. 419 1/8" Standard tapered Microtip probe.
- 3.4 A Sonabox is recommended for use with the above disrupter for decreasing sound (Heat Systems-Ultrasonics, Inc. Model 432 13 or equivalent).
- 3.5 Nitrogen evaporator with high purity (grade 4.5 or equivalent) nitrogen gas source.
- 3.6 Reagent water: Carbon-filtered deionized water which has been shown to be free from Diesel Range Organic compounds -- a Millipore system or equivalent is recommended.
- 3.7 Methylene chloride, hexane, acetone (pesticide grade or equivalent).
- 3.8 Sodium sulfate: ACS grade, granular, anhydrous. Purify by heating at 400°C for 4 - 8 hours in a shallow tray, or by extracting three times with methylene chloride and drying at 105°C.
- 3.9 Stock standard solution: Prepare the stock standards listed below. Unless noted, all are prepared in the methylene chloride listed in 7.2 above. Standard preparation should follow guidelines in Method 8000 (11.1).
- 3.9.1 Surrogate Control Standard: 1500 µg/ml Methyl Arachidate in MeCl₂.
- 3.9.2 Diesel Calibration Standard: Commercial certified stock -- 5 pt. curve.



- 3.9.3 Normal Alkane Standard (NAS): A stock solution of C₁₀, C₂₈, and surrogate at minimum which may contain other alkanes. This multi-component blend of alkanes serves as a retention time window defining mix for DRO.

4.0 Documentation

N/A

5.0 Inhouse Modifications to Referenced Method

N/A

6.0 Procedures

6.1 Sample Preparation

- 6.1.1 Waters are extracted according to SW-846 Method 3510 (Separatory Funnel Liquid-Liquid Extraction). Soil samples are extracted using Method 3550 (Sonication).

6.1.2 Water Extraction — Separatory Funnel

- 6.1.2.1 Measure a 1 liter portion of the sample and transfer to the 2 liter separatory funnel. If the sample is in a 1 liter or smaller bottle, mark the water meniscus on the side of the sample bottle for later determination of the sample volume. (See appropriate Extractions SOP for further details.)

- 6.1.2.2 Check and note the pH.

- 6.1.2.3 Add Methyl Arachidate surrogate standard. Recommended level is 75 µg/L in water samples.

- 6.1.2.4 For every batch or 20 samples extracted, whichever is more frequent, prepare Laboratory Control Samples by adding 0.3 ml of 5000 µg/ml LCS to 1 liter of carbon-filtered water. Daily (or for every 20 samples, whichever is more frequent) prepare a blank/surrogate control standard using 1 liter of carbon-filtered, organic-free water.



- 6.1.2.5 Carefully concentrate the extract to 3 ml under a gentle stream of nitrogen, using the N-evap apparatus. If the extract is highly colored, forms a precipitate, or stops evaporating, the final volume should be higher (5 - 10 ml). Transfer 1 ml to a GC autosampler vial for analysis.
- 6.1.2.6 Record information for the extraction and concentration steps.
- 6.1.3 Soil Preparation — Sonication
- 6.1.3.1 Decant any water layer which may accompany the solid layer in the sample. Note what percent of the sample the water represents and, if sufficient volume exists, analyze the water using the appropriate methods. Also document the apparent condition of the sample (e.g., presence of foreign materials, variable particle size, presence of oil sheen, multiple phases, etc.)
- 6.1.3.2 Since final numbers are reported as mg/dry Kg, a moisture determination must be made. Pre-weigh an aluminum weighing boat. Weigh 5 - 10 g of the sample into the boat and record both weights on a percent moisture worksheet. Dry the sample in a 105° C oven overnight. If necessary, cool in a desiccator until the sample reaches room temperature, and re-weigh for the moisture determination.
1. $\% \text{ Moisture} = (A-C)/(A-B) \times 100$, where A = weight of boat + wet sample, B = weight of boat, and C = weight of boat + dry sample.
- 6.1.3.3 Weigh 10-25 g of the original sample into a 250 ml centrifuge bottle and record the weight to the nearest 0.001 g. Add 25 g of dried Na_2SO_4 and stir the mixture well with a steel spatula (do not use plastic). The sample should have a grainy texture. If it forms a large clump, add more Na_2SO_4 and note the total weight of dehydrant used.
- 6.1.3.4 Add 100 ml of CH_2Cl_2 to all samples.



- 6.1.3.5 Add 0.05 ml of 1500 $\mu\text{g/ml}$ methyl arachidate to all samples and controls. Mix the samples immediately. Also see section 10.5.
- 6.1.3.6 Add 0.5 ml of 5000 $\mu\text{g/ml}$ LCS to the laboratory control sample. These samples should contain approximately 25 g of Na_2SO_4 .
- 6.1.3.7 Sonicate the samples for 1.5 minutes at an output setting of 10, with the 3/4 inch sonicator horn 1/2 inch below the surface of the solvent. The sonicator should be in the 1 second pulse mode, with the duty cycle set at 50%.
- 6.1.3.8 Decant and filter the extracts through Whatman No. 41 filter paper, using vacuum or pressure filtration, into a solvent-rinsed 500 ml graduated cylinder.
- 6.1.3.9 Repeat the extraction twice more using 100 ml aliquots of CH_2Cl_2 each time. Collect these extracts in the same cylinder described above.
- 6.1.3.10 Carefully concentrate the extract to 5.0 ml using the N-evap. apparatus. Vial approximately 1 ml for GC analysis.

6.2 Gas Chromatography

6.2.1 Recommended Conditions

Set helium column pressure to 7 psi. Set column temperature to 50°C for 3 minutes, then ramp at a rate of 15°C/min. to 280°C and hold for 15 minutes. Set FID Detector to 350°C and injector to 250°C .

6.3 Calibration

- 6.3.1 Calibrate the GC with at least 5 concentration levels using Diesel Calibration Standard (3.9.2). Tabulate the area response of the diesel against mass injected. The ratio of the response to the amount injected, defined as the response factor (RF), can be calculated for the standard at each concentration. If the percent relative standard deviation (%RSD) is less than 25% over the working range, linearity through the origin can be assumed, and the continuing calibration response factor can be used in place of a calibration curve. If the %RSD is greater than 25%, the continuing calibration response may not be used for quantitation.



- 6.3.2 The working response factor or calibration curve must be verified on each working day by the injection of a continuing calibration standard (CCS) at a concentration mid-point on the calibration curve. If the response for this standard varies from the predicted response by more than 25%, a new calibration curve must be prepared.

$$6.3.2.1 \text{ Percent Difference} = \frac{\text{Measured Value}}{\text{Actual Value}} \times 100$$

6.4 Gas Chromatograph Analysis

- 6.4.1 If initial calibration (6.3.1) has been performed, verify the calibration by analysis of mid-point CCS (6.3.2). With each day's run, open a 24 hour analysis window. This is done by running the midpoint curve STD.
- 6.4.2 Calculate the percent difference of the daily STD from the curve. This is done for diesel range organics as a group. If the response factors have a percent difference greater than 25%, the instrument must be recalibrated (6.3.1).
- 6.4.3 A midpoint continuing calibration standard must also be run at least once every twenty samples and at the end of each sequence. If the result does not fall within 25% of the true value, all samples run before the failed QC must be reanalyzed.
- 6.4.4 A method blank must be run every sequence to determine the area generated on normal baseline bleed under the conditions prevailing in the 24 hour period. This area is generated by projecting a horizontal baseline between the retention times observed for C₁₀ and C₂₈. This laboratory control sample is integrated over the DRO area in the same manner for the field samples, and is reported as the solvent blank (11.4). Do not baseline subtract. This information is for data interpretation purposes.
- 6.4.5 Rinses should be run after any samples suspected of being highly concentrated to prevent carryover. If the blank analysis shows contamination, the column must be baked out, and subsequent blanks analyzed until the system is shown to be free from contaminants.



6.4.6 If the product concentration exceeds the linear range of the method (as defined by the range of the calibration curve) in the final extract, the extract must be diluted and reanalyzed. The response of the major peaks should be kept in the upper half of the linear range of the calibration curve.

6.4.7 Qualitative Identification (Pattern Recognition):

6.4.7.1 Although the RT window for diesel range organics is +/- 0.2 minutes, identification of diesel or other products is achieved by direct comparisons of sample chromatograms to retention times and peak patterns of standard product chromatograms.

6.4.7.2 The analyst should generate a value for diesel range organics, and should qualitatively identify diesel or other products when reporting data. The experience of the analyst weighs heavily in the interpretation of the chromatogram. The analyst should identify each sample as fast as possible, and should explain any problems or comments in the Analyst Notes or the cover letter.

7.0 Review

7.1 The analyst will review project documentation to determine if there are any special requirements for sample handling or analysis.

7.2 Data are reported and reviewed as detailed in the "Data Reporting and Review" SOPs.

8.0 Quality Control

8.1 After successful calibration (6.3), analyze a method blank. This blank is also the reagent blank sample and is analyzed with every analytical batch (20 samples) or sequence, whichever is more frequent. The surrogate recovery should be within established limits (8.7), or within the limits established by the project plan, whichever are more stringent. The method blank should not have Diesel Range Organics above the practical quantitation limit.

8.2 Every batch of 20 samples, a Laboratory Control Standard must be analyzed, using organic-free water or Sodium Sulfate as is appropriate to the samples.

8.3 If any of the criteria in 6.3, 8.1, or 8.2 are not met, the problem must be corrected before samples are analyzed.



- 8.4 Calculate the surrogate standard recovery in each sample. If recoveries are outside established limits, verify calculations, dilutions, and standard solutions. Also verify instrument performance.
- 8.4.1 High recoveries may be due to a coeluting matrix interference. Examine the sample chromatogram.
- 8.4.2 Low recoveries may be due to adsorption by the sample matrix (muskeg, tundra, forest loam, etc.).
- 8.4.3 If the surrogate recovery is outside established limits due to matrix effects, DRO results must be flagged as such.
- 8.5 Field blanks, travel blanks, matrix blanks, duplicates, and matrix spikes are recommended for specific sampling programs.
- 8.6 More stringent quality control criteria may be required by specific project plans.

9.0 Corrective Actions

9.1 Continuing Calibration

- 9.1.1 All continuing calibration standards must meet %D limits. If a standard does not meet QC limits, all samples run after the standard that last met QC limits must be rerun.
- 9.1.2 If corrective maintenance can be performed to bring the offending standard back within limits, the run may be continued at that point.
- 9.1.3 If the out of control event cannot be reconciled, a new initial calibration sequence must be run.

9.2 Recovery limits

- 9.2.1 All surrogates, LCS extracts, and matrix spikes must meet Quality Assurance Project Plan (QAPP) recovery limits or be reextracted and/or rerun.
- 9.2.2 Before reanalysis, the analyst should attempt to determine the cause of the problem and correct it.
- 9.2.3 Because the internal QC limits have been determined for soil and water matrices only, they may not apply to other matrices such as oily soils, sludges, etc.

- 9.3 See Method 8000 for further corrective action procedures.



10.0 Miscellaneous Notes and Precautions

- 10.1 Other organic compounds including, but not limited to, animal and vegetable oil and grease, chlorinated hydrocarbons, phenols, phthalate esters, and biogenic terpenes are measurable under the conditions of this method. Heavier petroleum products such as lubricating oil and crude oil also produce a response within the retention time range for DRO. As defined in the method, the DRO results include these compounds.
- 10.2 Method interferences are reduced by washing all glassware with hot, soapy water and then rinsing it with tap water, methanol, and methylene chloride. Heating the glassware to reduce contaminants should not be necessary if this cleaning method is followed. At least one method blank must be analyzed with each extraction batch to demonstrate that the samples are free from method interferences.
- 10.3 High purity reagents such as Burdick and Jackson GC² methylene chloride or Baker capillary grade methylene chloride must be used to minimize interference problems.
- 10.4 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a solvent blank to check for cross-contamination.
- 10.5 Based on screen runs or historical data from a particular project, the GC Supervisor may decide to modify the usual extraction level. Such modifications may include decreased sample amount, increased final extract volume, and increased surrogate level. The analyst will also have discretion to dilute sample extracts prior to analysis based on visual inspection.

11.0 Method References

- 11.1 Alaska Department of Environmental Conservation, "Method for the Determination of Diesel Range Organics", AK102, Draft, 1 July 1992.

12.0 Appendices

- 12.1 Acceptance Criteria for Quality Control



12.1 ACCEPTANCE CRITERIA FOR QUALITY CONTROL

Analyte	Spike Concentration	
	Water mg/L	Soil mg/Kg
<u>Lab Control Samples</u>		
Diesel Range Organics	1.5	100
<u>Lab Control Samples</u>		
Methyl Arachidate	0.075	30
<u>Field Samples</u>		
Methyl Arachidate	0.075	30

Analyte	Control Limits	
	Water mg/L	Soil/Sediment (mg/Kg)
<u>Laboratory Control Samples</u>		
<u>Matrix Spike/Matrix Spike Dup.</u>		
Diesel Range Organics	60-120	60-120
<u>Laboratory Control Samples</u>		
Methyl Arachidate	52-138	50-150
<u>Field Sample Surrogate Recovery</u>		
Methyl Arachidate	32-157	33-160



ANALYTICAL
RESOURCES
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Standard Operating Procedure

Determination of Gasoline Range Organics (AK101 - 2/92)

422S

Revision 1

7/6/94

PROPRIETARY

Prepared By:

[Signature]

Approvals:

NA
Section Manager

[Signature]
Laboratory Manager

[Signature]
Quality Assurance Manager

[Signature]
Laboratory Director

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Standard Operating Procedure

Determination of Gasoline Range Organics - Alaska Method AK101 (1992)

1.0 Scope and Application

1.1 Analytes

- 1.1.1 This method is designed to measure the concentration of gasoline range organics in water and soil. This corresponds to an alkane range of C₆ - C₁₀ and a boiling point range between approximately 60°C and 170°C.
- 1.1.2 Components greater than C₁₀ which are present in products such as diesel or fuel oil are detectable under the conditions of the method. If, based on a review of the chromatogram, the presence of these product types is suspected, the client should be informed. Gasoline or other specific products or compounds may be identified by the use of pattern recognition techniques. This may include, but is not limited to, analysis of additional reference materials. These additional efforts are not contained within this method.
- 1.1.3 With the optional photolionization detector (PID), this method can be extended for specific determination of volatile aromatics (BTEX) as specified in EPA method 602/8020.

1.2 Quantitation Limits

- ~~1.2.1~~ The Method Reporting Limit (MRL) of this method for gasoline range organics is approximately 4 mg/kg for soils and 0.1 mg/L for ground water.

1.3 Dynamic Range

- 1.3.1 Dilutions should be performed as necessary to put the chromatographic envelope within the linear range of the method. In general, the approximate range is 0.25 to 25 mg/L of gasoline.

1.4 Experience

- 1.4.1 This method is based on a purge-and-trap, Gas Chromatography (GC) procedure. This method should be used by, or under the supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatographs. The analysts should be skilled in the interpretation of gas chromatograms and their use as a quantitative tool.



2.0 Definitions

- 2.1 Gasoline Range Organics (GRO): All chromatographic peaks, both resolved and unresolved, eluting between C₆ and C₁₀. Quantitation is based on a direct comparison of the baseline - baseline integrated area within this range to the total area of the calibration standard using FID response.
- 2.2 Surrogate Control Standard (SCS): Bromobenzene and trifluorotoluene are used as a laboratory control and to normalize GRO concentrations.
- 2.3 Laboratory Control Sample: A reagent water or method blank sample spiked with gasoline at a concentration equal to the calibration standard. The spike recovery is used to evaluate method control.
- 2.4 Pattern Recognition Standards: Various commercial gasolines and other petroleum products used by the laboratory to identify petroleum products.
- 2.5 Normal Alkane Standard (NAS): A normal alkane standard (C₆ and C₁₀) which is analyzed with each analytical batch, a batch not exceeding 20 samples. This standard is used to verify the gasoline quantitation range.
- 2.6 Other terms are as defined in SW-846 (11.1)

3.0 Equipment

- 3.1 40 mL amber glass VOA vials with Teflon-lined septa and screwcaps.
- 3.2 Volumetric flasks, class A: 10 mL, 50 mL, 100 mL, 500 mL, and 1000 mL with ground glass stoppers.
- 3.3 Disposable pipets: Pasteur.
- 3.4 5 mL Luerlock glass syringe and 5 mL gas-tight syringe with shutoff valve.
- 3.5 For purging large sample volumes for low detection limit analysis, 25 or 50 mL syringes may be used. Remember to adjust other volumes as necessary throughout the method.
- 3.6 Microsyringes: 1, 5, 10, 25, 100, 250, 500, and 1000 μ L.
- 3.7 Analytical balance capable of accurately weighing to the nearest 0.0001 g for preparation of standards, and a top-loading balance capable of weighing to the nearest 0.1 g for samples.
- 3.8 Stainless steel spatula.



- 3.9 Gas Chromatograph: HP 5890 GC with an OI 4460 concentrator and all required accessories, including detectors (FID required, additional PID optional), column supplies, gases, and syringes. Also required is a data system capable of determining peak areas using a forced baseline and baseline projection.
- 3.10 Column 1: 30 m x 0.53 mm I.D. J & W DB-624
- 3.11 Reagent Water: Carbon-filtered, purged water which has been shown to be free from purgeable compounds. (Referred to as organic-free water.) Helium is the purge gas.
- 3.12 Reagent grade Methanol (or equivalent). Store away from other solvents.
- 3.13 Stock Standard Solutions: Prepare the following stock standards. Unless noted, all are prepared using the methanol listed above as a solvent. Standard preparation should follow guidelines in SW 846 (11.1). All standards must be stored without headspace at -10 to -20°C and must be protected from light. Properly stored standards must be replaced within 6 months of preparation. Standards should be checked regularly to assure their integrity.
- 3.13.1 Recommended Surrogate Standard: 2.5 µg/mL of bromobenzene and 5.0 µg/mL trifluorotoluene. Add 140 µL of this surrogate directly into the 14 mL autosampler vial with every water sample and reference standard analyzed. Surrogate is spiked into soil samples during extraction.
- 3.13.2 Stock Standard for Laboratory Control Samples: From a certified gasoline solution, prepare a dilution of 5000 µg/mL in methanol. Addition of the following amounts yields the indicated concentrations:
- | | |
|--------------------------------|-----------|
| 0.007 mL added to 14 mL water: | 2.5 mg/L |
| 0.25 mL added to 5 g soil: | 250 mg/Kg |

4.0 Documentation

N/A

5.0 Inhouse Modifications to Referenced Method

- 5.1 The method section on sample collection techniques for soils has been omitted.
- 5.2 Section 6.7.3: Retention time windows are set at ±0.15 minutes.

6.0 Procedures

- 6.1 Volatile compounds are introduced into the gas chromatograph by purge-and-trap. The purge gas (helium) should be set at a flow rate of 35 - 40 mL/minute. Purge time is set at 11 minutes.



6.2 Waters:

- 6.2.1 Purge-and-trap may be used directly on most water samples.
- 6.2.2 Water samples high in dispersed sediments (non-settling or slow settling solids) must NOT be filtered before analysis, as this results in loss of volatiles. In most cases, a muddy water sample can be left undisturbed until the solids settle. Then an aliquot of the sample can be taken with a 5 mL syringe, as long as the sediment layer is left undisturbed. Introduction of the sediment into the purge device can result in occlusion of the frit, leading to incomplete purging of the sample and low-biased results. In any case, sample preparation should be noted, and an approximate volume given for the solids, if they are present.

6.3 Soils and Sediments:

- 6.3.1 Soils and solids are methanol extracted. An aliquot of the extract is added to reagent water, and is analyzed according to section 9.8, Gas Chromatograph Analysis.
- 6.3.2 Samples may be collected into tared, methanol-containing VOA vials.
- 6.3.3 Weigh the sample vial upon receipt and record the total filled weight. Shake the vial for 2 minutes and allow the sediment to settle. Transfer an aliquot of the extract into an amber glass vial with a Teflon-lined septum in the screw cap and store without headspace at 4°C.

6.4 Normally Collected Soils and Sediments:

- 6.4.1 When solids are collected by the sampling techniques in SW-846 (11.1), volatile results are biased low. Therefore, data from these samples (collected without methanol preservative) must be reported as "greater than or equal to" ($\geq$) the calculated mg/Kg GRO, and they may not be accepted as valid by State project managers.
- 6.4.2 In order to prepare extracts from these types of collection containers, gently mix the contents of the sample container with a narrow metal spatula. Do not discard any supernatant liquids, as the entire contents of the sample container must be represented.
- 6.4.3 For sediment/soil and waste that are insoluble in methanol, weigh 5.0 g (wet weight) of sample into a tared 20 mL vial, using a top loading balance. Note and record the actual weight to 0.1 g.



- 6.4.4 Quickly add 4.75 mL of methanol and 0.25 mL of the 100/50 µg/mL stock surrogate spiking solution to the vial. Or, after adding spiking solution, fill to the line on the vial. Cap and shake for 1 minute. Centrifuge the extract for 10 minutes at 1/2 speed. Transfer 140 µL of the extract to a 14 mL water-filled autosampler vial.
- 6.4.5 Allow sediment to settle, pipet an aliquot to an amber glass vial for storage at 4°C with zero headspace.
- 6.4.6 These steps MUST be performed rapidly and without interruption, in a laboratory free from solvent fumes, to avoid loss of volatile organics or cross contamination.
- 6.5 Sample Screening: It is highly recommended that all samples be screened prior to analysis, as they may contain enough petroleum product to overload the column or the detectors.
- 6.6 Gas Chromatography Conditions (recommended):
- 6.6.1 Column 1: Set helium column pressure to 6 psi. Set column temperature to 45°C for 3 minutes. Then ramp at a rate of 6°C/minute to 100°C then 20°C/minute to 240°C, and hold for 5 minutes. Conditions may be altered to improve the resolution of gasoline range organics.
- 6.7 Analysis
- 6.7.1 Tabulate the area response of the gasoline against mass injected. The ratio of the response to the amount injected, defined as the response factor (RF), can be calculated for the standard at each concentration. If the percent relative standard deviation (%RSD) is less than 25% over the working range, linearity is assumed and the continuing calibration standard may be used in place of the curve. If the %RSD is greater than 25%, the calibration curve must be used.

$$\text{Response Factor} = \frac{\text{Total Area of gasoline standard}}{\text{Gasoline standard amount (µg/mL)}}$$

- 6.7.2 Continuing calibration standards are run after every 10 samples to verify the working curve. Calculated amounts must be within $\pm 25\%$ D from the true amount.



$$\%D = \frac{\text{measured concentration}}{\text{actual concentration}} \times 100$$

6.7.3 Retention Time Windows and Pattern Recognition: The RT window for individual compounds within the gasoline range is ± 0.15 minutes. However, the experience of the analyst weighs heavily in the interpretation of the chromatogram. References 11.6, 11.7, and 11.8 contain some information on hydrocarbon pattern recognition. Environmental samples may contain more than one type of product, and loss of light-end components may indicate that the product has been in the subsurface a longer period of time. It may also make product identification tentative at best. The analyst should make a determination of Yes or No for the ID of gas. Any further explanation will be taken care of in the analyst notes or cover letter.

6.7.3.1 Quantitation of the gasoline range organics is based on summed, baseline-baseline integration of all resolved and unresolved peaks eluting between C₆ and C₁₀. Qualitative identification of gasoline may include all the same peaks or the analyst may eliminate some peaks. For instance, peaks could be deleted due to unusual peak shape. Other analyses, such as GC/MS, may be used to identify interferences.

6.7.3.2 Note: Although the retention time window definition introduces a low bias (55 to 75% for gasoline in Ottawa Sand), it improves precision and reduces interferences from heavier petroleum components.

6.8 Gas Chromatograph Analysis:

6.8.1 Samples are analyzed by GC/FID. 5 mLs of water from the 14 mL autosampler vials is introduced into the programmed gas chromatograph (section 6.2) using purge-and-trap sample concentration.

6.8.2 If a new run is being started, verify the calibration curve by analysis of the initial calibration standard.



- 6.8.3 Calculate the percent difference of the calibration standard response factor from the midpoint curve standard response factor (as in 6.7.1). This is done for gasoline as a "group" from the CCS. Percent difference should be $\leq 25\%$.
- 6.8.4 A reagent water blank or method blank must be run in every sequence to determine the area generated from normal baseline noise under the conditions prevailing within the 12 hour period. Addition of the 100 μL of methanol to the blank is made when soil/sediment extracts are to be analyzed. This area is generated by projecting a horizontal baseline between the retention times observed for C_6 and C_{10} . This lab control sample is integrated over the GRO area in the same manner as for the field samples, and is reported as the instrument or reagent blank. Do not blank subtract. This information is for data interpretation purposes only.
- 6.8.5 Blanks should also be run after samples suspected of being highly concentrated to prevent carryover. If the blank analysis shows contamination, the trap and/or column must be baked out, and subsequent blanks must be analyzed until the system is shown to be free from contaminants.
- 6.8.6 Dilutions:
- 6.8.6.1 If the product concentration exceeds the linear range of the method as defined by the range of the calibration curve, the sample (or extract or dilution) must be diluted and reanalyzed. The response of the major peaks should be kept in the upper half of the linear range of the calibration curve.
- 6.8.6.2 Inject the proper aliquot of sample from the syringe into the 14 mL vial. Aliquots of less than 1 mL are not recommended for dilution of water samples using this method. Make sure aliquot is introduced well below the surface of the reagent water in the volumetric flask to minimize sample loss.



6.8.6.3 Alternative Dilution Technique: The dilutions can be made directly in the glass syringe to avoid loss of volatiles. If diluting methanol extracts, follow 6.2.2 using a smaller volume of extract in the 5 mL purge volume or the procedure outlined for the dilution of water samples.

6.9 Moisture Determination for Solids

6.9.1 Moisture determinations should accompany all soils data (reported in mg/dry Kg) so the client can determine the results in the original soil condition. Reporting in mg/dry Kg can be done only if an unpreserved portion of the sample has been provided.

6.9.2 In order to determine percent moisture, pre-weigh an aluminum weighing boat. Weigh 5 - 10 g of the sample into the boat and record both weights to the nearest 0.01 g. Dry the sample overnight in an oven at 105°C.

6.9.3 Remove the sample from the oven and cool in a desiccator until the sample reaches room temperature, and weigh to the nearest 0.01 g. Record the weight.

6.10 Calculations:

6.10.1 External Standard Calibration:

The concentration of Gasoline Range Organics in the sample is determined by calculating the absolute weight of analyte purged from a summation of peak response for all chromatographic peaks, resolved and unresolved, eluting between C₆ and C₁₀. Refer to section 6.7.3. The concentration of Gasoline Range Organics is calculated as follows:

$$\text{Soil Sample Conc. mg/kg} = \text{As/A}_G \times 2.5 \times 100^*/\text{PS}$$

$$\text{Water Sample Conc. } \mu\text{g/L} = \text{As/A}_G \times 2.5$$

where: 2.5 = concentration standard (ng/mL)

A_G = Group area of gasoline calibration standard (minus Bromobenzene surrogate area)

A_s = Group area of sample (minus Bromobenzene surrogate area)

Ps = Percent solids (as fraction of 1.00)



Note = * Indicates that 100 is the correction factor for soils.
It corrects for the discrepancy between the
amount purged for soil samples versus the
standards. (0.05 g vs. 5 mL).

6.10.2 Moisture Determination (%)

$$\text{Moisture (\%)} = (A-C)/(A-B) \times 100$$

Where:

- A = weight of aluminum boat + wet sample
- B = weight of boat
- C = weight of boat + dry sample

7.0 Review

- 7.1 The analyst will review project documentation to determine if there are any special requirements for sample handling or analysis.
- 7.2 Data are reported and reviewed as detailed in the "Data Reporting and Review" SOPs.

8.0 Quality Control

- 8.1 The laboratory must, on an ongoing basis, demonstrate through the analysis of quality control check standards that the operation of the measurement system is in control. This should include the analysis of QC check samples, plus the calculation of average recovery, and the standard deviation of the recovery as outlined in Method 8000, Section 8.0.
- 8.2 After successful calibration, begin analysis with the method blank and LCS for the sample batch. The surrogate and spike recoveries for each blank should be within internal limits (see 12.3).
- 8.3 After every batch (no more than 20 samples), a Laboratory Control Sample must be analyzed. The matrix for this sample should be reagent water for aqueous samples or methanol for soil samples.
- 8.4 With every batch of samples extracted, a method blank must be analyzed. The blank should have GRO less than the detection limit.
- 8.5 If any of the criteria in 8.2 and 8.3 are not met, the problem must be corrected before samples are analyzed.



- 8.6 Calculate the surrogate standard recovery in each sample. If recoveries are outside established limits, verify calculations, dilutions, and standard solutions. Verify instrument performance.
- 8.6.1 High recoveries may be due to a coeluting matrix interference examine the sample chromatogram.
 - 8.6.2 Low recoveries may be due to adsorption by the sample matrix (i.e. high humus soils).
 - 8.6.3 Low recoveries may also be due to a poor purge (clogged purge tube or frit). If this is suspected, check the purge tube with a blank before reanalyzing the sample.
 - 8.6.4 If the surrogate recovery is outside established limits due to suspected matrix effects, GRO results must be flagged to note this fact.

9.0 Corrective Actions

9.1 Continuing Calibration

- 9.1.1 All continuing calibration standards must meet 25 %D limits. If a standard does not meet QC limits, all samples run after the standard that last met QC limits must be rerun.
- 9.1.2 If corrective maintenance can be performed to bring the offending standard back within limits, the run may be continued at that point.
- 9.1.3 If the out of control event cannot be reconciled, a new initial calibration sequence must be run.

9.2 Recovery limits

- 9.2.1 All surrogates, LCS extracts, and matrix spikes must meet Quality Assurance Project Plan (QAPP) recovery limits or be reextracted and/or rerun.
- 9.2.2 Before reanalysis, the analyst should attempt to determine the cause of the problem and correct it.
- 9.2.3 Because the internal QC limits have been determined for soil and water matrices only, they may not apply to other matrices such as oily soils, sludges, etc.

- 9.3 See Method 8000 for further corrective action procedures.



10.0 Miscellaneous Notes and Precautions

10.1 Safety Issues: The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets is available to all personnel involved in chemical analyses. Additional references to laboratory safety are available and identified for the information of the analyst.

10.2 Interferences

10.2.1 High levels of heavier petroleum products such as diesel or heating fuel may contain some volatile components, which will produce a response within the retention time range for GRO. Other organic compounds, including chlorinated solvents, ketones, and ethers are also detectable by this method. As defined in the method, the GRO results include these compounds.

10.2.2 Samples can become contaminated by diffusion of volatile organic through the sample container septum during shipment and storage. A trip blank prepared from organic-free water or methanol (for soils) and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

10.2.3 Glassware prepared in advance to accept soil samples (methanol-containing VOA vials) may lose its seal from changes in ambient temperature which result in changes in vapor pressure within the vials. In order to prevent loss or contamination of methanol solvent, sampling containers must be kept at 4°C from the time they are prepared through the time that analysis of the collected sample is completed.

10.2.4 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe and/or purging device must be rinsed between samples with reagent water or methanol. Whenever an unusually concentrated



sample is encountered, it should be followed by analysis of a solvent blank or reagent water to check for cross contamination. For volatile samples containing high concentrations of water-soluble materials, suspended solids, high boiling compounds, or organohalides, it may be necessary between analyses to wash the syringe or purging device with a detergent solution, then rinse with distilled water and methanol, and dry in a 105°C oven. The trap and other parts of the system are also subject to contamination. Therefore, frequent bake-out and purge of the entire system may be required. A screening of all samples prior to analysis is recommended to protect analytical instrumentation (section 6.5).

11.0 Method References

- 11.1 Alaska Department of Environmental Conservation, "Method for the Determination of Gasoline Range Organics", AK101, Draft, 1 July 1992.

12.0 Appendices

- 12.1 Recommended purge and trap operating parameters
- 12.2 Acceptance criteria for quality control



Appendix

12.1 Recommended purge and trap operating parameters (For GRO)

<u>Parameter</u>	<u>Setting</u>
Purge Gas	Helium
Purge Gas Flow Rate (mL/min.)	35 - 40
Purge Time (min.)	11 min.
Purge Temperature (°C)	Ambient
Desorb Temperature (°C)	180
Backflush Inert Gas Flow (mL/min.)	20 - 60
Desorb Time	4
Trap Bake-out time	7 min.
Bake Temperature (°C)	180



12.2 Acceptance Criteria for Quality Control

<u>Analyte</u>	<u>Spike Concentration</u>	
	<u>Water mg/L</u>	<u>Soil mg/Kg</u>
<u>Lab Control Samples</u>		
Gasoline Range Organics	2.5	250
<u>Laboratory Control Samples</u>		
Trifluorotoluene and Bromofluorobenzene	0.05/0.025	5.0/2.5
<u>Field Sample Surrogate Recovery</u>		
Trifluorotoluene and Bromofluorobenzene	0.05/0.025	5.0/2.5
<u>Continuing Calibration</u>		
See 3.13	2.5	125

<u>Analyte</u>	<u>Water mg/L</u>	<u>Control Limits</u>	<u>Soil/Sediment (mg/Kg)</u>
<u>Laboratory Control Samples</u>			
Gasoline Range Organics	89-111		79-112
<u>Laboratory Control Samples</u>			
Trifluorotoluene	79-110		80-112
Bromofluorobenzene	70-117		73-117
<u>Matrix Spike/Matrix Spike Dup.</u>			
Gasoline Range Organics	60-120		60-120
<u>Field Sample Surrogate Recovery</u>			
Trifluorotoluene	76-111		50-150
Bromofluorobenzene	71-121		50-150



ANALYTICAL
RESOURCES
INCORPORATED

Standard Operating Procedure

Total Organic Carbon
Method 9060A - (United States Air Force)

602S

Revision 1

4/4/94

PROPRIETARY

Prepared By:

M. K. Kuhn

Approvals:

[Signature]
Section Manager

[Signature]
Laboratory Manager

Michelle J. Turner
Quality Assurance Manager

[Signature]
Laboratory Director

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STANDARD OPERATING PROCEDURE TOTAL ORGANIC CARBON

METHOD: UV PERSULFATE OXIDATION, DIRECT COMBUSTION (AQUEOUS)

DIRECT COMBUSTION (SOLIDS)

RANGE: 10 ppb - 30,000 ppm NPOC

HOLDING TIME: Aqueous: 28 days

Soils: 28 days

PRESERVATIVE: pH < 2 with H₂SO₄ TEMP @ 4C

1.0. Scope and Application

1.1. General Information. The total carbon (TC) content of either aqueous solutions or solids may be divided into inorganic and organic forms. Inorganic carbon (IC) consists predominantly of bicarbonate and carbonate or mineral complexes thereof. Total organic carbon (TOC) includes all reduced, covalently bonded carbon atoms in organic molecules. Dependent upon sample matrix, these can be operationally defined: Aqueous samples include a separation into dissolved (DOC) and non-dissolved (particulate or NDOC) fractions based upon a 0.45µm filtration. These fractions can be further separated into purgeable (POC) and non-purgeable (NPOC) fractions based upon their behavior under acidic conditions and the general volatility of many organic compounds. Solid phase samples contain both volatile and non-volatile species.

In the analysis of organic carbon, reduced carbon compounds are oxidized to carbon dioxide (CO₂) using either wet oxidation or direct combustion technique. Specific reference methods for the analysis of organic carbon in either aqueous or solid phase samples are all basically the same (see Section 11). Each method addresses issues related to the removal or measurement of inorganic carbon (IC) and sample pretreatment prior to the actual analysis of the organic carbon fraction. Measurement of evolved organic carbon as carbon dioxide or methane is dependent upon the capabilities of the analytical instrumentation and all referenced methods defer to the specific manufacturers instructions for detailed operating procedures and protocol.

We use two different organic carbon analyzers, a Dohrmann DC-180 for low level aqueous samples and a Dohrmann DC-190 for high level aqueous samples (see Appendix for simplified flow diagrams). The DC-180 employs internal sparging of IC with UV-persulfate wet oxidation for the conversion of remaining organic carbon to CO₂. As presently configured, the instrument is not capable of a separate analysis for POC. The DC-190 uses external sparging of IC and direct catalytic combustion for the conversion of organic carbon to CO₂. The DC-190 is configured for a separate analysis for POC. Both analyzers use non-dispersive infrared detection (NDIR) for the analysis of CO₂ evolved as a result of the oxidation process. The analytical modes for both instruments relative to the form of carbon measured is operator selectable (TC, IC, POC, NPOC, TOC). The service request for analytical services should specify the desired form of carbon. Unless otherwise specified, our standard analytical mode for aqueous samples is for non-purgeable organic carbon (NPOC) in which inorganic carbon is sparged from the sample prior to oxidation. There will be an unavoidable loss of purgeable organics (POC) during the sparging operation.



Both instruments are equipped with external boat samplers for the analysis of solid phase samples by catalyzed combustion in a resistance furnace, the DC-190 having a higher operating range. Solid phase samples are processed independently for the removal of inorganic carbon and the resulting analysis is for NPOC (purgeable organics being lost during the pretreatment).

1.2. Interferences.

1.2.1. Inorganic carbon. Inorganic carbon consists predominantly of bicarbonate and carbonate which will evolve as CO_2 during the analysis and hence constitute a positive interference unless corrected for or removed by purging with dilute acid. Inorganic carbon must always be accounted for in either aqueous or solid phase samples.

1.2.2. Chloride. For aqueous solutions, chloride concentration in excess of 0.1% (1,000 ppm) will interfere with the oxidation rate of organic material using the UV-persulfate procedure and result in low recoveries and poor response time (a noticeable tailing of the CO_2 peak during the analysis). This effect can be reduced by complexation of chloride with mercuric salts. Mercuric salt solution (described below) should be used for all marine samples and those samples suspected to have a high chloride concentration.

2.0. Definitions

2.1. TC (Total Carbon). The sum of both inorganic and organic carbon present in a sample. It is equivalent to $\text{TOC} + \text{IC}$.

2.2. IC (Inorganic Carbon). The sum of all oxidized forms of carbon present in a sample consisting primarily of carbonates, bicarbonates and carbon dioxide (CO_3^{2-} , HCO_3^- , CO_2).

2.3. TOC (Total Organic Carbon). The sum of all reduced, covalently bonded carbon atoms present in a sample. It is equivalent to $\text{TC} - \text{IC}$.

2.4. POC (Purgeable Organic Carbon). That fraction of the organic carbon in a sample which is lost as a result of the gas stripping for removal of inorganic carbon.

2.5. NPOC (Non Purgeable Organic Carbon). That fraction of the organic carbon content which remains in a sample following gas stripping for removal of the inorganic fraction. It is equivalent to $\text{TOC} - \text{POC}$.

2.6. IDL (Instrument Detection Limit). This is the minimum concentration of substance that can be detected as being significantly different from the background noise (Blank) level for a given instrument configuration. The value is set at approximately 3 standard deviations of the mean blank concentration for replicate analyses of the blank.



2.7. LDL (Lower Detection Limit). This is the constituent concentration that will produce a response which is 3.290 standard deviations above the mean blank response. It is determined by replicate analyses of a known standard concentration at a level near the IDL (usually < 5X the IDL).

3.0. Supplies and Equipment

3.1. General supplies and glassware

Carbon analyzers, Dohrmann DC-180, DC-190
platinum combustion boats
Analytical balance
Mortar and pestle
Microsieves (100 - 140 mesh)
30 mL glass scintillation vials
pipettes and microliter syringes
Vacuum desiccators
oxygen gas cylinder, regulator, flow manifold

3.2. Reagents

3.2.1. PHOSPHORIC ACID (20%)

3.2.1.1. PHOSPHORIC ACID (10%). Dilute the 20% solution 1:1. Use this acid for removal of inorganic carbon from solid phase samples (Lloyd Kahn technique)

3.2.2. NITRIC ACID (20%).

3.2.3. HYDROCHLORIC ACID (10%).

3.2.4. POTASSIUM PERSULFATE (2%). Dissolve 40 grams potassium persulfate ($K_2S_2O_8$) in 1 liter organic free water (finished DI). Transfer to premarked, amber persulfate storage bottle, add 4 mL concentrated phosphoric acid, mix and dilute to 2 liters. The solution should have a pH of approximately 3. Replace monthly.

3.2.5. MERCURIC SALT REAGENT. Dissolve 5 grams mercuric chloride ($HgCl_2$) and 5.9 grams mercuric nitrate monohydrate ($Hg(NO_3)_2 \cdot H_2O$) in 50 mL organic free water contained in a 100 mL volumetric flask. Add 3 mL concentrated nitric acid (HNO_3) and mix until salts have dissolved. Dilute to 100 mL. THIS REAGENT IS USED TO COUNTER THE EFFECTS OF HIGH CHLORIDE CONCENTRATIONS (MARINE SAMPLES) AND SHOULD BE ADDED TO SUCH SAMPLES AT A RATE OF 0.25 mL PER 50 mL OF SAMPLE.

3.2.6. PERSULFATE-MERCURIC SALT SOLUTION. Dissolve 8.2 grams mercuric chloride ($HgCl_2$) and 9.6 grams mercuric nitrate monohydrate ($Hg(NO_3)_2 \cdot H_2O$) in 400 mL organic free water contained in a 1000 mL volumetric flask. Add 5 mL concentrated nitric acid (HNO_3) and mix until salts have dissolved. Add 20 grams potassium persulfate ($K_2S_2O_8$), mix to dissolve and then bring to volume. THIS REAGENT IS USED TO COUNTER THE EFFECTS OF HIGH CHLORIDE CONCENTRATIONS (MARINE SAMPLES) AND SHOULD BE ADDED TO THE UV REACTOR IN PLACE OF THE USUAL POTASSIUM PERSULFATE REAGENT.



3.2.7. ORGANIC CARBON STANDARD Potassium Hydrogen Phthalate, (C₈H₅O₄K)

3.2.7.1. Stock KHP Standard (2000 ppm carbon). Dissolve 0.425 grams dried KHP (dried at 120 C and stored in desiccator) in 50 mL organic free water contained in a 100 mL volumetric flask. Add 0.1 mL 85% phosphoric acid and mix to dissolve. Dilute to volume with organic free water and store in an amber glass bottle under refrigeration. Prepare fresh stock monthly.

3.2.7.2. Calibration Standard (5 ppm carbon). Add 0.5 mL of the 2000 ppm stock to 150 mL organic free water contained in a 200 mL volumetric flask. Mix and dilute to volume. Prepare fresh with each use. (Follow the calibration instruction on page A2 of the Dohrmann manual to compensate for the system blank)

4.0. Documentation

N/A

5.0. In-house Modifications from Referenced Method

See comment above regarding specified methods and instrumentation

6.0. Procedure

6.1. Aqueous Samples

6.1.1. Calibration must be done daily and when completed must be immediately followed by a minimum of 3 blanks and 3 verification standards (5ppm). Compute 3X the standard deviation of the blanks and the check standards to establish the daily IDL and LDL respectively. The mean blank value must be < MDL and the check standard recovery must be within $\pm 10\%$. If these criteria are not satisfied, you must recalibrate. Follow the Dohrmann manuals for calibrating either instrument

6.1.2. Review the analytical service request to determine the form of organic carbon required. For relatively clean, low level samples use the Dohrmann DC-180. For high level samples and those containing significant particulate materials, use the DC-190. Following the Dohrmann manuals, program the instruments to run the required carbon fractions. Obtain a blank copy of the TOC, Aqueous Data Analysis sheet. Record all processing information on this sheet as you run each sample or prepare the autosampler vials. The sheet must correspond exactly to the output from the Dohrmann.

6.1.3. Dependent upon how you have programmed the instrument, samples may be processed by either manual injection or by autosampler. All samples must be thoroughly mixed, homogenizing in a blender if necessary, prior to withdrawing the aliquot for analysis. For analysis by autosampler, mix the samples and transfer 50 mL to the sampling tubes. Place in the autosampler tray (keeping track of the sequence numbers) and cover each tube with aluminum foil. When all blanks, standards and samples have been placed in the tray, Press (RUN) and the autosampler will start.



- 6.1.4. Special prep for high chloride marine samples (DC-180 only!!)
- 6.1.4.1. Add 10 drops mercuric salt reagent to each 50 mL sample tube and cap with plastic film and aluminum foil, mix gently.
- 6.1.4.2. The regular potassium persulfate oxidizing solution must be replaced with the persulfate-mercuric salt solution and the 20% phosphoric acid solution must be replaced with 20% nitric acid.
- 6.1.4.3. Collect and properly dispose of the mercury wastes!
- 6.1.5. Select at least one sample from each job number for duplicate and matrix spike analysis. Matrix spikes are conducted by adding 50 μ L of the 2,000 mg/L KHP standard to 5 mL of sample. This yields a spike level of 20 mg/L
- 6.2. Solid Samples (soils and sediments)
- 6.2.1. TOC in solid samples is determined by direct combustion in a medium temperature (850C) resistance furnace in an oxygen atmosphere. Each TOC analyzer is equipped with a Dohrmann DC-183 Boat Sampler module for solids analysis. Combustion products are carried in the oxygen stream through a catalytic converter to assure complete oxidation to CO₂. Samples are purged of inorganic carbon by acidification, dried at 70C and then ground to pass a 120 mesh sieve.
- 6.2.2. Pre treatment to remove inorganic carbon. Obtain a blank copy of the Solids TOC, Solids Prep Log Sheet. Transfer 1-5 grams (record exact weight) of well homogenized sample to scintillation vial. Add 4 mL of 10% HCl and observe for effervescence of CO₂. If there is any effervescence, add an additional 2 mL of acid. Place the treated vials in a vacuum desiccator and allow effervescence to stop. Transfer vials to a 70C oven to dry for 24 hours. Repeat the effervescence test and re-treat any sample which test positive. Repeat this procedure until all sample yield a negative effervescence test. Re dry the samples at 70C and return to vacuum desiccator and allow to cool. Reweigh to determine the percent solids after drying at 70C.
- 6.2.3. After the 70C dry weight is determined, grind the sample to pass a 120 mesh sieve and return the same to its vial, cap and store under vacuum desiccation until analysis.
- 6.2.4. Sample replicates (usually three) should be run through the entire pretreatment process.
- 6.2.5. From the original sample jar, take a separate sample aliquot (approximately 10 grams) of homogenized sample for the analysis of percent solids after drying at 104C.



6.2.6. Instrument set-up. Follow the Dohrmann manuals for instructions on programming the instrument for boat sampling. Turn on the NDIR, combustion furnace, printer and oxygen supply. Allow a sufficient warm-up period for the furnace (should be a bright orange glow, not yellow). When the furnace is up to temperature, pre-combust (approximately 2 minutes) the platinum combustion boats to remove any residual organics. Remove the boat and cool to RT. Obtain a blank copy of the TOC Solids Data Analysis sheet. Enter all processing data on this sheet as you run each sample. This sheet must correspond exactly to the output from the Dohrmann.

6.2.7. When cooled, transfer the empty boat to the analytical balance and zero to remove the tare weight. Transfer 0.2 - 0.8 mg of sample to the boat and reweigh. Record the exact sample weight on the TOC Run Log Benchsheet.

6.2.8. Add cupric oxide accelerator to the sample and place the boat in the push rod assembly of the combustion train. Follow the on-screen directions and slide the boat into the furnace when instructed.

6.2.9. Matrix spike analysis is conducted on post-prep samples by adding 10 μ L of the 2,000 ppm KHP (0.02 mg C) standard to a known weight of sample (0.2 - 0.8 mg). This yields a spike of 25,000 to 100,000 ppm, dependent upon sample weight used.

6.3. DATA REDUCTION

Output from the instruments will provide ppm C (mg/l or mg/kg, aqueous and solid samples respectively) uncorrected for the blank determination. These data must be further reduced on the Macintosh. Benchsheets for both aqueous and solid phase samples are the same as those you have previously filled out for the sample run.

The benchsheets are setup to calculate the mean blank determination for the days run and to correct the samples for this mean blank (by subtraction). Additionally, the benchsheets will allow for the calculation of both the Instrument Detection Limit (IDL) and the Lower Detection Limit (LDL). The IDL is based upon replicate determinations of the blank and is calculated as three times the standard deviation of those determinations. The LDL is based upon replicate determinations of either a 5 ppm check standard (aqueous) or 2,000 ppm check standard (solids) and is calculated as 3.29 times the standard deviation for those replicates. These values are used to track overall instrument performance and to update MDLs.

An additional note relative to TOC in solids. The values generated from the analyzer will be ppm C for a sample which has been purged of inorganic carbon and dried at 70C (to prevent volatilization of lower molecular weight organics). TOC values are normally reported on the basis of dry weight at 104C. A separate aliquot of sample for the determination of dry weight at 104C should have been taken. The TOC value from the Dohrmann will have to be corrected for this dry weight or reported on the basis of dry weight at 70C. Most reporting is done on the basis of dry weight at 104 C. This calculation is done by the data section during preparation of the final report.



7.0. Review

- 7.1. The supervisor reviews Service Request, enters information into the Conventional database and assigns samples to the analyst.
- 7.2. The analyst verifies Service Request, reviews the SOP and proceeds with the analysis.
- 7.3. The final computer generated result is placed into the method folder in chronological sequence and a copy is placed into the job folder.
- 7.4. The supervisor reviews the job folder for completeness of analysis (all requested parameters have been run) and sufficiency of Quality Control.
- 7.5. Completed analysis is given to the Data Section for final report preparation.
- 7.6. The final report is reviewed for accuracy and completeness and then signed by the Division Manager or other authorized person.

8.0. QC Limits

- 8.1. Initial Calibration Verification (ICV) and Calibration Blank (ICB) must be run at the beginning of each batch. Continuing Calibration Verification standards and blanks (CCV, CCB) must be run after every ten analytical samples in the batch and at the end of each run. The calibration verification standards must agree within $\pm 10\%$ of the "true" value and the concentration of the blanks should be less than the detection limit.
- 8.2. Matrix spike and duplicate analyses are run with each job number or once for every 20 samples in a job.
 - 8.2.1. Duplicate analysis. If both the original and duplicate sample concentrations are greater than 5X the detection limit, the calculated RPD should be less than 20%. If either concentration is less than 5X the detection limit, then the absolute difference between the two should be less than or equal to the detection limit. If these criteria are not satisfied, corrective actions must be taken.
 - 8.2.2. Matrix Spikes. The acceptance limits for matrix spike recoveries are $\pm 25\%$ if the original concentration is less than 4X the spike concentration added. If the original concentration is greater than 4X the added spike level, the spike is invalid and must be repeated.

9.0. Corrective Actions

- 9.1. If Initial Calibration Verification (ICV) and Initial Calibration Blank (ICB) are out of QC limits, new calibration standards or new ICV solution should be made and the instrument re calibrated. If the Continuing Calibration Verification (CCV) and Continuing Calibration Blank (CCB) are out of QC limits, all samples between the last in control condition and the out of control condition must be re-run. All samples in any batch run must be bracketed by in control verification standards.



- 9.2. After the above corrective actions, if the results are still outside the limits, the supervisor will review the entire procedure with the analyst to verify that correct procedures are being followed or check the instrument to make sure it is working properly.
- 9.3. If RPD or matrix spike recoveries are outside the prescribed limits, the analysis will be repeated to confirm the outlying condition. The sample analysis will be flagged and reported in the final report to the client.
- 9.4. If any of the following situations arises, the supervisor will be immediately notified and the project manager be informed for resolution with the client:
- Samples have exceeded holding times.
 - Samples have been improperly preserved.
 - There is insufficient sample to run the analysis.

10.0. Miscellaneous Notes and Precautions

10.1. Hazardous Wastes Streams.

11.0. Method Reference

Methods for Chemical Analysis of Water and Wastes. EPA-600/4-79-020 (Rev Mar 83).

Method 415.1. *This is a generic document which defines the basic procedures and precautions for the analysis of TOC in aqueous samples using either catalytic combustion or wet oxidation with NDIR (CO₂) or GC-FID (CH₄) detection. Specific attention is given to procedures for addressing inorganic carbon relative to the capabilities of the instrument being used. The form of carbon being measured should be stated. This method defers to instrument manufacturers instructions for detailed operating protocol.*

Standard Methods for the Examination of Water and Wastewater. 1992. 18th ED. Method 5310 B. Combustion-Infrared; Method 5310 C. Persulfate-UV Oxidation. *These are generic methods which define the basic procedures and precautions for the analysis of TOC in aqueous samples using either catalytic combustion or UV-persulfate oxidation with NDIR (CO₂) or GC-FID (CH₄) detection. Specific attention is given to procedures for addressing inorganic carbon relative to the capabilities of the instrument being used. The preferred method is to measure TC and IC and then calculate TOC by difference. Otherwise, the analysis is for NPOC. The methods defer to instrument manufacturers instructions for detailed operating protocol.*



Methods of Soil Analysis. American Society of Agronomy. Chapter 29-3. Organic Carbon. This a detailed description which defines the basic procedures and precautions for the analysis of TOC in soils and other solid phase samples. Particular emphasis is given to sample pre-treatment for the removal of inorganic carbon (5% sulfurous acid). Wet oxidation and dry combustion (>900C for total carbon) procedures are described. The methods for the final analysis of organic carbon are varied (NDIR, GC-FID, GC Thermal conductivity, gravimetric) and defer to specific instrument manufacturers instructions for operating protocol. As defined, the method will provide an estimate of NPOC

Lloyd Kahn. 1988. "Determination of Total Organic Carbon in Sediment". USEPA, Region II, Edison, NJ. This procedure is for pyrolytic combustion of sediment samples which have had inorganic carbon removed by addition of 1:1 phosphoric acid and heating to 75C. Samples are combusted wet. The methods for the final analysis of organic carbon are varied (NDIR, GC-FID, GC Thermal conductivity) and defer to specific instrument manufacturers instructions for operating protocol. As defined, the method will provide an estimate of NPOC

Plumb, R.H., 1981. "Procedures for Handling and Chemical Analysis of Sediment and Water Samples". USEPA, USACOE. Environmental Laboratory, USAE, Waterways Experiment Station. This is a generic document which defines the basic procedures and precautions for the analysis of TOC in aqueous and sediment samples using either catalytic combustion or wet oxidation with NDIR (CO₂) or GC-FID (CH₄) detection. The sediment procedure is for pyrolytic combustion (500 - 650 C for organic, >950C for inorganic) of sediment samples which have had inorganic carbon removed by addition of 10% hydrochloric acid. Samples are combusted after drying at 70C. The methods for the final analysis of organic carbon are varied (NDIR, GC-FID, GC Thermal conductivity) and defer to specific instrument manufacturers instructions for operating protocol. As defined, the method will provide an estimate of NPOC

Puget Sound Estuarine Protocol. March 1986. Total Organic Carbon. This procedure is for Induction furnace combustion (950 C) of sediment samples which have had inorganic carbon removed by addition of 10% hydrochloric acid. Samples are combusted after drying at 70C. The methods for the final analysis of organic carbon are varied (gravimetric, Thermal conductivity) and defer to specific instrument manufacturers instructions for operating protocol. As defined, the method will provide an estimate of NPOC

Test Methods for Evaluating Solid Wastes. EPA, SW-846. Volume 1C. Method 9060A. Rev. Nov. 1990. This document defines the basic procedures and precautions for the analysis of TOC in aqueous samples using either catalytic combustion or wet oxidation with NDIR (CO₂) or GC-FID (CH₄) detection. Specific attention is given to procedures for addressing inorganic carbon relative to the capabilities of the instrument being used. The preferred method is to measure TC and IC and then calculate TOC by difference. Otherwise, the analysis is for NPOC. Quadruplicate analysis of aqueous samples is required. This method defers to instrument manufacturers instructions for detailed operating protocol.

Total Organic Carbon
602S

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12.0 Appendices

Dahrmann DC-180 Flow Diagram

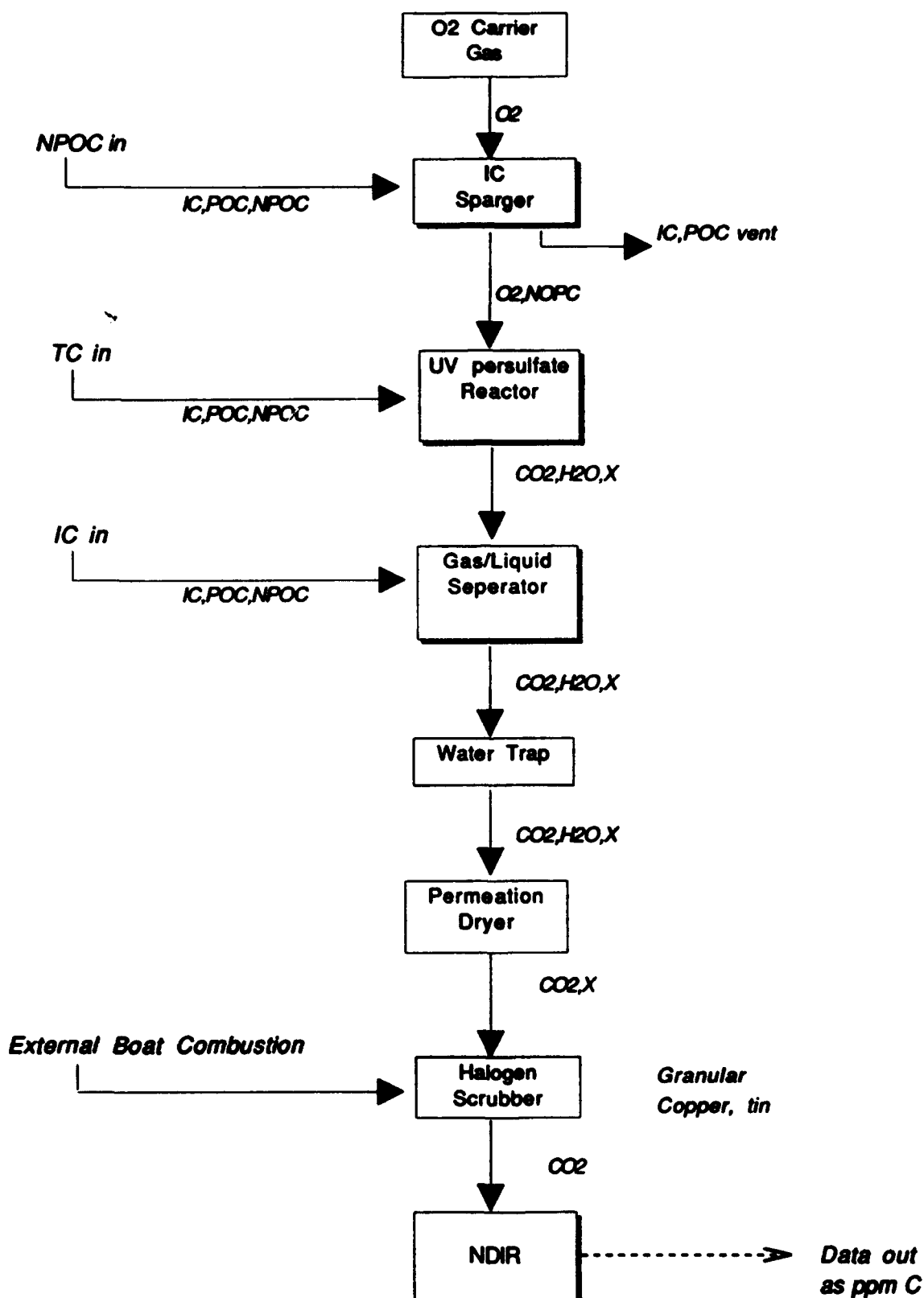
Dahrmann DC-190 Flow Diagram

TOC, Solids Prep Log

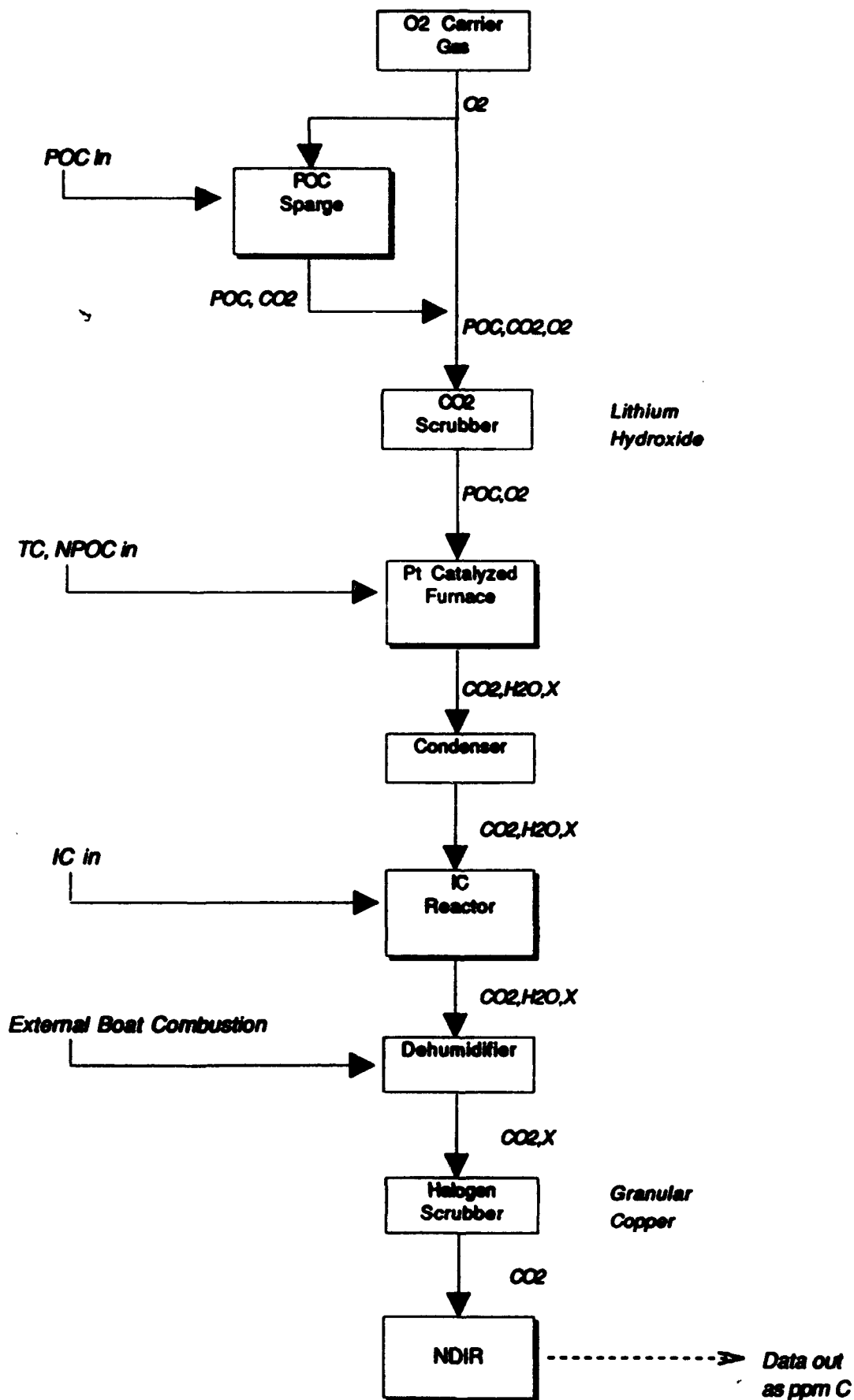
TOC, Solids Data Analysis

TOC, Aqueous Data Analysis

Dohrmann DC-180 Flow Diagram



Dohrmann DC-190 Flow Diagram



TOC Solids Prep Log

DATE:

ANALYST:

General notes regarding prep method and samples

[illegible]

[illegible]

TOC, Aqueous Data Analysis

Check the appropriate box for the method used

UV/Persulfate Ox (DC-180)

Direct combust (DC-190)

DATE:

ANALYST:

Verification Data

BLANKS		CHK STD (5 ppm)	
#	CARB (ppm)	CARB (ppm)	CORRC (ppm)
1	0.03		-0.22
2	0.58		-0.22
3	0.06		-0.22
4			-0.22
5			-0.22
6			-0.22
7			-0.22
8			-0.22
9			-0.22
10			-0.22
MEAN	0.22	#DIV/0!	-0.22
STDEV	0.31	#DIV/0!	0.00
IDL =	0.93	LDL =	0.00

Detection Limits (IDL & LDL) are calculated as 3 times the std dev of replicate determinations of the blank and 5 ppm check standard, respectively.

-4.47% RECOVERY

SAMPLE DATA

ppm C = Mean sample value - Mean blank value

Spike Level =

20

ppm C

[illegible]