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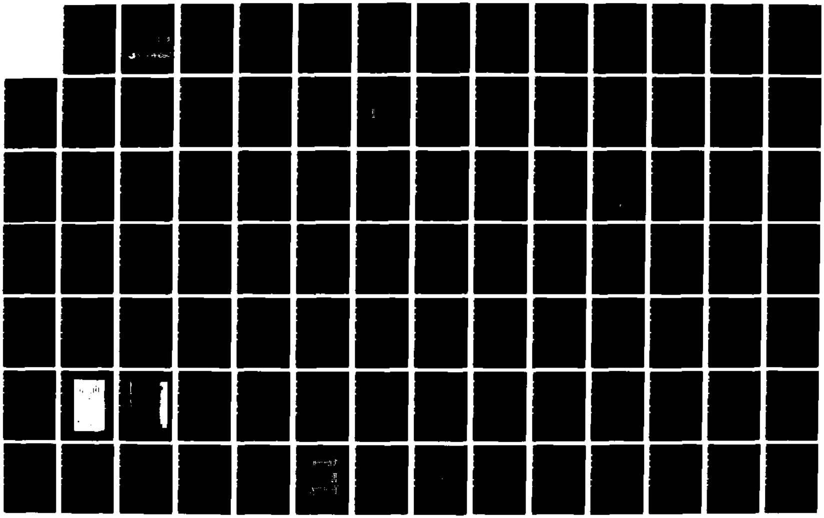

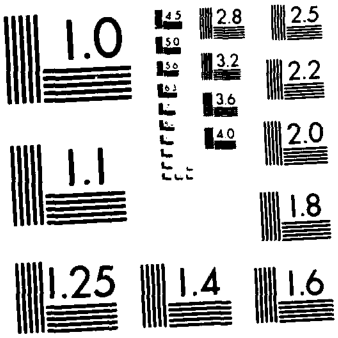
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VOL I

PROTOTYPE TECHNOLOGY FOR MONITORING VOLATILE ORGANICS, VOLUME I

V. TAYLOR, J. WANDER

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MARCH 1988

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19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

This report describes the development and implementation of the phase I prototype volatile organic compound (VOC) monitor, a turn-key system for analyzing trichloroethylene (TCE) in water. The system incorporates commercial purge and trap and gas chromatography instruments, a microcomputer, and custom-written software. Because this monitor is planned (for installation at base facilities and for use by nonspecialized personnel,) driving design considerations were reliability and simplicity of operation.

Assembly and lab testing of the unit were completed in September 86, and the monitor was transitioned to the sewage plant (379 CES/DEMH) at Wurtsmith AFB MI for evaluation by base personnel. Most logistical accommodations had been made within 6 months, and, except for one construction related accident, the system worked exactly as planned.
Companion documents, including schematics and operating and maintenance instructions, are included in Vol. 1; Vol 2 is a complete downlisting of the software. (Keywords: —

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PREFACE

This report was prepared by S-CUBED, a Division of Maxwell Laboratories, Inc., 3398 Carmel Mountain Road, San Diego, California 92121, under Contract Number F08635-84-C-0298, for the Air Force Engineering and Services Center, Engineering and Services Laboratory (AFESC/RDVS), Tyndall Air Force Base, Florida 32403-6001.

This report summarizes the work done between August 23, 1984, and June 30, 1987. The HQ AFESC/RDVS Project Officers were Lt. Robert C. Beggs (1984-February 1985), Maj. Kenneth T. Denbleyker (February 1985 - June 1986), and Dr. Joseph Wander (July 1986 - 1987). Volume I contains the project report and two handbooks written to accompany the system in the field; Volume II contains a complete source code listing of the data acquisition software (in C), written by Ms. Barbara Lentz.

This report has been reviewed by the Public Affairs Officer (PA) and it may be released to the National Technical Information Service (NTIS). At NTIS, this document will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.

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TABLE OF CONTENTS

Section	Title	Page
I	INTRODUCTION	1
II	LITERATURE SURVEY	3
III	SYSTEM DESIGN	6
IV	METHOD DEVELOPMENT	12
	A. Evaluation of Analytical System	12
	B. Evaluation of Available Detector Options	12
	C. Linearity and Reproducibility of the Purge and Trap System	16
	D. Development of an Internal Standard Option	17
	E. Conclusion and Determination of Additional VOCs	19
V	SOFTWARE DEVELOPMENT	22
	A. Menu Control	22
	B. Parameter Control	26
	C. Automated Analysis of TCE	27
	D. System Control and Data Collection	28
	E. Peak Detection	31
	F. Peak Identification	31
	G. Quantitative Analysis	33
	H. Quality Control/Quality Assurance	35
VI	PERFORMANCE EVALUATION	37
VII	TRANSITION TO THE FIELD	41
VIII	CONCLUSION	45
IX	REFERENCES	46
Appendixes		
A	Bibliography	47
B	Procedural Guide	53
C	Operation and Maintenance Manual	101

LIST OF FIGURES

Figure	Title	Page
1	VOC Monitor Option 1	7
2	VOC Monitor Option 2	8
3	VOC Monitor Option 3	9
4	Schematic of Computer - Controlled Instrument	11
5	Purge and Trap/ECD Chromatogram of Blank	13
6	Chromatogram of Blank and a 1-ppb Solution of TCE using Purge and Trap Sampling with FID on a Hewlett-Packard 5880 Gas Chromatograph	14
7	Chromatogram of a 1-ppb Solution of TCE on a Varian GC by Purge and Trap	15
8	System Response versus Concentration of TCE Over a Range of 0.5 to 1000 ppb	18
9	System Response versus Concentration of TCE Over a Range of 0.5 to 200 ppb	18
10	Chromatogram of TCE and Three Internal Standards	19
11	Example of Seven VOCs Separated on Prototype VOC Monitor	21
12	Data System Main Menu	22
13	Sample Parameter Listing	26
14	Sample Table for Calibration Run	27
15	Sample Table for TCE Analysis	28
16	Schematic of Instrumentation Control Interface Box	29
17	Sequence of Signals to Start Data Collection	30
18	Example of Multiple Internal Standard Pattern Recognition	34
19	Measured Concentration as a Function of Expected Concentration for TCE Determined by Two Methods	39

LIST OF TABLES

Table	Title	Page
1	VOC MONITOR SUMMARY OF OPTIONS	6
2	INSTRUMENT OPERATING PARAMETERS	16
3	REPRODUCIBILITY AT 1 PPB TCE ON THE TEKMAR PURGE AND TRAP	16
4	MINIMUM CONCENTRATION OF VOLATILE COMPOUNDS DETECTABLE BY PURGE AND TRAP/GC/FID	20
5	DESCRIPTION OF SOFTWARE SUBROUTINES	23
6	RESULTS OF SPIKED SAMPLE ANALYSIS	35
7	RESULTS OF SPLIT SAMPLE ANALYSIS	38
8	RESULTS OF REGRESSION ANALYSIS OF SPLIT SAMPLE DATA	40

LIST OF ABBREVIATIONS

ECD	Electron capture detector
EPA	United States Environmental Protection Agency
FID	Flame ionization detector
NTIS	National Technical Information Service
PID	Photoionization detector
ppb	Part-per-billion
TCE	Trichloroethylene (1,1,2-trichloroethene)
VOC	Volatile Organic Compound
VOA	Volatile Organic Analysis

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SECTION I

INTRODUCTION

A. OBJECTIVE

The objective of this project was to design, develop, and field-evaluate an analytical system that can provide rapid, accurate, reliable determinations of trace levels of TCE in water samples under conditions of unsupervised operation by enlisted Air Force personnel having no formal training in analytical chemistry or in the use of computers.

B. BACKGROUND

Wurtsmith Air Force Base is located in northeastern lower Michigan. Significant trichloroethylene (TCE) contamination of local ground water exists as a result of leakage of underground storage tanks, leaching from landfills and seepage lagoons, and disposal of wastewater effluent from treatment plants. The Air Force began decontamination of affected wells by air stripping, in an effort to prevent localized aquifer contamination from spreading to unaffected areas. To ascertain the extent of well water contamination and the effectiveness of decontamination by air stripping, the Air Force required development of an analytical system that would permit nonspecialized, enlisted Air Force personnel to perform timely, accurate determinations of trace levels of TCE in water.

In response to this need, S-CUBED designed and delivered a computer-controlled analytical system capable of providing rapid-turnaround analyses of TCE in ground water. The system is based on accepted methods for the analysis of volatile organics in water and on novel data acquisition and data reduction software, which enables operators with minimal training to produce accurate and meaningful results that will be acceptable to regulatory agencies.

C. SCOPE

This project, *Prototype Technology for Monitoring Volatile Organics*, was initiated to provide the Air Force with a turn-key system suitable for determining trace levels of TCE in ground water. The project was originally organized into four tasks as follows:

- Task 1 - Literature survey of the techniques, hardware, and software available for volatile organic compound analysis.
- Task 2 - Design of a system that will function for minimally trained operators and will meet the sensitivity (1 ppb) and precision (10 percent standard deviation) specifications for determination of TCE in ground waters.
- Task 3 - Development of a procedure to perform the analysis.
- Task 4 - Demonstration of the protocol at Wurtsmith AFB and delivery of the instrumentation and procedural manuals.

Before the instrument was installed at Wurtsmith AFB, Task 4 was expanded by a contract amendment to include evaluation of the performance of the system by duplicate analysis of well water and aqueous TCE standards by Wurtsmith AFB personnel using the prototype VOC monitor, and by S-CUBED employees using an EPA-approved method.

Volume I of this report summarizes the results of the software development, system design, and application to the analysis of TCE in water. An initial literature search was conducted and several options for instrumental configuration were developed. These options were thoroughly evaluated with respect to the Air Force need. As a result of the literature search, the following major components were assembled:

- a Tekmar Liquid Sample Concentrator with a 10-position Auto-sampler.
- a Varian 3400 Gas Chromatograph with a flame ionization detector (FID).
- an IBM personal computer with a complete software package for instrument control and data reduction.

A dedicated software package was developed with unique features, which include complete, user-friendly menus for ease of operation by untrained personnel. In addition to system design and software development, an extended performance evaluation was conducted, including a comparison of results of water sample analyses performed at Wurtsmith AFB and at S-CUBED.

Volume II of this report contains a complete source code listing of the "C" language program which is used to control and execute all steps and the automated analysis operation.

SECTION II

LITERATURE SURVEY

Many successful methods for determination of a class of compounds termed volatile organic compounds (VOCs), including TCE, in aqueous solution are documented in the scientific literature. Literature surveys of the National Technical Information Service and Chemical Abstracts were conducted and over 205 articles reviewed. References were considered relevant if the work presented focused on practical techniques for the determination of VOCs, especially organohalides, in aqueous solution. Of this collection of references, 43 were considered relevant to this project. References that included sample introduction procedures, standardization procedures unique to VOC analysis, and sample collection were also reviewed and the methods evaluated. A complete bibliography compiled as a result of this literature survey is included in Appendix A.

A number of different sample preparation techniques may be applied to the removal of volatile compounds from aqueous solution for subsequent gas chromatographic analysis. Contained in the literature list are references which describe the following sample preparation and introduction techniques, all of which were considered for use on this project.

- Liquid/liquid extraction.
- Purge and trap (dynamic headspace) sampling.
- Closed loop stirring.
- Static (equilibrium) headspace sampling.
- Direct aqueous injection.
- Sorbent extraction.

As these methods were reviewed, certain criteria were considered in deciding whether a given method would be appropriate for the purposes of this project. The criteria considered essential for sample introduction techniques for this project were:

- The method must be simple enough that minimally trained technicians will obtain reproducible results.

- The method should be acceptable to Federal and State regulatory agencies.

- The method must possess a minimum detection limit of not less than 1 ppb for TCE.

- The bulk of instrument control and data manipulation must be automatic.

Purge and trap sampling of aqueous samples meets all the above criteria and is best suited for this project. This type of sample preparation meets the requirements for simplicity, suitability to trace analysis, and compatibility with automation. The purge and trap technique has undergone considerable scrutiny and is the method of sample introduction specified in EPA Method 601 (Purgeable Halocarbons), which includes TCE on the target analyte list. This sampling method is easily automated and requires only that the operator learn to fill a syringe quantitatively from a sample container and to control evaporative losses of TCE. (Reference 1)

For separation and detection, gas chromatography with flame ionization detection was chosen. EPA methods 601 and 602 specify packed columns. Since only one analyte, TCE, was to be determined, packed column analysis provides sufficient resolution, therefore, capillary column methods were rejected. Several detectors are suitable for this type of analysis, including electron capture (ECD), flame ionization (FID) and photoionization (PID). The FID is the favored choice for this project. The FID is a relatively universal detector for organic compounds and may be used for detection of both halocarbons (e.g., TCE) and aromatics (e.g., toluene). The FID is also a relatively simple detector to operate and maintain. Using purge and trap sampling techniques, the FID has been reported to exhibit a signal-to-noise ratio of 11.5 ± 1.1 for samples containing 1 ppb of TCE. (Reference 2)

Since the data system for this project is designed to meet a very user-specific purpose, little published literature was found which presented relevant applications. A complete description of software development is presented in Section 5.0.

Hardware options for each system component were evaluated, based on a review of manufacturers' product literature. In choosing a gas chromatographic system, the following criteria were considered pertinent:

- Sufficient microprocessor capacity to store analytical methods and enable operators to switch easily from method to method.
- Possession of continuous self diagnostics.
- Good service accessibility to minimize downtime.
- Digital flow controllers for carrier gas.
- Easy to establish hydrogen and air flows.

The criteria used to select purge and trap sampling systems were cost, simplicity of operation, and compatibility with automation.

For this project, no product or scientific literature presented a clearly relevant data system option for this highly user specific task. The basic criteria used in making a selection of data system hardware and software were as follows:

- Ability to store different methods.
- Ability to coordinate the operating sequence of an autosampler with data acquisition.
- Easily accessed self-diagnostics.
- Ability to function with minimal operator involvement or judgment.

Various equipment options were considered as a result of the literature survey. A thorough description of the options evaluated for application to this project is presented in the following section.

SECTION III

SYSTEM DESIGN

Three specific system options were developed which vary both in cost and in complexity. Each option was based on the use of purge and trap sample introduction, since the method is well documented in the literature and has gained the acceptance of regulatory agencies. Also common to the three options is the specific gas chromatograph to be used, a low-cost model suiting the needs of this project, which was identified during the review of the manufacturers' literature.

The major differences in the three options are in the method of data acquisition and signal processing. Option 1 provides for a simple, low-priced integrator and optional chromatogram obtained from a strip-chart recorder. Option 2 uses an integrator and optional strip-chart recorder, but in addition connects to a data system, which can provide instructions to the operator, statistics, and a final report. Option 3 is to connect a data system in the form of a personal computer directly to the gas chromatograph, and to output instructions, statistics, and reports directly from that data system. Table 1 summarizes some of the requirements, advantages, and disadvantages of the three options, and these options are diagrammed in Figures 1 through 3.

TABLE 1. VOC MONITOR SUMMARY OF OPTIONS

	Option 1	Option 2	Option 3
Relative hardware cost	Low	Moderate	Moderate
Relative development time	Low	Moderate	High
Ease of use	Poor	Good	Excellent
Data handling capability	Limited	Good	Excellent
Ease of extendability to other analytes	Fair	Good	Good
Recommendations	Not Recommended	Acceptable Option	Recommended Option

Advantages of Option 1 are relatively low hardware cost and development time. The reasonable price of integrators and detailed instruction for their use are already outlined in the various manufacturers' manuals; however, the requirements for the analyst to understand the use of the integrator (which may be extensive) and the limited data storage capacity are disadvantages, which eliminate the use of commercially available integrators from consideration for this application.

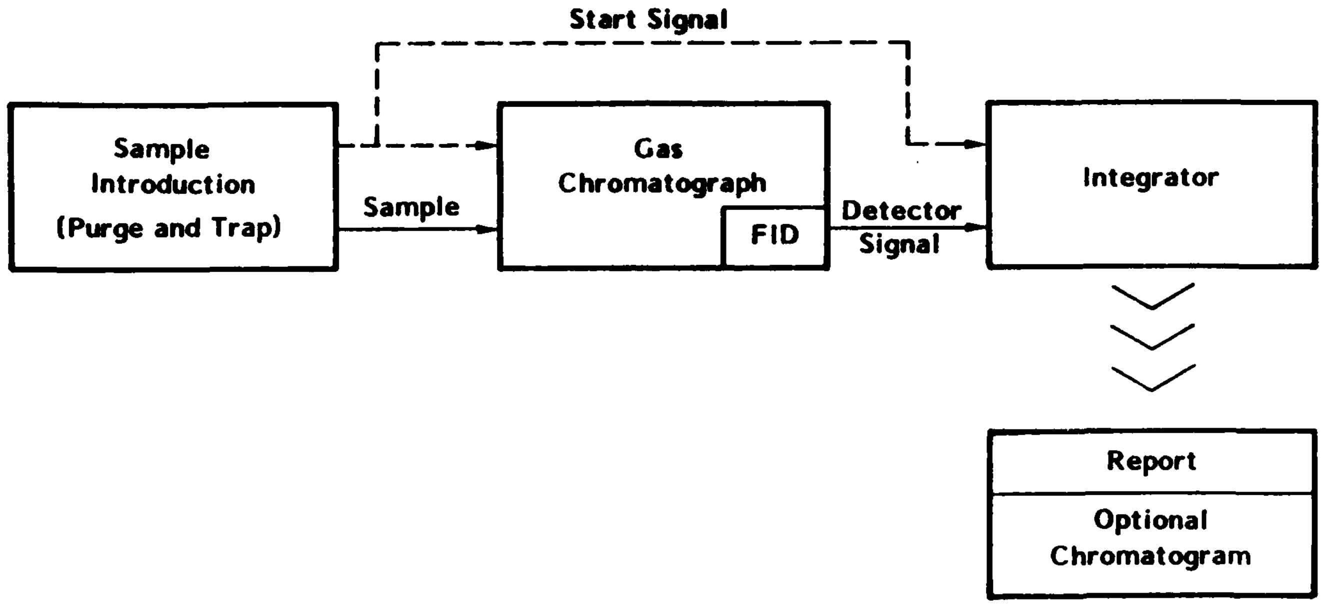


Figure 1. VOC Monitor Option 1.

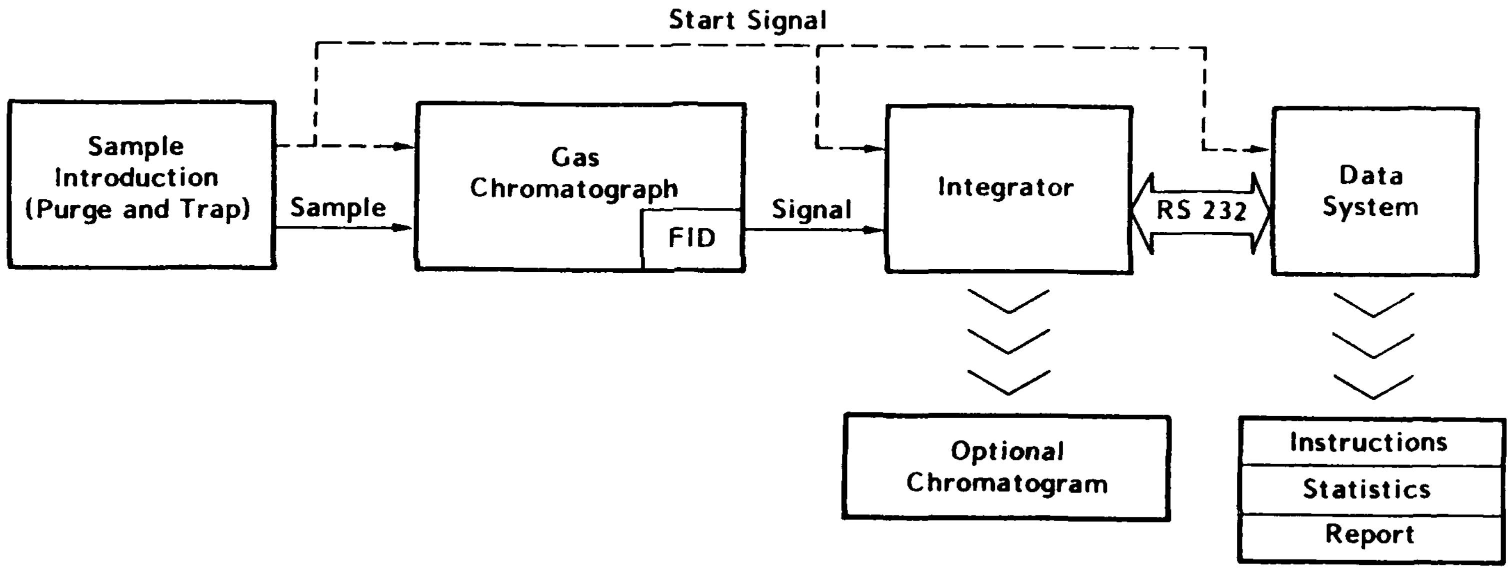


Figure 2. VOC Monitor Option 2.

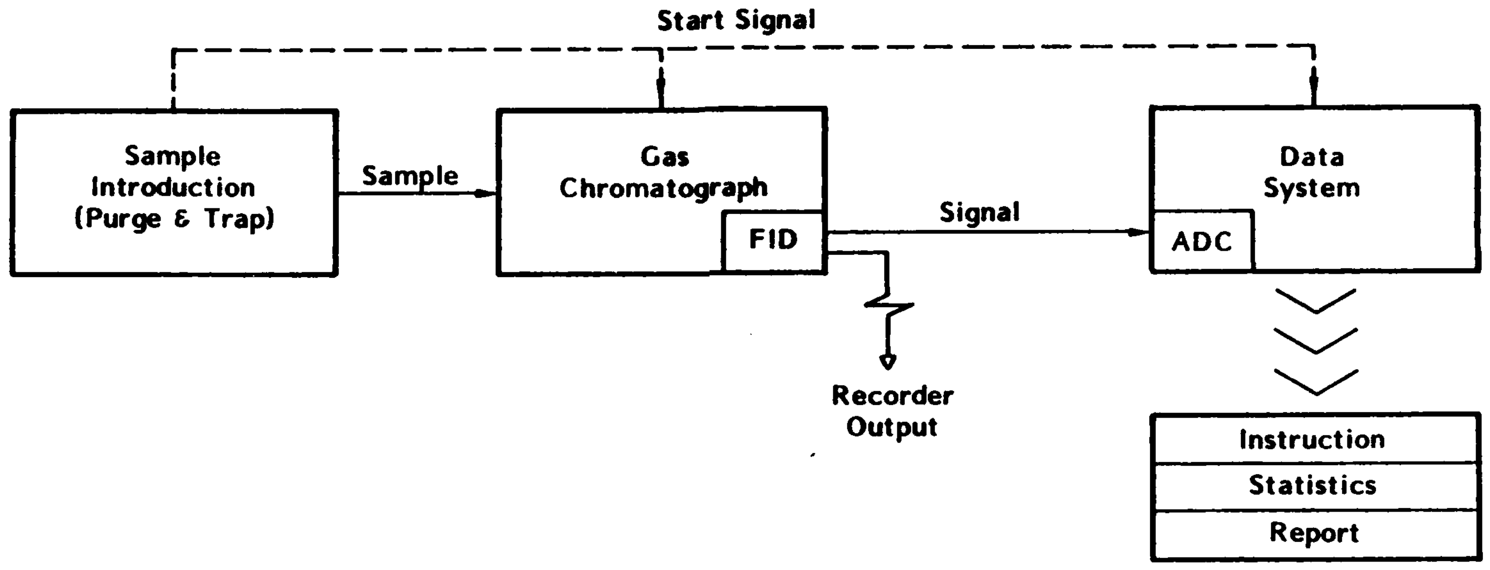


Figure 3. VOC Monitor Option 3.

Option 2 would involve greater cost and longer development time as a consequence of the need to interface various pieces of equipment; however, the addition of a data station permits one to use menu-driven programs, which would decrease the requirements upon the user.

Option 3 also involves moderate hardware costs, but the development time is substantial because much more extensive software must be developed. The significant advantage of Option 3 is the ability to incorporate the greatest number of systems automatically. Based on this evaluation of three proposed system configurations, Option 3 was selected as being the most suitable.

Final hardware choices were made,based on the preceding considerations, and the final system was assembled from:

- A Tekmar Liquid Sample Concentrator with a 10-position Tekmar Autosampler.
- A Varian 3400 Gas Chromatograph.
- An IBM Personal Computer-based data acquisition system.

A schematic of the final system configuration is presented in Figure 4.

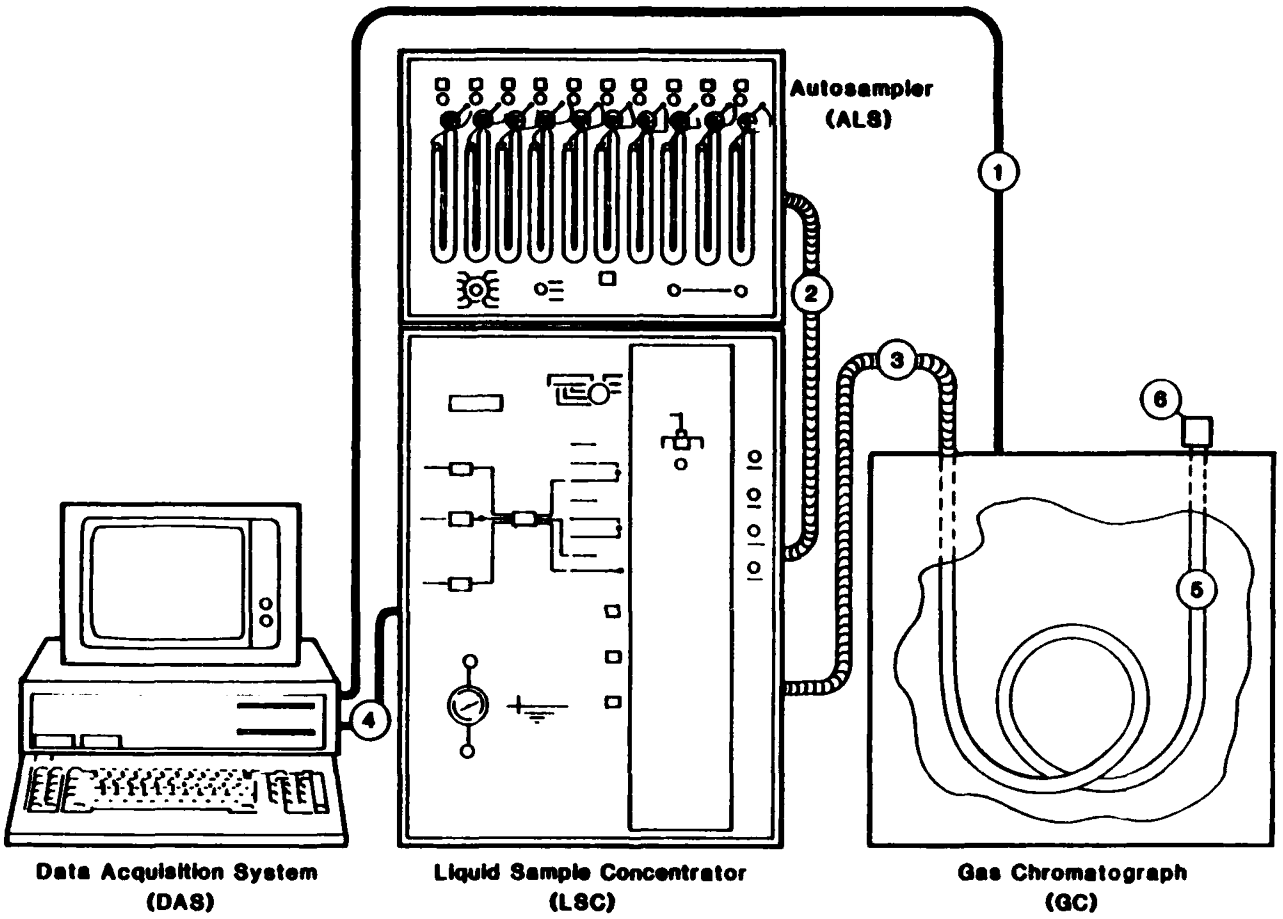


Figure 4. Schematic of Computer - Controlled Instrument.

SECTION IV

METHOD DEVELOPMENT

S-CUBED's system design for determination of trichloroethylene in groundwater is based on an initial purge and trap concentration step. The purge and trap procedure effects extraction of volatile organics from aqueous solution into a stream of inert gas and concentrates the extracted volatiles on an adsorbent trap, in this application, Chromosorb WHP (60/80 mesh). Once the volatile organics are deposited on the adsorbent trap, the trap is heated quickly to 180°C and flushed with nitrogen. The gas stream carrying the desorbed analytes is swept through heated transfer lines onto the gas chromatograph, where separation and detection are accomplished.

A. EVALUATION OF ANALYTICAL SYSTEM

In general, the S-CUBED procedure for determination of TCE in ground water follows EPA Methods 601 (chlorinated hydrocarbons) and 602 (volatile aromatics). Because only TCE is to be determined by this procedure, minor deviations have been introduced into the method to minimize run times. Details of the S-CUBED procedure are summarized in Appendix B, the *Procedural Guide for Automated Analysis of Trichloroethylene in Ground Water.*

The essential requirements for an analytical method to be suitable for this project were:

- Sufficient chromatographic resolution to determine TCE in the presence of three internal standards and nonspecific interferences.
- Appropriate mixture of internal standards that bracket the target analyte without interference.
- Sufficient sensitivity and acceptable reproducibility at the 1-ppb detection limit.

Based on the literature and product evaluation (pp. 3-5), the analytical system was assembled from a Tekmar Liquid Sample Concentrator and a Varian 3400 GC. The column selected for this work was a 6-foot x 1/8-inch stainless steel column packed with 1 percent SP-1000 on 60/80 Carbopak B. This column is similar to the one required by EPA Method 601.

B. EVALUATION OF AVAILABLE DETECTOR OPTIONS

A necessary condition required of this system is measurement of trace levels of TCE to a minimum detection limit of 1 ppb. Before making a final decision on the type of detector to be used, several experiments were performed to evaluate the available options. Three detector options were evaluated:

- Electron capture detector (ECD).
- Photoionization detector (PID).
- Flame ionization detector (FID).

The choice of detector option was made based on the requirements of ruggedness, ease of operation, and attainment of adequate sensitivity.

An ECD was evaluated for TCE determination by using standard purge and trap parameters which conformed to EPA Method 624 for volatile organic priority pollutants. The ECD has great sensitivity to chlorinated compounds, based on the electron affinity of halogen atoms, but is relatively insensitive to hydrocarbons. The chromatograms obtained from the analysis of blank water samples showed a large, off-scale detector response, possibly from the effect of water on the ground current of the ECD or from the presence of other halogenated compounds. A dry purge cycle was added but proved to be ineffective in eliminating these nonspecific interferences. Chromatograms obtained on a blank water sample with the ECD are shown in Figure 5. Based on these results, the ECD was rejected as a candidate detector for this application.

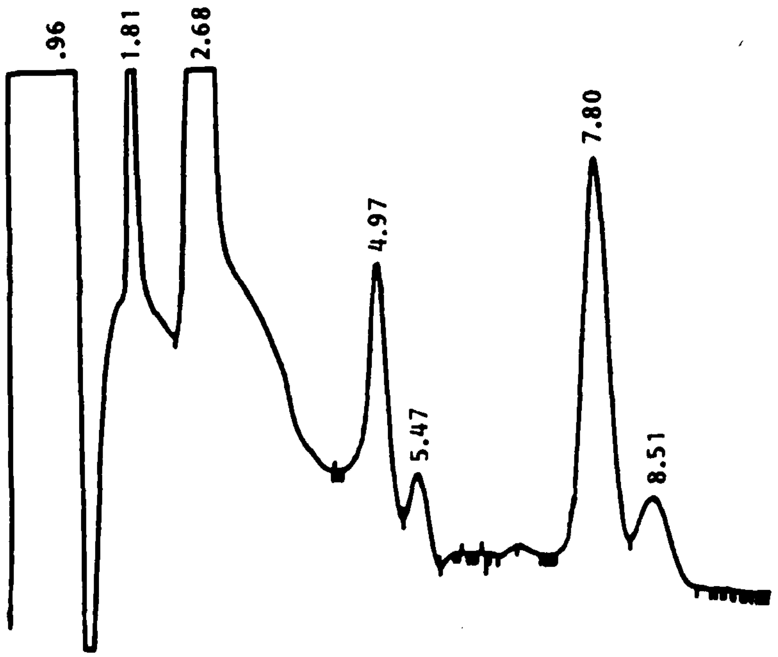


Figure 5. Purge and Trap/ECD Chromatogram of Blank.

A preliminary evaluation of a flame ionization detector was performed by interfacing a Tekmar Purge and Trap Liquid Sample Concentrator to a Hewlett-Packard 5890 Gas Chromatograph fitted with a FID (see Figure 6).

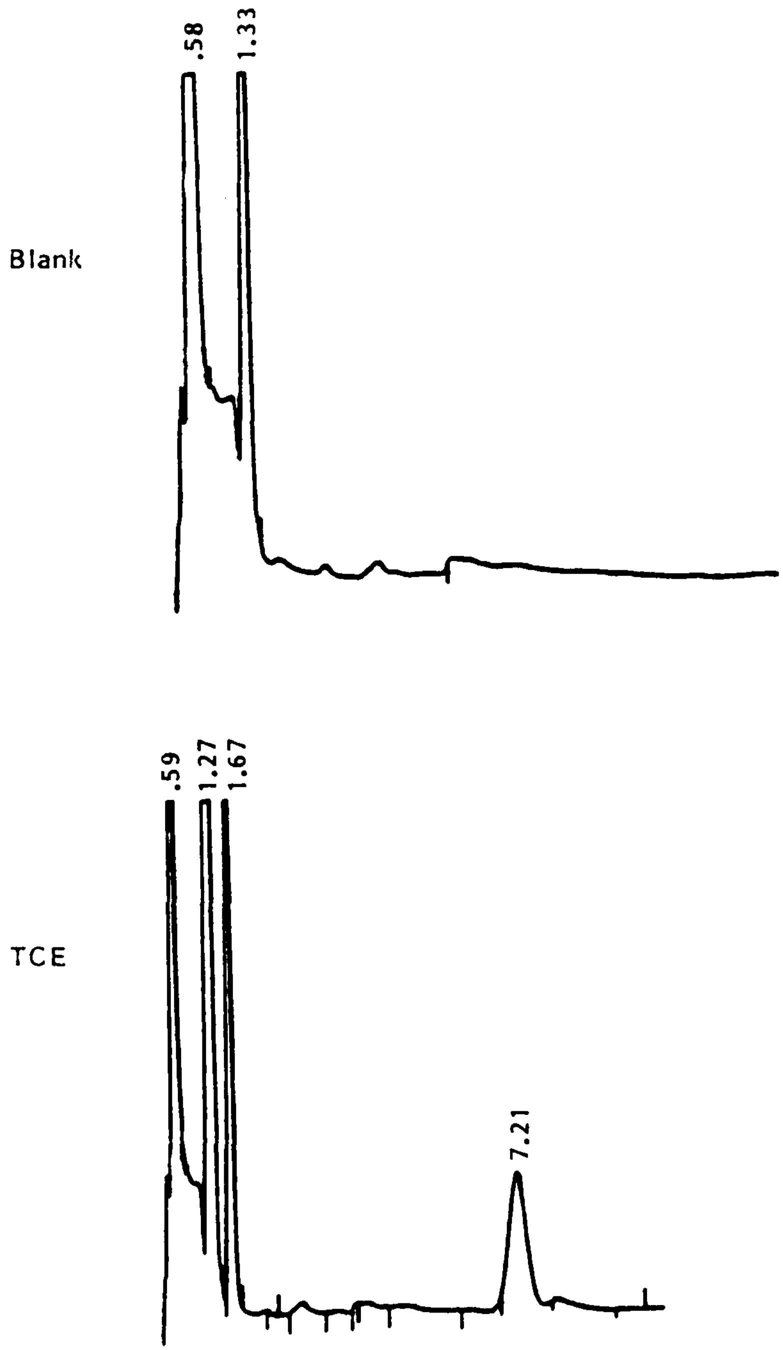


Figure 6. Chromatogram of Blank and a 1-ppb Solution of TCE Using Purge and Trap Sampling with FID on a Hewlett-Packard 5880 GC.

Organic-free water was obtained through extensive purging of laboratory organic-free water. Both a blank and a sample spiked at 1 μg/L (1 ppb) were analyzed using this system, and the chromatograms are presented in Figure 6. The Hewlett-Packard 5890 and purge and trap sampling demonstrated that the 1-ppb detection limit is attainable using a flame ionization detector. Subsequently, a similar evaluation of a Varian FID was conducted. As illustrated by the chromatogram in Figure 7, equally acceptable sensitivity was obtained using the Varian GC.

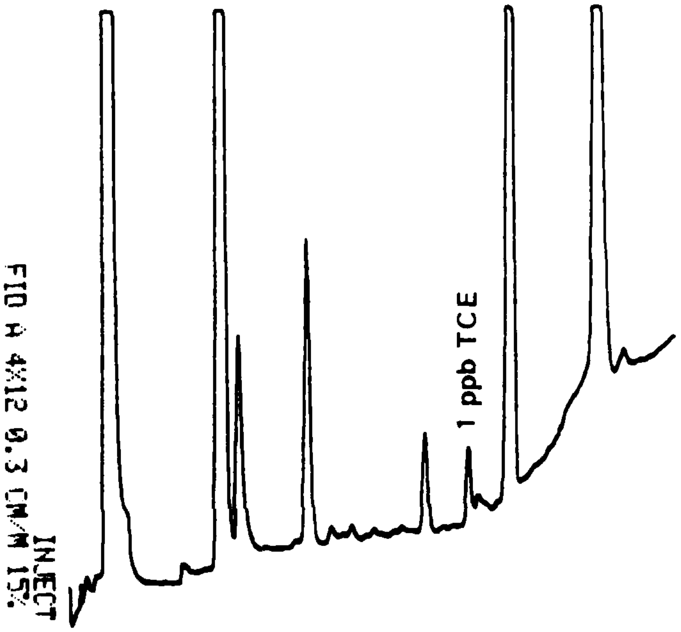


Figure 7. Chromatogram of a 1-ppb Solution of TCE on Varian GC by Purge and Trap.

A PID is required by EPA Method 602 for purgeable aromatics. The PID is a nondestructive detector that is especially sensitive to aromatic molecules. Although it is suitable in principle for the applications of this project, it was considered somewhat less rugged than the FID and was therefore rejected.

In this evaluation of the three available detector options, the FID fulfilled all the requirements for a rugged, easily operated detector that possesses sufficient sensitivity for the needs of this project. Development of a suitable protocol continued on evaluation of the purge and trap system and identification of a suitable internal standard option.

C. LINEARITY AND REPRODUCIBILITY OF THE PURGE AND TRAP SYSTEM

Once the complete system hardware had been configured, experiments were performed to study the reproducibility of purge and trap analysis and the linear range of the detector. Reproducibility at the 1-ppb detection limit was determined by replicate purge and trap concentration and GC/FID analysis of six individual samples prepared from standards. The samples were analyzed according to the parameters listed in Table 2. The mean area for the six determinations is 316 ± 32 integration units, a relative standard deviation of 10 percent, to two significant figures. These results are presented in Table 3.

TABLE 2. INSTRUMENT OPERATING PARAMETERS

Tekmar Purge and Trap	
Purge Time	8.0 min
Desorb Time	5.0 min
Desorb Temperature	180°C
Bake Time	3.0 min
Bake Temperature	200°C
Purge Pressure	20 psi
Purge Flow	40 mL/min
Varian Gas Chromatograph	
Initial Temperature	40°C
Initial Time	5 min
Ramp	8°C/min
Final Temperature	180°C
Final Time	5 min
Carrier Gas (N_2)	30 mL/min

TABLE 3. REPRODUCIBILITY AT 1 PPB ON THE TEKMAR PURGE AND TRAP

	Retention Time (min)	Area
	10.60	303
	10.62	306
	10.62	321
	10.62	339
	10.60	267
	10.60	359
mean ± sd.	10.61 ± 0.01	316 ± 32

Once the specified precision and minimum detection limit were achieved, the linear response of the instrument was established. To determine the linear range of the system, dilutions of an aqueous 1,000-ppb TCE standard were prepared to cover the range of 0.5 ppb to 1,000 ppb and analyzed; the resulting plot of instrument response versus concentration is presented in Figure 8. This plot shows that the response is linear from 0.5 ppb to approximately 150 ppb. To determine the linear response range more precisely , more data points were collected in the range of 0.5 to 150 ppb, and a plot prepared over this concentration range is presented in Figure 9.

D. DEVELOPMENT OF AN INTERNAL STANDARD OPTION

Effective identification and quantitation of the target analyte, TCE, with minimal operator intervention was accomplished by development of a pattern-matching algorithm based on the presence of multiple internal standards in the chromatogram. The peak detection and quantitation software is discussed in Section V; however, since the software peak identification routine depends on pattern matching, an appropriate internal standard option was investigated. An internal standard must satisfy the following requirements:

- Stability
- Inertness to analyte
- Linear concentration/response on compatible scale
- Elution in clean windows and over the retention time range of interest.
- Low probability of coelution with other nontarget compounds present in water samples.

A solution containing 20 mg/mL each of bromochloromethane, 1-chloro-2-bromopropane, and 1,4-dichlorobutane is commercially available and meets all these criteria. This solution is specified for EPA Method 601, and it has been widely applied to the analysis of volatile organics. A sample chromatogram of TCE and the three internal standards is presented in Figure 10.

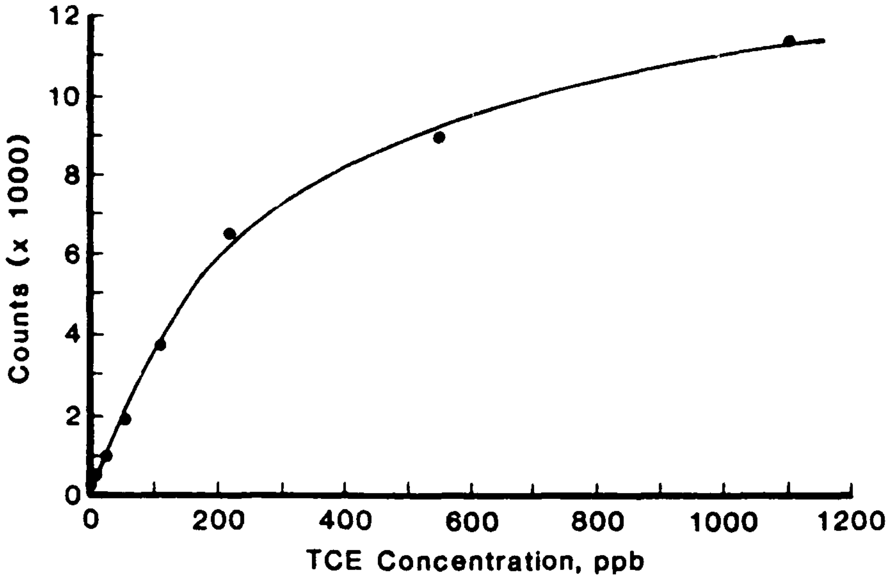


Figure 8. System Response vs. Concentration of TCE over a Range of 0.5 to 1000 ppb.

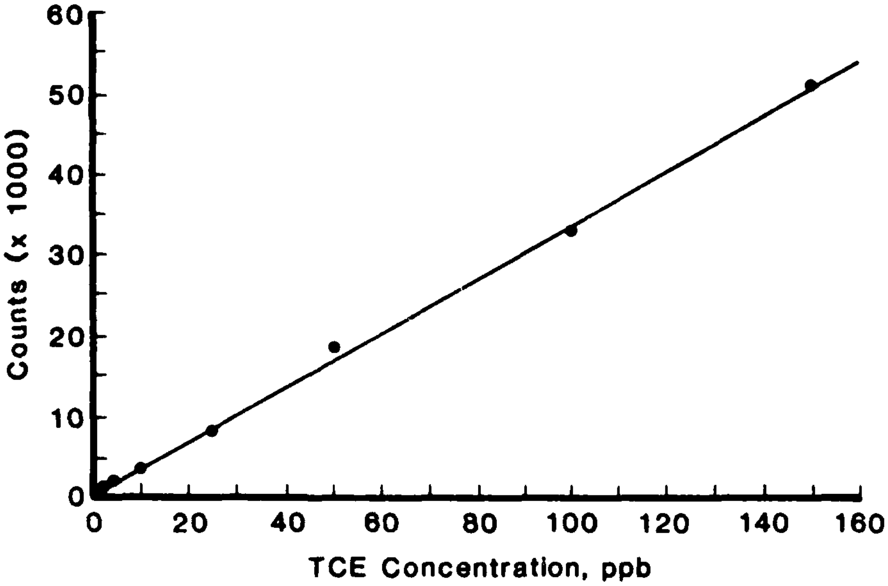


Figure 9. System Response vs. Concentration of TCE over a Range of 0.5 to 150 ppb.

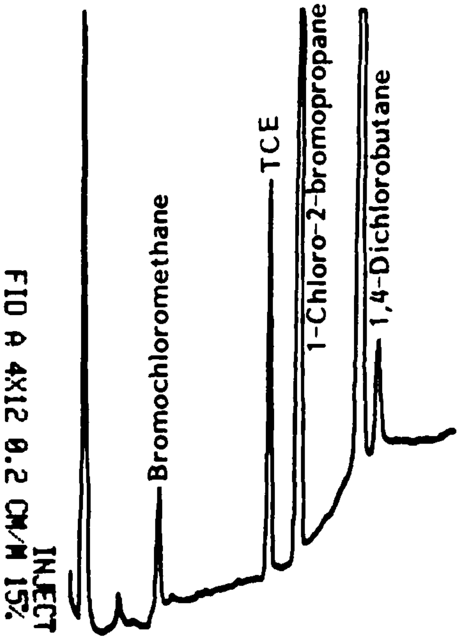


Figure 10. Chromatogram of TCE and Three Internal Standards.

E. CONCLUSION AND DETERMINATION OF ADDITIONAL VOCS

The analytical system performed well and met the criteria for reproducibility and reliability. Testing of this method was performed using other VOCs to several ends: to demonstrate that the system could be used to measure any one of a variety of different VOCs; to demonstrate that quantitation of TCE is practical in the presence of other common VOCs; and to establish that system expansion is possible at a later date. Retention times of the compounds analyzed on this system to date are presented in Table 4 together with the estimated minimum detection limit. Additional compounds qualitatively determined using this system include methylene chloride, *trans*-1,2-dichloroethylene and ethylbenzene. The precision achieved for five replicate analyses of five VOCs ranges between 4-17 percent relative standard deviation. Figure 11 presents a chromatogram of a mixture of seven VOCs determined with this system, on which the approximate positions of the internal standards are indicated.

TABLE 4. MINIMUM CONCENTRATION OF VOLATILE COMPOUNDS DETECTABLE BY PURGE AND TRAP/FID DETECTION

Compound	Concentration (ng/mL)	Retention Time (min)	Response (mm)	Detection Limit
1,1-Dichloroethylene	0.95	4.5	16	0.30
Chloroform	1.22	6.6	10	0.61
Trichloroethylene	1.02	11.1	12	0.51
Benzene	0.34	11.5	27	0.07
1,1,2,2-Tetrachloroethane	1.52	16.5	10	0.76
Toluene	0.02	5.0	18	0.02

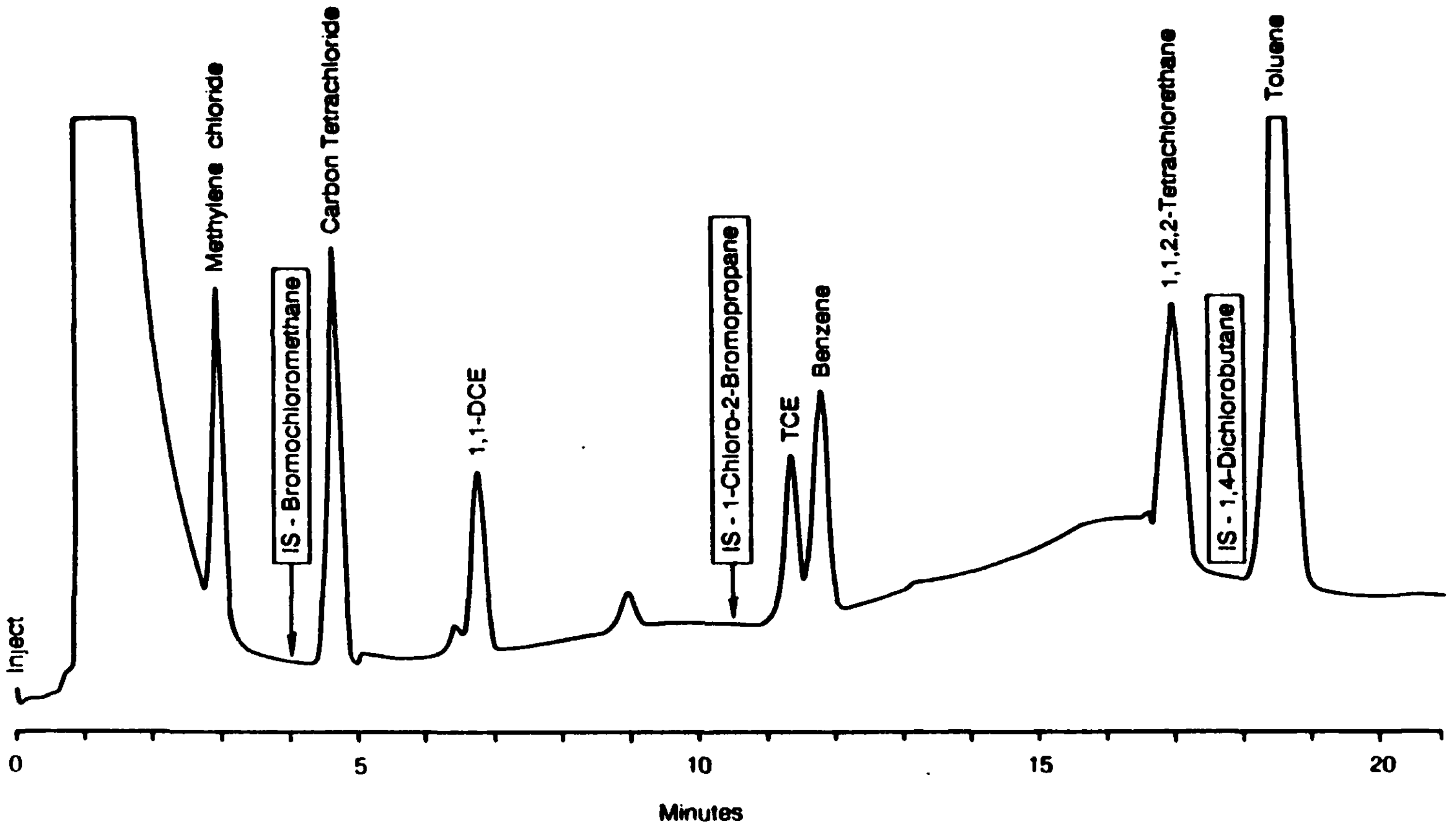


Figure 11. Example of Seven VOCs Separated on Prototype VOC Monitor.

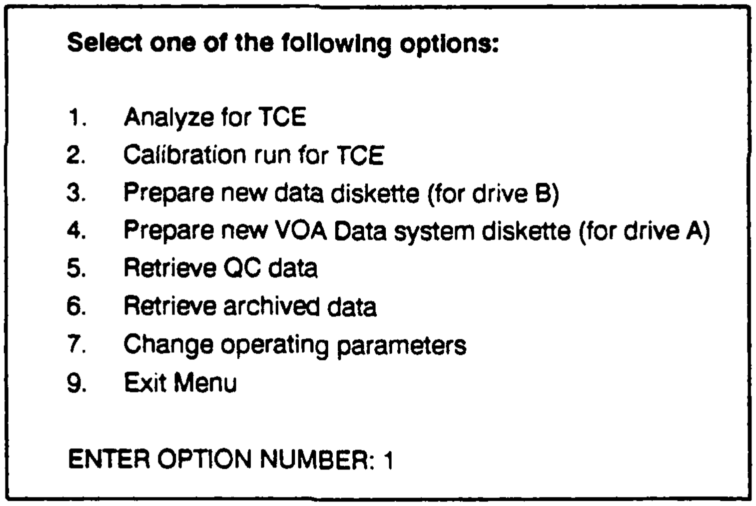
SECTION V

SOFTWARE DEVELOPMENT

The high degree of automation of this S-CUBED system is a result of unique software developed specifically for this application. The development of the software was directed toward establishing efficient instrument control, ease of operation, and independent data reduction. The source code is included in Appendix D, Volume II; each option of the menu-driven software is described below, and a description of the major software subroutines is presented in Table 5.

A. MENU CONTROL

The software runs under a complete system of control menus. This design enables operators without computer expertise quickly to gain operational skill with the system. All analysis options are initiated by entering the Data System Main Menu (illustrated in Figure 12.)



```
Select one of the following options:

1.   Analyze for TCE
2.   Calibration run for TCE
3.   Prepare new data diskette (for drive B)
4.   Prepare new VOA Data system diskette (for drive A)
5.   Retrieve QC data
6.   Retrieve archived data
7.   Change operating parameters
9.   Exit Menu

ENTER OPTION NUMBER: 1
```

Figure 12. Data System Main Menu.

Nine options are presented in the main menu. The two analytical options presented, *Analyze for TCE* and *Calibration Run for TCE*, provide for analysis and quantitation of standards and samples. Options 3 through 6 provide the operators with automated data storage and retrieval operations, as well as preparation of data diskettes. Specific instructions for execution of these system options are included in the *Operation and Maintenance Manual* (Appendix C). In addition to operating the system and storing data, the analyst is able to adjust operating parameters by invoking Option 7.

TABLE 5. DESCRIPTION OF SOFTWARE SUBROUTINES

Software Subroutine	Description
adtconv.c	Collects data from GC and converts it to digital voltage.
analyz.c	Controls sample collection and analysis modules.
caldate.c	Checks date of last calibration.
calib.c	Calibrates chromatographic response based on the ratio of the response of the target compound to the internal standards. All three standards are used in the final concentration calculations in order to improve the results (the three values are averaged).
change.c	Changes values of user parameters in "parm" file.
chgtgt.c	Changes target parameters.
collect.c	Collects raw data and analyzes it. Displays retention times and areas.
column.c	Calculates and prints column factor. (This factor provides an indication of the condition of the column. The value decreases as the column deteriorates.)
copsys.c	Formats a new diskette and copies operating system and data system files on to it.
error.c	Prints error messages.
filelist.c	Gets list of data files on floppy disk.
fixseq.c	Corrects any errors made during sequence entry (i.e., sample numbers and positions for the purge and trap) and is called by "sequenc.c" and "stdseq.c".
fmtdis.c	Formats a new diskette for data collection.
getdate.c	Gets current system date and time.
getname.c	Checks valid filename - alphanumeric only.
getnum.c	Prompts user for numerical input and then verifies it. If valid string is found, returns length of number string, otherwise returns zero.
g_fnum.c	Prompts user for floating point numerical input and then verifies it. If valid string is found, returns length of number string, otherwise returns zero.
g_ parm.c	Reads text file which contains sample parameters into "user" structure.
g_spec.c	Reads text file which contains target parameters into structure "samp".
initdio.c	Sets digitial I/O bit 0 of port 0 for output and initializes to open relay switch (set to 1). This state will cause the Tekmar to wait for the switch closure to begin desorb.
ioerr.c	Reads status registers for error reporting from data translation board.
match.c	Locates standard peaks (internal and target) within standard samples and determines actual retention times and response factors for each standard.

TABLE 5. DESCRIPTION OF SOFTWARE SUBROUTINES (continued)

Software Subroutine	Description
pkstart.c	Determines if a new peak (called by pk_det.c.)
pk_det.c	Initializes data segments and calls subroutines to establish peak start, peak end and peak max.
integr.c	Integrates peak areas.
segm.c	Sets local baselines by recursive algorithm.
pk_end.c	Predicts peak end for pk_det.c.
prnparm.c	Prints current user-defined parameters.
prnres.c	Sends sample results to printer.
prnseq.c	Prints sample sequence to screen or printer.
prntype.c	Prints sample types available to the screen.
qcexec.c	Calls QC data retrieval routines.
qcretrv.c	Retrieves spike data from floppy disk files.
qcwrite.c	Opens archive file for writing spike concentrations for QC analysis. QC filename format: qc<month> <year>.dat
readdate.c	Waits for user to enter in date string and check for valid entry. String should be in format: month/year.
readday.c	Waits for user input and check for valid day.
reply.c	Gets yes or no reply from user. Returns true on yes and false on no.
resflpy.c	Stores results in floppy disk file.
retriev.c	Retrieves information from data files on floppy disk.
sampler.c	Performs necessary calculations and sends results to appropriate location.
samptype.c	Sets sample numbers for all sample types.
select.c	Selects numerical menu selection.
seqenc.c	Prompts user for sample numbers, collection date/time and analyst. Indicates which positions are to be filled with standards, blanks, and samples. This information is stored in a structure which is passed to the other routines.
setcalib.c	Sets switches to require recalibration on the next run.
setdate.c	Sets date and obtains operator ID for run.

TABLE 5. DESCRIPTION OF SOFTWARE SUBROUTINES (concluded)

Software Subroutine	Description
setdio.c	Sends signal to Tekmar to control desorb start (contact closure). Opens relay switch (set to 1), or set to 0 to close relay switch. This state will cause the Tekmar to wait for the switch closure to begin desorb.
smooth.c	Smooths raw data for further processing using Savitzky Golay least squares fit. 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, and 25-point smoothing equations are available. (Anal. Chem. 1964, 36(8) 1627-39).
stddev.c	Calculates standard deviation of concentrations and discards outliers. Acceptance criterion - must be within 2 s.d.
stdseq.c	Establishes sample sequence for the calibration.
stocalib.c	Changes values in "permanent" parameter file for slope and intercept and changes calibration flag to indicate that calibration was successful.
stoflpy.c	Stores sample information, retention time, and areas on floppy disk "b".
temp.c	Tests remaining modules without the need to collect data each time.
umenu.c	Controls sample automation on the GC.
valfile.c	Checks for presence of file.
wrparm.c	Writes new value of parameter to "parm.dat".

B. PARAMETER CONTROL

Certain data acquisition and data reduction operations are controlled by operating parameters stored in a file that may be accessed from the System Main Menu. By invoking Option 7 of the main menu, the operator may obtain a list of all current operating parameters, as presented in Figure 13. Sample parameters that may be changed by the analyst as the result of changing analytical conditions include: internal standard peak area, retention times, and such data acquisition parameters as the gain and the data smoothing factor. An additional menu may be entered at this point, Option M, which presents a similar listing of specific operating parameters that pertain only to the target compound, in this case TCE. These acquisition parameters are available to the operator if operating conditions change to such an extent that current parameters are no longer valid. This situation may arise when a new column is installed or the instrument response changes, producing significant deviations in retention times or peak areas. By establishing a separate file to store method parameters, flexibility is established to accommodate a change in internal standards employed or in the type or number of target analytes.

```
Listing of Current Operating Parameters

a)  Verbose option is ON.
b)  Gain is set to 1.
c)  Frequency is set to 4.000000 points/second.
d)  Smoothing factor is 11.
e)  Threshold levels for peak detection:
        Threshold Level #1 is at 1.
        Threshold Level #2 is at 0.
        Threshold Level #3 is at 1.
        Threshold Level #4 is at 2.
f)  Chromatography sample time is 1.500000 minutes.
g)  Number of internal standard 3.
h)  Number of target compounds 1.
i)  Number of standard samples (levels) 3.
j)  Retention time of internal standards.
        Standard #1 at.
        Standard #2 at.
        Standard #3 at.
k)  Areas of internal standards (used for match calculation).
        Standard #1 at.
        Standard #2 at.
        Standard #3 at.
l)  Minimum area required for Standard 10.
m)  Change target compound parameters.

ENTER LETTER OF OPTION TO CHANGE (USE "X" TO EXIT):
```

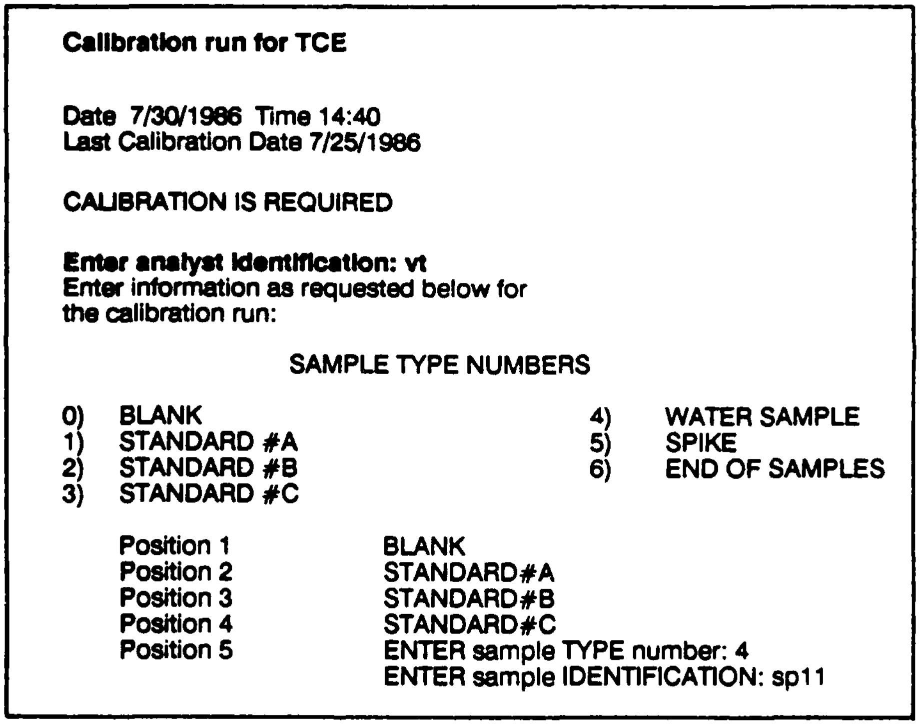
Figure 13. Sample Parameter Listing.

C. AUTOMATED ANALYSIS OF TCE

Automated analysis of TCE may be accomplished by invoking either of two main menu options. From the data system main menu, the operator may choose two analysis options:

- Analyze for TCE (Option 1).
- Calibration Run for TCE (Option 2).

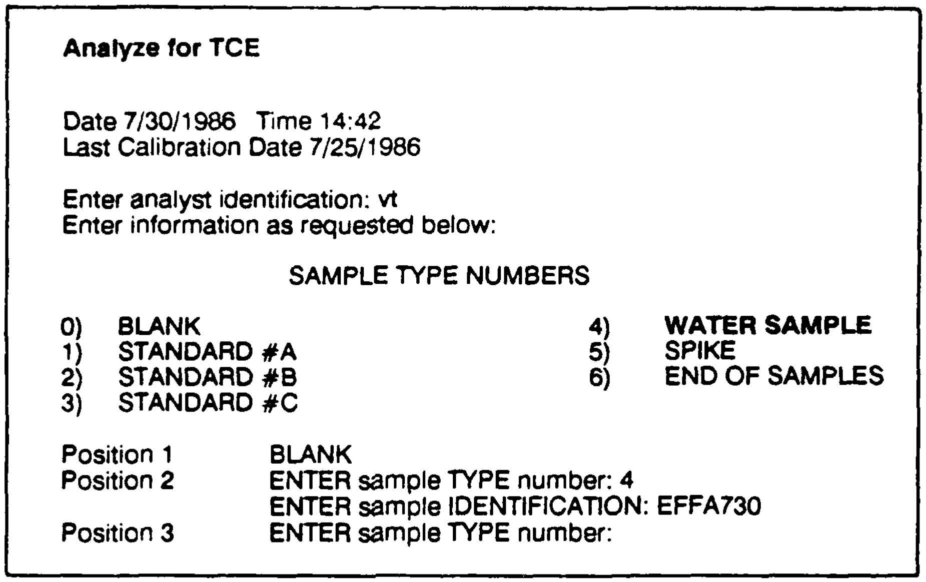
A *Calibration Run for TCE* is required under certain conditions, which are detailed in the section on quality control (Section 5.7). When a calibration run is begun, a calibration menu or sample table appears on the screen (Figure 14).



```
Calibration run for TCE


Date 7/30/1986 Time 14:40
Last Calibration Date 7/25/1986

CALIBRATION IS REQUIRED

Enter analyst identification: vt
Enter information as requested below for
the calibration run:

                    SAMPLE TYPE NUMBERS

0)  BLANK                                  4)  WATER SAMPLE
1)  STANDARD #A                            5)  SPIKE
2)  STANDARD #B                            6)  END OF SAMPLES
3)  STANDARD #C

    Position 1        BLANK
    Position 2        STANDARD#A
    Position 3        STANDARD#B
    Position 4        STANDARD#C
    Position 5        ENTER sample TYPE number: 4
                      ENTER sample IDENTIFICATION: sp11
```

Figure 14. Sample Table for Calibration Run.

If calibration is not required, the operator may choose main menu Option 1, *Analyze for TCE*. For TCE analysis, a similar menu is displayed and is presented in Figure 15.



```
Analyze for TCE

Date 7/30/1986  Time 14:42
Last Calibration Date 7/25/1986

Enter analyst identification: vt
Enter information as requested below:

                    SAMPLE TYPE NUMBERS

0)   BLANK                              4)    WATER SAMPLE
1)   STANDARD #A                        5)    SPIKE
2)   STANDARD #B                        6)    END OF SAMPLES
3)   STANDARD #C

Position 1        BLANK
Position 2        ENTER sample TYPE number: 4
                  ENTER sample IDENTIFICATION: EFFA730
Position 3        ENTER sample TYPE number:
```

Figure 15. Sample Table for TCE Analysis.

Again the operator is prompted to enter certain pertinent information such as analyst and sample identification. Both the calibration and TCE analysis menus are displayed on the screen with certain sample positions fixed. For calibration runs, the first four autosampler positions are assigned in sequence and without deviation to contain a blank, Standards A, B, and C. When TCE analysis is to be conducted under an existing calibration, the only required sample is a blank in autosampler position 1, and the remaining positions may be used for analysis of up to nine samples.

D. SYSTEM CONTROL AND DATA COLLECTION

An IBM personal computer with a Data Translation analog-to-digital converter is used to collect data from the Varian GC. A personal computer was chosen as the data system and control device to support operation as a turn-key system requiring little user input; an interface, containing relay switches and other interface circuitry necessary to communicate with the instrumentation, was designed to control the entire system from the computer. A schematic of the circuitry is shown in Figure 16.

Once the operator has selected the type of analysis and entered the sample type and identification number, the computer will wait for the user to verify that the samples have been loaded in the order specified, or to amend the list to match the actual samples loaded. The user will then be instructed to start the purge and trap analysis. System start is initiated by pressing the *start* button on the Tekmar LSC and the *First Cycle* button on the Tekmar ALS. After this step, all operations in the analysis are automatic, and no further user input is required. During a typical run the following

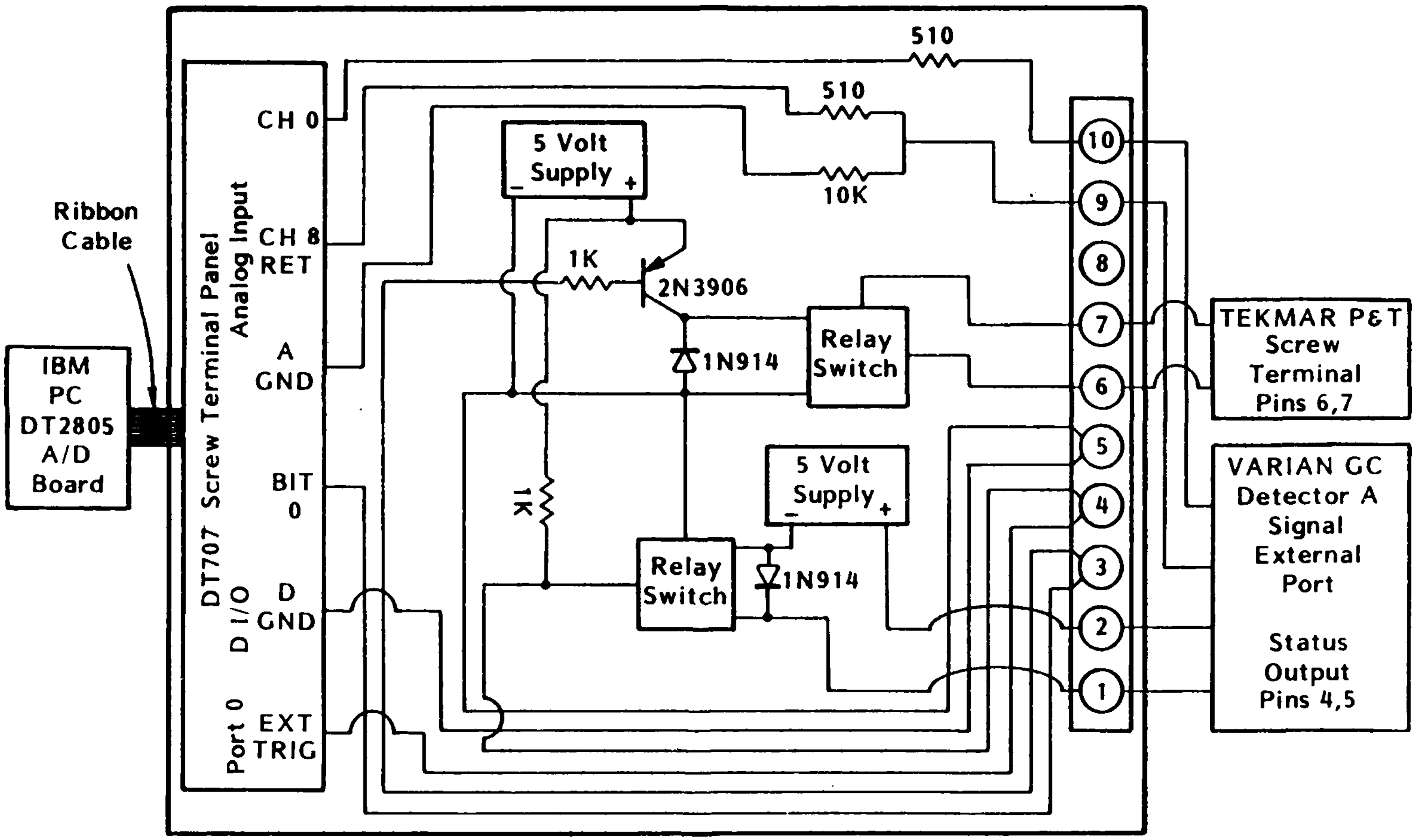


Figure 16. Schematic of Instrumentation Control Interface Box.

sequence of events occur under computer control:

- The LSC-2 purges the sample, and then stops and waits at Desorb Ready until a signal is received from the computer.
- The Tekmar LSC-2 monitors the GC oven temperature and waits for it to return to the initial value before continuing. It then waits to receive the "Desorb Begin" signal from the computer, at which time it simultaneously sends a "Begin Chromatogram" signal to the Varian GC and the desorb cycle begins.
- The GC responds by starting a chromatographic run and returning an acknowledging signal to the computer.
- The computer continues its "Desorb Begin" signal to the Tekmar and starts data collection from the Varian GC.
- After desorption is complete, the Tekmar completes a bake cycle, advances to the next sample, and begins the purge cycle at the first step of this sequence while data are collected for the current sample.
- When data collection and analysis are complete, the computer sends a "Desorb Begin" signal to the Tekmar to start the next chromatographic analysis.
- The process continues until all samples are run.

The flow of control signals between the purge and trap apparatus, gas chromatograph, and computer is shown in Figure 17.

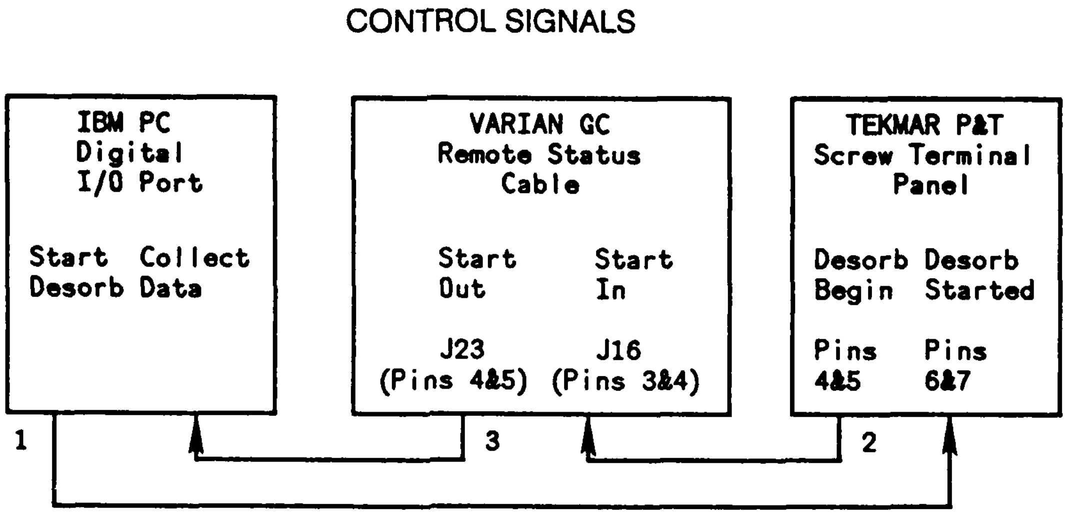


Figure 17. Sequence of Signals to Start Data Collection.

E. PEAK DETECTION

Our peak-detection software uses the increasing tangent search method as described by Woerlee and Mol, (Reference 3) which is basically a second-derivative test featuring decreased sensitivity to noise. When the tangents of the angles constructed between a fixed data point and the next four data points are increasing, a peak is detected. Peak validity is checked with first- and second-derivative tests. Peak apex detection is based on determining the maximum value before the downslope side of the peak is found. For flat-topped peaks, the center of the region is chosen as the apex. Peak end is based on the peak width and the slope. This method was tested on actual data and proved to be very reliable.

Basic peak-detection software is based on the intensity of the gas-chromatographic signal, relative to a linear baseline. When the signal attains a predetermined threshold value above the baseline value, a peak is recognized and integration begins. Even though this method requires minimal development time and subsequently lower cost, it is very susceptible to noise and is limited to isothermal chromatographic conditions. These limitations excluded this method from consideration.

For the development of the VOC software package, baseline correction was designed with nonideal gas chromatographic conditions and temperature-programmed analysis in mind. The chromatographic baseline is established by finding a straight line which will join one or more valleys without passing through any of them. An iterative process is conducted which initially joins the first valley of the chromatogram with the last valley and then checks all valleys within that range. If any valleys fall below this baseline, a new baseline is drawn from the first valley to this valley, and again a check is made. The next baseline segment begins where the last one left off, and continues until a baseline has been established for all the peaks.

As the peaks are identified, their areas are integrated from the system baseline. After the chromatographic baseline has been established, perpendiculars are dropped from the peak start and end positions on the chromatographic baselines to the system baseline. Corrected areas are calculated by subtracting this area from the initial integrated area.

F. PEAK IDENTIFICATION

S-CUBED has developed peak identification software using pattern recognition based on a multivariant statistics function usually referred to as the cosine theta (cos θ) function:

$$\cos \theta_{u,r} = \frac{\sum_{k=1}^{m} U_k \quad R_k}{\left[\sum_{k=1}^{m} U^2_k \quad \sum_{k=1}^{m} R^2_k\right]^{1/2}}$$

where theta is defined as the angle formed between the two vectors *U* and *R* in *m* dimensions. (Reference 4)

In this approach one adds known amounts of three or four internal standards to the sample. An internal standard is a reference compound, of which a fixed quantity is added to the sample. The internal standards were selected to be widely spaced in the chromatogram and to coelute with no known target compounds. Several methods for *peak identification and quantitation are available, and each was evaluated with respect* to the needs of this project.

Peak identification may be accomplished by using external or internal standard procedures. In the external standard procedure, the retention time of the compound of interest recorded is in memory. During sample data reduction the program *looks* for a GC peak in the retention time region of the target compound within a window of a few percent of the absolute retention time expected. Typically, three or four percent is used. If a peak is found within that window, it is labeled as the compound, a positive identification is reported, and quantitation follows.

However, retention time can change, and a peak that is not the target compound can drift into the retention time window and be identified in error. Alternatively, the target compound may drift out of the time window and be missed completely. Even under normal operating conditions, an interfering compound could be found within the window and result in misidentification of the target compound.

The use of internal standards reduces errors of this sort by analyzing a standard during the same chromatographic run as the sample. In the internal standard procedure, one adds to the sample a fixed quantity of a reference compound that is known not to coelute with the target compound. The internal standard is searched for within a time window. Once the internal standard is found, a search is made for the target compound based on its retention time relative to the internal standard. The advantages to the internal standard procedure are (1) relative retention time (RRT) is more precise, i.e., more predictable than absolute retention time, so fewer misidentifications are made, and (2) under normal operating conditions one can obtain quantitation based on response factors scaled to the internal standard. These values are generally more accurate and precise than external standard results. Even so, if retention times vary by more than a few percent, this method may also fail to find the internal standard and produce meaningful data. Therefore, the pattern-recognition algorithm was chosen as the best peak identification method for the turn-key system.

Under normal operating conditions (top of Figure 18) the pattern recognition program looks for the first internal standard in a relatively large window and then tries to identify the second and third internal standards at expected relative retention times based upon that first internal standard peak. In addition to finding the internal standards at their proper retention times, the areas of the other two internal standards relative to the first must also be within certain limits. Should chromatographic conditions change dramatically, as under the reduced flow conditions illustrated in the bottom of Figure 18, the extreme shift in retention times will not prevent correct identification of internal standards or target analyte.

If two or more peaks appear in the first absolute retention window, the algorithm will calculate a cosine theta value for each peak in that window. The peak whose calculation yields the highest cosine theta value is chosen as the correct primary internal standard peak. In this method, both retention times and relative areas are used to identify correctly the three internal standards and thus to calculate expected retention times for the compound of interest.

In addition, using multiple internal standards provides the ability to quantitate target compounds referenced to either one or all three internal standards. Using multiple reference peaks decreases the chances for error caused by material coeluted under an internal standard peak. Using this pattern-recognition algorithm, the VOC monitor can accommodate retention times that vary by 30 or 40 percent (Figure 18) and still produced useful data.

G. QUANTITATIVE ANALYSIS

To determine the amount of TCE in a sample, four response factors are calculated, one for TCE and one for each of the internal standards. The ratio of the peak area of the target compound to each internal standard peak is calculated. In a calibration run, three concentrations of TCE are determined while the concentration of all three internal standards is held constant. A linear relationship is developed between the response of TCE and the response of each of the internal standards. From these curves a correlation coefficient is calculated and checked against a predetermined acceptance criterion. An acceptable calibration is stored on disk and used to determine the TCE concentrations of all subsequent samples within a predetermined QC window, after which a new calibration is required.

In effect, three calibration curves are generated from the relationship of TCE response to that of the internal standards. Three concentrations are calculated for each sample, the standard deviation calculated and any outliers identified and removed. This distinguishes the effect of an occasional impurity coeluting with one of the internal standards. The sample result is reported as the mean of the accepted concentration values.

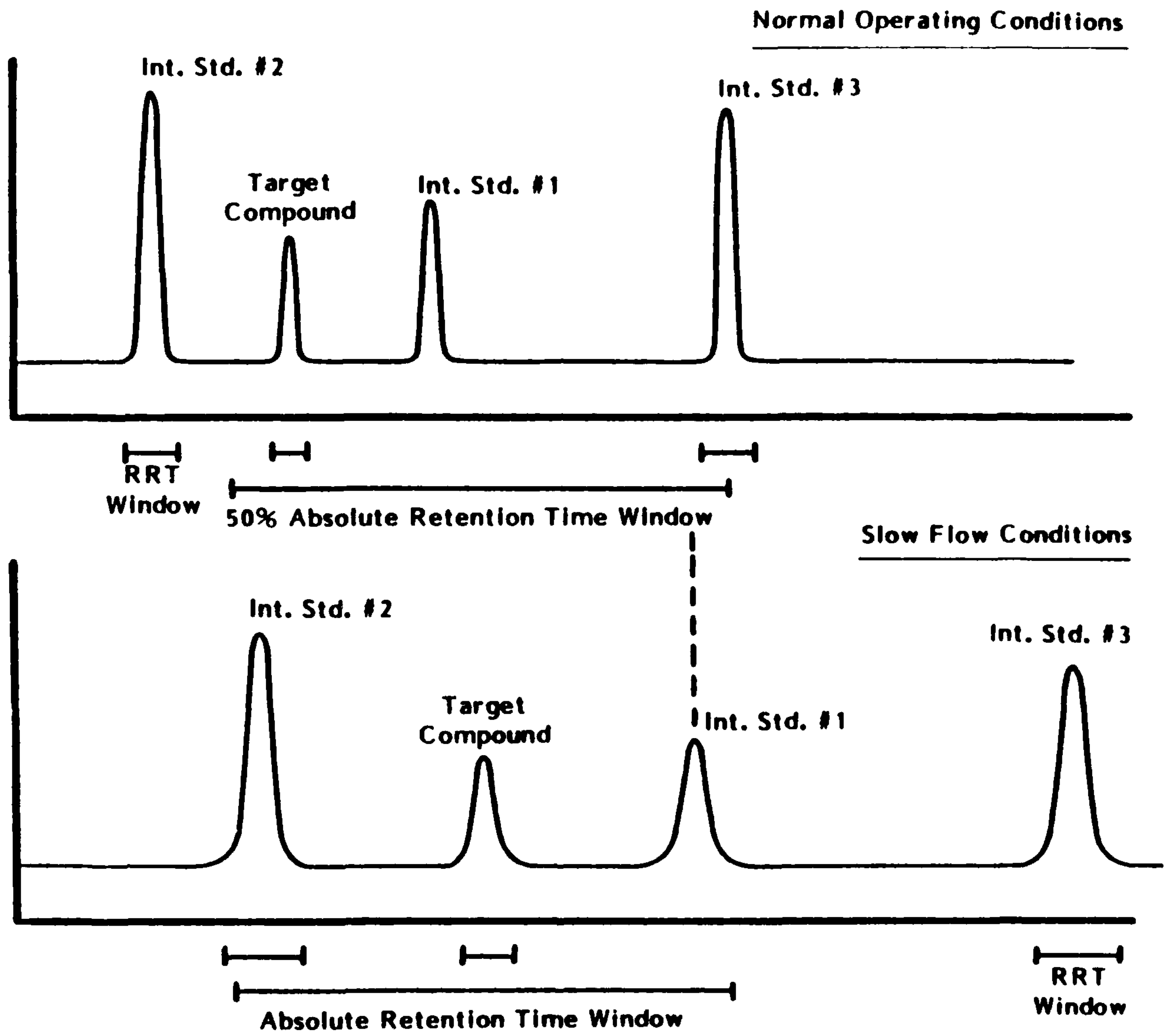


Figure 18. Example of Multiple Internal Standard Pattern Recognition.

H. QUALITY CONTROL/QUALITY ASSURANCE

A system designed to perform automated analyses with minimal operator participation must be able to perform complete self diagnostics and data evaluation. The software designed for this project compares sample results to a preestablished set of criteria that must be met before results are determined to be acceptable. These criteria include:

- The correlation coefficient of the calibration curve must be greater than 0.9.
- A calibration check is performed by daily analysis of STD B.
- A blank sample must be run with each set of ten samples.
- Duplicate spike samples are run after every ten samples.

Evaluation of the system performance during spike sample analysis was accomplished by analysis of three replicate samples and three spike samples. The samples were prepared to contain an absolute amount of 10 ng TCE in 5 mL and each spike sample was fortified with an additional 10 ng TCE. The results of this spike recovery experiment are summarized in Table 6. The mean recovery was 9.8 ± 3.2 ng TCE. The large coefficient of variation (cv = 33 percent) is a result of the expected variation among measurements made at or near the instrument detection limit and represents a real analytical limitation on any trace analytical procedure.

TABLE 6. RESULTS OF SPIKED SAMPLE ANALYSIS

Sample	Amount Expected (ng)	Amount Spiked Recovered (ng)	% Recovered
Sample-1	10	–	–
Sample-1 + Spike	20	8.5	85
Sample-2	10	–	–
Sample-2 + Spike	20	7.5	75
Sample-3	10	–	–
Sample-3 + Spike	20	13.5	135
Average Spike Recovery			98

Correlation Coefficient of Standard Curve; 0.999

The quality of analytical data may be monitored by control charts. To create a control chart, the analyst plots the results of an analysis of a sample of known concentration against the particular day or time at which the result was obtained. In this way, the quality of data from unknown samples may be estimated by considering the deviation of the control sample from the expected value. When the control sample deviates unacceptably from the expected value, the system is considered *out of control* and corrective action must be taken before sample analysis may proceed.

The Prototype VOC Monitor has a control chart type QA/QC feature built into the software. Spiked samples are used as control samples and the results are evaluated using the following criteria:

- Reproducibility - The difference between the pair of spike results must be less than 25 percent of the expected TCE value.
- Accuracy - The mean recovery of TCE from the pair of spiked samples must be greater than 75 percent.

If the spike and duplicate spike determinations fail these criteria, recalibration of the system is required. Should a calibration fail during unattended operation, the system will calculate TCE concentrations based on the last successful calibration to prevent loss of sample data. These results, however, will be flagged as estimates *only*. This default feature will prevent complete loss of data in cases where additional sample is not available. A quality control archive file is automatically updated each time a set of spiked samples is run. In this way, system performance may be monitored over time by retrieving the archived quality control data. Each month a new archive file is automatically created so a complete record of system performance is available to provide an estimate of the quality of sample results during a specific QC period.

SECTION VI

PERFORMANCE EVALUATION

The final application of the VOC monitor is to provide rapid turnaround analysis of groundwater to determine the level of TCE with respect to regulatory limits. To establish the validity of the results generated by this automated system an interlaboratory comparison was performed. A set of water samples was prepared at a range of TCE concentrations and analyzed at Wurtsmith by the VOC monitor and at S-CUBED by EPA Method 624, GC/MS analysis with purge and trap sampling.

Duplicate sets of samples were prepared at S-CUBED to contain quadruplicate aliquots of aqueous TCE solutions at concentrations of 1, 2, 3, 4, and 5 ppb. One set of samples was shipped to Wurtsmith AFB and one set was retained at S-CUBED. The results obtained by each laboratory are presented in Table 7.

For each concentration level the mean and standard deviation are presented for all measurements except where noted. In general, the average result for each data set presents acceptable precision, and agreement between the two methods is good. The sample set provided by Wurtsmith AFB contains only one duplicate result for the 3-ppb level and three results for the 4-ppb level. The four 1-ppb and 5-ppb aliquots were split and duplicates analyzed on the VOC monitor and therefore eight results are reported for those samples.

A plot of measured concentration as a function of expected concentration was prepared for both data sets and is presented in Figure 19. Two data points from the VOC monitor 1-ppb data set were rejected as outliers as were both measurements of the 3-ppb sample. These values were excluded from subsequent regression analysis; otherwise, all measurements were included. A second curve in Figure 19 fits Wurtsmith's data set less the same 1-ppb points and the 3-ppb determination. The results of the regression analysis are presented in Table 8.

Based on the good correspondence between the slope of the regression line for both data sets, the VOC monitor is an acceptable alternative to standard EPA methods for TCE analysis in aqueous samples, and an application has been submitted to EPA Region V for acceptance of this method as an Alternative Test Procedure for TCE determinations at Wurtsmith AFB.

TABLE 7. RESULTS OF SPLIT SAMPLE ANALYSIS

Normal Concentration	TCE (ppb)	
	Method 624	VOC Monitor
1	0.68	0.92
	2.11	0.71
	0.83	0.77
	1.08	1.23
		1.04
		6.00[a,b]
		6.64[a,b]
		0.77
mean	1.17	0.99
SD	0.64	0.19
2	1.53	1.34
	1.46	1.61
	1.46	1.78
	1.01	1.19
mean	1.37	1.48
SD	0.24	0.26
3	2.38	5.72[b]
	2.14	5.26[b]
	2.30	-
	1.84	-
mean	2.16	NA
SD	0.25	NA
4	0.89	2.21
	3.17	2.64
	2.28	2.84
	2.94	-
mean	2.32	2.56
SD	1.02	0.23
5	3.79	3.93
	3.97	4.81
	2.70	5.11
	3.58	3.59
		3.50
		3.42
		3.45
		3.01
mean	3.51	3.85
SD	0.56	0.73

[a] Not used in computation of mean and standard deviation.

[b] Excluded from plot and regression analysis.

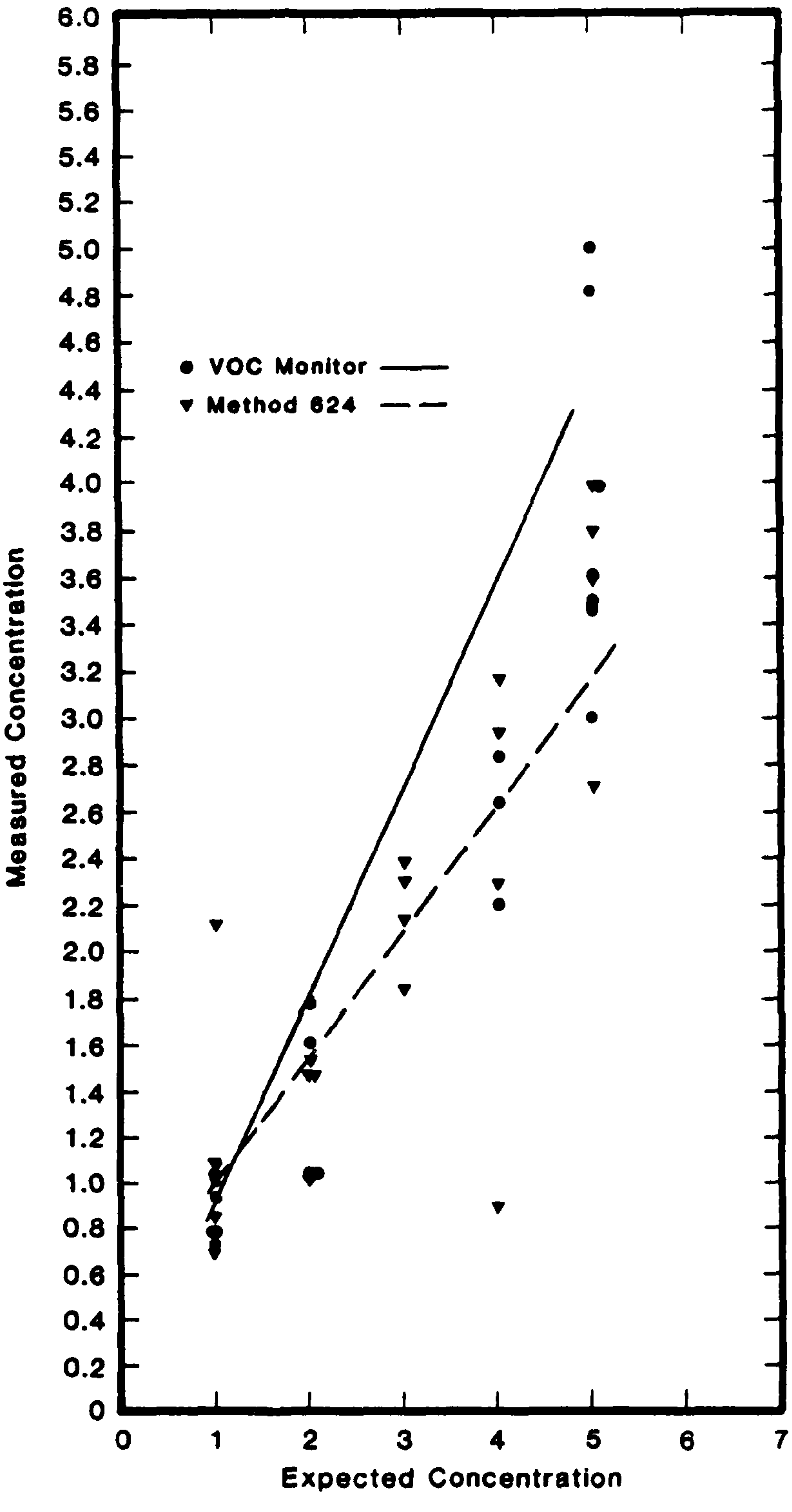


Figure 19. Measured Concentration as a Function of Expected Concentration for TCE Determined by Two Methods.

TABLE 8. RESULTS OF REGRESSION ANALYSIS OF SPLIT SAMPLE DATA

Analysis	VOC Monitor	EPA Method 624
Number of data points	20	20
Slope	0.724	0.562
y-Intercept	0.103	0.419
Correlation coefficient (r^2)	0.925	0.807

SECTION VII

TRANSITION TO THE FIELD

After disassembly into its components, each of which was packaged carefully in the original manufacturer's crate or an equivalent carton, the VOC monitor was shipped directly from S-CUBED's facility to the site at Wurtsmith AFB via commercial carrier. Except for repairable distortion of a few metal parts, a couple of loose screws, and a chip knocked out of one sparging vessel, the system arrived in perfect condition and was assembled in a day. The shipment included all manufacturer's documentation to accompany the units purchased, and sufficient glassware, supplies, and chemicals to support the system for more than a week after the installation.

A preliminary site survey had determined that the laboratory area of the sewage plant appeared to be adequate for installation of the prototype VOC monitor. Working from experience in a well-prepared, dedicated laboratory environment, S-CUBED assembled a set of pre-installation instructions specifying ancillary (two refrigerators, oven for drying clean glassware, fume hood, vacuum pump, and analytical balance), environmental (30-A 110-V AC service, dust- and organic-free room air), and consumable requirements (ultraclean solvents, compressed gases, spare small equipment items and supplies) to be available on site at or immediately following installation.

During the actual installation on site, a wall-mounted cabinet was raised several inches to accommodate components underneath. A 3.5-V current measured from neutral to ground in the IBM PC repeatedly caused ground-fault-interrupt breakers to trip; conventional breakers were not affected by the ground current (which presented no problem at S-CUBED's site), and an isolated, dedicated AC circuit protected by a 3-kVA line conditioner was required to protect the VOC monitor from destructive surges and from interference of smaller transients with data transmission. Restraints for gas cylinders (OSHA requirement) were requested at the same time, and both modifications were installed afterward by the cognizant base shops.

Normal lags in procurement of supplies attended the installation and initial provisioning of the VOC monitor. Emergency procurements were invoked on several occasions, and Wurtsmith AFB personnel extended wholehearted cooperation throughout the installation and evaluation period. Even so, at least a month of operating time was lost in waiting for delivery of supplies, and the standard procedure of requisitioning replacements whenever supplies on hand are within 6 months of exhaustion was strongly recommended. It may be useful to note that timely lines of supply for gases were established through Defense General Supply Center (Richmond, VA). As similar learning curves for procurement and maintenance of supplies will occur at any new site, site modifications and procurements should be initiated several months prior to the date of installation, and not less than a three-month supply of any item not on site at the time of delivery should be included in the initial installation package.

Environmental conditions at the sewage plant have proved to be generally adequate, with the following exceptions:

- A background of about 100 parts-per-trillion of benzene appears in outputs from the VOC monitor on site. Efforts to locate and suppress the source of this contamination have failed so far, but it is suspected to be intermittent airborne contamination; however, chromatographic separation is sufficient that the monitor produces accurate results except when the concentration of TCE is below the threshold for detection, in which event a false positive result, recognizable by the operator, is reported. Relocation of the VOC monitor to a *clean* area, ideally in a setting like a clinic, in which strenuous environmental control is already exercised, would be an approach to the problem of background contamination, but such facilities may not be available at all candidate locations. Accordingly, this problem will be addressed in the Phase II development, and this unit will be retrofitted afterward to include improvements.

- Transient signals, associated with automatic switching on and off of electrical equipment in the vicinity (and presumed to be transmitted in the 110-V AC supply), occasionally interfere with control of event timing by the computer. The line conditioner is intended to suppress such interference in the AC service, but, prior to its arrival, significant improvements in performance were obtained by moving a small refrigerator away from the area of the VOC monitor and by amending the software to narrow the time window during which such interferences can act. Testing for short- and long-term instabilities in the electrical service should be incorporated into initial site surveys preceding future such installations; a line conditioner is recommended as a standard precaution and, in any event, sites in which a reliable power source cannot be established prior to installation should be avoided.

- Personnel unfamiliar with environmental requirements of electronic equipment have practically uncontrolled access to the area housing the VOC monitor. In one disastrous episode, canvas dust covers were put over the components on the VOC monitor, in place, while a hole was chiseled into an adjacent cinder-block wall to permit the installation of an air conditioner. Prompt cleanup efforts by the instrument technician salvaged several of the component units, but extensive damage to one of the disc drives put the computer out of commission for nearly a month, and a catastrophic failure of the line conditioner occurred shortly afterward. Where protective isolation is impractical, emergency instruction and a telephone number for a POC should be posted prominently.

Operator training during the evaluation period was a face-to-face process involving expert project personnel and base personnel with minimal experience in techniques and principles related to the VOC monitor. Three visits were made to the site to deliver training to operators, and during each visit one operator (different each trip) was the primary recipient. In addition, instructional guidebooks (Appendices B and C) were provided, and contractor personnel and the project officer were available by telephone and on call to return to the site in an emergency.

Each of the three operators (two uniformed personnel and one civilian) learned the operation of the system satisfactorily, and each was able to generate data independently during the periods when the VOC monitor was up and running. Both the quality of the companion documents and the visible support from project personnel were significant factors in the acceptance and implementation of this concept. Although the companion documents provide sufficient information to introduce new operators to the operation of the system, most trainees will prefer to learn procedures while an experienced operator is available to consult. Maintenance by operators of a loose-leaf book detailing specific procedures might serve as a basis for preserving some experience.

During the 11 months eventually committed to field evaluation of the prototype VOC monitor, the system was in service about 30 percent of the time; however, most of the down time was spent waiting for logistical support during the procurement and maintenance learning processes. During the evaluation period, only three spontaneous failures of VOC monitor components exceeded the experience level of the operator and required the intervention of project personnel: a broken wire in the transfer line heater in the ALS-10, misalignment of the six-port valve in the LSC-2, and occlusion of the surface of one (or more) of the contacts on a printed circuit board in the GC; total repair time was a couple of days, and the only part required was a common wire connector available from the Electrical Shop. The operator managed the recovery from the construction incident, but in so doing inadvertently incorporated an ungrounded extension cord that fed the computer's 3.5-V ground current into the data channel and created a bizarre constellation of symptoms in data outputs that ultimately resulted in another site visit; however, this sequence of events involved no failures on the part of the VOC monitor. Numerous other minor patches and adjustments were accomplished by site personnel using local resources or telephone instructions.

The issue of long-term maintenance remains to be determined. At Wurtsmith AFB (or almost any other) military installation, support shop resources are limited and not set up to be readily accessible for timely response to maintenance requirements of an unfamiliar instrument system. The service organizations of the manufacturers of the components have outstanding reputations for supporting their individual units, and our experience with them during this transition to the field is consonant with their reputations. A service contract has been purchased from Varian to cover the cost of parts and labor for repairs to both the Varian and the Tekmar components, primarily to shorten the response time by taking Procurement out of the reflex arc. No contracted service calls (except to repair the computer after the construction incident) were required during the evaluation period.

The mechanical ability and involvement of the operators will play a significant part in the success or failure of this system in the field. During the evaluation period, the civilian operator was more alert in perceiving when maintenance was needed, and more competent in the mechanical aspects of identifying and performing repairs or knowing where to go for help. A sample this limited will not support a generalization, but some consideration of mechanical aptitude and of expected time left on site must be included in the selection of personnel as candidate operators of such an unusual instrument system. If such units achieve wide acceptance in the field, a self-propagating fund of experience will evolve within a large population of operators; in the interim, much of the experience carried away by former operators will have to be rediscovered by their successors. The current NCOIC at this installation is exploring the possibility of creating a permanent civilian position for a laboratory technician, whose primary function would be to provide continuity of experience.

SECTION VIII

CONCLUSION

The prototype volatile organics monitor designed and assembled by S-CUBED is capable of unattended sampling and analysis of up to nine samples. The system possesses sufficient on-line diagnostic capability to aid novice operators in real time assessment of system performance. The results of the split sample analysis illustrate the equivalence of this prototype system to accepted EPA methodologies.

In the course of the transition phase of this project, a major portion of the total effort was directed at coordination between the personnel at Wurtsmith AFB and S-CUBED contractors. The conditions of the contract under which this effort was performed included inadequate provisions in the area of site preparedness and overestimated the aptitude of site personnel for system maintenance and operation. This required a number of procedural adjustments during the on-site evaluation phase which resulted in delays in completion of the project.

Should the Air Force elect to continue in the area of monitoring equipment such as the prototype VOC monitor developed under this contract, some guidelines for site preparation should be observed to facilitate transition to the field. These recommendations include:

- Establishment of a dedicated laboratory for the installation and operation of the system with appropriate facilities for associated sample preparation and storage.
- Preparation of the designated installation site with all necessary equipment as listed in the Procedural Guide and Operation and Maintenance Manuals prior to delivery and training.
- Commitment of Air Force and on-site civilian personnel to receive training during installation and to continue as operators throughout the course of the project with the support and cognizance of all supervisory personnel.

The system designed by S-CUBED fully meets the Air Force need for an automated system capable of trace level analysis of TCE in ground water. The system provides extensive built-in QA/QC functions to assure the quality of the final results. In additional, significant flexibility has been built into the S-CUBED system so eventual expansion to analysis of additional volatile organic compounds may be accomplished.

SECTION IX

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APPENDIX B

PROCEDURAL GUIDE

Material contained in this appendix has been published without change from its original format.

S-CUBED
A Division of Maxwell Laboratories, Inc.

PROCEDURAL GUIDE FOR AUTOMATED PURGE AND TRAP ANALYSIS OF TRICHLOROETHYLENE IN WATER

Contract CN F08635-84-C-0298

S-CUBED Report No. SSS-R-86-8083
S-CUBED Reference No. 11272-03

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September, 1986

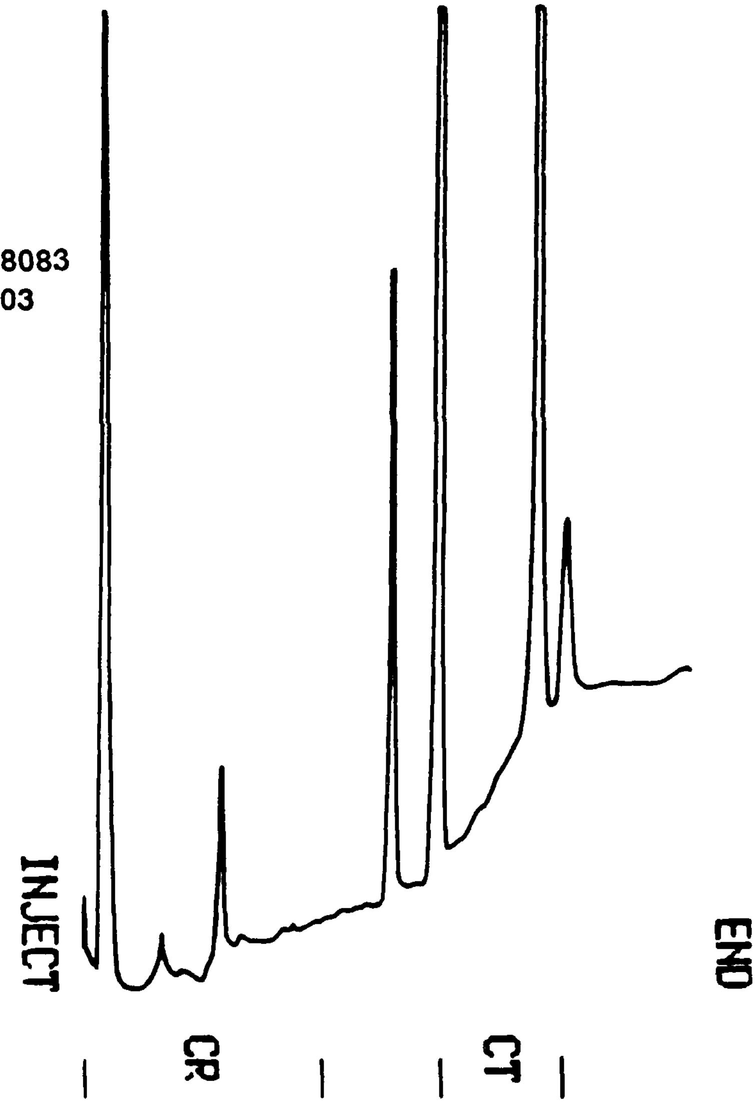

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TABLE OF CONTENTS

1.0 INTRODUCTION 1
1.1 Gas Chromatography 1
1.2 Concentration of Volatile Organics by Purge and Trap Techniques ... 4
1.3 Computer-Controlled Data Acquisition 7

2.0 APPARATUS 8
2.1 Sample Collection Vials 8
2.2 Purge and Trap Equipment 8
2.3 Gas Chromatograph 8
2.4 GC Column 8
2.5 Syringes and Valves 8
2.6 Storage Vials 8
2.7 Data Acquisition System 8

3.0 REAGENTS, CHEMICALS AND COMPUTER SUPPLIES 9
3.1 Sorbent Traps 9
3.2 Organic-Free Water 9
3.3 Stock Standards 9
3.4 Methanol 9
3.5 Diskettes 9
3.6 Paper 9
3.7 Reagent Gases 9

4.0 GENERAL LABORATORY PROCEDURES FOR VOLATILE ORGANICS ANALYSIS 10
4.1 Glassware Cleaning 10
4.2 Cleaning of Sparging Vessels 10
4.3 Cleaning of Sample Vials for Volatile Organic Analysis (VOA) 10
4.4 Preparation of Organic-Free Water 12
4.5 Storage of VOA Samples and Standards 12
4.6 Opening Sealed Ampules 12

5.0 FIELD SAMPLING PROCEDURES 15
5.1 Preparation of Field Blanks 15
5.2 Filling and Sealing VOA Vials 15
5.3 Direct Collection of Volatile Organics from a Flowing Stream or Tap . 15

TABLE OF CONTENTS (Continued)

6.0 PREPARATION OF STANDARDS 17
- 6.1 Preparation and Storage of Trichloroethylene (TCE) Stock Standards 17
- 6.2 Storage of Internal Standard Stock Solution and Purchased TCE Standard Stock Solution 19
- 6.3 Preparation of TCE Working Standard 19
- 6.4 Preparation of Internal Standard Working Standard 20
- 6.5 Preparation of TCE Daily Calibration Standard 20
- 6.6 Preparation of Internal Standard Daily Standard 21
- 6.7 Preparation of Calibration Samples 21

7.0 DATA SYSTEM OPERATION 22
- 7.1 System Cold Start (Power Off) 22
- 7.2 Calibration Run 26
- 7.3 Routine TCE Analysis 28
- 7.4 Duplicate Spike Samples 29

8.0 OPERATION OF PURGE AND TRAP APPARATUS 31
- 8.1 Loading Syringes 31
- 8.2 Loading Automatic Liquid Sampler (ALS) 31
- 8.3 Preparation of TCE Spike and Duplicate Spike Samples 34
- 8.4 Dilution of High-Concentration Samples 34
- 8.5 Instrument Start Procedure 35

APPENDICES

- I Standard Log Sheets
- II Abbreviated Operating Instructions

LIST OF FIGURES

1 Schematic of Computer-Controlled Instrument for Purge and Trap Analysis of Volatile Organics 2
2A Chromatogram of Organic-Free Water 3
2B Chromatogram of Water Sample 3
3 Tekmar Liquid Sample Concentrator and Automatic Liquid Sampler 5
4 Status Panel for Process Monitoring on the LSC-2 6
5 Cleaning Autosampler Spargers 11
6 Apparatus for Preparation of Organic-Free Water 13
7 Opening Sealed Standard Ampules 14
8 General Procedure for Preparation of Volatile Organic Standards 18
9 Keyboard 23
10 Special Keyboard Keys 24
11 Correct Procedure for Insertion of Floppy Diskette into Drive A 25
12 Data System Main Menu 26
13 Sample Table for Calibration Run 27
14 Sample Table for TCE Analysis 29
15 Sample Table for Spike and Duplicate Spike Analysis 30
16 5-mL Needle Sparge Vessel and Sample Introduction Valve 32
17A Loading Samples into Automatic Liquid Sampler 33
17B Top View of Sample Introduction Valve 33

1.0 INTRODUCTION

Several synthetic halogenated organic compounds may be introduced into the water supply as the result of various industrial processes. The nature of these compounds (low molecular weight, limited aqueous solubility and ready volatilization from solution) make careful procedures for sampling and analysis crucial for accurate determinations.

Trichloroethylene (TCE) is one such halogenated organic compound, which is regulated as a hazardous substance. Where TCE is detected in a water supply, proper monitoring and evaluation of required clean-up procedures is required.

This manual outlines the operation of an instrumental system to determine TCE at parts-per-billion (ppb) concentrations in water. The system consists of:

(1) A gas chromatograph.

(2) A purge and trap liquid sample concentrator and a ten-position automatic sampler.

(3) An IBM PC programmed to operate the components and to acquire, analyze, and report data.

The entire system is diagrammed in Figure 1. Competent operation of this system requires no detailed knowledge of chemistry or computers; however, a general understanding of the analytic procedures used to determine TCE in water will aid the operator in learning to operate the system and produce reliable data.

1.1 Gas Chromatography

Gas chromatography (GC) is a technique used to separate components of a mixture. In general, a sample is introduced (at [3] in Figure 1) onto a column (at [5] in Figure 1) contained in the GC oven. The column contains a packing material onto which each compound of the mixture is adsorbed. Nitrogen gas flows continually through the column and, as the oven heats, each individual compound enters the stream of nitrogen at a rate depending on: (1) its boiling point; and (2) its affinity for the packing material. This results in a separation in time of components of the mixture. As each individual compound arrives at the detector (at [6] in Figure 1), it produces a response proportional to the amount of that material in the mixture. The detector signal is received by the data acquisition system, which calculates the concentration of the material in the sample. Figure 2 illustrates the separation of components in a mixture

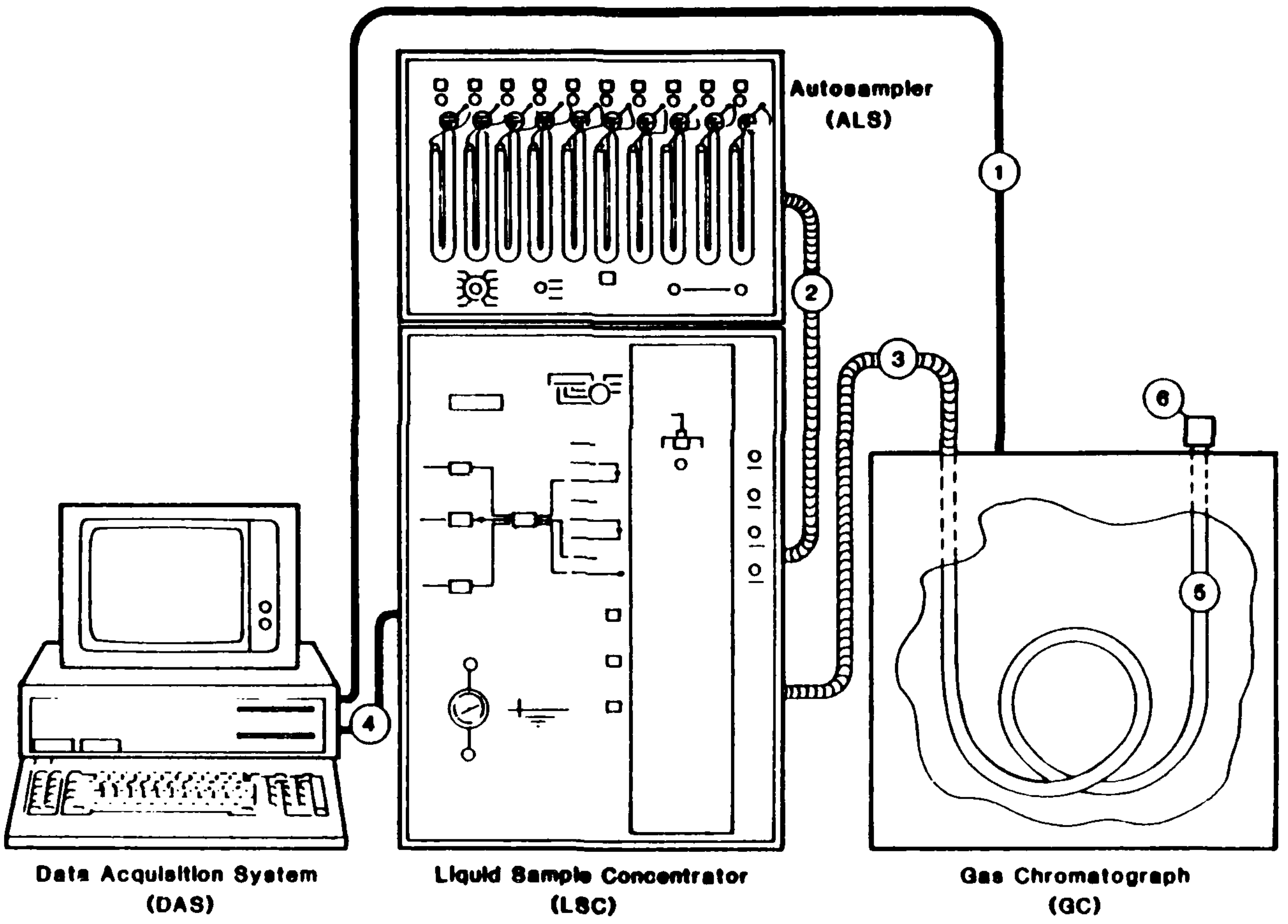


FIGURE 1. Schematic of Computer-Controlled Instrument for Purge and Trap Analysis of Volatile Organics

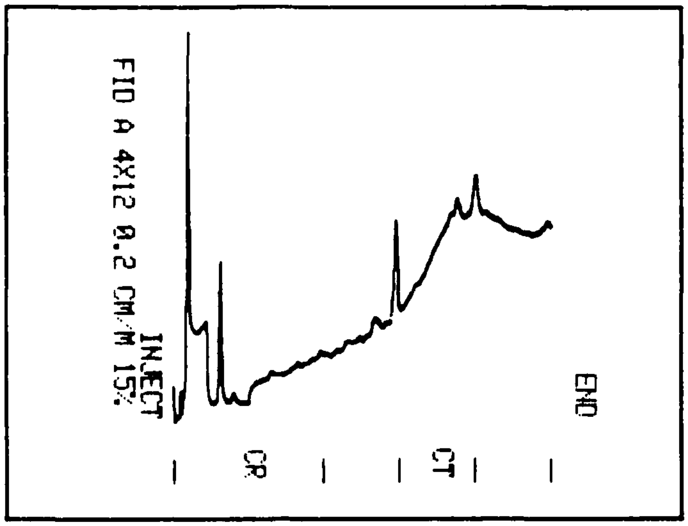


FIGURE 2A. Chromatogram of Organic-Free Water

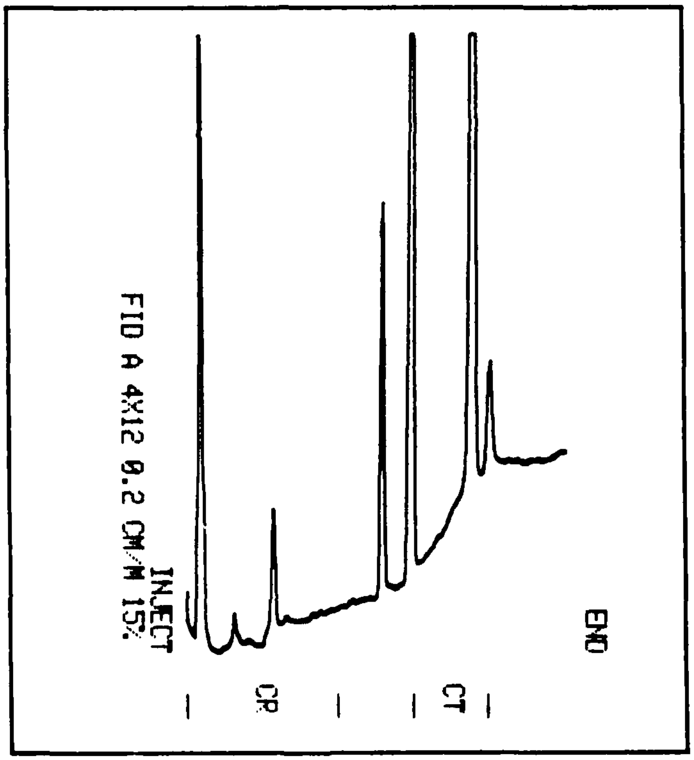


FIGURE 2B. Chromatogram of Water Sample

with a representative chromatogram of an actual water sample (bottom) collected at Wurtsmith AFB, and the result of analyzing a sample of organic-free water (top) to evaluate the response to a "zero-concentration" sample.

1.2 Concentration of Volatile Organics by Purge and Trap Techniques

Successful analysis of volatile organic compounds in aqueous solution at ppb levels requires a concentration step. The technique known as purge and trap is based on the ability of an inert gas to "extract" certain compounds from water and transfer them quantitatively to the GC.

The system described in this manual consists of a controlling unit, the LSC-2, and an auto sampler (ALS). The LSC-2 houses the trap where the volatile organics are deposited after purging, the pneumatics that divert the gas flow during each step, and the heated transfer line by which the volatile compounds are delivered to the GC. A picture of the purge and trap system is provided in Figure 3.

The purge and trap procedure is automatic. Once the samples are loaded and purging is initiated, the following steps occur:

1.	Purge Ready:	The trap temperature has returned to near room temperature.
2.	Purge:	Nitrogen is bubbled through the sample and the volatiles are deposited on the trap.
3.	Purge Complete:	
4.	Desorb Ready:	After automatic purging, the system waits for the GC to finish its run and for the GC oven to cool before proceeding to the next step.
5.	Desorb Preheat:	The trap is quickly heated to 100°C.
6.	Desorb:	The trap is heated to 180°C and the volatile compounds adsorbed on the trap are transferred via the heated line to the GC.
7.	Bake:	The trap is heated to 200°C for three minutes to remove any remaining material.
8.	Standby:	The system waits for the trap to return to room temperature before proceeding to Purge Ready.

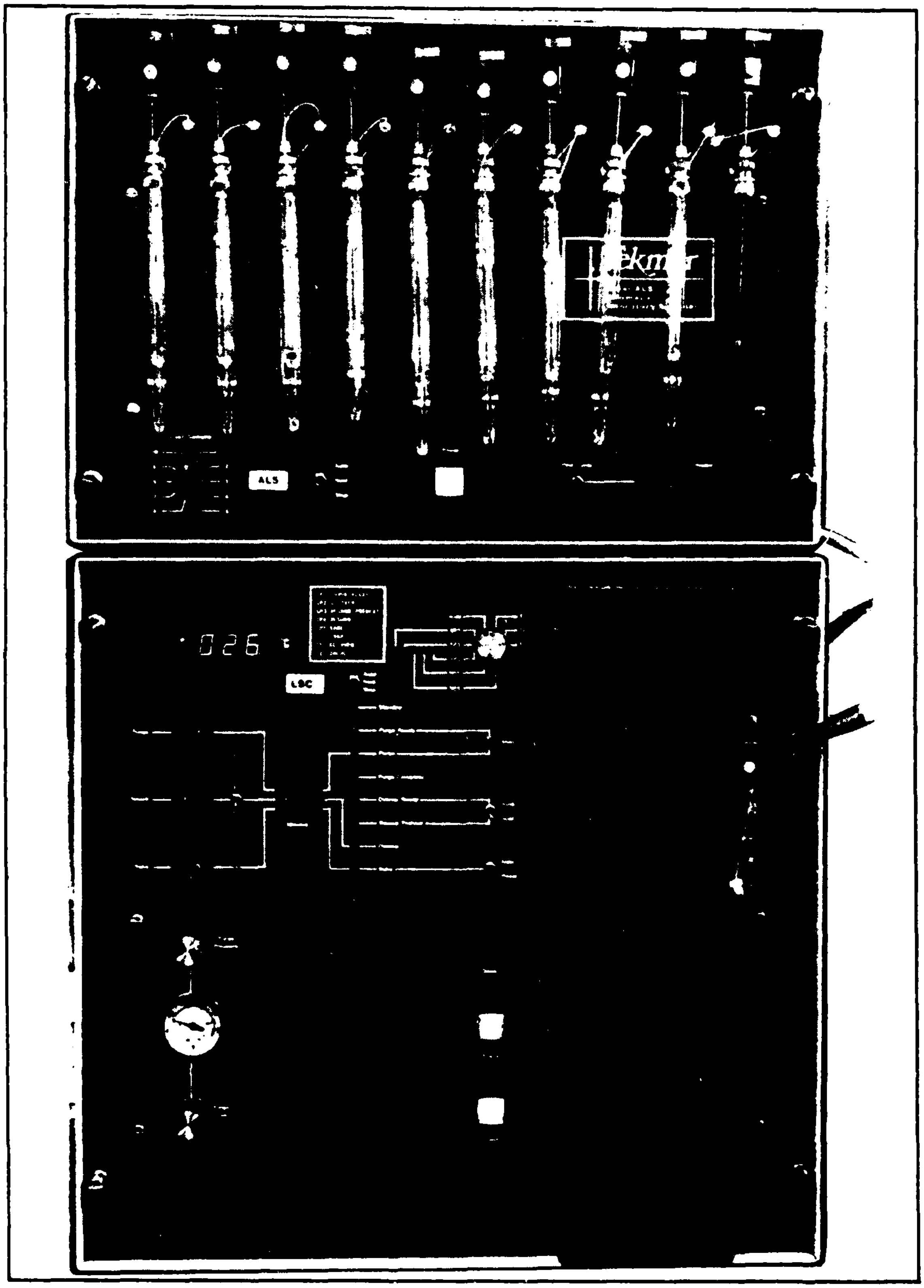
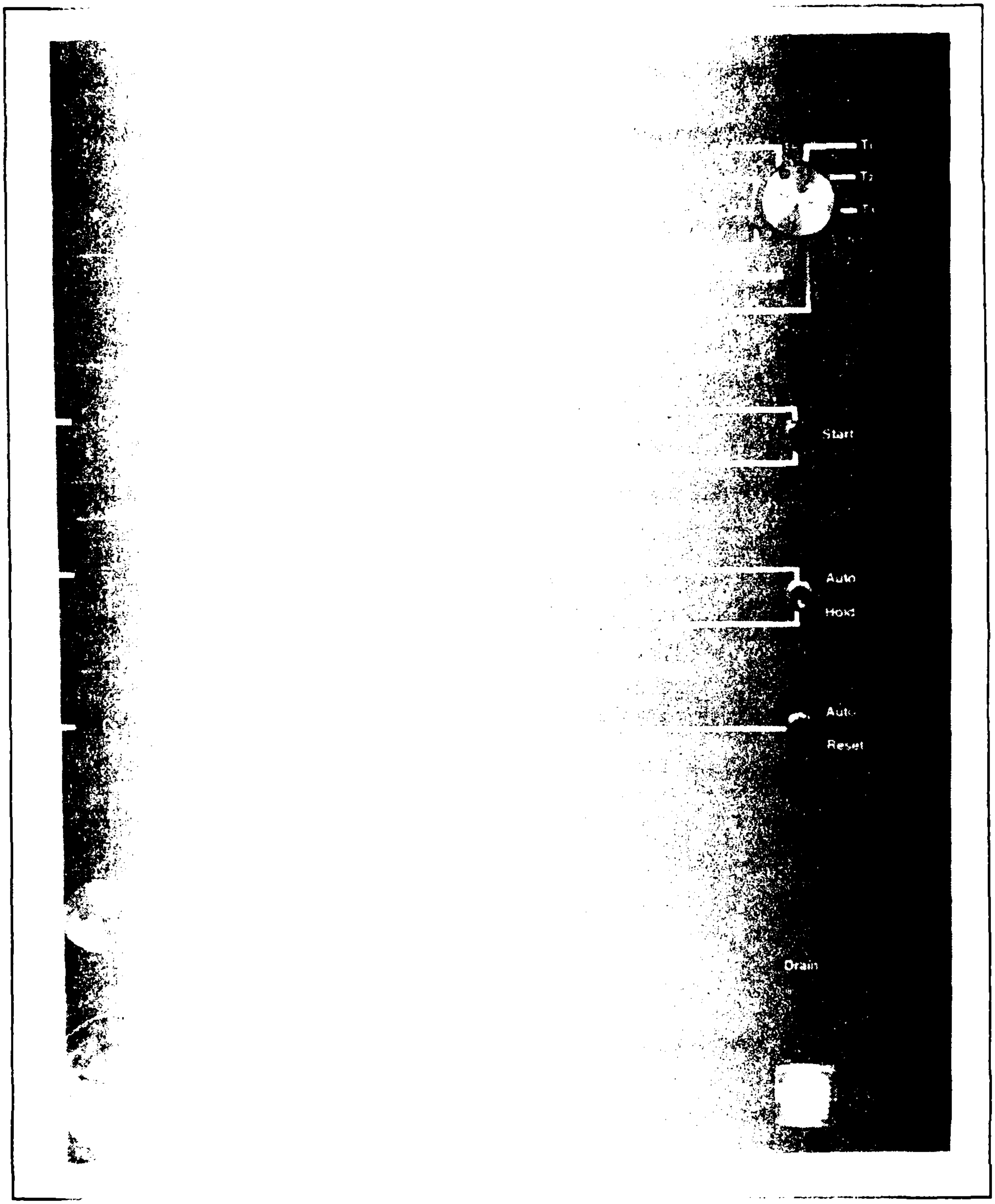


FIGURE 3. Tekmar Liquid Sample Concentrator and Automatic Liquid Sampler



LSC-2

The progress of the analysis may be monitored by observation of the status lights and digital temperature display on the front panel of the instrument as illustrated in Figure 4.

1.3 Computer-Controlled Data Acquisition

A number of analysis options are available through the data acquisition system. In general, *TCE Analysis* and *TCE Calibration Run* will be the options used most often. The other available options may be required occasionally, and instructions for their use are found in the Operating and Maintenance Manual.

The data acquisition software has been developed to provide the user with step-by-step instructions to insure ease of operation and production of accurate results. To determine the quantity of TCE in a sample, the response for that sample must be compared to the response of a solution of known concentration. Before any samples may be run, the system must be calibrated by analyzing three TCE solutions of known concentration over a preset concentration range. The data system will require that a calibration run be performed if:

1. Daily standard did not meet specifications,
2. The previous calibration did not meet specifications, or
3. More than ten days have elapsed since the last calibration.

The data acquisition system is based on an IBM PC with dual disk drives. When data collection and analysis are not in progress, the PC may be used for other tasks.

2.0 APPARATUS

2.1 Sample Collection Vials

Screw cap vial of 40 mL with Teflon-faced silicone septa.

2.2 Purge and Trap Equipment

LSC-2 with a ten-position autosampler (ALS).

2.3 Gas Chromatograph

Varian 3400 GC with flame ionization detector.

2.4 GC Column

Six-foot stainless steel column packed with one percent SP1000 on 60/80 mesh Carbopack B.

2.5 Syringes and Valves

2.5.1 Gas-tight micro syringes: 10, 25, 100 μL.

2.5.2 Gas-tight Luer Lock syringe (5 mL).

2.5.3 Stainless steel cap to fit each Luer Lock syringe.

2.6 Storage Vials

Screw cap vial of 1.5 mL with Teflon-faced silicone septa. Screw-cap vials of 7 and 25 mL with Teflon stop-and-go valve screw caps.

2.7 Data Acquisition System

2.7.1 IBM PC.

2.7.2 Communications Interface.

2.7.3 Epson FX-80 Printer.

3.0 REAGENTS, CHEMICALS AND COMPUTER SUPPLIES

3.1 Sorbent Traps

Stainless steel (25-cm x 1/8-inch OD) packed with Tenax GC (60-80 mesh).

3.2 Organic-Free Water

Prepared according to Section 4.4 from HPLC grade water.

3.3 Stock Standards

Reagent trichloroethylene and internal standards solution purchased from Supelco to prepare stock standards.

3.4 Methanol

HPLC grade, or equivalent.

3.5 Diskettes

Diskettes (5-1/4-inch), single-sided, double density, soft sector, 48TP1.

3.6 Paper

Fan fold paper (9-1/2 to 10-inch wide) for Epson printer.

3.7 Reagent Gases

Nitrogen (99.999 percent minimum purity); Air, dry; and Hydrogen (99.9 percent minimum purity).

4.0 GENERAL LABORATORY PROCEDURES FOR VOLATILE ORGANICS ANALYSIS

4.1 Glassware Cleaning

Each piece of glassware used for volatile analysis must be cleaned thoroughly prior to use.

4.1.1 Using a good quality lab glassware cleaner (Liquinox or equivalent) and water, wash each piece of glassware.

4.1.2 Rinse the glassware sequentially with tap water, with deionized water, and with methanol.

4.1.3 Rinse the glassware one final time with distilled water and place in a 110°C oven for two to three hours. Remove from oven and allow to cool to room temperature, in a clean area.

4.1.4 Store the glassware either stoppered or covered with aluminum foil in an area free of organic solvent contamination.

4.2 Cleaning of Sparging Vessels

Each sparging vessel should be cleaned individually prior to use to prevent carry-over contamination as follows.

4.2.1 Attach a vacuum line from an aspirator to one end of the sparger. Draw some hot tap water through the vessel (Figure 5).

4.2.2 Continue cleaning by drawing sequentially, 5 mL each of hot water, soapy water, a tap water rinse, methanol, and, finally, a distilled water rinse through each sparging vessel.

4.2.3 Place the spargers in a 100-110°C oven for two to three hours.

4.2.4 Remove the spargers from the oven and allow them to cool completely before use.

4.3 Cleaning of Sample Vials for Volatile Organic Analysis (VOA)

4.3.1 Clean 40-mL VOA sample vials, caps, and Teflon-faced silicone septa as described in Section 4.1.

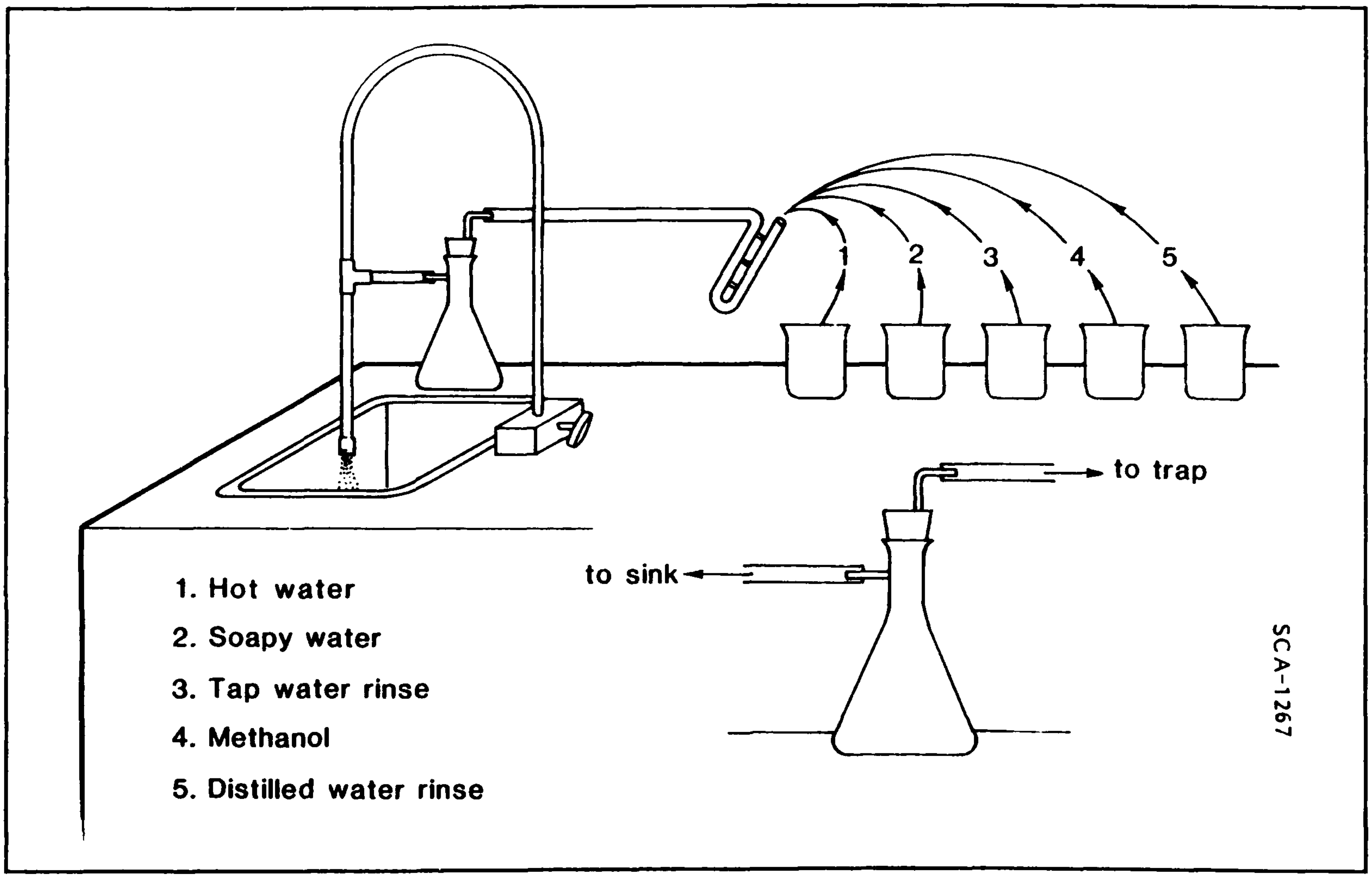


FIGURE 5. Cleaning Autosampler Spargers

4.3.2 Once vials, caps, and seals are cool, assemble the vials and store.

4.4 Preparation of Organic-Free Water

4.4.1 Fill a 500-mL gas washing bottle, cleaned by the method in Section 4.1, with HPLC grade water. Assemble the apparatus as illustrated in Figure 6.

4.4.2 Connect the tube that runs to the frit at the base of the gas washing bottle to a source of compressed Ultra Pure nitrogen.

4.4.3 Bubble nitrogen through the water for approximately one hour.

4.4.4 Store this purged water in a narrow mouth bottle, cleaned by the method in Section 4.1, with a Teflon-lined cap.

4.4.5 Organic-free water should be prepared by this procedure prior to use; it may be stored at room temperature for use without repurging for a maximum of two days.

4.5 Storage of VOA Samples and Standards

VOA samples and standards must be stored in an area free of organic solvent vapors.

4.5.1 All samples and standards must be refrigerated at 4°C. In addition, samples must be refrigerated and stored in an area apart from standards.

4.5.2 Sample holding time must not exceed 14 days. (Refer to Table 1, Section 6.0 for recommended storage time for standards.)

4.6 Opening Sealed Ampules

Some standards are provided in sealed amber glass ampules. A special technique is required to open them safely and correctly.

4.6.1 Hold the sealed ampule with your thumbs pressing against the scored neck of the ampule, protected from the breaking glass by a slip of paper toweling, so that it will break away from you (Figure 7).

4.6.2 Using a strong, even force, snap the ampule at the scored line.

4.6.3 Transfer the material to a clean VOA vial of appropriate volume and seal.

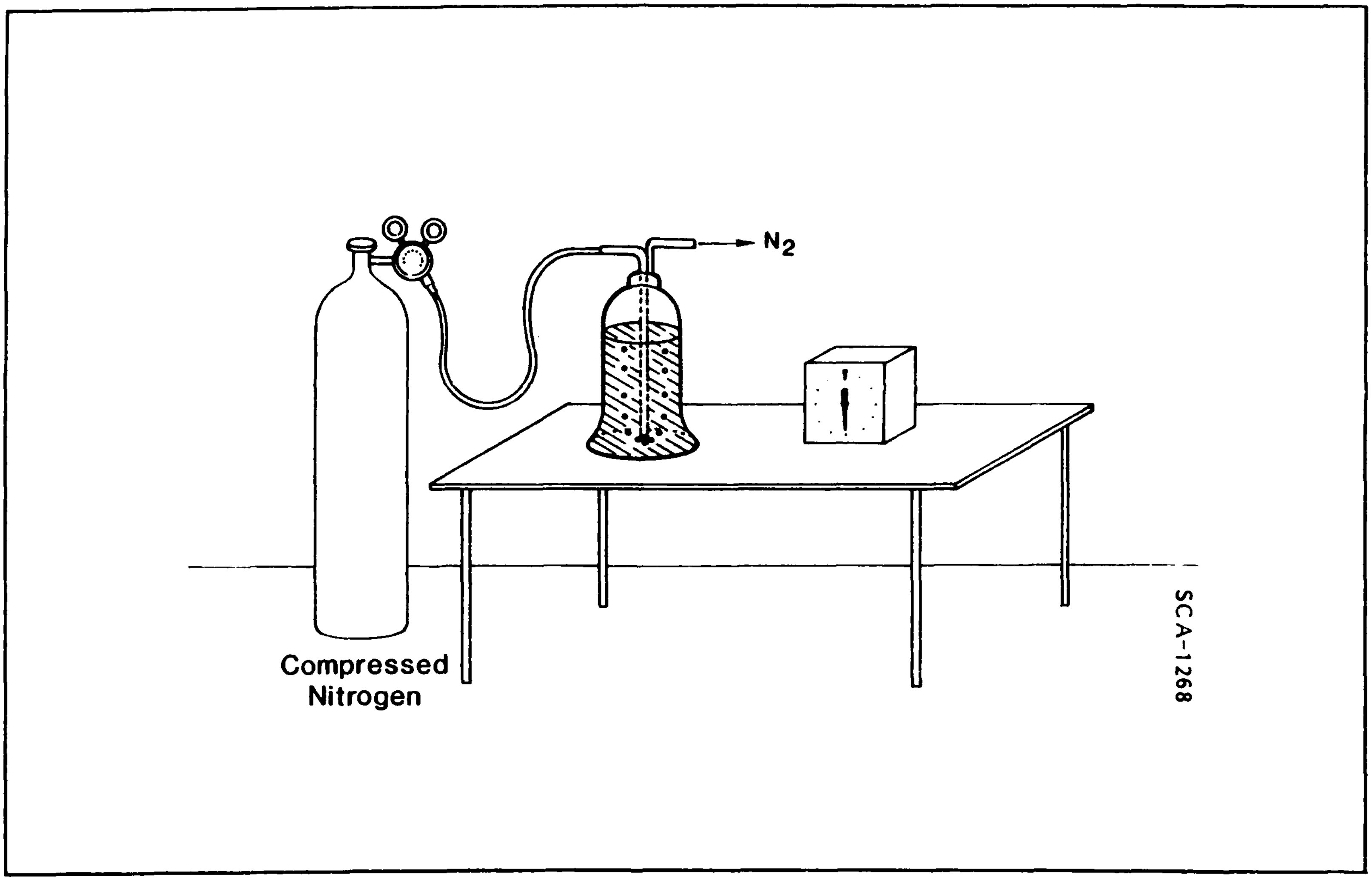


FIGURE 6. Apparatus for Preparation of Organic-Free Water

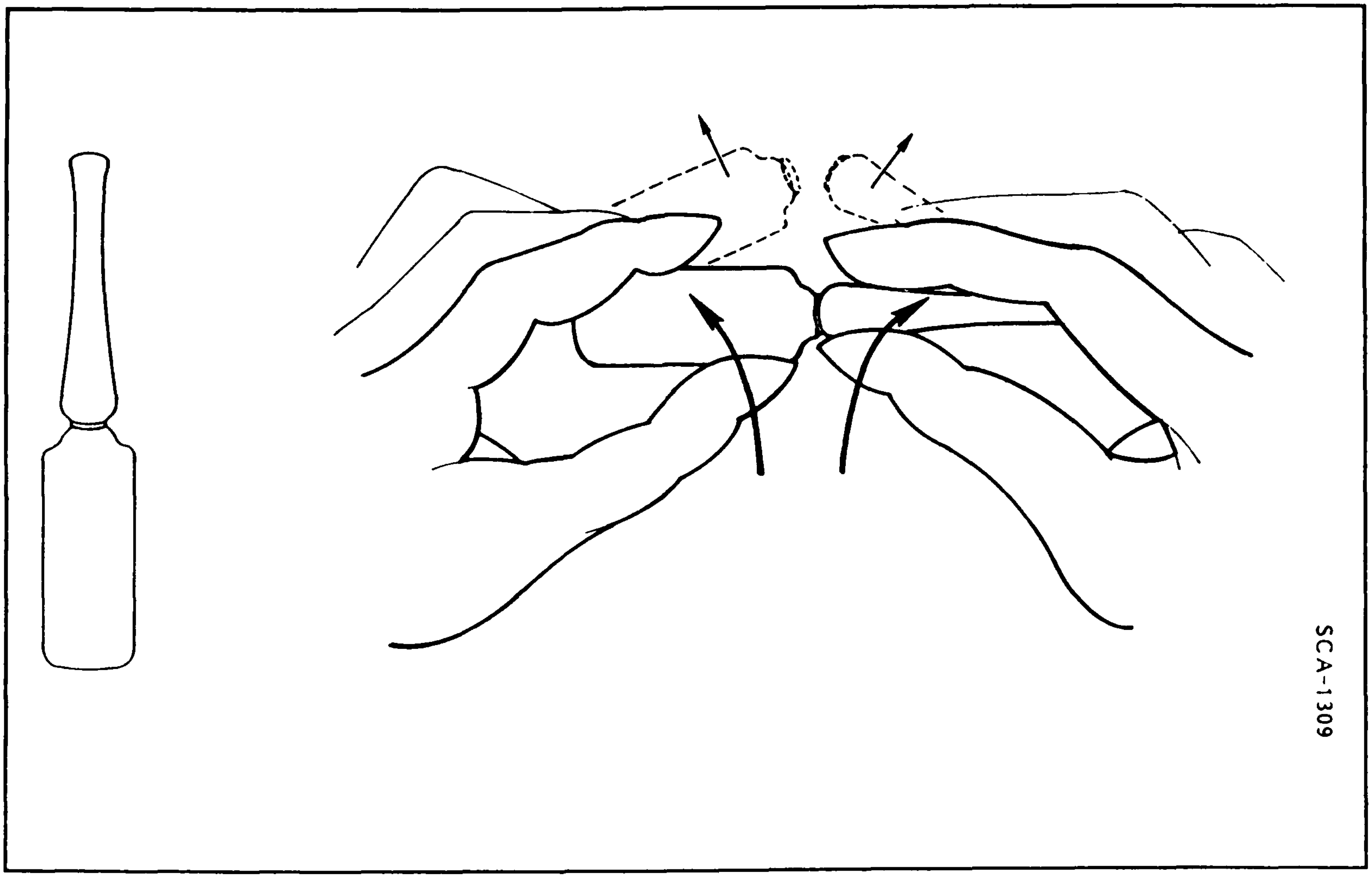


FIGURE 7. Opening Sealed Standard Ampules

5.0 FIELD SAMPLING PROCEDURES

5.1 Preparation of Field Blanks

Field blanks should be prepared in the laboratory prior to field sampling to determine the occurrence of sample contamination in transit.

5.1.1 Field blanks are shipped to the sampling location with the sample vials and remain with the samples during shipping, collection and storage.

5.1.2 Blanks are prepared from organic-free water (Section 4.4) and loaded into 40-mL sample vials according to Section 5.2.

NOTE: If samples are analyzed within 12 hours of sampling, field blanks are not required.

5.2 Filling and Sealing VOA Vials

Vials are filled and sealed to eliminate the air in the sample and form a hermetic seal.

5.2.1 Carefully fill each vial in such a way that no air bubbles pass through the sample solution.

5.2.2 Overfill the vial so that when the septum is placed on the vial, no air space is created.

5.2.3 Place the septum on the vial, being certain the Teflon face is in contact with the sample and no headspace is created. Seal the vial with the plastic cap.

5.2.4 If an air pocket is visible, open the vial, add more sample, and reseal.

5.2.5 Samples are to be refrigerated immediately after collection and must remain refrigerated at 4°C until analysis.

5.3 Direct Collection of Volatile Organics from a Flowing Stream or Tap

5.3.1 Open the sample vial and rinse several times in the solution to be sampled. Discard the rinses.

5.3.2 Fill the sample vial and seal according to Section 5.2.

5.3.3 Samples are to be refrigerated immediately after collection and must remain refrigerated until analysis.

6.0 PREPARATION OF STANDARDS

Refer to Figure 8 for a general description of procedures for preparation of standards and Table 1 for a summary of standard type, concentration, and frequency of preparation. Master copies of worksheets are in Appendix 1.

TABLE 1. Standards for TCE Analysis and Frequency of Preparation

Standard	Concentration	Solvent	Lifetime After Initial Use
TCE Stock Standard	20 mg/mL*	MeOH	1 Month
TCE Working Standard	20 µg/mL	MeOH	1 Week
Internal Standard Stock Standard	20 mg/mL*	MeOH	1 Month
Internal Standard Working Standard	1000 µg/mL	MeOH	1 Week
Internal Standard Calibration Standard	10 µg/mL	MeOH	Daily

*Used as purchased from Supelco.

Note: Two sets of syringes should be kept, one set for TCE standards and one set for internal standard solutions.

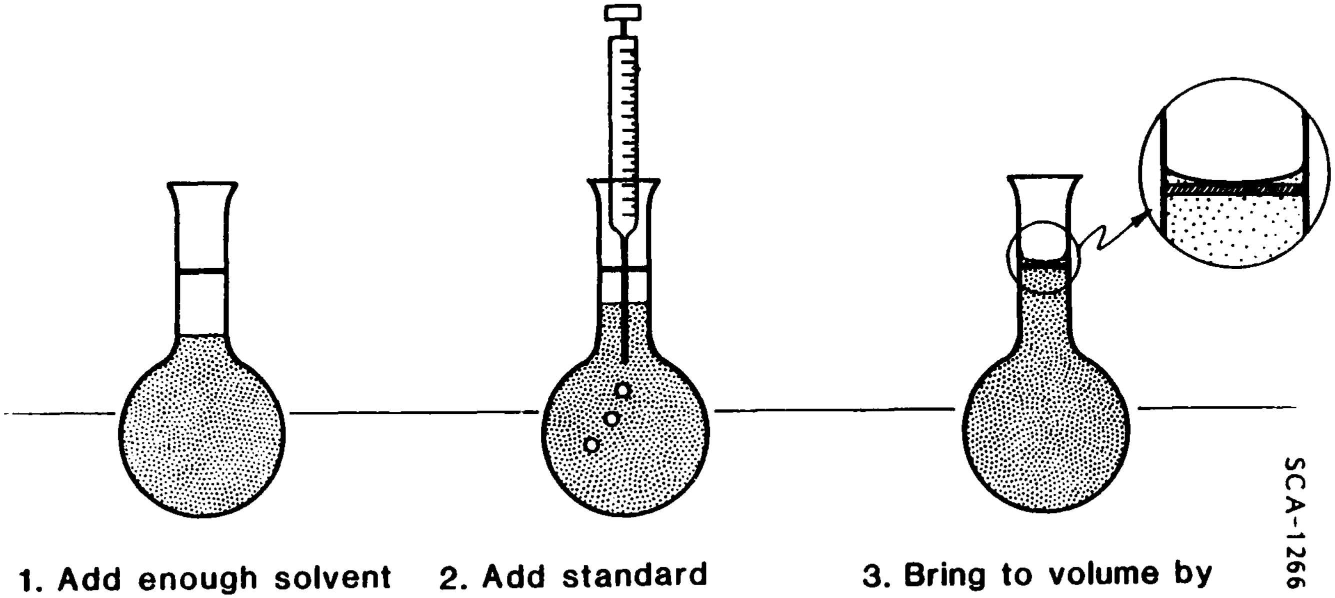
TCE stock standards may be purchased at 20 mg/mL, or prepared by dilution of a known weight of reagent TCE as described in Section 6.1. Instructions are included for preparation and use of both types of stock standards.

6.1 Preparation and Storage of Trichloroethylene (TCE) Stock Standards

All volumetric glassware used for standard preparation should be thoroughly cleaned and completely dry before use (Section 4.1).

6.1.1 To a 25-mL volumetric flask, add approximately 20 mL methanol. Allow the flask to stand unstopped for about ten minutes to allow all wetted surfaces inside the flask to dry.

6.1.2 Weigh the stoppered volumetric flask on an analytical balance to the nearest 0.1 mg. Record this value on the Data Sheet for Preparation of TCE Stock Standards.



1. Add enough solvent (water or methanol) to a volumetric flask to enable a syringe needle to be dipped into the solvent and still remain below the line of the flask.

2. Add standard beneath the surface of the solvent.

3. Bring to volume by adding solvent to bring the bottom of the meniscus to the line.

FIGURE 8. General Procedure for Preparation of Volatile Organic Standards

6 1.3 Using a 500-µL syringe, transfer 350 µL of TCE reagent to the volumetric flask, being certain to deliver the TCE beneath the surface of the methanol into the wide protion of the flask. Do not inject into the neck.

6.1.4 Replace stopper, reweigh the flask, and record this weight to the nearest 0.1 mg on the Data Sheet for Preparation of TCE Stock Standards.

6.1.5 Add methanol to the flask to bring the bottom of the meniscus to the line (Figure 8).

6.1 6 Stopper the flask and invert gently once to mix.

6.1.7 Calculate the concentration of the TCE standard as instructed on the Data Sheet for Preparation of TCE Stock Standards. The concentration of TCE should be near 20 mg/mL. If it is not, recheck the calculations and, if necessary, prepare a new standard.

6.2 Storage of Internal Standard Stock Solution and Purchased TCE Standard Stock Solution

The standard stock solutions used to prepare working standards are purchased at a concentration of 20 mg/mL in methanol and should be transferred to an appropriate vial for storage.

6.2.1 Open the sealed ampule as instructed in Section 4.7.

6.2.2 Transfer the solution into a 1.5-mL vial and seal with a Teflon-lined septum and cap.

6.2.3 Store in refrigerator. Internal standard stock solution may be used to prepare working standards for up to one month.

6.3 Preparation of TCE Working Standard

Working standards are prepared on a weekly basis by dilution of a 20-mg/mL purchased TCE stock standard or stock standard prepared as in Section 6.1.

6.3.1 Partially fill a clean 10-mL volumetric flask with methanol (see Figure 8.)

6.3.2 Using a micro syringe, deliver 10 µL of a TCE stock standard beneath the surface of the methanol (see Figure 8). Add additional methanol to bring the bottom of the meniscus to the line. Stopper the flask and mix.

6.3.3 Discard the standard in the neck of the flask and transfer the solution to a 7-mL vial fitted with a stop-and-go screw cap.

6.3.4 Complete the Data Sheet for Preparation of TCE Standard Working Solution. The concentration of the TCE working standard is 20 µg/mL.

6.3.5 Label the vial with the log number and the date prepared.

6.3.6 Store working standard in refrigerator.

6.4 Preparation of Internal Standard Working Standard

Internal standard working standards are prepared by dilution in methanol of a 20-mg/mL purchased internal standard solution.

6.4.1 Partially fill a 10-mL volumetric flask with methanol (see Figure 8).

6.4.2 Using a micro syringe, deliver 500 µL of the internal standard stock solution beneath the surface of the methanol.

6.4.3 Add enough methanol to the flask to bring the meniscus to the bottom of the line. Stopper the flask and mix.

6.4.4 Discard the solution in the neck of the flask and transfer the solution to a 7-mL vial with a stop-and-go screw cap.

6.4.5 Record the appropriate information on the Data Sheet for Preparation of Standard Working Solution and label the vial with the log number and date.

6.4.6 The concentration of the internal standard working standard is 1000 µg/mL.

6.5 Preparation of Internal Standard Calibration Standard

6.5.1 Internal standard daily standards are prepared by dilution of internal standard working standard in 10 mL of methanol.

6.5.2 Partially fill a 10-mL volumetric flask with methanol.

6.5.3 Using a 100-µL syringe, deliver 100 µL of internal standard working standard beneath the surface of the water in the volumetric flask (see Figure 8).

6.5.4 Add enough methanol to the volumetric flask to bring the bottom of the meniscus to the line.

6.5.5 Stopper the flask and gently invert once to mix.

6.5.6 The concentration of the internal standard daily standard is 10,000 ng/mL.

6.7 Preparation of Calibration Samples

Calibration samples are prepared by dilution of the TCE working standard in appropriate volumetric glassware to produce final concentrations of 1.5, 4, and 10 ng TCE/mL, STD A, STD B, and STD C, respectively.

6.7.1 Fill to approximately 80 percent capacity a 10-, 25- and 100-mL volumetric flask with organic-free water.

6.7.2 Using a 10-μL syringe, add 7.5 μL of the TCE working standard to the 100-mL flask. Add 5 μL of the TCE daily calibration standard to the 25-mL and 10-mL flasks.

6.7.3 Label the 100-mL flask STD A, the 25-mL flask STD B, and the 10-mL flask STD C.

6.7.4 Bring each of the volumetric flasks to volume by adding additional organic-free water so that the bottom of the meniscus of each flask reaches the line.

6.7.5 Stopper each flask and invert once gently to mix.

7.0 DATA SYSTEM OPERATION

The data acquisition system is easy to use and will provide instructions to the user by a series of screen prompts.

Enter

Each time the operator is requested to "enter" information, the typewriter area of the Keyboard should be used along with the "backspace" key to correct any mistakes in typing. See Figures 9 and 10. When the information is correct, press the "Enter" key. In this manual, the enter key will be represented as a left arrow ←.

Screen Restore

The computer is equipped with a screen saver facility which will cause the computer screen to go dark when no keyboard entry has been made for awhile. To restore the screen display, press the "shift" key (see Figures 9 and 10).

Floppy Diskette Insertion

Make sure that the diskette label is facing up and is close to you when you insert the diskette into the drive. The label side of the diskette DOES NOT go in the drive first. Close the diskette drive door. See Figure 11.

7.1 System Cold Start (Power Off)

7.1.1 Raise the lift load lever and insert the VOA data system operating floppy diskette into Drive A. Make sure that the diskette label is facing up and is close to you when you insert the diskette into the drive. The label side of the diskette DOES NOT go into the drive first. See Figure 11 for the correct position. Lower the lift load lever to engage the diskette.

7.1.2 Turn on the system power switch located on the right hand side of computer.

7.1.3 The computer will execute a series of internal tests and proceed to load the data analysis software.

All keys are typematic, that is, they repeat as long as you hold them down.

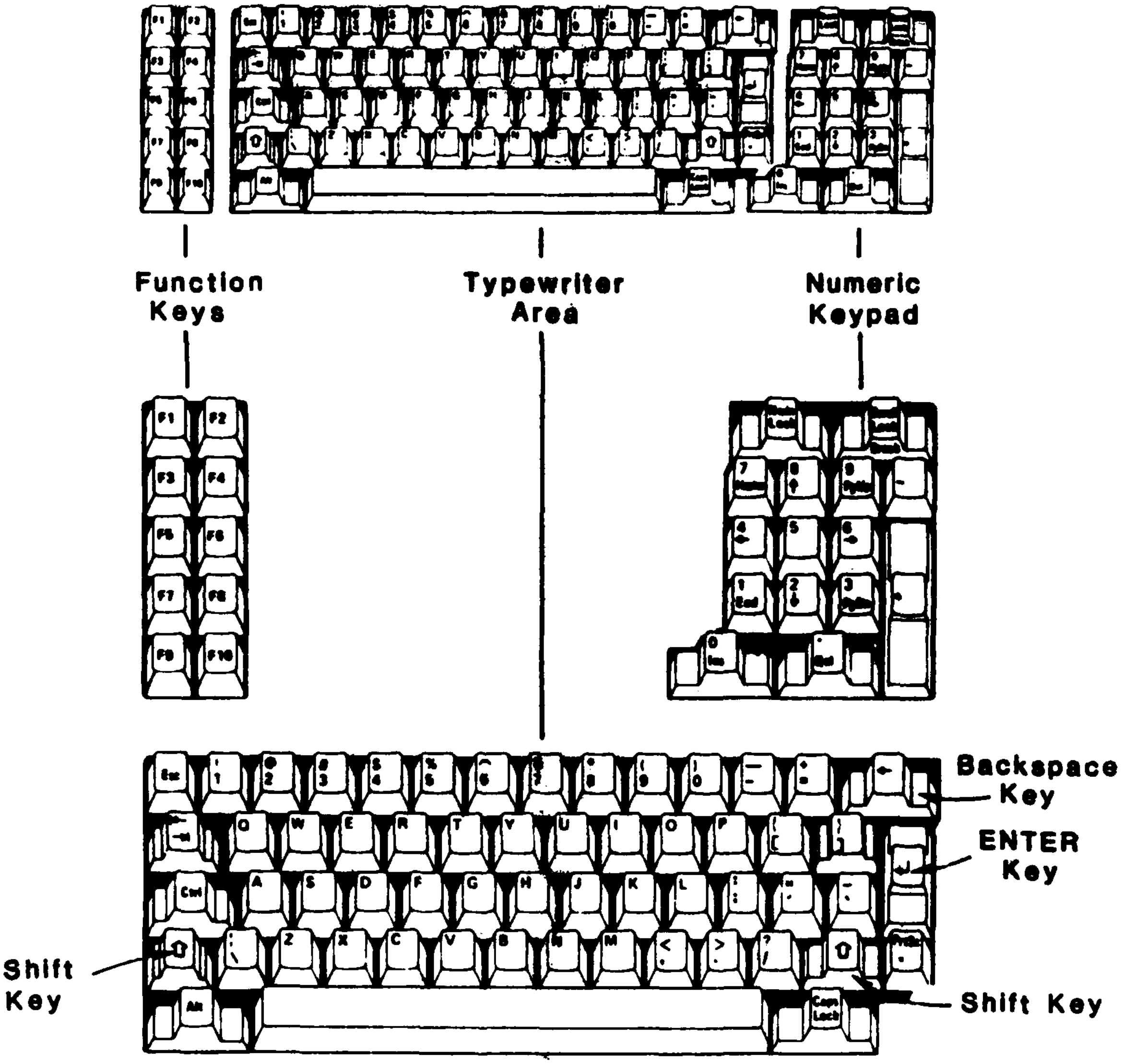
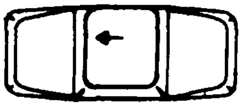
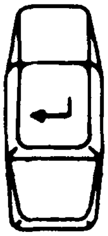


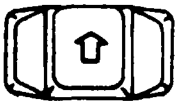
FIGURE 9. Keyboard



The Backspace key moves the cursor one position to the left. The character to the left of the cursor is erased.



This is the ENTER key. Each time information has been correctly entered using the keyboard, this key must be pressed next for the computer to respond to the input.



The keyboard has two shift keys, which are in the typewriter area. Pressing either of these changes the keys in the typewriter to the uppercase mode. When alphabetic keys are pressed, the characters appear as capital letters. When other keys in the typewriter are pressed, the characters shown on the upper portion of the keys appear. This key is also used to restore the screen display after it blanks out.

FIGURE 10. Special Keyboard Keys

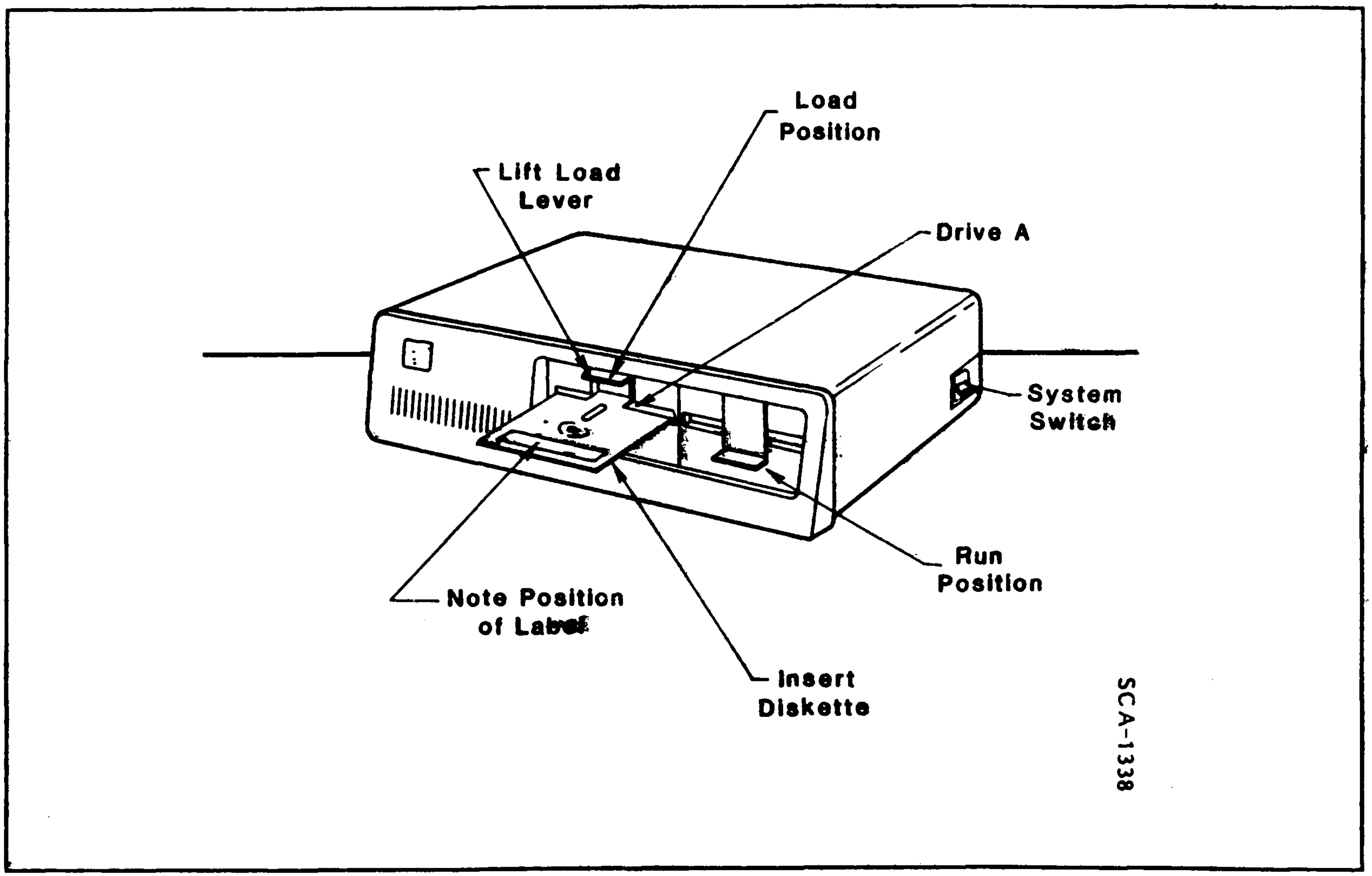


FIGURE 11. Correct Procedure for Insertion of Floppy Diskette into Drive A

7.1.4 The main menu of the data system will appear on the screen as shown below:

```
Select one of the following options:

     1.  Analyze for TCE
     2.  Calibration run for TCE
     3.  Prepare new data diskette (for drive B)
     4.  Prepare new VOA Data system diskette (for drive A)
     5.  Retrieve QC data
     6.  Retrieve archived data
     7.  Change operating parameters
     9.  Exit Menu

     ENTER OPTION NUMBER: 1
```

FIGURE 12. Data System Main Menu

7.1.5 If the computer display does not resemble the above, turn the power off, wait about 30 seconds, and then restart the system.

7.1.6 Check for sufficient paper in the printer and see that the printer is "on line". The power switch is located on the left side of the printer and the "on line" button must be pressed if the green "ready" light is not illuminated.

7.2 Calibration Run

7.2.1 Before beginning data collection, insert a data storage diskette in Drive B. Each diskette is capable of storing results for 100 samples. New diskettes must be initialized before using. Select Option 3, "Prepare new data diskette (for Drive B)", follow the instructions on the screen, and then label the diskette with the date and "TCE data".

7.2.2 To begin a calibration run, select Option 2 of the main menu by typing on the keyboard:

2 ←

7.2.3 Enter operator identification (name or initials) as shown in Figure 13. This is limited to eight characters and/or numbers and must not contain any blanks.

```
Calibration run for TCE

Date 7/30/1986 Time 14:40
Last Calibration Date 7/25/1986

CALIBRATION IS REQUIRED

Enter analyst identification: vt
Enter information as requested below for
the calibration run:

                    SAMPLE TYPE NUMBERS

0)  BLANK                               4)  WATER SAMPLE
1)  STANDARD #A                         5)  SPIKE
2)  STANDARD #B                         6)  END OF SAMPLES
3)  STANDARD #C

    Position 1          BLANK
    Position 2          STANDARD#A
    Position 3          STANDARD#B
    Position 4          STANDARD#C
    Position 5          ENTER sample TYPE number: 4
                        ENTER sample IDENTIFICATION: sp11
```

FIGURE 13. Sample Table for Calibration Run

7.2.4 In a calibration run, the first four autosampler positions will always be the same. A blank and the three levels of standards will always occupy these positions in a calibration run as outlined in Section 8.2.6.

7.2.5 Enter the correct sample type by number. The data system automatically prompts the operator to load the correct samples in the first four autosampler positions as shown below:

7.2.6 Up to six samples may be analyzed as part of the calibration run. When setting up the sample table, starting with Position 5, enter Option 4 and an appropriate sample identifier (see Section 7.3.5).

7.2.7 The data system will require a spike and duplicate spike sample to be run every ten samples. If this should occur, refer to Section 8.3 for spike sample preparation and Section 7.4 for appropriate data system set up.

7.2.8 If fewer than 10 positions on the autosampler are to be used for samples, enter sample type number 6 for the position following the last sample to be analyzed.

7.2.9 All sample analysis runs must include a standard as the last sample run in a sample set. If the last sample is a spiked sample, no additional sample is required. If the last sample to be run is not a spiked sample an additional Standard A is to be run to verify continuous acceptable system performance.

7.2.10 After all entries have been made, the computer will list the sample table. If an error has been made it may be corrected at this time by entering the information as requested.

7.2.11 The system will display, "Load Blank in Position 1 and start Tekmar Purge and Trap."

7.2.12 Start the Tekmar autosampler as described in Operation of Purge and Trap Apparatus - Instrument Start Up Procedure, Section 8.5.

7.2.13 Now you should respond to the query, "Has the Tekmar Purge and Trap been started?" by entering:

y ←

7.2.14 Load the remaining samples in sequential order.

7.2.15 After all samples have been analyzed, the data system will return to the main menu and all sample results will be recorded on a printout. Check the printed results for warnings and error messages before beginning a new run. Consult the Operating and Maintenance Manual for explanation of error messages and appropriate corrective action.

7.3 Routine TCE Analysis

Routine TCE analysis will be performed after an acceptable calibration run has been completed and additional sample analysis is required.

7.3.1 Before beginning data collection, insert a data storage diskette in Drive B. See Section 7.2.1.

7.3.2 For routine TCE analysis, select Option 1 of the main menu by entering:

1 ←

7.3.3 A sample of organic-free water (blank) will always be required in Position 1.

7.3.4 Standard A will always be run in Position 2 for the first run in a 24-hour period. Standard A will also be included as the last sample at the end of an analysis set for system verification.

7.3.5 Samples are designated by selecting Option 4 for the corresponding autosampler position as shown below.

```
Analyze for TCE

Date 7/30/1986  Time 14:42
Last Calibration Date 7/25/1986

Enter analyst identification: vt
Enter information as requested below:

                     SAMPLE TYPE NUMBERS

0)  BLANK                               4)  WATER SAMPLE
1)  STANDARD #A                         5)  SPIKE
2)  STANDARD #B                         6)  END OF SAMPLES
3)  STANDARD #C

Position 1      BLANK
Position 2      ENTER sample TYPE number: 4
                ENTER sample IDENTIFICATION: EFFA730
Position 3      ENTER sample TYPE number:
```

FIGURE 14. Sample Table for TCE Analysis

7.3.6 An appropriate sample identification should be chosen such as EFFA730 which would refer to an effluent sample collected on 7/30. The sample identification is limited to eight characters which may be a combination of numbers and letters.

7.3.7 Complete the sample table and initiate analysis by following steps in Section 7.2.6 to 7.2.16.

7.4 Duplicate Spike Samples

7.4.1 To verify that the system is operating correctly, the data system will require that a TCE spike be added to every tenth sample (see Section 8.3).

7.4.2 The spike and duplicate spike will be added to the sample immediately preceding the position in which the first spike sample is loaded. That is, the tenth sample to be analyzed as part of the current calibration and analysis being run will be the sample to which the spike will be added. The sample table entries (prompts) are shown below:

SAMPLE TYPE NUMBERS

0) BLANK
1) STANDARD #A
2) STANDARD #B
3) STANDARD #C
4) **WATER SAMPLE**
5) **SPIKE**
6) END OF SAMPLES

Position 1	BLANK
Position 2	ENTER sample TYPE number: ***4*** ENTER sample IDENTIFICATION: ***iffa730***
Position 3	**SPIKE** of sample **iffa730.dat**
Position 4	**Duplicate SPIKE** of sample **iffa730.dat**
Position 5	ENTER sample TYPE number:

FIGURE 15. Sample Table for Spike and Duplicate Spike Analysis

7.4.3 When a spike is to be run, it should be added to a low-concentration sample. If the situation should occur where the data system requires a spike be added to a sample suspected to be high, for example, an influent sample, the sample should be diluted according to Section 8.4 or that sample should be replaced with another low-concentration sample and the sample table corrected according to Section 7.2.10.

7.4.4 Complete the sample table and initiate analysis by following the appropriate steps in Sections 7.2.7 to 7.2.14.

8.0 OPERATION OF PURGE AND TRAP APPARATUS

8.1 Loading Syringes

Syringes must be loaded in such a way to prevent air from passing through the sample or creation of a vacuum headspace over the sample.

8.1.1 Rinse the syringe with sample by drawing about 3 mL of sample through the syringe and discarding the rinse into a waste beaker.

8.1.2 Remove the plunger from the barrel of the syringe. Seal the outlet of the syringe with a syringe cap.

8.1.3 Pour approximately 10 mL of the sample into the syringe barrel and replace the plunger without putting force on the plunger.

8.1.4 Turn the syringe upright, supporting the barrel and plunger, and remove the syringe cap.

8.1.5 Expel excess air and adjust the volume to 5 mL, discarding the excess sample into a waste beaker.

8.1.6 Rinse syringe three times with organic-free water for loading the next sample.

8.2 Loading Automatic Liquid Sampler (ALS)

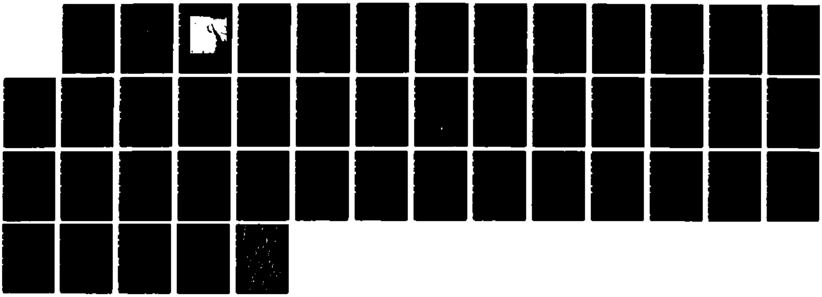
8.2.1 Place a clean sparger at each sample position to be used on the ALS. Carefully tighten the nut at the top of the sparger only finger tight. Use no tools! (Figure 16).

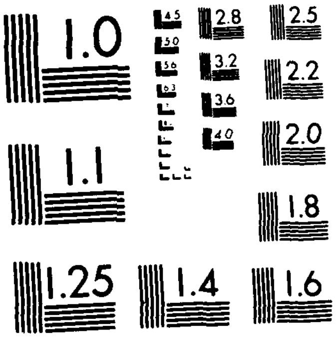
8.2.2 Fill the syringe with appropriate sample, according to 8.1 above.

8.2.3 To each 5-mL blank, standard, spike sample, or sample add 5 μL internal standard calibration standard by introducing the internal standard through the tip of the sample syringe. The internal standard concentration in each blank and sample is 10 ng/mL of each compound.

8.2.4 Load the sample as illustrated in Figure 17, being sure to establish a secure connection between the Luer Lock fitting on the syringe and the sample introduction valve.

AD-A195 120 PROTOTYPE TECHNOLOGY FOR MONITORING VOLATILE ORGANICS 2/2
VOLUME 1(U) S-CUBED LA JOLLA CA V TAYLOR ET AL MAR 88
SSS-R87-8515-VOL-1 ESL-TR-88-01-VOL-1 F08635-84-C-0298
UNCLASSIFIED F/G 7/3 NL




1.0
4.5
5.0
5.6
6.3
2.8
3.2
3.6
4.0
2.5
2.2
2.0
1.1
1.8
1.25
1.4
1.6

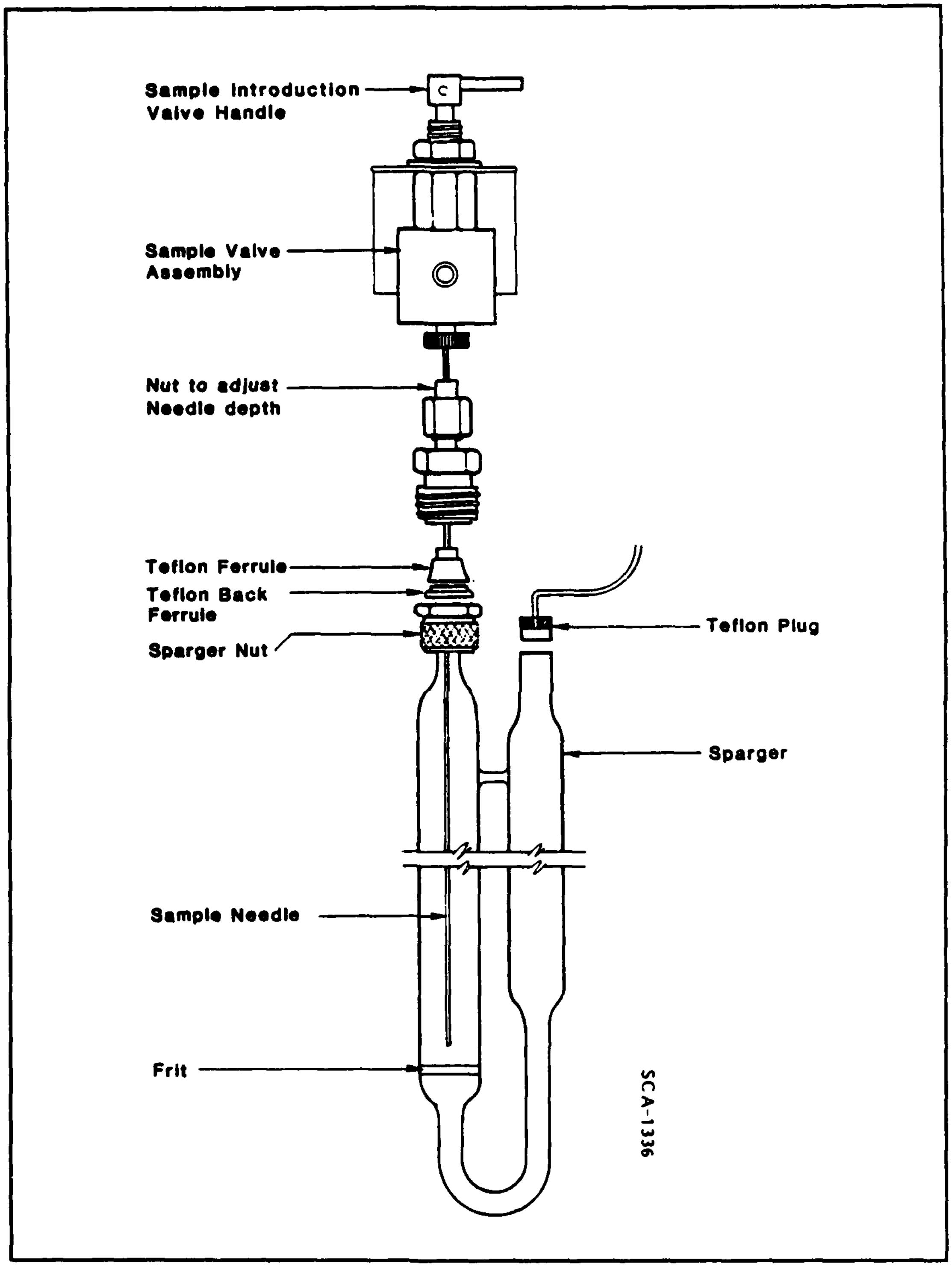


FIGURE 16. 5-mL Needle Sparge Vessel and Sample Introduction Valve.

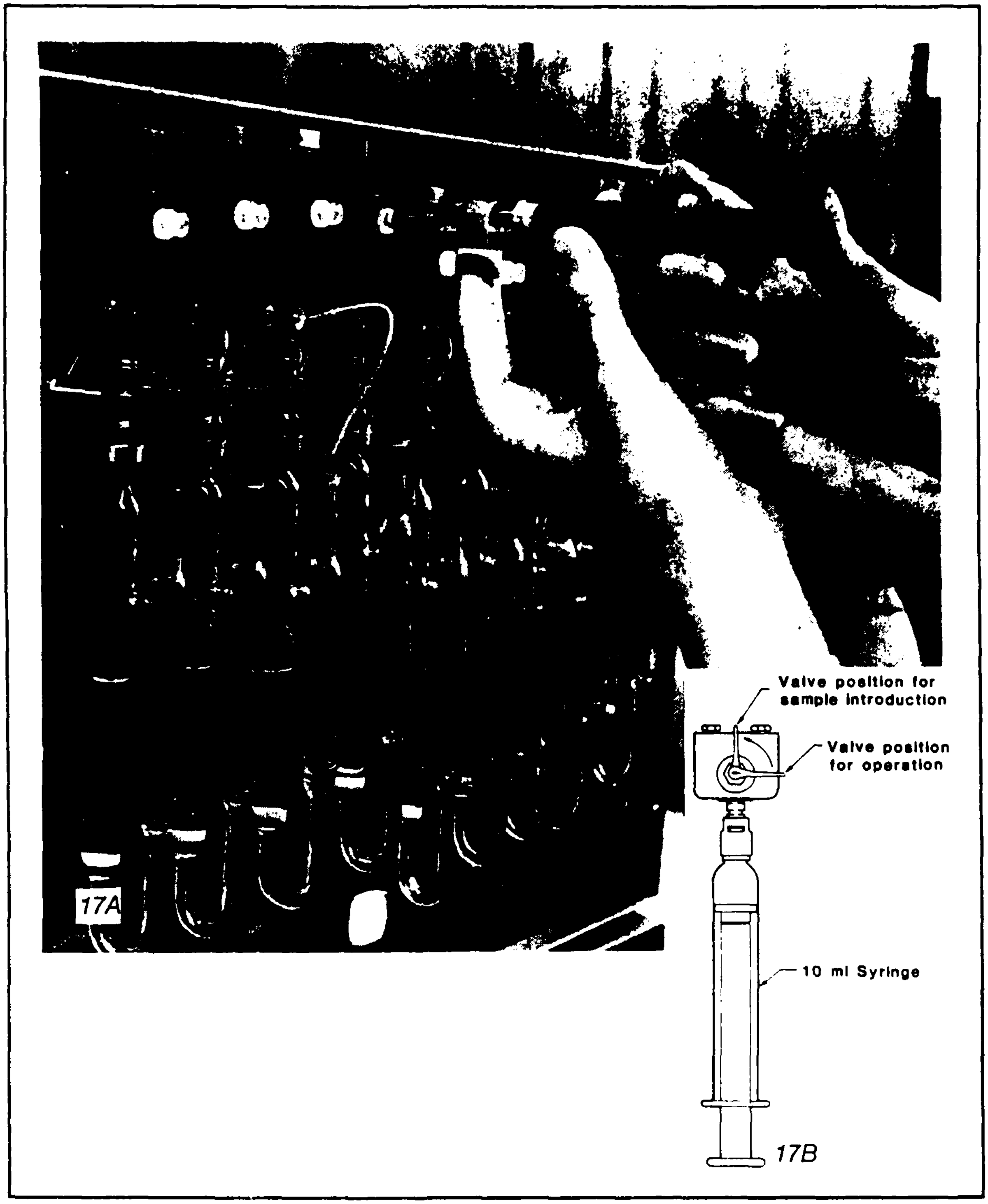


FIGURE 17A. Loading Samples into Automatic Liquid Sampler
FIGURE 17B. Top View of Sample Introduction Valve

8.2.5 Turn the sample introduction valve handle so the arrow points to the syringe, inject the sample, and immediately turn the valve handle back so the arrow points left before removing the syringe.

8.2.6 For a calibration run, load each of the first four positions with the correct solution as follows:

Position 1:	Blank, 5 mL of purged organic-free water used to prepare standards.
Position 2:	Standard A, 1.5 ng TCE/mL.
Position 3:	Standard B, 4 ng TCE/mL.
Position 4:	Standard C, 10 ng TCE/mL.

The proper position for these calibration samples will be confirmed by the data system prompts.

8.2.7 The remainder of the samples should be loaded to correspond with the sample table.

8.3 Preparation of TCE Spike and Duplicate Spike Samples

Spike and duplicate spike samples will be required by the data system every tenth sample.

8.3.1 Prepare a 1:1 dilution of the TCE working standard by adding 1 mL of methanol to 1 mL TCE working standard. The concentration of this TCE spiking standard is 10 μg/mL.

8.3.2 Load syringe as in Section 8.1 with designated sample to be used for spiking.

8.3.2 Add internal standard as in Section 8.2.3.

8.3.3 To both spike and duplicate spike sample add 5 μL of the TCE spiking standard as prepared in Section 8.3.1. The concentration of the TCE spike is 10 μg/mL.

8.3.4 Load each spiked sample in its assigned position in the autosampler.

8.4 Dilution of High-Concentration Samples

The situation may arise that certain samples contain TCE at a concentration too high for accurate quantitation by the data system. The data system will print out a message warning the operator when this is the case. Samples will require dilution.

8.4.1 The appropriate dilution may be estimated by looking at the area of STD B and estimating a dilution of the sample which would produce an equal response. Estimate the required dilution as in the following example:

Area of STD B: 3000

Area of High-Concentration Sample: 30000

Dilution Factor: 30000 ÷ 3000 = 10

Required Dilution: 1 part sample in 9 parts organic-free water

This is a ten-fold dilution and will produce a sample signal approximately equal to the signal produced in this example by STD B.

8.4.2 The results calculated by the data system will not include the dilution factor. Once the analysis is completed, the operator must adjust the reported concentration by the required dilution factor. For example, if the dilution factor had been calculated as in 8.4.1, and the result of the analysis of the diluted sample is reported as 9.8 ng/mL, the operator must correct this result by the dilution factor, that is:

Final Result: 9.8 ng/mL x 10 = 98 ng/mL

Where: ng/mL = ppb

8.5 Instrument Start Procedure

Check for sufficient gas pressure on all gas regulators before starting the run. For appropriate settings consult Operation and Maintenance Manual Section 3.3.

8.5.1 After the blank has been loaded into Position 1, and the rest of the autosampler positions have been designated on the data system, analysis of the blank can begin.

8.5.2 Set the Auto/Hold/Step switch on the Tekmar LSC-2 to Auto (Figure 3).

8.5.3 Step the Auto/Hold/Step switch on the Tekmar ALS autosampler, until the light under Position 1 is illuminated; leave switch at Hold.

8.5.4 Set the Last Sample switch on the ALS autosampler to the number of the last position to be used.

8.5.5 Press the First Cycle button on the ALS autosampler.

8.5.6 Set the Auto/Hold/Step switch on the Tekmar ALS to Auto.

8.5.7 Set the Auto/Hold/Step switch on the ALS autosampler to Auto.

8.5.8 You may now respond to the prompt ("Are samples loaded as designated?") by entering

y ←

8.5.9 Analysis of the blank should begin

8.5.10 Load the remaining samples in numerical order.

APPENDIX I

STANDARD LOG SHEETS

Date:____________________
Log No.:__________________
Prepared by:_______________

DATA SHEET FOR PREPARATION OF TCE STOCK STANDARDS

A.	Weight of 25-mL volumetric flask and 20 mL methanol	__________ g
B.	Weight of 25-mL volumetric flask and methanol with 350 μL TCE reagent	__________ g
C.	Difference (B - A)	__________ g
D.	Concentration of TCE = (B - A) x 40	__________ mg/mL

DATA SHEET FOR PREPARATION OF TCE STANDARD WORKING SOLUTION

Log No.	Lot No. Standard	Date Prepared	Dilution Volume	Aliquot Standard
001				
002				
003				
004				
005				
006				
007				
008				
009				
010				
011				
012				
013				
014				
015				
016				
017				
018				
019				
020				
021				
022				
023				
024				
025				
026				

DATA SHEET FOR PREPARATION OF INTERNAL STANDARD WORKING SOLUTION

Log No.	Lot No. Standard	Date Prepared	Dilution Volume	Aliquot Standard
001				
002				
003				
004				
005				
006				
007				
008				
009				
010				
011				
012				
013				
014				
015				
016				
017				
018				
019				
020				
021				
022				
023				
024				
025				
026				

APPENDIX II

ABBREVIATED OPERATING INSTRUCTIONS

ABBREVIATED OPERATING INSTRUCTIONS

1. Start the computer with the Data System Operating Diskette in Drive A.
2. Check printer paper supply and verify that the printer is "on-line".
3. Check gas regulators for adequate pressure.
4. Select Option 1 or 2 for a regular run or a calibration run.
5. Insert a Data Diskette into Drive B (prepare a new data diskette about once a week).
6. Enter the information as requested on the screen (be sure to use a low-concentration sample for spikes).
7. Load the blank sample with added internal standard onto Position 1 on the autosampler.
8. Set the Auto/Hold/Step switch on the Tekmar LSC-2 to Auto.
9. Step the Auto/Hold/Step switch on the Tekmar ALS autosampler until the light under position #1 is illuminated. Leave the switch in Hold.
10. Set the Last Sample switch on the ALS autosampler to the number of the last position to be used.
11. Press the First Cycle button on the ALS autosampler.
12. Set the Auto/Hold/Step switch on the ALS autosampler to Auto.
13. You may now respond to the computer prompt ("Are samples loaded as designated?") by entering

    y ←

14. Analysis of the blank should begin.
15. Load the remaining samples in numerical order.

APPENDIX C

OPERATION AND MAINTENANCE MANUAL

Material contained in this appendix has been published without change from its original format.

S-CUBED
A Division of Maxwell Laboratories, Inc.

OPERATING AND MAINTENANCE MANUAL FOR AUTOMATED PURGE AND TRAP ANALYSIS OF TRICHLOROETHYLENE IN WATER

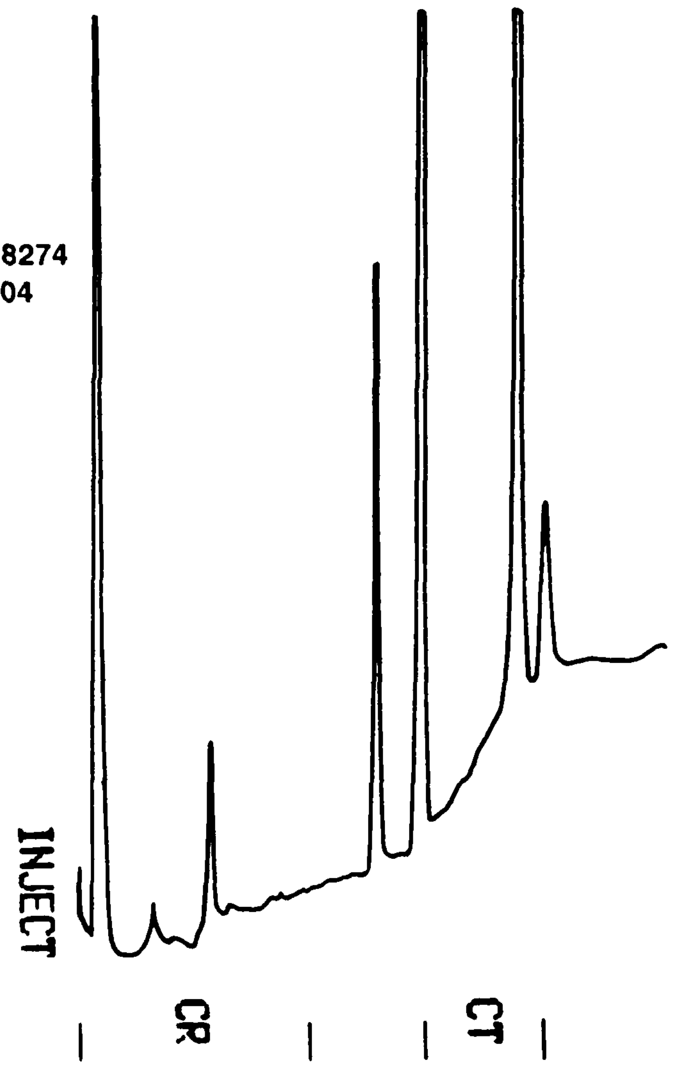
Contract CN F08635-84-C-0298

S-CUBED Report No. SSS-R-86-8274
S-CUBED Reference No. 11272-04

Prepared by:

V. Taylor
B. Lentz

October, 1986



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(619) 453-0060

TABLE OF CONTENTS

1.0 SITE PREPARATION 1
  1.1 Space Requirements 1
  1.2 Gas Line Requirements 1
  1.3 Tools 1
  1.4 Specifications for Gas Regulators 2
  1.5 Supplies Required for Interface Box Construction 2
  1.6 Miscellaneous 3

2.0 INSTRUMENT INSTALLATION 4
  2.1 Gas Lines 4
  2.2 Cabling Connections 4

3.0 RECOMMENDED INSTRUMENT OPERATING PARAMETERS 10
  3.1 Tekmar Purge and Trap 10
  3.2 Varian Gas Chromatograph 10
  3.3 Gas Cylinder Regulator Pressures 10

4.0 MAIN MENU COMPUTER OPTIONS 11
  4.1 Prepare New Data Diskette (for Drive B) 11
  4.2 Prepare New VOA Data System Diskette (for Drive A) 11
  4.3 Retrieve QC Data 12
  4.4 Retrieve Archived Data 12
  4.5 Change Operating Parameters 13

5.0 MAINTENANCE 16
  5.1 Gas Flow Measurement 16
  5.2 Gas System Leak Checking 18
  5.3 System Decontamination 18
    5.3.1 Glassware Decontamination Procedures 19
    5.3.2 Decontamination by Repetitive Blank Analysis 19
    5.3.3 Methanol Decontamination Procedure 19
  5.4 *Installation of New Sorbent Trap* 20
  5.5 Installing a New Gas Chromatographic Column 20
  5.6 Printer Paper Loading 21
  5.7 Printer Ribbon Installation 21
  5.8 Resetting Computer System Clock 22
  5.9 Installing a New Battery for Computer System Clock 22

6.0 INSTRUMENT LOG 24

7.0 SAMPLE LOG 25

8.0 TROUBLESHOOTING 26
  8.1 Chromatography Problems - Warnings 26
  8.2 Computer Troubleshooting 26
    8.2.1 Diagnostic Tests (Hardware) 26
    8.2.2 Software Tests 30

1.0 SITE PREPARATION

Required chemicals and glassware are listed in the Procedural Guide in Sections 2.0 and 3.0.

1.1 SPACE REQUIREMENTS

Minimum uninterrupted bench top for installation: 7' x 3' long with suitable area for securing four gas cylinders.

Note: the cable connections between some units are fixed; therefore, there is little flexibility in configuration of the instrumentation.

1.2 GAS LINE REQUIREMENTS

Sufficient 1/8-inch copper tubing and brass or stainless steel ferrules, back ferrules, and column nuts for installing the following gas lines.

- Nitrogen carrier (with *on-line tee to purge line*).
- Hydrogen and air for detector operation.
- Air for pneumatic valve on automatic sampler

In-line hydrocarbon filters should be installed on carrier gas lines and renewed according to manufacturer's recommendations.

1.3 TOOLS

- One medium flat-head screwdriver.
- One small flat-head screwdriver.
- Two 1/4" x 5/16" open end wrenches.
- Two 3/8" x 7/16" open end wrenches.
- Two 7/16" x 1/2" open end wrenches.
- Two 1/2" x 9/16" open end wrenches.
- One 1 1/8" x 1 1/16" open end wrench.

1.4 SPECIFICATIONS FOR GAS REGULATORS

Two-stage gas regulators for H_2, N_2, and air with the following specifications:

Maximum inlet pressure	3,000 psig
Outlet pressure	0-75 psig
Operating temperature	0-94°C
Flow Capacity	140 mL/minute (air)

1.5 SUPPLIES REQUIRED FOR INTERFACE BOX CONSTRUCTION

- Two power supplies, 5 volt, 3 amp.
- Two relays, PC mount, SPDT, type T#20P1-05.
- Two resistors, 1/4 watt, 1 kΩ.
- Two resistors, 1/4 watt, 510 Ω.
- One resistor, 1/4 watt, 10 kΩ.
- One transistor, type 2N3906.
- Two diodes, type 1N914 or 1N4003.
- One barrier terminal block (screw terminal), 20 terminals, for #16 wire.
- One piece blue-board, approximately 4" x 6".
- One grounded power cord (for power supplies).
- Approximately two feet each of #16 black, white, and green wire, for wiring power supplies.
- Approximately 20 feet of #21 or #22 wire, assorted colors.
- Aluminum housing, approximately 8" x 12" x 4".
- One strain relief busing to fit grounding power cord.
- Stand-offs, screws, nuts, and washers as needed.

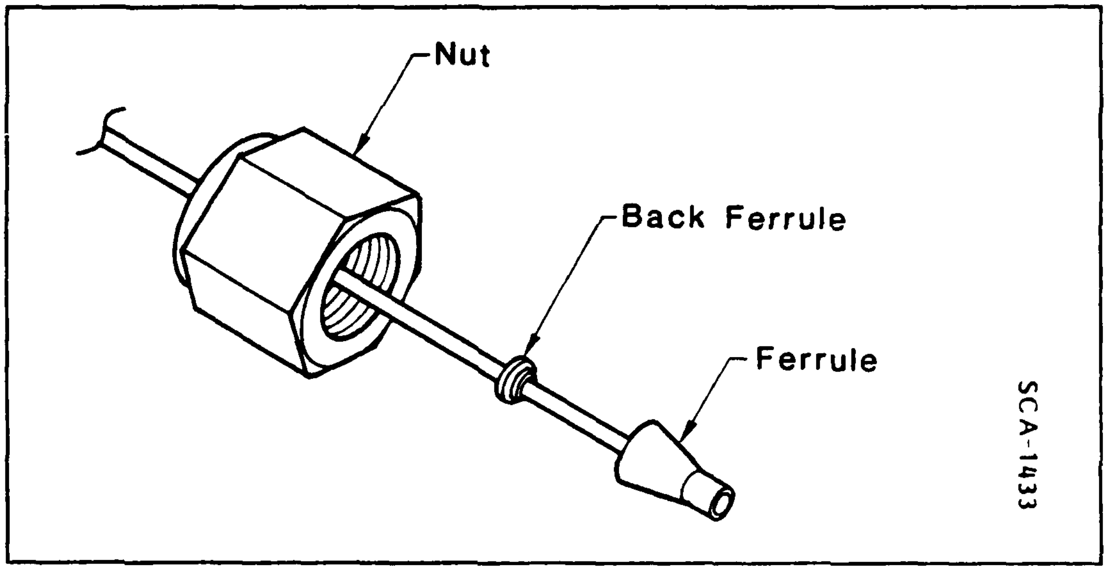
1.6 MISCELLANEOUS

- Oven - suitable for glassware drying (200°C maximum).
- Refrigerator - small table-top model for storage of standards.
- Refrigerator - separate unit for samples. Size will be dependent upon sample load.
- Analytical balance (optional) - accurate to 0.1 mg.
- Vacuum line or aspirator.
- Harness for gas cylinders.
- Soap bubble flow meter - Supelco catalogue #2-0433 or equivalent.
- Stop watch.
- Dedicated (30-A 110-V) electrical circuit, protected by a 3-kVA isolation transformer (Topaz 53406-00P3 or equivalent) without ground loop detection.
- If a supply of HPLC-grade water is not readily accessible, a water purification system (Millipore RO-15 and MilliQ or equivalent) is recommended.
- Heat gun.
- Multimeter
- Desk top cabinet with small, transparent drawers for small parts storage.

2.0 INSTRUMENT INSTALLATION

2.1 GAS LINES

The gas lines should be connected as shown in the schematic in Figure 2.1 with the ferrules and nuts configured as shown below. Care should be taken not to overtighten gas line connections. All gas lines should be leak tested according to Section 5.2.



Configuration of Hardware for Gas Line Connections to Instrument

2.2 CABLING CONNECTIONS

All lines between the computer, the Varian GC, and the Tekmar purge and trap pass through the interface box, the silver-colored box connected by a ribbon cable. Figure 2.2 is a schematic diagram of the interface box. A TTL level digital output from the A/D board controls the Tekmar purge and trap through the 2N3906 transistor and relay. The transistor amplifies the TTL output current enough to drive the relay coil which, in turn, provides the isolated contact closure required by the purge and trap. The analog output of the Varian detector is directly input to an analog input of the A/D board, and the status output is isolated by the second relay, so as to avoid possible ground loop problems.

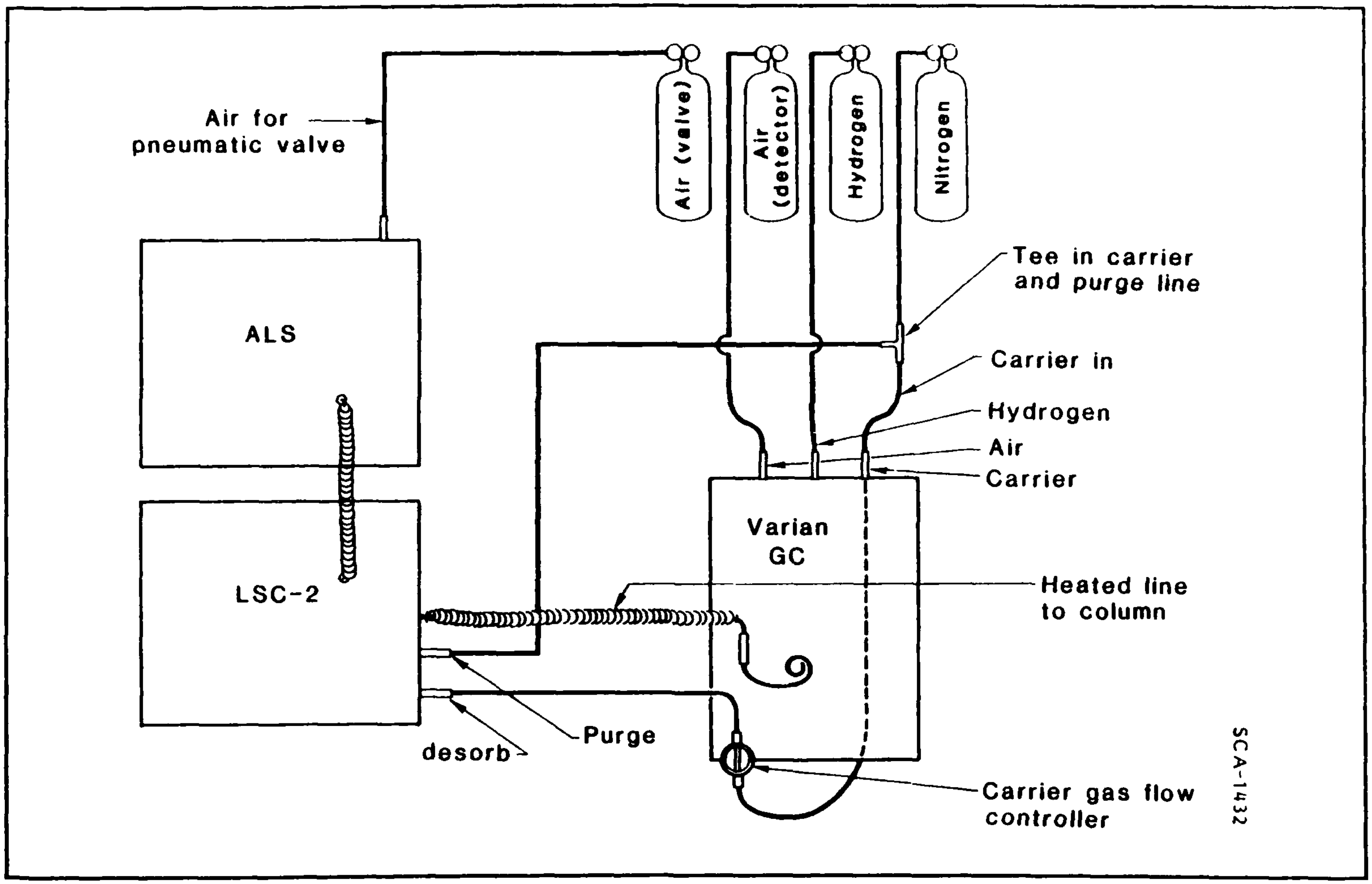


FIGURE 2.1 Schematic of Gas Line Connections to Instrument

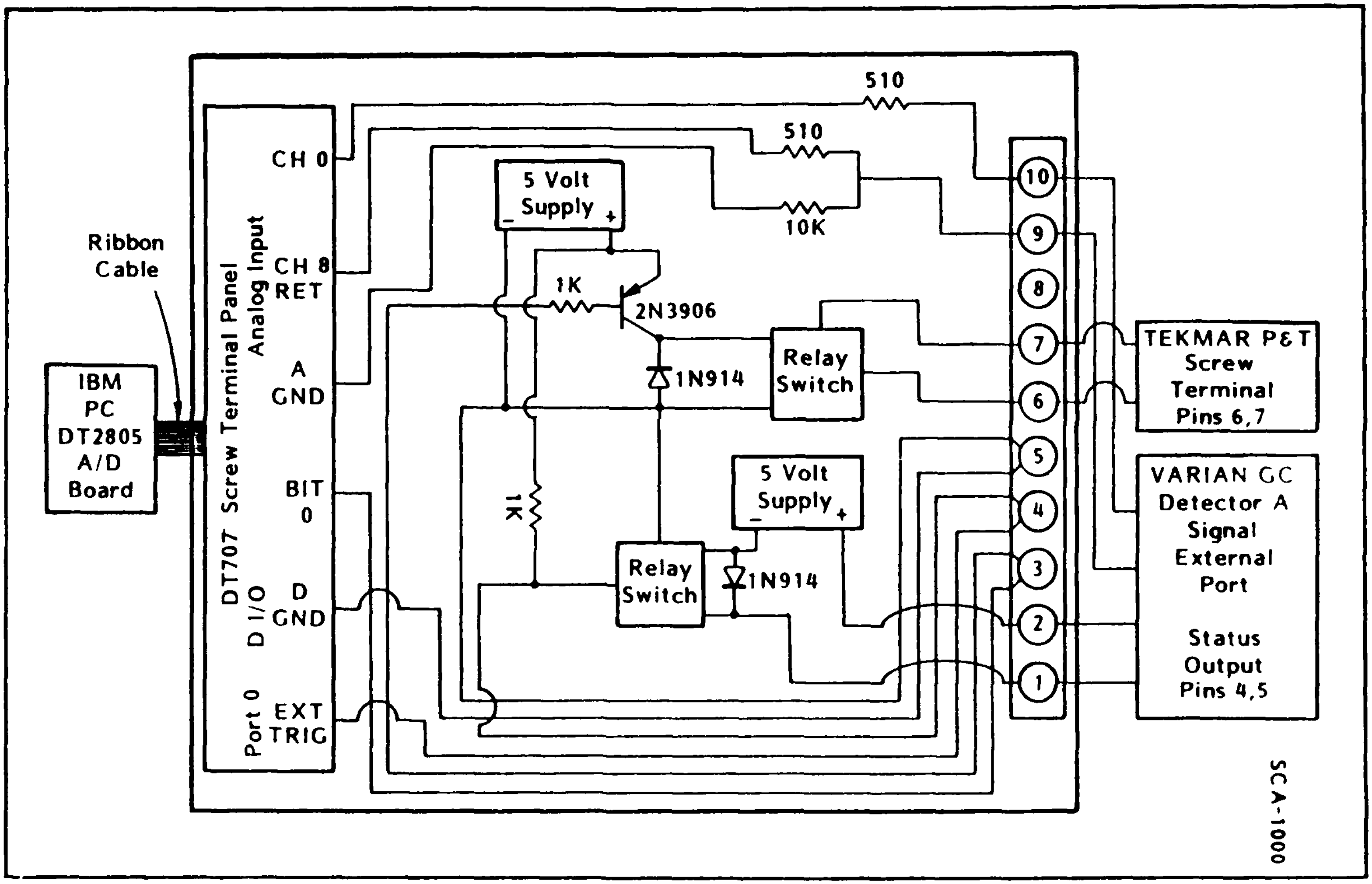


FIGURE 2.2 Schematic of Interface Box Used to Communicate between the Computer and the Instrument

The cables connecting the Varian GC and the Tekmar purge and trap to the interface box are connected to a ten-terminal strip that can be seen inside the interface box when its cover is removed. The terminals are numbered and each wire is labeled with the number of the terminal to which it should be connected; Figure 2.3 represents these connections schematically.

Data are collected on a three-wire cable that originates from the left side of the Varian GC from a slot labeled "DETECTOR A COMPTR"; the female end of this cable is plugged in at this point with the green ring terminal attached to the knurled thumbscrew below the connector. The other end of this cable is connected to the interface box as follows:

Wire	Interface Box
Black	9
Silver	10
Green	Remains disconnected

This cable carries the analogue signal from the detector output to the analogue to digital conversion board in the IBM PC. The other cables which are connected to the interface box screw terminals carry the data collection start and stop signals. They are connected as follows:

Wire	Interface Box
Brown	1
Red	2
Black	6
White	7

Behind the Tekmar LSC purge and trap unit, there is another screw terminal panel. Communication between the Varian GC and the Tekmar purge and trap unit is carried by two cables connected here. One cable originates from the Varian GC and the red and black wires are connected to terminals 4 and 5, respectively. The other set originates from the silver interface box with the cluster of five wires in the cable. The black and white wires of this cluster connect to positions 6 and 7 of the Tekmar screw terminal connector.

The relay switches located in the silver interface box emit an audible click when activated. To troubleshoot the switches, momentarily short the screw terminal

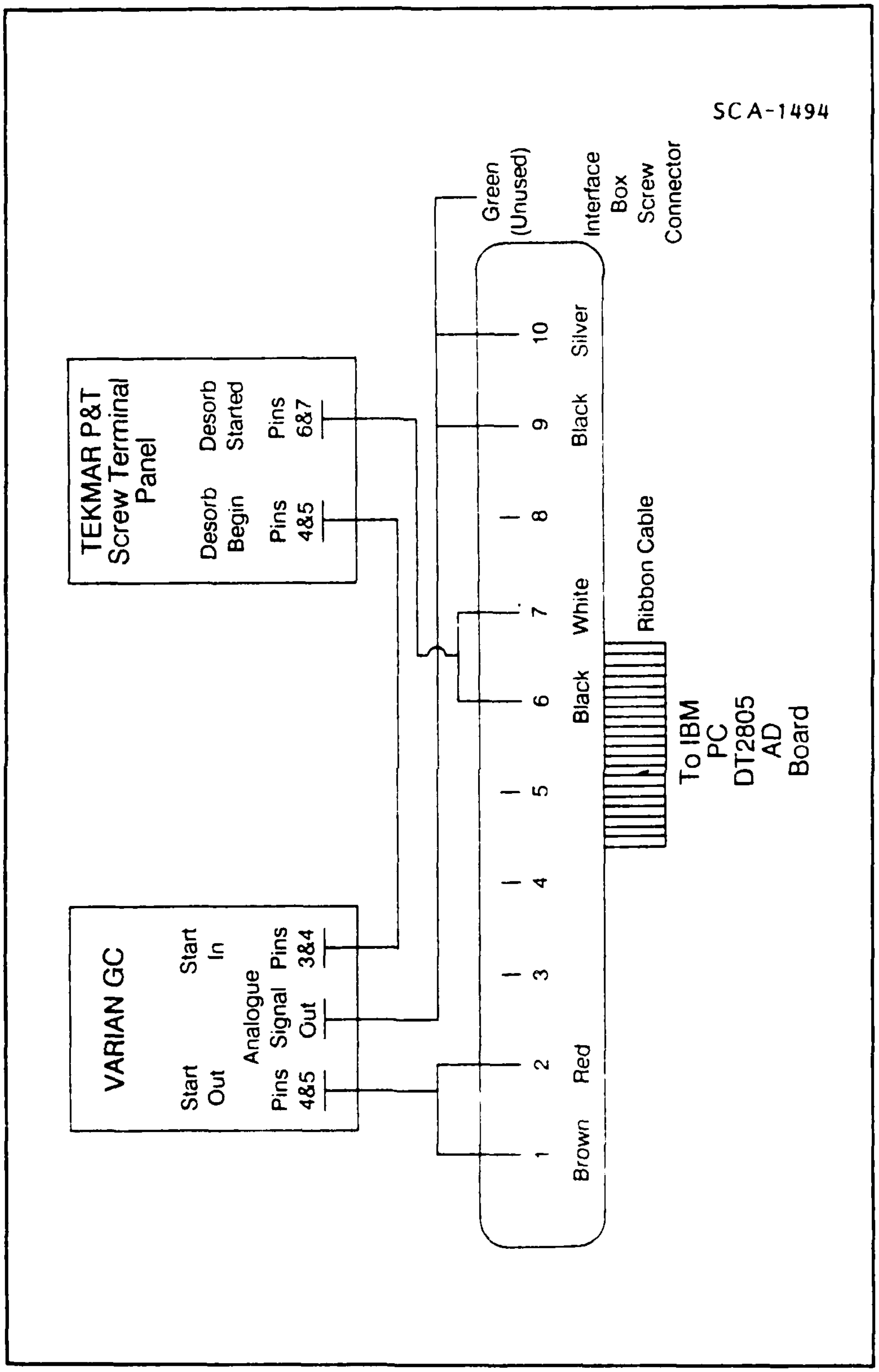


FIGURE 2.3 Schematic Terminal Connections

connections 1 and 2 in the interface box. Do not short out any of the other screw terminal connections. To check the other relay switch, manually step the Tekmar LSC unit to Desorb Ready. This relay will be activated when the LSC advances to "Desorb". If the switches do not operate properly, contact technical support and be prepared to describe what has been done.

3.0 RECOMMENDED INSTRUMENT OPERATING PARAMETERS

3.1 TEKMAR PURGE AND TRAP

• Purge time	8.0 minutes
• Desorb time	5.0 minutes
• Bake time	3.0 minutes
• X1m X.1 toggle switch	X.1
• Auto/Hold switch for Desorb Ready/Preheat	HOLD
• Auto/Reset switch for Bake	AUTO
• Purge pressure	20 psi
• Purge flow	40 mL/minute

3.2 VARIAN GAS CHROMATOGRAPH

• Initial temperature	40°C
• Initial time	5 minutes
• Ramp	8°C/minute
• Final temperature	180°C
• Final time	5 minutes
• Total time	27.5 minutes
• Chart speed	0.2 cm/minute
• Run log	ON
• Annotation	ON
• Carrier gas (digital dial inside oven door)	250

3.3 GAS CYLINDER REGULATOR PRESSURES

• Hydrogen	40 psi
• Air (for flame -GC)	60 psi
• Nitrogen	80 psi
• Air (Tekmar - ALS)	70 psi

4.0 MAIN MENU COMPUTER OPTIONS

The following options appear when the computer has been booted from the VOA Data System diskette:

(1) Analyze for TCE.
(2) Calibration Run for TCE.
(3) Prepare New Data Diskette (for Drive B).
(4) Prepare New VOA Data System Diskette (for Drive A).
(5) Retrieve QC Data.
(6) Retrieve Archived Data.
(7) Change Operating Parameters.
(9) Exit Menu.

The first two options, Analyze for TCE and Calibration Run for TCE, are described in the Procedural Guide (Section 7.0). If it becomes necessary to halt an analysis after data collection has begun, the computer must be re-booted to terminate data collection. Simultaneously press CTRL, ALT, and DEL keys to re-boot.

4.1 PREPARE NEW DATA DISKETTE (FOR DRIVE B)

Sample results are archived on the data diskette following sample analysis. Since approximately 100 data files can be stored on a single diskette, a new diskette should be prepared about once a week depending upon the number of samples analyzed.

The previously used data diskette should be labeled with the date of the last sample collection and stored in an appropriate place. The new diskette should be labeled with the start date (today's date), "TCE data diskette", and volume number (add 1 to the number of the previous diskette). Record the information in the sample log book. After the computer instructs you to insert a new diskette, the remainder of the operation is automatic.

4.2 PREPARE NEW VOA DATA SYSTEM DISKETTE (FOR DRIVE A)

The VOA data system diskette contains the programs that collect and analyze the data from the purge and trap/gas chromatograph.

Under daily operation of the data system, the VOA data system diskette should be replaced every 1-2 months. A new diskette should be inserted into Drive B as instructed by the computer prompts. When the new diskette is ready for use, label it with the date and "VOA data system".

Next the program will request that the QC archive diskette be inserted into Drive B. Information from the spike samples is temporarily stored on the VOA data system diskette and is copied to the QC archive diskette for permanent storage during this operation. When complete, return the QC archive diskette to storage and begin using the new VOA data system diskette in Drive A.

4.3 RETRIEVE QC DATA

This module prints out the spiked sample results for the designated period. The QC archive diskette must be placed in Drive B. Following an update of the disk, you will be prompted for the month and the year of the data you wish to recover. If there are data for the month specified, you will be asked to specify the first date of the month you wish to retrieve and then the last day. A table will be printed out with the TCE concentration values recorded in that date range.

To retrieve more data, simply enter another month and year and continue as before. When you are finished retrieving data, enter "X" to exit when prompted for another month and year. The system will ask you to remove the QC archive diskette from Drive B and will return to the main menu.

4.4 RETRIEVE ARCHIVED DATA

Besides retrieving archived data, this routine can also be used to obtain a listing of the files on a specific data diskette. This option will provide a printed report of the results for the selected sample. Place the appropriate TCE data diskette into Drive B. The program begins by displaying a list of the data files. If you wish to have a printout of the names, enter "y" in response to the query. Next it prompts the operator for a filename. The filename must be entered exactly as it appears in the listing with the extension included. The filename extensions indicate the sample type as follows:

File Extension	File Type
.blk	Blank
.stA	Standard A
.stB	Standard B
.stC	Standard C
.dat	Water Sample
.spk	Spiked sample
.dsp	Duplicate spike

Water samples are named by the operator, but the other sample types are assigned names by the computer. The first number of the assigned name corresponds to the position (minus 1) on the autosampler, the next four values comprise the month and day analyzed, and the last two digits indicate the hour in the day the run was started. For example, 3091910.stC would represent standard C run in position 4 (3 + 1), analyzed on September 19 (0919) at 10 A.M. The printer must be "on line" to receive the report. When you have finished printing reports, simply press the enter key when prompted for another filename, and the system will return to the main menu. Be sure to place the current data diskette back into Drive B before continuing.

4.5 CHANGE OPERATING PARAMETERS

The operating parameters should be changed ONLY by the designated maintenance person, and ONLY when operating conditions have been changed. Some instances of when this will be necessary include a GC column change, a change in the levels of standards, or a change in the spike concentration. A list of the parameters that can be changed will be displayed with their current values when Option 7, "Change Operating Procedures," of the Data system main Menu is selected. Enter the letter of the option you wish to modify. Retention times may drift if gas flows should vary or if analytical conditions, such as installation of a new column, are changed. The areas of target peaks may also change to reflect a change in analytical conditions or as a result of a change in standard concentration. If these parameters change, the retention times and *areas of all pertinent analytes must be updated with current information.*

Target compound parameters are listed in a separate table (select option "t") to facilitate addition of other compounds of interest at a later time. This table contains retention time and concentration information along with spike sample information for TCE.

Options:

- **Verbose**
  Used to obtain intermediate results for toubleshooting when set to "on". This is useful if all other efforts towards finding the problem have failed (see Section 8.0 on troubleshooting).

- **Chromatography sample time**
  This is the length of time in minutes that data will be collected for each sample. This should correspond to the total run time on the Varian gas chromatograph.

- **Retention time of internal standards**
  Retention time in minutes of each internal standard. The centrally located internal standard should be declared as internal standard #1. The order of the remaining internal standards is not critical.

- **Areas of internal standards**
  The area values reported on the printouts should be used for this parameter. The areas of the internal standards should correspond to the same order as the retention times above.

- **Minimum area required for standards**
  The area of each of the internal standards must be greater than this value to be identified by the system.

- **Change target compound parameters**
  Will display the current values of the parameters for the target compounds (currently only TCE). These parameters include:

  - **Target compound name**
    Name reported on printout (e.g., TCE).

  - **Retention time**
    In minutes.

  - **Units of concentration**
    Units name for report (e.g., ppb).

  - ***Maximum allowable water sample limit (warning limit)***
    Designed as a regulatory limit to warn the operator that the concentration is above this set limit.

  - **Concentration of spike added**
    Should be modified only if procedure is changed.

  - **Standard concentration**
    Concentration of target compound (TCE) in all three levels of standards (A, B, & C) in the units specified above.

The following parameters should not be changed by the operator (they are established prior to installation):

- Precision
- Accuracy
- Linear Range
- Quantitation limit

Error messages:
If invalid responses are entered (e.g., non-numerical values) the original values of the parameters are not changed.

- **Invalid selection**
  Enter letter of parameter to modify.

- **Invalid input**
  Enter numerical value (input must not contain letters or spaces).

- **Invalid retention time, larger than runtime**
  Specified retention time must be less than chromatographic runtime. If chromatographic conditions are changed so that the standards elute at a later time and the runtime is extended, the chromatographic sample time should be changed along with the retention times as described in Section 4.5.

5.0 MAINTENANCE

5.1 GAS FLOW MEASUREMENT

Prior to gas flow measurement, turn off detector gases and cool detector and oven to ambient temperature. Flow rates for the air, hydrogen, or detector gas flow are set individually to avoid compounding errors in flow rate measurement.

Set air, hydrogen, or detector gas inlet pressure to the recommended values given in Section 3.3. Gas pressures are indicated on the second stage regulator of the gas supply cylinder.

Each gas (hydrogen, air, and nitrogen) used has different optimum flow rates and should be checked individually. Consult Varian manual Section 8.3.3.1 for recommended rates and complete description of adjustment procedures. For example, flow through the column is measured at the detector with detector at room temperature with the air and hydrogen turned off at the regulator. Place the rubber stopper (provided for flow measurement) into the detector tower outlet, as shown in Figure 5.1. Securely attach a soap bubble flowmeter to the stopper and force a bubble above the inlet of the flowmeter. Using a stopwatch, measure the elapsed time it takes the bubble to move from zero to an appropriate volume mark (for accuracy, choose volumes giving at least 10 to 20 seconds elapsed time).

CAUTION

To avoid contamination of the detector, do not allow soap solution from flowmeter to flow into detector exit tube.

WARNING
EXPLOSION HAZARD

Shut off hydrogen flow immediately after making the flow adjustment unless hydrogen is to be ignited. Escaping hydrogen gas is both a waste and a potential hazard.

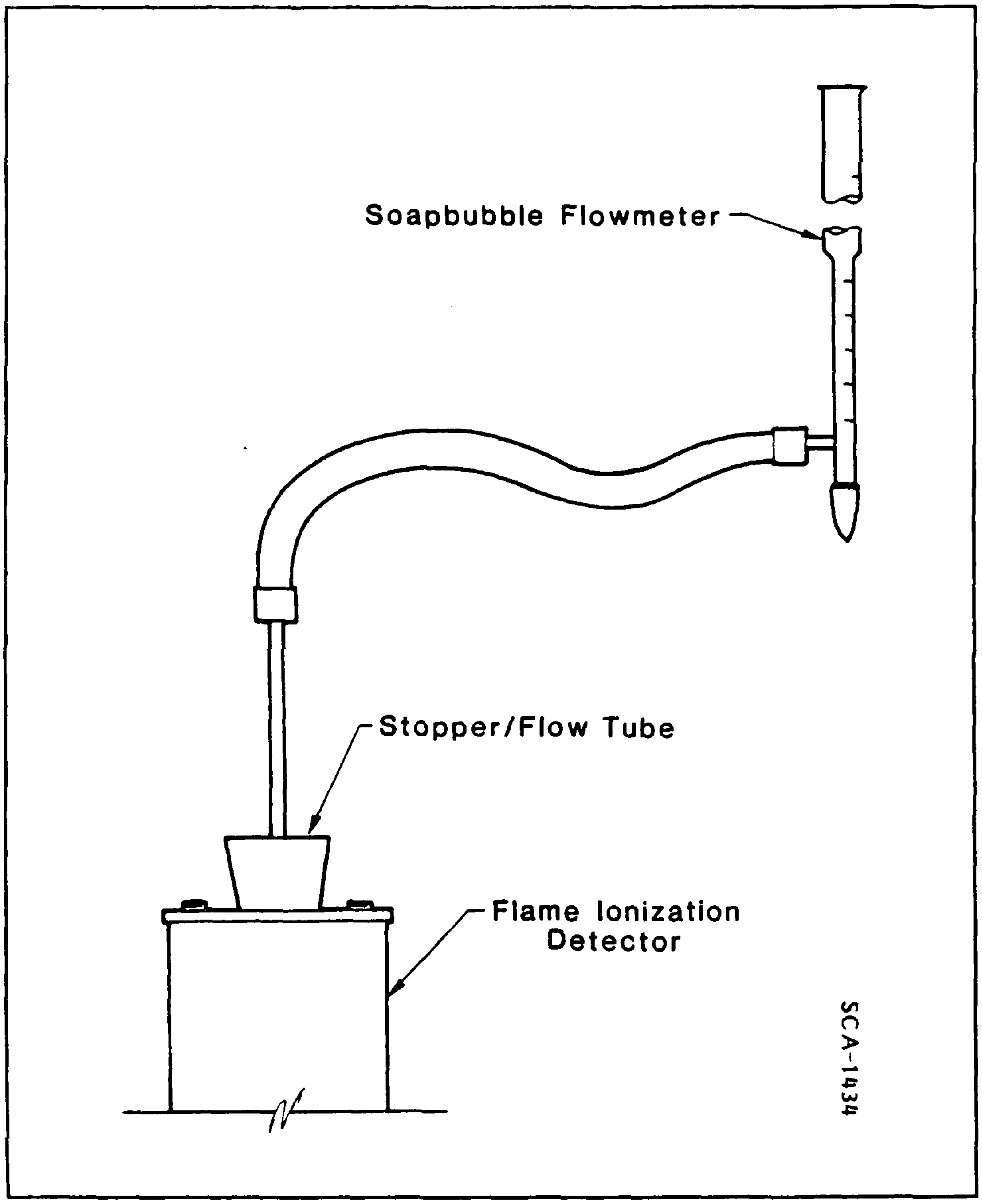


FIGURE 5.1 Gas Flow Measurement Setup

Calculate flow rate as shown in the following example:

- Volume: 10 mL
- Time: 20 seconds
- Flow rate: $\frac{\text{Volume}}{\text{Time}} = \frac{10\text{ mL}}{20\text{ sec}} = \frac{0.5\text{ mL}}{\text{sec}}$
- Convert flow rate in mL/sec to mL/min $\frac{0.5\text{ mL}}{\text{sec}} \times \frac{(60\text{ sec})}{\text{min}} = \frac{30\text{ mL}}{\text{min}}$

The purge gas flow on the Tekmar LSC-2 is determined in a similar manner at the vent outlet with the system in the purge mode. The recommended purge flow is 40 mL/min

5.2 GAS SYSTEM LEAK CHECKING

Generally, the fittings from the gas supply to the instruments will not develop leaks. Occasionally leaks may develop at these points, and these can be located by squirting a leak checking solution on the fittings and tightening them as needed.

Both the gas chromatograph and purge and trap apparatus may develop leaks where gas fittings are connected. Soapy water should not be used to leak check this system. A solution of 50 percent isopropyl alcohol in water may be used sparingly for this purpose.

The LSC-2 may develop leaks at the top and bottom of the sorbent trap. With the system in the purge mode, use a small amount of isopropyl alcohol - water and check for leaks. Tighten the fittings as necessary.

The gas chromatograph may develop leaks where the transfer line is connected to the GC column or where the GC column connects to the detector. Cool off the tranfer line, injector, and GC oven then leak check these fittings with the isopropyl alcohol - water solution and tighten as necessary.

5.3 SYSTEM DECONTAMINATION

This section will cover the probable sources of hardware contamination and corrective action.

5.3.1 Glassware Decontamination Procedures

The most probable sources of hardware contamination are as follows:

- Sparging vessels
- Sparging needles
- Volumetric glassware
- Syringes
- Sorbent Trap

All glassware and spargers should be thoroughly cleaned and baked out between runs according to Sections 4.1 and 4.2 of the procedural guide. The sparging needles must be rinsed between samples with a few milliliters of organic-free water.

Syringes may be rinsed with methanol and warmed by a heat gun to remove residual volatile organics. Do not overheat Teflon-faced plungers, and do not place syringes in the oven. If high-concentration samples have been run and the sorbent trap is contaminated, bake the trap at 200°C for several hours or overnight. This is done by stepping the LSC-2 to Bake and leaving the Auto/Hold/Step toggle switch in Hold.

5.3.2 Decontamination by Repetitive Blank Analysis

If the system remains contaminated (blanks continue to appear contaminated after the procedures in Section 5.3.1 have been followed) the problem may be in the valves in the transfer lines. Check to see that the valves in the ALS and LSC-2 and both sample transfer lines are heated. If either the lines or valves are not heated, take steps to correct the problem. If the lines and valves are heated and all spargers and sparger needles are clean, set up 10 blanks (organic-free water) to run as samples. If this procedure does not produce clean blank runs, additional decontamination may be carried out as follows.

5.3.3 Methanol Decontamination Procedure

This decontamination procedure should not be used unless it is absolutely necessary. Be certain to understand the entire procedure before starting. First, be certain the GC oven is cool to avoid damage to the GC column packing material by oxidation. Then disconnect the heated transfer line connecting the LSC-2 to the GC. Replace sorbent trap with an empty trap. Place a few milliliters of purged methanol in each sparging vessel on the ALS. With the ALS in Position 1, place the LSC-2 into the bake mode and gently heat the first sparger. **Avoid overheating the sparger and instrument panel.** Step the ALS to the next position, and heat the sparger in Position 2. Continue this procedure until all positions have been heated. Remove the spargers, rinse with purged water and bake to remove residual methanol. Rinse each sparging needle with purged water and heat gently to remove residual methanol. Reconnect the heated transfer line to the GC. Set up ten blanks (organic-free water) to run as samples This should produce clean chromatograms. If the system still produces contaminated blanks, service may be required.

5.4 INSTALLATION OF NEW SORBENT TRAP

(1) Remove front panel/cover from LSC-2 to expose trap.

(2) Unplug heater and disconnect connections on screw terminal panel.

(3) Loosen one-eighth-inch nuts at top and bottom of trap.

(4) Remove trap and heater assembly from instrument and slide sorbent trap from heater sheath.*

(5) Replace new sorbent trap by sliding it into the heater sheath.

(6) Replace one-eighth-inch Teflon ferrule and back ferrules at top of trap.

(7) Reconnect trap and heater assembly to LSC-2.

(8) Plug in heater and connect.

(9) Condition the trap in the bake mode for several hours as determined by the setting on the digital dial or overnight by leaving the Auto/Hold/Step toggle switch in hold.

5.5 INSTALLING A NEW GAS CHROMATOGRAPHIC COLUMN

Occasionally, gas chromatographic columns may deteriorate. Symptoms of a spent column include poor resolution, peak broadening, and unacceptable retention time shifts. If it is determined that the column requires changing, it is performed as follows:

(1) Cool the column and fittings to room temperature (turn off power to Varian GC).

(2) Turn off carrier gas.

(3) Disconnect the heated transfer line from the head of the GC column.

---

* Occasionally the stainless steel trap may have bent or become difficult to remove from the heater sheath. If this is the case the trap heater will have to be replaced also

(4) Disconnect the column from the detector port.

(5) Remove column from GC oven.

(6) Install new brass Swagelok nuts, ferrules, and back ferrules on the new column.

(7) Install new column by loosely connecting the detector end to the detector port and the inlet end to the heated transfer line. The stainless steel columns used in this system are fairly rugged and will withstand considerable flexing.

(8) Turn on carrier gas.

(9) Tighten column connections.

(10) Leak check connections and tighten as necessary.

(11) Turn on power to Varian GC, wa[illegible] system to attain set point temperatures, and operate as normal.

(12) Prior to operation, the new column must be conditioned. With carrier gas on and detector lit, program the oven temperature from ambient temperature to maximum operating temperature at approximately 2°C/minute. Hold the GC at the maximum operating temperature for four to six hours. If manufacturer directions for conditioning the column are supplied, they should be followed. **NEVER CONDITION THE COLUMN WITH THE FID UNLIT.**

5.6 PRINTER PAPER LOADING

See Page 18 of the "Epson FX+ Series Printer User's Manual Volume 1 Tutorial". Read the section entitled "FX-80: built-in tractor feed" and refer to Figures 1-1 and 1-2 of the printer manual.

5.7 PRINTER RIBBON INSTALLATION

See top of Page 12 of the "EPSON FX+ Series Printer User's Manual Volume 1 Tutorial" for ribbon installation instructions and see Page H-1 of the "EPSON FX+ Series Printer User's Manual Volume 2 Reference" for routine printer maintenance.

5.8 RESETTING COMPUTER SYSTEM CLOCK

It will be necessary to change the date and time for the computer clock whenever the clock battery is replaced (see "installing a new battery for computer system clock", Section 5.9), or for a change to/from Daylight Savings Time

(1) Insert a copy of your DOS Master Diskette in Drive A and a copy of the PC Accelerator Diskette in Drive B and turn on the computer power switch. Wait for system prompt (A >). Enter the following statement: *BASIC B:SETCLOCK*. The program will ask you whether you want to set "chip" clock or the DOS clock. Specify the "chip" clock and enter the correct date and time when prompted.

(2) Remove the diskettes from the drives and replace them in their storage sleeves.

(3) Place the VOA data system diskette in Drive A and simultaneously press the CTRL, ALT, and DEL keys to re-boot the system.

5.9 INSTALLING A NEW BATTERY FOR COMPUTER SYSTEM CLOCK

Tools needed:

- Medium sized screwdriver.
- Alkaline AA battery.

(1) Turn off and unplug IBM PC and disconnect the monitor and keyboard as shown in Figure 5.2

(2) Remove the five screws holding the main unit's top cover (see Figure 5.3 for location of screws). Remove the cover by sliding it forward and off.

(3) The battery holder is mounted along the center back of the computer. Check that the polarity of the battery and the holder are matched. **Installing the battery in the holder backwards can damage the clock circuit!!**

(4) Replace the computer cover and the five screws.

(5) Plug in all peripherals that were disconnected in Step 1.

(6) Follow the instructions on resetting the computer system clock (Section 5.8).

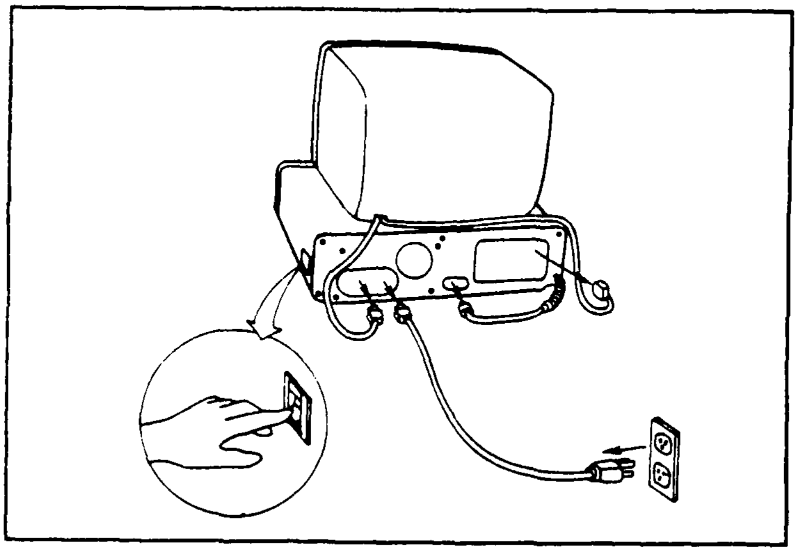


FIGURE 5.2 Disconnecting the Computer

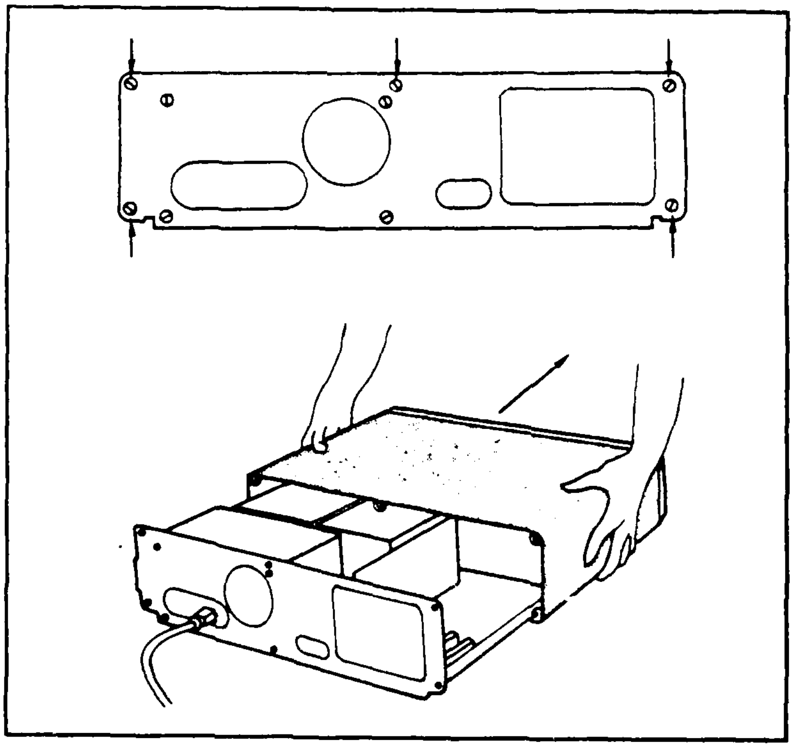


FIGURE 5.3 Remove the Computer Cover

6.0 INSTRUMENT LOG

Every time a problem arises or maintenance is conducted on the instrumentation, the information should be recorded in an instrument log book. Record the date, instrument (Tekmar ALS, Varian GC, etc.) operator, what was observed, and what was done to correct the problem. An entry should also be included every time a gas cylinder is replaced.

7.0 SAMPLE LOG

The following information should be recorded for each sample:

Date	Diskette No.	Analyst	Sample Name	Lot No. Int. Std.
9/19/86	1	Doug	EFLP2919	919AST
9/19/86	1	Doug	DFLP3919	919AST
9/20/86	1	Ron	EFLP105B	919BST
9/27/86	2	Doug	INFG10KF	874LMT

8.0 TROUBLESHOOTING

8.1 CHROMATOGRAPHY PROBLEMS - WARNINGS

Occasionally, problems will arise that will be automatically flagged by the data acquisition system as shown in Table 8.1. Those warnings which are addressed in this section are as follows:

- Chromatography problem, too few peaks detected.
- Sample too complex (> 50 peaks).
- Internal standard peaks not found.
- Contaminated blank.
- Calibration unsuccessful for TCE.
- System out of calibration, re-calibration required.

For other chromatography problems, see Varian Operation Guide, Section 15.8.

8.2 COMPUTER TROUBLESHOOTING

8.2.1 Diagnostic Tests (Hardware)

To determine if the problem is hardware related, it will be necessary to conduct the diagnostic tests provided by IBM. The IBM "Guide to Operations Manual" explains the diagnostic tests in greater detail in Section 4. You will need a copy of the IBM diagnostic diskette and two "scratch diskettes". Scratch diskettes are formatted diskettes with no data on them.

Insert the diagnostics diskette in Drive A and turn the power switch on. If you do not have any scratch diskettes, use two new, unused diskettes and the option "format diskette" (Option 1). After both diskettes have been formatted, enter 0 to select the diagnostic routines. Next the screen should display "System Checkout" along with a series of options. Enter 1, "Run tests multiple times", and have the system cycle through the tests 2 or 3 times. Follow the instructions, being sure to insert the scratch diskettes in the Drives and remove the diagnostic diskette. If any error messages are displayed, write down the error number and call the IBM Service Center.

If no errors are found while running the diagnostic routines there may be a software problem.

TABLE 8.1

Data System Warning	Possible Causes	Corrective Action
1. **Chromatography Problem** *Detected too few peaks*	• Standards made correctly?	• Remake daily standards and standards A, B and C (re. Procedural Guide Sections 6.5, 6.6, and 6.7).
	• Internal standard spikes and/or TCE spikes added to sample?	• Rerun sample with appropriate spikes (re: Procedural Guide Sections 7.3, 7.4, and 8.3).
	• All fittings connected to sparging vessel?	• Reconnect all fittings.
	• Sufficient purge gas flow?	• Check purge pressure and adjust to 20 psi.
		• Determine purge flow (re: Operations and Maintenance Manual Section 5.1).
	• Sorbent trap heating in desorb mode?	• Check electrical connections.
		• Check fuses.
		• Replace trap heater.
		• If none of the above solves the problem, service may be required.
	• LSC-2 trace switch on?	• Turn trace on.
	• LSC-2 and ALS transfer lines hot?	• Check fuses.
		• If none of the above corrects problem, service may be required.
	• GC temperature program running correctly.	• Monitor status during run and correct temperature program.
		• If oven is not heating, service may be required.
	• Sorbent trap leaking?	• Check top and bottom trap fittings for leaks (re: Tekmar Manual Section 4.5.2).
	• Early triggering of data acquisition?	• Verify that all line cords are connected through isolation tranformer.

TABLE 8.1 (Continued)

Data System Warning	Possible Causes	Corrective Action
2. **Sample too Complex** (> 50 peaks)	• Blank contaminated?	• Run a blank of freshly purged water.
	• Standards or reagents contaminated?	• Remake standards with new, clean reagents.
	• Syringes contaminated?	• Thoroughly clean syringes.
	• System including glassware contaminated?	• Thoroughly clean system (re: Operating and Maintenance Manual Section 5.3).
	• Carrier gas contaminated?	• Replace with uncontaminated carrier gas.
3. **Internal Standard Peaks Not Found**	• Internal standard added?	• Rerun sample with appropriate internal standard spike.
	• *Loss of resolution?*	• Change GC column (re: Operating and Maintenance Manual, Section 5.5).
	• See Item 1.	• As in Item 1.
4. **Contaminated Blank**	• Water freshly purged?	• Purge water according to Section 4.4 of Procedural Guide.
	• Syringes clean?	• Clean syringes (re: Operating and Maintenance Manual Section 5.3).
	• Internal standard contaminated?	• Prepare new internal standard (re: Procedural Guide Section 6.6).
	• Transfer lines heated?	• Check as in Item 1.
	• Purge gas contaminated?	• If nitrogen tank replaced coincident with appearance of contamination, replace tank.
	• Hydrocarbon trap expended?	• Replace with new hydrocarbon trap (re: Tekmar Manual 3.4.1).
	• Sorbent trap contaminated?	• Bake sorbent trap at 200°C for two hours.

TABLE 8.1 (Continued)

Data System Warning	Possible Causes	Corrective Action
4. Contaminated Blank (continued)	• System contaminated?	• Operations and Maintenance Manual Section 5.3.
5. Calibration Unsuccessful for TCE	• Blank standard A, B, and C in correct autosampler positions? • Calibration standards prepared correctly? • TCE peak clearly resolved in chromatogram?	• Reload standards and try again. • Remake standards A, B, and C (re: Procedural Guide Section 6.0). • Determine source of non-target peaks and take appropriate decontamination steps.
6. System out of Calibration, Recalibration Required	• System operating correctly?	• See previous Troubleshooting sections.

8.2.2 Software Tests

Boot the system from the VOA data system diskette and select Option 7 (change operating parameters). Change the verbose option, a, to "on". This will permit intermediate values of the results to be displayed. Set up a short analysis run and just prior to starting the Tekmar purge and trap, set the printer to capture all output sent to the screen. To print all screen output, press the CTRL key and the PrtSc key simultaneously. To turn off print capture, press the CTRL key and PrtSc Key simultaneously again. It acts as toggle switch and can be set at any time, but printing does consume lots of paper. Continue operation as normal and check the output for error messages.

If any of the following messages are displayed, record the information, reboot the computer (cold start), and try the operation again. If the problem persists, call S-CUBED at (619) 453-0060 and describe the problem.

For the following error messages, <name> represents a variable name that is dependent upon the error condition.

Error Messages:
```
ERROR opening parameter file
ERROR closing <name>
<name> not found in file
Address error - improper seek.
ERROR writing to file
Buffer not cleared
ERROR sending information to output device
Illegal value for gain
FATAL ERROR - illegal status register value
FATAL BOARD ERROR
ERROR - denominator is zero
ERROR opening <name>
ERROR opening control archive file
ERROR opening QC file
ERROR transmitting data to printer file
ERROR transmitting data to printer
```

These messages are displayed on the screen during sample analysis.

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END
DATED
FILM
8-88
DTIC