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ALTERNATE TECHNIQUES FOR WEAR METAL ANALYSIS

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Abstract: Wear metal measurements were performed on various type lubricant samples obtained from operating engines and laboratory prepared samples using AE, AA, ICP, graphite furnace AA, ferrography and a particle size independent method. Also, the effect of 3-micron filtration on the analytical capability of the various methods was investigated. Considering the data from all samples, all spectrometric techniques were Fe particle size sensitive. None of the spectrometers offered any significant improvement over AE with respect to analyzing large particles, monitoring capability with and without 3-micron filtration, analysis time or analysis cost or person-power. The data also indicated that 3-micron filtration could have small effect on spectrometric oil analysis results.

Key Words: Ferrography, Fine filtration, Oil analysis, Particle size, Spectrometers

Introduction: Spectrometric oil analysis programs for determining wear metals in used aircraft turbine engine lubricants have been used for the last three decades for detecting those engines experiencing abnormal wear and the removal of those engines from service prior to catastrophic failure. The program requires lubricant samples to be periodically taken from engines and analyzed in a laboratory for various wear metal concentrations. Abnormal operating engines are identified by the level and/or rate of change in specific wear metal concentrations. Many reports and papers have been published on the success (or failure) of the various monitoring techniques and programs. Many different methods and techniques have been developed and used for monitoring the wear metals in used lubricants depending on such factors as the type equipment being monitored, monitoring organization, equipment usage, etc.

For many years oil filters were used having nominal filtration capabilities of 35 to 50 microns and in some cases much greater than 50 microns. In recent years "finer" filtration has been investigated for the purpose of inhibiting secondary wear caused by the primary or initial wear particles and external contamination. Currently, finer filtration is being considered for use in aircraft turbine engine lubrication systems. These "fine" filters have the potential of greatly reducing the metal content of SOAP samples and current techniques for oil analyses may prove unsatisfactory for use in monitoring turbine engines equipped with these filters.

The objective of this investigation was to conduct an evaluation and comparative analysis of currently used AE and AA techniques with various wear metal analysis techniques such as inductively coupled plasma (ICP) spectrometry, graphite furnace atomic absorption (PWMA), ferrography and particle size

distribution using the acid dissolution method (ADM). The effect of 3-micron filtration on the analysis capability of the various methods was investigated using a test rig equipped with a 3-micron operational "in-depth" type oil filter and using parameters of pressures, temperatures and flow rates typical of operating turbine engines.

Microfiltration Test Rig: A detailed description of the microfiltration test rig (MFR) has been previously reported [1] and only a brief description of the test rig and filter will be given in this paper. The test rig consists mainly of a 5 gallon capacity conical bottom oil reservoir, a constant speed gear pump for oil circulation and a 3/4 inch stainless steel oil circulation system incorporating a turbine flow meter, in-line thermocouples and pressure transducers and a pressure relief valve. A 7 gallon seamless stainless steel container is used for collecting the fluid after passing through the filter. A small scavenger gear pump is used for transferring the filtered fluid back into the oil reservoir for subsequent passes through the filter. The test fluid can be circulated in a by-pass mode prior to filtering for obtaining an uniform (mixed) sample. An "upstream" filter sample can be taken either from the oil reservoir or sampling port while the filtered sample is obtained immediately after filtering from the 7 gallon collection container using a precleaned vacuum flask. The filter elements (3 micron absolute, $\beta_3 > 200$) were operational type "in-depth" elements capable of withstanding temperatures in the range of -65°F to 350°F. The pressure drop across the filter at a rated flow of 4 GPM is 4 psi at 100°F and has an element collapse differential pressure of 100 psi.

Wear Metal Analysis Techniques: Two different atomic emission (AE) spectrometers were used for determining the trace metal concentrations of the various samples. Both instruments employ a rotating disk lower electrode, no sample dilution, AC spark excitation, multi-element simultaneous analysis, data reporting and each using SOAP oil standards R-19 for instrument calibration. Normal SOAP procedures were used during the operation of both spectrometers.

Trace element concentrations of the samples were made using a single element mode atomic absorption (AA) spectrophotometer and only iron determinations were conducted on this instrument since iron was the most prevalent metal present in most of the samples. These analyses were made using a 1 part sample to 4 parts methylisobutyl ketone (MIBK) dilution, nitrous oxide-acetylene flame, and 1:4 diluted SOAP oil standards for instrument calibration.

Inductively coupled plasma (ICP) analyses were made using 1 part sample and 9 parts kerosene dilution, spray nebulizer using argon gas, multi-element simultaneous analysis and diluted SOAP standards for calibration.

The portable wear metal analyzer (PWMA) is a graphite furnace atomic absorption spectrophotometer. It is a microprocessor controlled automatic sequential multielement instrument that will analyze for nine elements (Fe, Cu, Al, Cr, Ag, Mg, Ni, Si and Ti) using electrothermal element atomization. Analyses made with the PWMA required no dilution. Regular oil analysis standards in MIL-L-7808 lubricant were used for calibration.

The acid dissolution method (ADM) has been previously reported in detail [2] and only a brief summary of the method will be given in this paper. The appropriate amount of sample is combined with a HNO_3/HCL (1:3) acid mixture and hand shaken for 10 seconds. The mixture is then agitated in an ultrasonic bath for 5 minutes at 40°C (65°C if Mo analysis is required). The mixture is then diluted

with a long chain alkoxy alcohol/MIBK (or kerosene) solvent and analyzed by AA or ICP for selected wear metals.

Particle size distribution of iron wear debris was determined using a microfiltration technique. Aliquots of the sample were filtered through 12-, 8-, 5-, 3-, 2-, 1- and 0.4-micrometer membrane filters. The filtrate was then analyzed for iron by the ADM using an AA spectrophotometer.

Ferrography was used for magnetic separation and collection of wear debris (primarily iron) from lubricating fluids for the subsequent evaluation of the debris with respect to the amount and morphology (particle size, shape, source or type wear, etc.) of the debris [1]. All ferrograph analyses referenced in this report were conducted on the Analytical Ferrograph which involves depositing the debris onto a glass slide and subsequent microscopic evaluation as to particle morphology and densitometer measurements. The densitometer measurements provide a relative concentration of the various size particles deposited down the slide from which the ratio of large (L) to small (S) particles can be calculated.

Test Lubricants: The various type lubricant samples used in this investigation were obtained from operational engines, laboratory prepared samples using new lubricant blended with commercially purchased metallic powders and with new lubricant blended with wear debris generated by a pin-on-disk wear test rig. Some of the operational engine samples were obtained specifically for this program. In all cases, the samples were newly shaken and sonicated prior to analysis. Many of the samples consisted of such small volumes that only limited analyses could be conducted. In other cases, two or three samples were combined for providing sufficient sample for microfiltration rig studies.

Results and Discussion: Samples used to evaluate the analytical capabilities of the ICP, A/E JA, PWMA, AA, ADM, and ferrography and to perform particle size distribution analyses were heated and sonicated prior to analysis. A/E35U-3 emission analyses were conducted by SOAP laboratories using normal procedures. In general the data obtained by the various analysis techniques have been tabulated and arranged in order from high to low for initial iron content and percent iron loss. This approach provided for determining the relative rankings of the various analysis techniques to ADM values with respect to total iron content and iron loss due to three micron filtration. Correlation between all analysis techniques including ferrography were made only for MFR samples since no ferrography measurements were conducted on the SOAP samples.

Previous research [3] has shown that determined iron concentrations of ester base oils can be up to 2.5 times the actual iron concentration when determined using the A/E 35U-3 spectrometer calibrated with mineral oil base standards. This same research also showed decreasing emission sensitivities for particles above approximately eight microns. The data obtained during this study have shown similar matrix effects and changing of particle size sensitivity when using atomic emission analysis techniques. As shown in Table 1 samples having small iron particle sizes (less than 3 microns such as sample MFR-8) have much higher atomic emission values than corresponding ADM values. For samples having very large iron particles such as sample MFR-4 the ADM values are much higher than the corresponding emission values. Particle size distribution on MFR samples confirms the above findings. The original iron content and iron loss due to three micron test rig filtering (Table 1) show a wide variation between the various analysis techniques for both the original iron content and percent loss. As expected, the spectrometers' values diverge greatly from the ADM values at higher concentrations

where large particles exist. Samples having low initial iron concentrations can have as large of variations between percent loss analyses as high iron content samples due to the presence of large metallic particulates. Particle size can also have a greater effect on percent iron loss due to filtering than on initial iron concentration.

Table 2 gives a summary of rankings based on the highest iron content determined in the MFR samples by the analysis techniques. For example ADM analyses ranked in the highest position (6) two of twelve analyses, in fifth position three of the twelve analyses, etc. These data show that ADM, PWMA, A/E35 and A/EJA rank 3 and above 83% of the time while ICP, and AA ranks 2 and below 81% of the time. Table 3 gives similar type data for percent iron loss due to filtering. Again ADM, PWMA, A/E35 and A/EJA ranked 3 and above 73% of the time and ICP and AA ranked 2 and below 70% of the time. Table 4 gives the rankings for each analysis technique for MFR samples not filtered. In this case ADM, A/EJA, A/E35 and PWMA ranked 4 and above 72% of the time while ICP and AA ranked 3 and below 94% of the time.

Figure 1 represents all original iron test data using six different type analyses. Since the ADM analyses are particle size independent, various values obtained using the other analysis techniques are plotted against the appropriate ADM values. There is much data scattering at higher concentration but nevertheless the deviation from ADM values is quite evident. The slopes of these lines show AE instruments to be the highest followed by ICP, PWMA and AA. A slope of 1.00 would indicate a perfect correlation with ADM. It seems that A/E JA has a good correlation, slope of 1.02, but one should bear in mind that a correction factor has not been applied to the values which would significantly decrease the slope. In addition, particle size plays a significant role in the slopes. In order to minimize the particle size effect, samples having iron concentrations of < 15 ppm were plotted in Figure 2. Much smaller scatter is seen. Similar conclusions could be made from this plot since the two AE instruments gave the highest slope values which correspond to 2.0-2.5 accounting for the matrix effect. ICP slope also correlates well with ADM and AA is a distant last. PWMA shows a higher correlation due to sampling problems.

Figure 3 shows similar type curves for the 3-micron filtered samples. Again, a slope of one means perfect correlation with ADM. Slopes similar to those of Figure 2 were obtained when discounting MFR-5 high value. This indicates that all instruments did correlate well with ADM and each other for samples having small particle size.

A summary of the ferrographic analysis of the MFR filtered samples is shown in Table 5. Ferrographic data provide a comparative rating of the quantity of iron present and a comparative rating of large (entry position reading) to small (50 mm position reading). These data show several interesting points. First the level of iron content is ranked the same when using the percent area covered for the entry position, percent area covered for the entry plus 50 mm positions or the total of the percent area covered for the entry, 50, 40, 30, 20 and 10 mm positions. Secondly, these rankings are very close to the ADM iron content rankings considering the small differences in the iron content of some of the samples. Sample MFR-5-A appears to be the only sample out of order in ferrographs ranking. This could be due to this sample being the only automotive mineral oil having a very high iron content consisting of small (less than 3 micron) particles. The initial L/S rankings do not correlate to the percent area covered rankings which would be expected but do correlate to particle size [4]. It should be noted that the L/S (Initial) ranking correlate very well with the L/S loss due to filtration ranking.

Figure 4 illustrates the correlation between the ADM values (ratio of Fe concentrations before and after 3-micron MFR filtering indicated by L/S (ADM)) and decreases in L/S Ferrograph values. Slopes show good correlation between decreases in L/S Ferrograph values and percent loss due to filtration for most of the samples. Similar correlation is shown between initial ADM iron content and L/S ferrograph values for the same samples before MFR filtering.

Analysis of Wear Metals Other Than Iron: Very few MFR samples contained any significant concentrations of wear metals other than iron [4]. Silicon metal was present in several of the samples with the concentrations not being reduced by filtration. However, other studies have shown most silicon values are due to silicone contamination which is not filterable. Sample MFR-5-A (automotive oil) had very large quantities of Al, Cu, Mg and Pb with the concentrations of these metals not being affected by filtration. Samples MFR-6-A through MFR-9-A contained 3 to 30 ppm Mg and with samples MFR-6-A, MFR-8-A and MFR-9-A containing 1 to 3 ppm Cu. Again, filtration did not reduce the concentrations of these metals. This could be due not only to small particle size but part of the metals being in solution after reaction with oil breakdown products. Some of the SOAP samples contained 1 to 3 ppm Ag, 1 to 30 ppm Mg, 1 to 10 ppm Cu and 1 to 20 ppm Pb. These metals may have been dissolved since the three micron membrane filtration had only a very slight effect on reducing the concentration of the values for any samples. The above data indicate that the use of 3 micron absolute filters would primarily affect only the iron concentrations of lubricant systems.

Wear Metal Trending of SOAP Samples: Four hundred eighty four residual SOAP samples were submitted by the base level operating activities including their AE spectrometric analyses for additional studies. ICP concentrations were also determined on these residual SOAP samples to see if "trending" could be established by using either of the two analysis techniques and for comparing data obtained on lubricant systems having "fine" filtration when using both AE and ICP spectroscopy. These samples were obtained from 9 type of engines and from 2 transmission systems and two gearbox systems. Complete test data for these samples including system serial numbers, hours since overhaul and hours since oil change were reported previously [4]. Based upon information provided by the operating activities all engine lubricant systems utilized 10 micron oil filters except for the F404-GE-400 engines which utilized 5 micron filters. The SH-60B helicopter transmission lubricant system and the F404-GE-400 engine lubricant system were the only systems from which a significant total number of samples were obtained or systems from which consecutive samples were obtained. No increasing iron trends occurred for any of the consecutive sample series which should not be surprising since none of the oil systems being monitored were reported as having any problems. The average ratio of AE iron to ICP iron values of the 484 samples is very close to the average of the AE and ICP iron ratio values for the MFR samples. These AE/ICP ratios were approximately two for the MFR samples and SOAP monitoring samples with the one exception of the F404-GE-400 engines which had an AE/ICP iron ratio of 4.4. This ratio is probably high since many of the AE analyses were conducted on the high range setting of the AE spectrometer (the ICP iron range was 0.00 to 0.63 for these engines).

Concentrations of other trace elements such as Ag, Al, Cr, Cu, Mg, Ni, Si and Ti for all the 13 lubricant systems monitored are low using either the AE or ICP analysis technique with the AE analysis usually being slightly higher and much higher for Ti. Analyses for Pb and Sn were inaccurate due to a small number of intermittent unexplained very high ICP values of Pb and the Sn enhancement when using AE spectroscopy for specific formulations of ester base lubricants. Overall, monitoring of the 13 lubricant systems gave low analysis values for all metals, no iron "trending" data for either analysis

technique and with the similarity between the AE data and ICP data being about the same as that shown by the corresponding data obtained on the MFR samples

Conclusions: The comparative study of the various analysis techniques has indicated that microfiltration could have a small effect on spectrometric oil analysis results. Considering the data from all samples, all analysis techniques investigated (except ferrography and the acid dissolution method) were iron particle size sensitive with none showing significant improvement over the currently used emission spectrometric technique with respect to analyzing large particles. None of the analytical analysis techniques investigated offered any improvement over the currently used emission technique with respect to monitoring capability with or without microfiltration, analysis time or analysis cost, or man-power. Although the analytical ferrograph showed good correlation with iron particle size as well as total iron concentration it could be useful in supplementing the current SOA programs where specific lubricant related problem areas exist.

Recommendations: This study has shown that future research for improving the monitoring capability of lubricant systems would be best directed towards the following areas. Abnormal operating engines or lubricant systems which were not detected by SOAP should be drained and all the drained oil submitted to an appropriate laboratory for an in-depth evaluation including wear particle size distribution determination. Associated lubricant filters should be included for analyses. The data obtained would identify the reasons for the SOAP misses and identify specific type of measurements or data evaluation techniques which would reduce the number of SOAP misses.

Research effort should be directed towards improving the currently used atomic emission spectrometric technique. These improvements would include such factors as instrument and calibration stability, reduced instrument down time, reducing repair costs and equipment modifications such as incorporating computers for updating data acquisition and data evaluation capability.

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TABLE 1
ORIGINAL IRON CONTENT AND IRON LOSS DUE TO THREE MICRON
TEST RIG FILTERING

Sample	Orig. Fe & Loss due to Filt.	Method of analysis, ppm					
		ICP	A/E 35	A/E JA	PWMA	AA	ADM
MFR-1-A-1	Orig. Fe	9.28	25	25	60	7.5	31.8
	Filt. Loss	3.01	16	11	51	2.3	21.0
	% Loss	32	64	44	85	31	66
MFR-2-A-1	Orig. Fe	32.7	62	93	61	15.0	60.4
	Filt. Loss	10.9	22	39	27	3.0	30.7
	% Loss	33	37	42	44	20	51
MFR-3-A-1	Orig. Fe	11.1	22	32	15	9.0	13.8
	Filt. Loss	0.7	2	5	2	0.6	2.3
	% Loss	6	9	16	13	7	17
MFR-4-A-1	Orig. Fe	6.43	2	17	40	4.0	26.0
	Filt. Loss	5.90	1	17	38	2.4	25.8
	% Loss	92	50	100	95	60	99
MFR-5-A-1	Orig. Fe	96.1	94	110	54	89	110
	Filt. Loss	14.8	5	2	5	(3)	11.3
	% Loss	15	5	2	9	(3)	10
MFR-6-A-1	Orig. Fe	6.57	11	13	10	5.1	7.41
	Filt. Loss	1.67	1	2	5	1.0	2.79
	% Loss	25	9	15	50	20	38
MFR-7-A-1	Orig. Fe	0.49	2.0	0.80	0.8	0.6	0.61
	Filt. Loss	0.02	0.5	0.50	0.1	0	0.20
	% Loss	4	25	62	12	0	33
MFR-8-A-1	Orig. Fe	12.50	27	28	11	11	10.1
	Filt. Loss	(0.01)	6	6	0	0	(1.7)
	% Loss	0	22	21	0	0	(17)
MFR-9-A-1	Orig. Fe	3.61	5.6	6.2	2.7	2.2	3.41
	Filt. Loss	0.32	(0.1)	1.4	0.3	0.3	(0.2)
	% Loss	9	(2)	23	11	14	(6)
MFR-10-A-1	Orig. Fe	2.69	4.0	6.1	2.6	1.6	6.14
	Filt. Loss	0.78	2.0	2.8	0.8	0.4	2.81
	% Loss	29	50	46	31	25	46
MFR-18-A-1	Orig. Fe	2.30	3.2	8.6	2.4	1.9	5.31
	Filt. Loss	1.50	1.4	5.2	1.4	1.2	3.68
	% Loss	65	44	60	58	63	69
MFR-22-A-1	Orig. Fe	8.56	17	23	8.6	6.2	8.57
	Filt. Loss	1.20	2	4	1.6	1.1	1.39
	% Loss	14	12	17	19	18	16

Values in () show ppm and % increase in value after filtering

TABLE 2

**SUMMARY OF RANKINGS FOR EACH ANALYSIS TECHNIQUE
AND MFR FILTERED SAMPLES BASED ON IRON CONTENT
(12 SAMPLES EXCEPT AS NOTED)**

Measuring Technique	Number of Times Ranked in Position High to Low Readings					
	6	5	4	3	2	1
ADM	2	3	0	5	1	1
PWMA	2	1	4	1	2	1
A/E35	1	6	3	0	1	1
A/EJA	7	2	2	1	0	0
ICP	0	0	2	3	4	3
AA	0	0	0	0	0	12

TABLE 3

**SUMMARY OF RANKINGS FOR EACH ANALYSIS TECHNIQUE BASED
ON PERCENT LOSS DUE TO 3 MICRON FILTERING OF TEST RIG SAMPLES
(12 SAMPLES EXCEPT AS SHOWN)**

Measuring Technique	Number of Times Ranked in Position (High to Low Readings)					
	6	5	4	3	2	1
ADM	4	4	1	1	1	1
PWMA	3	1	3	2	3	0
A/E35	2	0	2	2	2	4
A/EJA	2	3	3	2	0	2
ICP	1	1	0	3	3	4
AA	0	2	1	0	2	7

TABLE 4

**SUMMARY OF RANKINGS OF EACH ANALYSIS TECHNIQUE
FOR MFR SAMPLES NOT FILTERED AND BASED ON IRON CONTENT**

Measuring Technique	Number of Times Ranked in Position (High to Low Readings)					
	6	5	4	3	2	1
ADM	2	1	3	1	1	0
A/EJA	4	3	0	0	1	0
A/E35	2	4	1	0	1	0
PWMA	0	0	3	4	1	0
ICP	0	0	1	2	3	2
AA	0	0	0	1	1	6

TABLE 5

**SUMMARY OF ANALYTICAL FERROGRAPH DATA AND EFFECTS OF
MFR FILTRATION ON THE RATIO OF LARGE TO SMALL PARTICLES**

Sample	ADM Iron ppm	Ferrograph Data				
		Entry Pos. % A.C. ⁴ Value	E ¹ +50 mm Pos. % A.C. Value	Total ² % A.C. Value	L/S3 (Init) Value	L/S (Filt. Loss) Value
MFR-5-A	110	444 ⁵	856 ⁵	1289 ⁵	1.08	0.05
MFR-2-A	60.4	1407	2217	3453	1.74	0.57
MFR-1-A	31.8	771	1086	1398	2.45	1.29
MFR-4-A	26.0	717	834	1323	6.13	4.79
MFR-3-A	13.8	25.9	62.7	267	0.77	(+0.11)
MFR-8-A	10.1	26.5	39.8	82.2	1.99	0.84
MFR-22-A	8.57	21.6	47.6	177	0.83	0.27
MFR-6-A	7.41	40.2	76.6	190	1.10	0.30
MFR-10-A	6.14	13.3	24.9	75	1.15	0.36
MFR-18-A	5.13	27.3	54.8	109	0.99	0.46
MFR-9-A	3.41	9.8	19.3	37.3	1.03	(+0.01)
MFR-7-A	0.61	5.4	7.3	11.5	2.84	1.84

¹ E= Ferrogram entry position; ² Total of % area covered readings at the entry, 50, 40, 30, 20 and 10 mm ferrogram positions; ³ L/S Ratio of large (Entry) particles to small (50 mm); ⁴ A.C. = Area Covered;

⁵ Values adjusted to normal 3 mL sample size

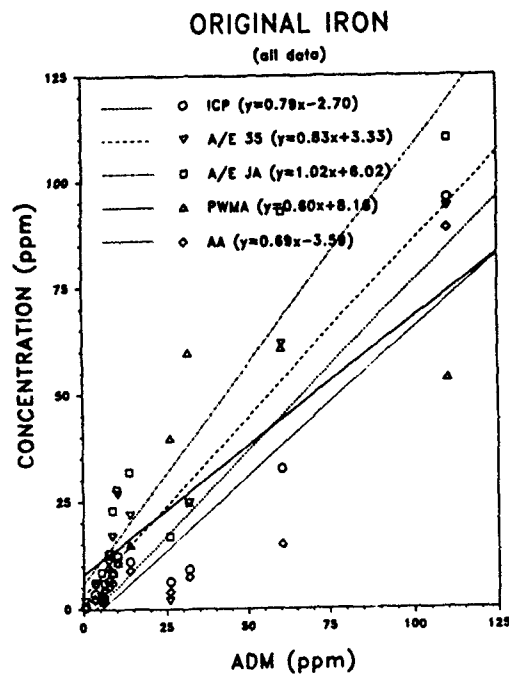


Figure 1. ADM Values of Iron Before Filtration from Five Different Type Analyses Against ADM Values

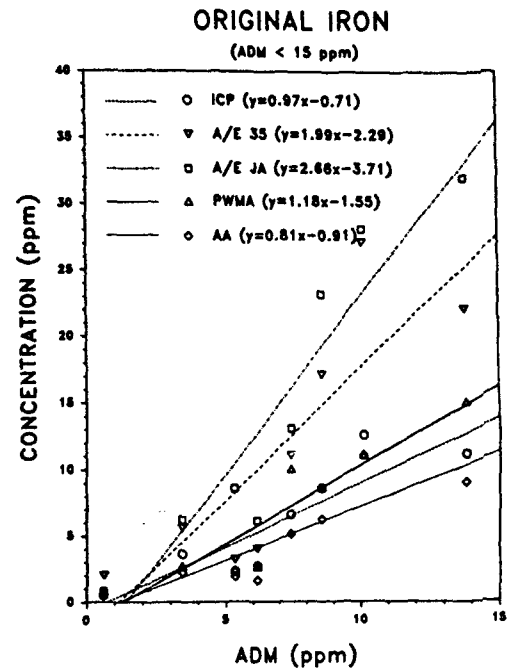


Figure 2. Data Similar to Figure 1 Except Original Iron Concentrations of < 15 PPM Were Considered

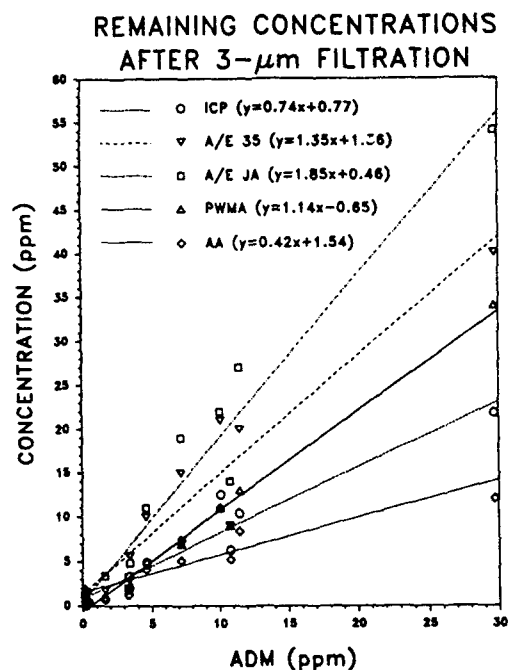


Figure 3. Iron Concentrations from Samples in Figure 1 Filtered Through Three Microns

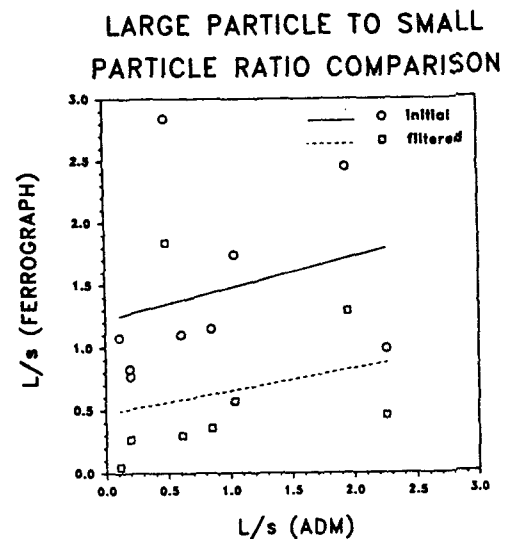


Figure 4. Large to Small Particle Size Ratios Before and After Filtration from Ferrographic Analyses Plotted Against Their Respective ADM Values