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AFWAL-TR-87-2061

CALIBRATION OF THE PORTABLE WEAR METAL ANALYZER

Captain Michael J. Quinn
Lubrication Branch
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December 1987

Final Report for Period March 1985 - December 1986

AERO PROPULSION LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
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This technical report has been reviewed and is approved for publication.

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	

4. PERFORMING ORGANIZATION REPORT NUMBER(S) AFWAL-TR-87-2051	5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION Aero Propulsion Lab, AFWAL AFSC	6b. OFFICE SYMBOL (If applicable) AFWAL/POSL	7a. NAME OF MONITORING ORGANIZATION

6c. ADDRESS (City, State, and ZIP Code) Wright-Patterson AFB OH 45433-6563	7b. ADDRESS (City, State, and ZIP Code)

8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO	WORK UNIT ACCESSION NO.
61101F/ 62203F	3048	06	26

11. TITLE (Include Security Classification)

Calibration of the Portable Wear Metal Analyzer

12. PERSONAL AUTHOR(S)
QUINN, MICHAEL JOHN

13a. TYPE OF REPORT Final	13b. TIME COVERED FROM Mar 85 TO Dec 86	14. DATE OF REPORT (Year, Month, Day) 1987 December	15. PAGE COUNT 63

16. SUPPLEMENTARY NOTATION
"This research was partially funded by the In-house Independent Research Fund."

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Turbine Engine Lubricants, Wear Metal Analysis, Atomic Absorption Spectrometer
11	08		
14	02		

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

The Portable Wear Metal Analyzer (PWMA), a graphite furnace atomic absorption (AA) spectrometer, developed under a contract for this laboratory, was evaluated using powdered metal particles suspended in oil. The PWMA is a microprocessor controlled automatic sequential multielement AA spectrometer designed to support the deployed aircraft requirement for spectrometric oil analysis. The PWMA will analyze for nine elements (Ni, Fe, Cu, Cr, Ag, Mg, Si, Ti, Al) at a rate of 4 min per sample. The graphite tube and modified sample introduction system increase the detection of particles in oil when compared to the currently used techniques of flame AA or spark atomic emission (AE) spectroscopy. The PWMA shows good-to-excellent response for particles in sizes of 0 to 5 and 5 to 10 μm and fair response to particles of 10 to 20 and 20 to 30 μm. All trends in statistical variations are easily explained by system considerations. Correction factors to the calibration curves are necessary to correlate the analytical capability of the PWMA to the performance of existing spectrometric oil analysis (SOA) instruments.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT [X] UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED
22a. NAME OF RESPONSIBLE INDIVIDUAL MICHAEL J. QUINN, CAPT, USAF	22b. TELEPHONE (Include Area Code) (513) 255-7230 22c. OFFICE SYMBOL AFWAL/POSL

DD Form 1473, JUN 86   *Previous editions are obsolete.*

FOREWORD

This work was performed during the period of March 1985 to December 1986 and funded through an Independent Laboratory In-House Research (ILIR) grant, Project Element No. 61101F/62203F, Project No. 3048, Task No. 06, Work Unit No. 26. The report was submitted in May 1987 under the principal investigator Capt Michael J. Quinn from the Lubrications Branch, Fuels and Lubrication Division of the Aero Propulsion Laboratory (APL), Air Force Wright Aeronautical Laboratories (AFWAL), Air Force Systems Command (AFSC) Wright-Patterson Air Force Base, Ohio 45433-6543.

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SECTION I

INTRODUCTION

For more than 20 yr, the United States Air Force (USAF) has used spectrometric oil analysis (SOA) of aircraft turbine engine lubricants to detect abnormal wear to remove those engines from service prior to catastrophic failure. This monitoring program allows engine overhaul "on condition" instead of "on time," thereby, reducing maintenance costs. The primary goal of the portable wear metal analyzer (PWMA) development program was to provide SOA for aircraft deployed in an austere environment, with an additional goal of improving particle detection. Although many engines have been saved by detecting abnormal wear prior to failure, we still see wear initiated failures that go undetected by SOA every year. Two instruments currently in use, the rotating disk electrode arc/spark atomic emission (AE) spectrometer and the flame atomic absorption (AA) spectrometer, require laboratory support and have very limited analytical response to particles greater than 3 μm (Reference 1, 2, and 3). The mass distribution by particle size of a "dirty" used oil is available (Reference 4). Situations have developed in which reanalysis of a sample taken prior to a failure that did not show high wear metal concentration had significant wear debris with particles too large to be seen by the current instruments (Reference 5). The factors that most affect an instrument's capability to "see" small particles are the sample introduction system, the rate and amount of energy put into the analysis zone, and the residence time of the sample in the analysis zone. The PWMA shows significant improvement in some of these factors, perhaps most notably in the sample introduction system.

Although graphite tube AA is not new to research laboratories (Reference 6), its field use in support of SOA is new. For large particles the analytical response is much superior to that of flame or spark techniques (Reference 6). Quality response has been observed for particles as large as 60 μm when placed directly in a graphite tube atomizer (Reference 7). A second significant difference to current technology is sampling undiluted turbine engine lubricant using a plastic and direct "blowout" injection into the graphite tube with argon gas. The one-time use disposable tip contains approximately 10 μl and delivers 7.4±0.2 μl. The sample is drawn into the inner bore (1.08-mm diameter) of the tip by capillary action in 3 or 4 s

and is injected into the PWMA by a puff of argon at about 4 lbf/in^2 gage pressure. The tip is pressed onto the end of a "gun" for control and consistent handling. Although the microprocessor will compute a calibration curve after standards are tested in the appropriate sequence and report the concentration of the sample tested in parts per million (p/m) concentration, the results of this study used the raw absorbance data for all tests. All tests were accomplished in a laboratory and do not represent possible environmental variation impact of field use. To avoid known variations encountered in SOA due to instrument and operator techniques, all samples were tested on the same spectrometer (although some repairs were required during the program) by the author alone. More than 2,000 samples were on the PWMA during this program.

SECTION II

EXPERIMENTAL DESCRIPTION

The PWMA is a rugged instrument, designed to provide SOA in a field environment, which a technician can operate with minimum training. The instrument consists of two containers (dimensions 29 by 48 by 49 cm) interconnected by power, data and argon lines and requires only external power to support the analysis of several hundred samples. Additional support equipment such as calibration standards, plastic sample delivery tips, special tools, and interface cords add approximately 7 kg. With a cylinder of argon to refill the internal bottle, a thousand samples can be analyzed without additional support. The "left" box (28.87 kg) contains the power supplies, polychrometer, graphite furnace, and electrometers that together make the essential functions of a graphite tube atomic absorption spectrometer. The "right" box (20.25 kg) contains the argon bottle and associated regulators, the microprocessor electronics which control the furnace and the data interpretation, and all the operator controls and data displays. The units are shock resistant and will operate in noncondensing atmospheres up to 57 C. Initial setup calibration takes about 1 h, subsequent cycles of off and on take about 15 min to recalibrate. The unit tested is a preproduction prototype. Full production rate units will meet or exceed the current specifications.

All samples were prepared in a turbine engine lubricant basestock, without additives, typical in quality to those commonly found in fully formulated oils. Approximately 94 percent by weight was trimethylolpropane triheptanoate (TMP) with most of the remaining material having C_6 alcohol substitutions on the main chain. A full analysis of the basestock is available (Reference 8). All of the powdered elements used were reagent grade, exceeding 99 percent purity in all cases. The powders were separated by size with an ultrasonic sieve separator using screens with microetched-square holes of 5, 10, 20, and 30 μm with typical dimensions +1 μm. Scanning electron micrographs of the powders used in this study are shown in Appendix A. For comparison, micrographs of real wear debris may be found in Reference 9. Samples were prepared by one-step dilutions from a stock solution of 150 to 200 p/m by weight. Each stock solution contained the powder of a single element in one size range. The final concentrations are referred to as the true concentration, whereas

the result by analysis is called the PWMA concentration. All samples were shaken by two methods prior to diluting stock solutions or analyzing the diluted samples. An ultrasonic dismembrator was modified from the normal probe configuration to be used inverted with a 50 mL titanium cup on top as the oil bath. When a 4-dr vial sample is immersed in this device, significant mixing and dispersion of agglomerated clumps is observed as the ultrasonic energy is increased to cavitation. Cavitation can be maintained inside the vial for a minute without appreciable heating. Five seconds was found to be adequate and was used as the standard procedure. Handshaking was used both before and after ultrasonic mixing. Samples were withdrawn from the vial between 5 and 10 s after handshaking. Several calibration samples were tested after each initial turn on to stabilize the operating temperature and confirm proper operation. Blank oil samples were tested alternately with each "unknown" sample to clean any residue from the graphite tube and avoid the common problem of sample "memory." One clean burn was found to be adequate to eliminate sample memory within the concentration and particle size range of these test samples. Titanium and silicon, the most refractory elements, were the most likely to exhibit memory, although all elements in the largest particle sizes and concentrations occasionally showed memory to some extent. Typical memory, when present, was approximately 2 p/m.

As a control measure, all samples were analyzed by a second method referred to as the acid dissolution method (ADM) (Reference 10). The results of this correlation test were good for those elements that dissolved completely, but 0.4-μm millipore filtration of the post-ADM treated samples showed undissolved material in several different samples. Chromium and silicon were the most difficult to dissolve. The ADM samples were analyzed on a flame AA spectrometer. All standards were in the form of organometallic concentrates diluted with clean oil so as to avoid the matrix effects occasionally found in AA spectroscopy. The results of ADM analysis are presented in Appendix B. The reported deviation of the ADM result is only a measure of the standard deviation of the result from the multiple sample tests on the flame AA and do not indicate any dilution, sampling, or preparation errors.

Standard calibration solutions for the PWMA were based on a single solution of all elements of interest (from 5,000 p/m organometallic concentrates) diluted with basestock oil to create a solution to match 100 percent of the design dynamic range of concentrations of each element. The maximum range of concentration for each element is given in Table 1.

TABLE 1. Maximum Concentration Range for the
PWMA Standard Solutions

Element	Maximum Concentration (p/m)
Ni	30
Fe	100
Cu	40
Cr	10
Ag	10
Mg	25
Si	20
Ti	20
Al	25

Additional solutions were made from this stock solution so as to make 70, 50, 40, 20 and 10 percent solutions. All unknown samples were tested in blocks of five and then the appropriate standards were tested which would bracket the analytically derived value, the PWMA concentration. This method defeats one of the strong capabilities of the PWMA, i.e., internal calibration and direct concentration readout, but this technique was used to avoid errors in that system and determine the PWMA's maximum capabilities. Additionally, drift in AA spectroscopy was avoided by having the standards tested in close conjunction with the unknowns. Standards were tested periodically by independent AE analysis and were found to be free of any change in concentration during the course of PWMA testing.

SECTION III

STATISTICAL FACTORS

The analyses of nonhomogenous systems, such as particles in oil, require special consideration be given to the statistical factors which affect the accuracy of the results. The concentration accuracy of the primary test samples was limited by the desire to use as few dilutions as possible as well as the use of 4-dr volume sample containers (holding 15 g neatly). The balance used was certified and calibrated to an accuracy of 0.1 mg. About 15 g of oil was added to approximately 2.5 mg of powder of each element in each size range so as to make the stock solutions in the range of 150 to 200 p/m. The particles in this concentration range are known to be well behaved with respect to agglomeration and other non-Newtonian fluid effects. The maximum concentration error for any stock solution was less than 5 percent.

The settling of particles in solution can be calculated from Stoke's law,

$$v = g(d^2) \ (\ \rho_p - \rho_f)/18\mu \qquad \text{Eq. 1}$$

where g is 980.7 cm/s^2, ρ_p is the particle density (ρ_p for Ag is 10.5 g/cm^3), ρ_f is the fluid density (TMP is 0.964 g/cm^3 at 250 C), μ is the fluid viscosity (TMP is 0.2410 g/cm s at 25 C), d is the particle diameter in cm, and the velocity of descent is v, in cm/s. From this relationship, a 30-μm diameter silver sphere will fall 2.0 mm in 10 s. The settling rate should, therefore, not be a factor in this experiment. Therefore, we assume that all samples have a particle size distribution identical to the stock solution.

To minimize the concentration error that would be introduced by small samples, the aliquot to be used for a dilution must have a statistically large number of particles. In mathematical terminology, one needs a population and not a sample. To develop a worst-case scenario, consider the most dense element of interest (Ag), all particles as spheres with a diameter of the largest sieve opening (30 μm), and the stock solution with the minimum concentration (150 p/m). From this stock solution a

0.1-g aliquot will have approximately 101-silver spheres, which will represent a statistical population. This 0.1-g sample, when diluted with 15 g of clean oil, will make a 1.0-p/m final solution. All final solutions used in this study were 2 p/m or greater, and should not be affected by the error of small sampling.

The number of particles in the injected sample does have a statistical impact on this system. A 7.4-μl sample of 1-p/m solution would contain 10-Ag spheres of 5-m diameter. As the particle size increases from this point, the small sample error will become a more significant factor. For example, a single 10-μm silver sphere would make a 0.8-p/m sample, while a 20-μm particle would make a 6.3-p/m sample. This small sample factor can be seen in the calibration plots by the size of the standard deviation for increasing particle sizes. Although lesser density, greater concentration, and less adverse particle morphology will decrease the small sample errors, the injected sample volume set the limit of investigation to the 20- to 30-μm particles.

SECTION IV

DISCUSSION OF RESULTS

All data points are the result of at least five independent trials and the standard deviation reported is calculated by Equation 2.

$$\text{Std Dev} = [\left\{ \Sigma x^2 - (\Sigma x)^2/N \right\} / (N-1)]^{1/2} \qquad \text{Eq. 2}$$

The calibration curves in Figures 1, 2, and 3 show the indicated absorbance of the PWMA (not scaled in the range of zero to one) against the concentration of the calibration standards made from organometallic standards. Although the ideal Beer's law straight line does not fit the data well, in all but two cases a simple curve fit with an order not exceeding three does fit. Magnesium shows significant saturation effects above 10 p/m, with total saturation at about 15 p/m. Silicon shows both high-concentration saturation, although not extreme, as well as poor low concentration sensitivity. This combination creates a point of inflection in the working curve, a very nonideal condition. More than 99 percent of all turbine engine oil field samples will have wear metal concentrations which will be on the linear range of each curve. (See Reference 5 for typical concentrations of hundreds of field samples.) The coefficients for the equation $y = a + bx + cx^2 + dx^3$ for each element are given in Table 2.

All of these curves (except silicon) are well behaved, i.e., all coefficients of a concentration decrease by more than an order of magnitude for each increase in power. Since samples were tested in series with standards having a concentration close to the sample which would bracket the analytically derived absorbance value, point to point straight line linear regression was used to determine the PWMA concentration from the absorbance data. The following use of terms such as excellent, good, and fair are subjective evaluations of the calibration data in three major respects: (1) repeatability of the PWMA from sample to sample, (2) linearity of the mean value over the concentration range, and (3) response to the element which is large enough to use small correction factors to replicate the ideal response line. The mean concentration and the associated standard deviation of all of the samples are the subject of Figures 4 through 12.
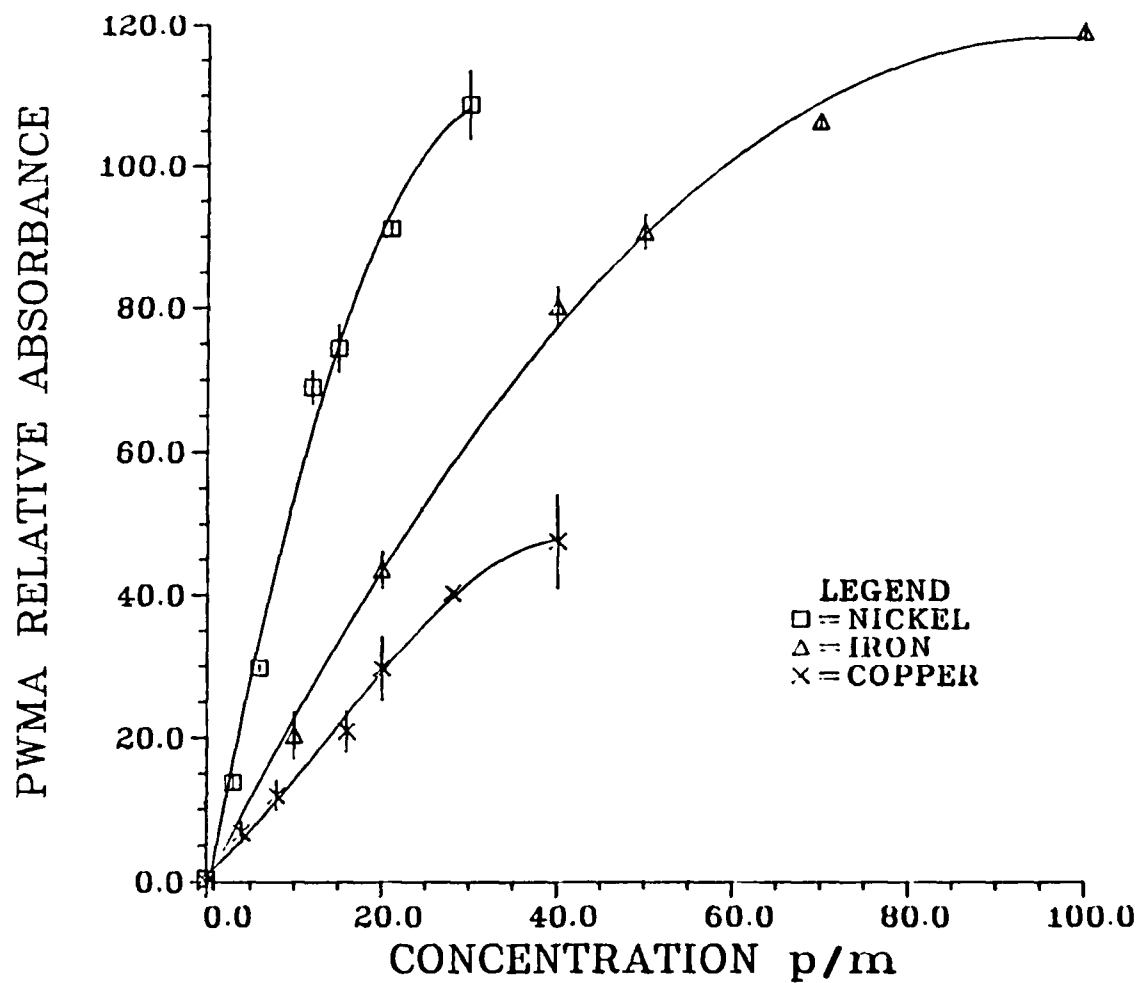
Figure 1. PWMA standard working curves for nickel, iron, and copper.
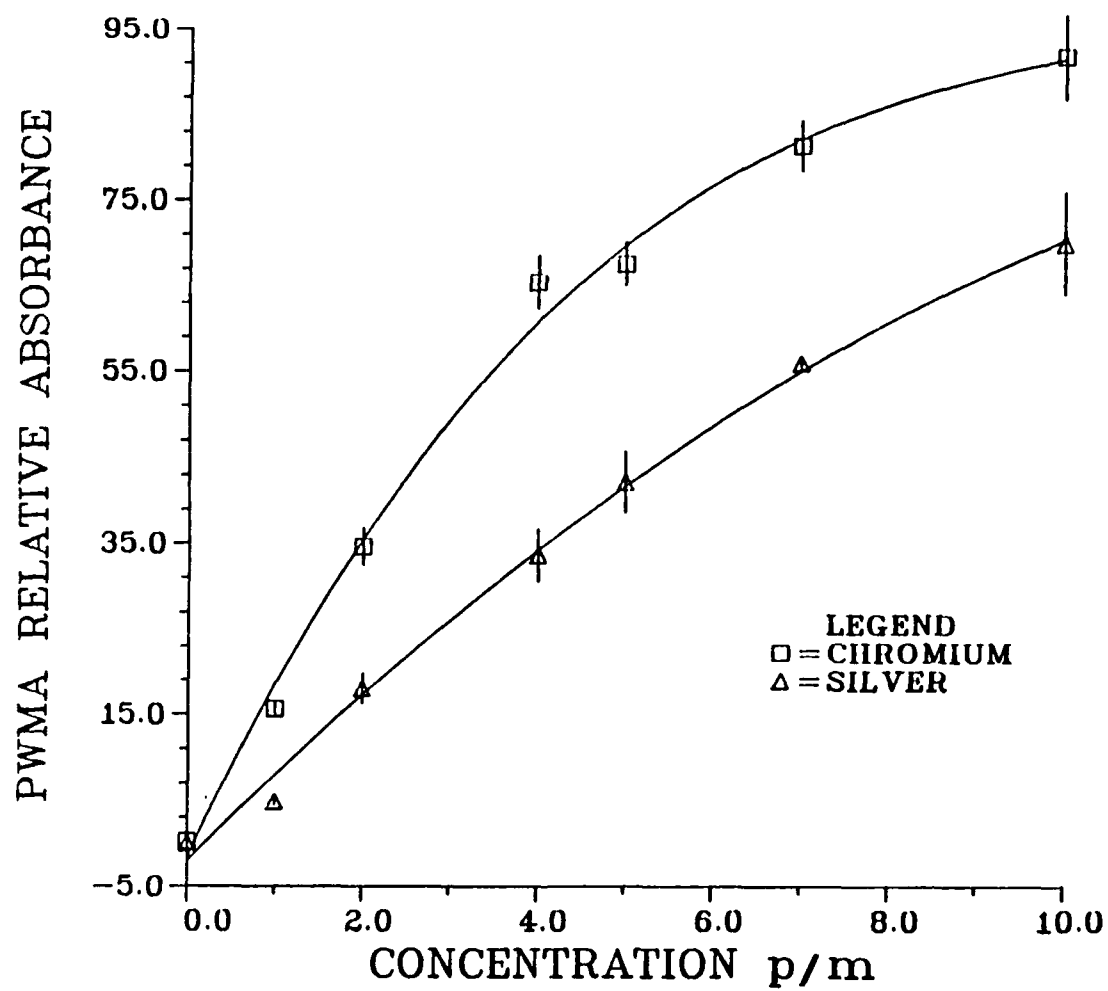
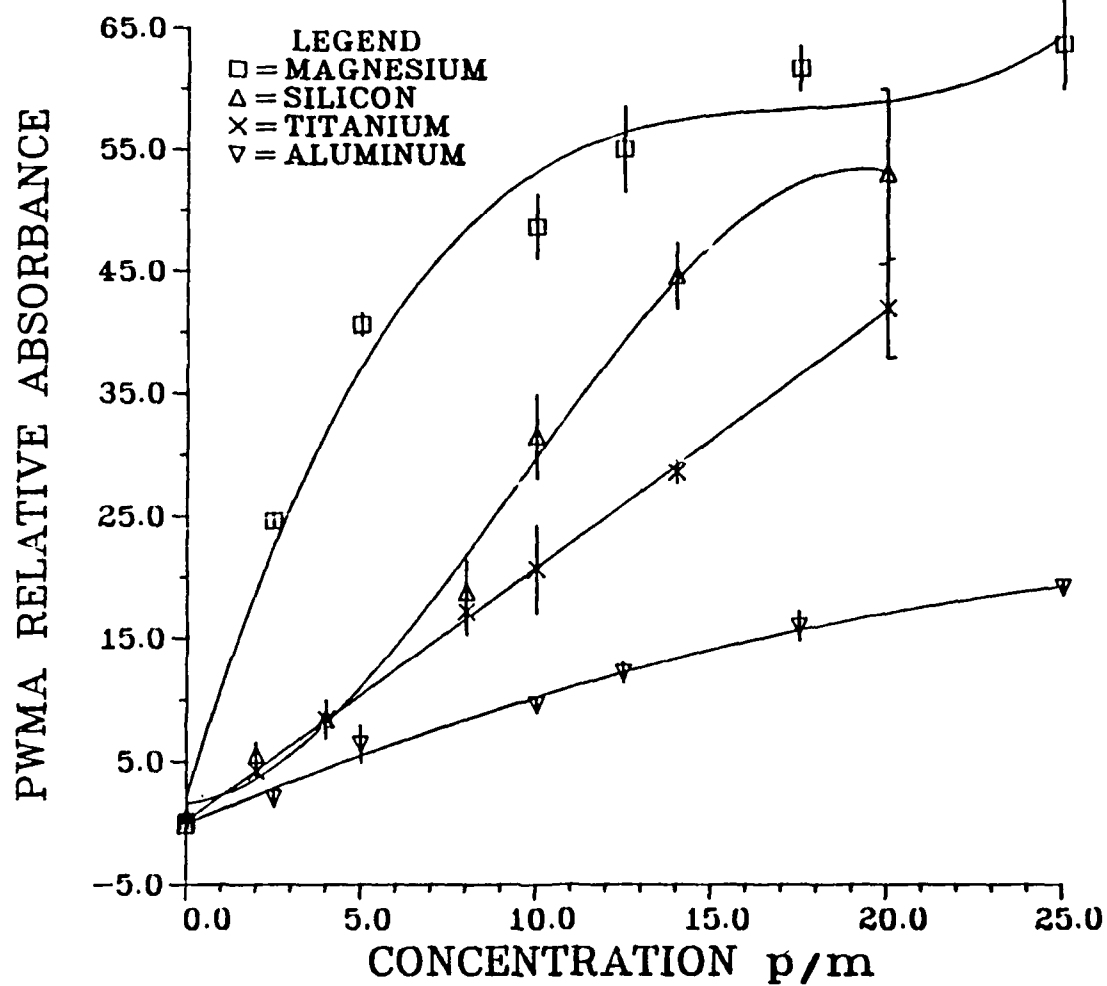Figure 2.   PWMA standard working curves for chromium and silver.

Figure 3. PWMA standard working curves for magnesium, silicon, titanium and aluminum.

TABLE 2.   Coefficients for Least Squares
Curve Fit of Working Curves

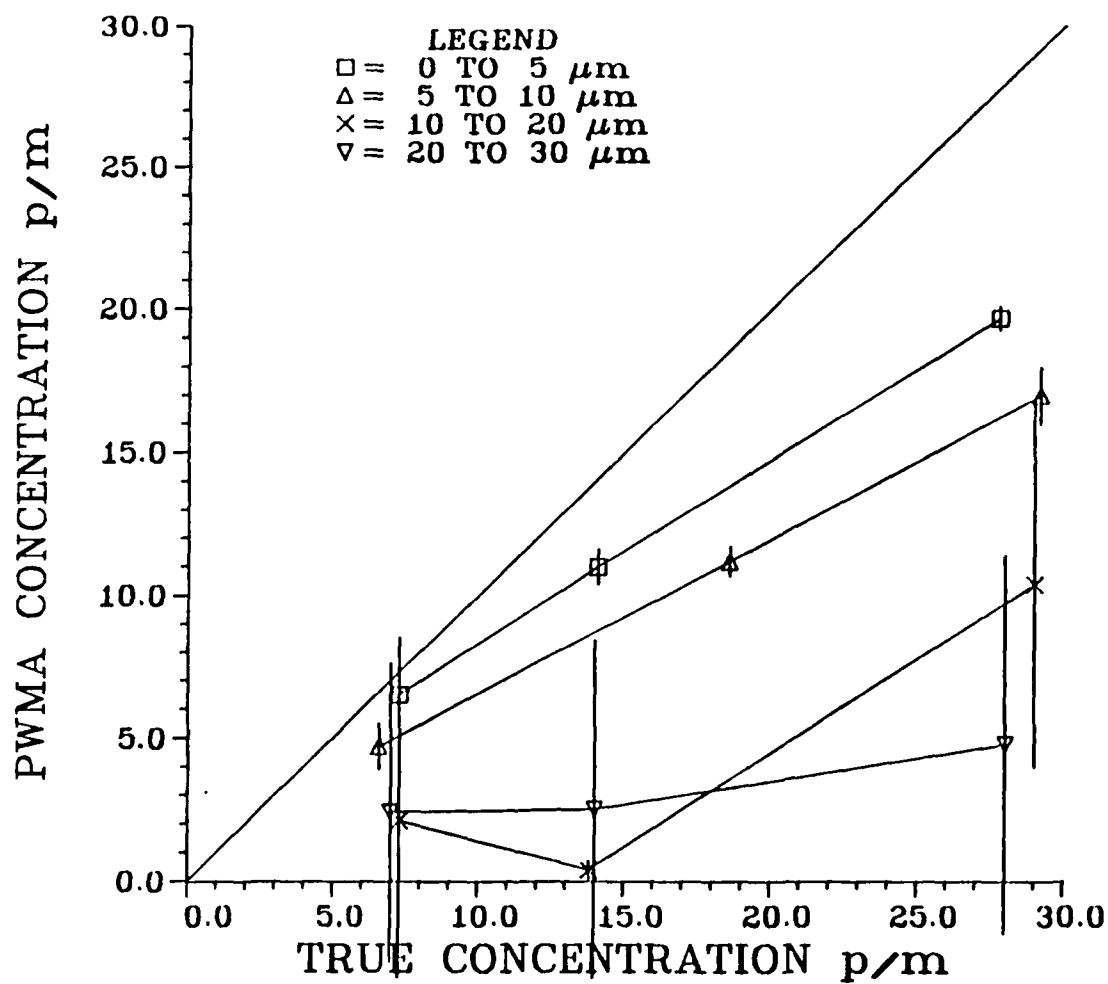| Element	a	b	c	d
Ni	-2.435243	6.610648	-0.09725336	
Fe	-0.539788	2.453616	-0.01266514	
Cu	0.876107	1.084035	-0.03097598	-0.000719155
Cr	-1.655033	21.92030	-1.792620	0.05324952
Ag	-2.071793	10.27792	-0.3023439	
Mg	2.085295	9.422857	-0.5350790	0.01030700
Si	1.547396	0.2875532	0.3909312	-0.01381702
Ti	0.1415940	2.040767	0.00210817	
Al	-0.1754047	1.208438	-0.01721758	

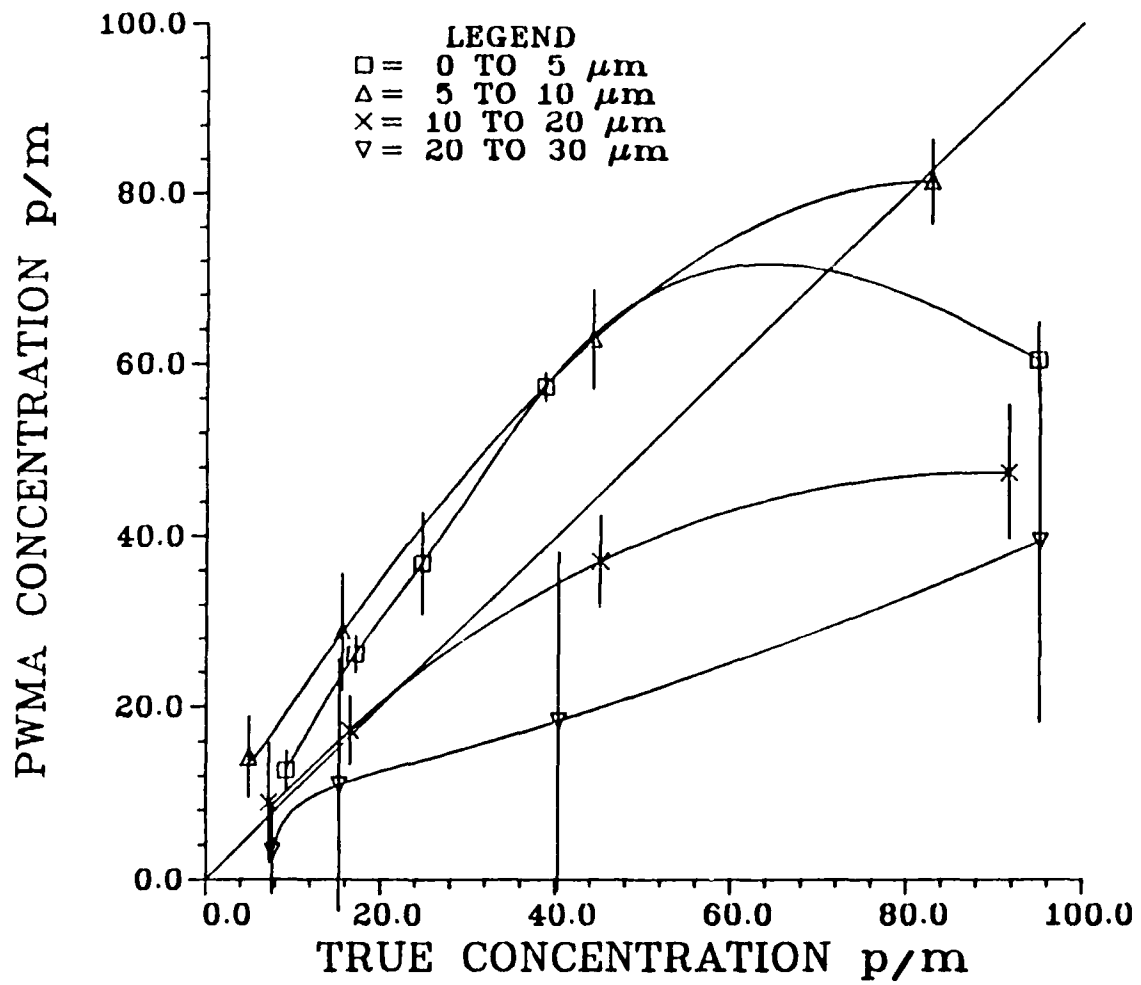Figure 4.   PWMA calibration - nickel particle solutions.

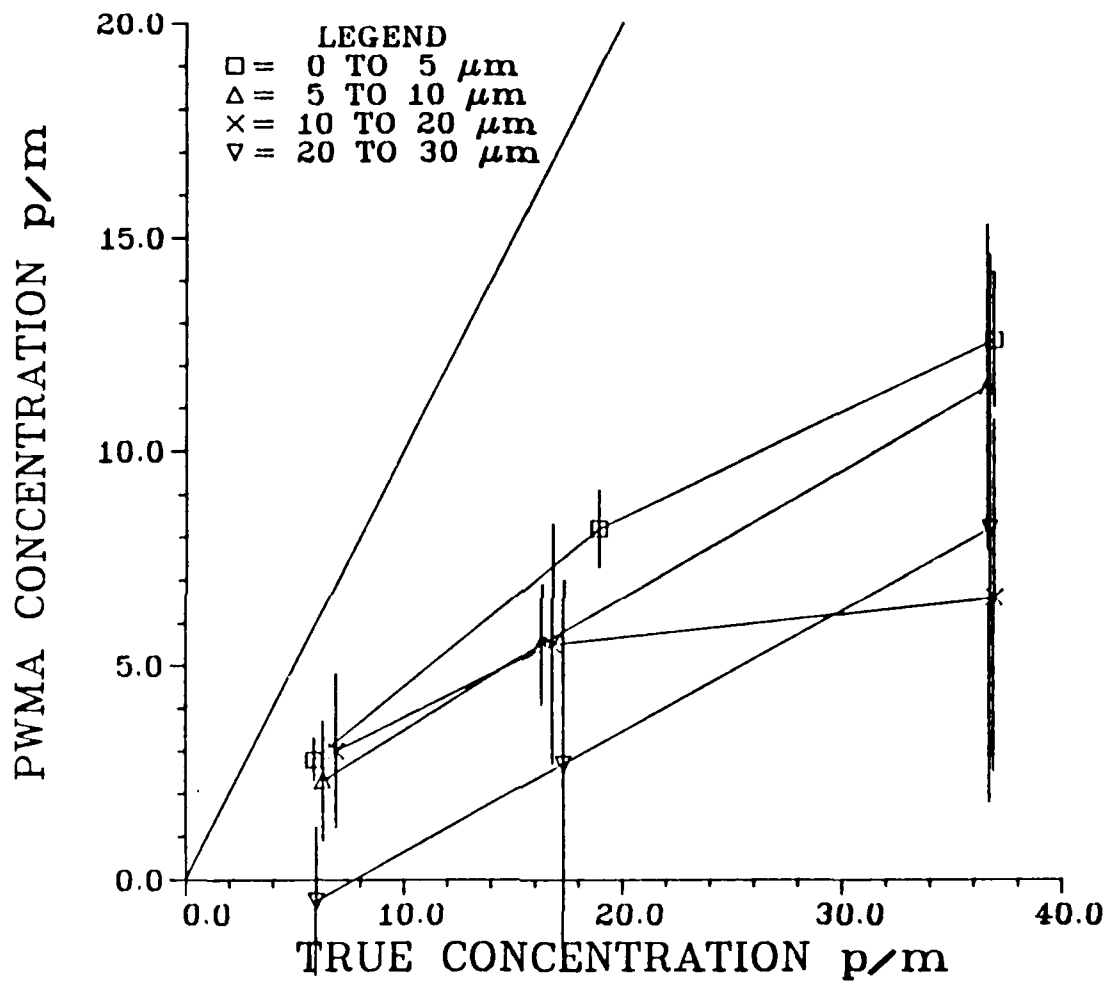Figure 5. PWMA calibration - iron particle solutions.

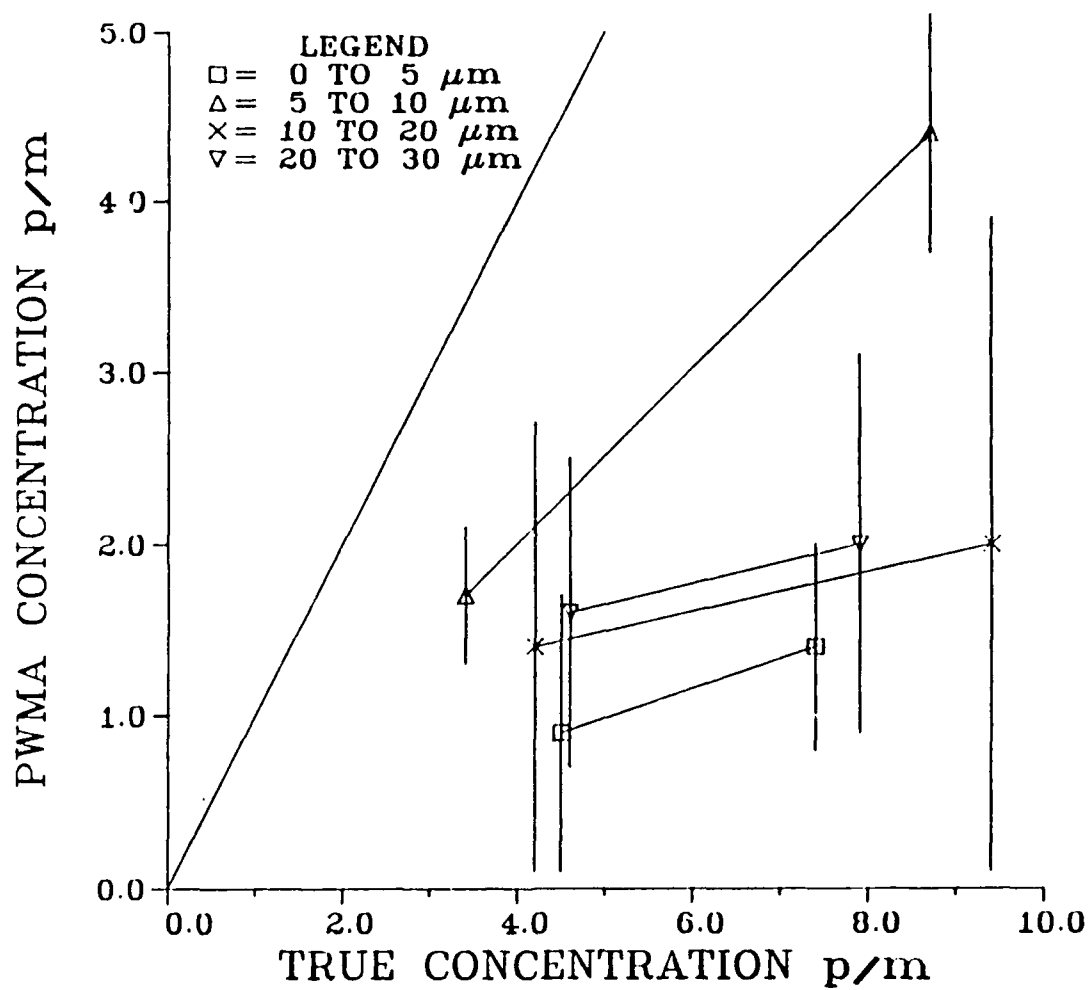Figure 6.   PWMA calibration - copper particle solutions.

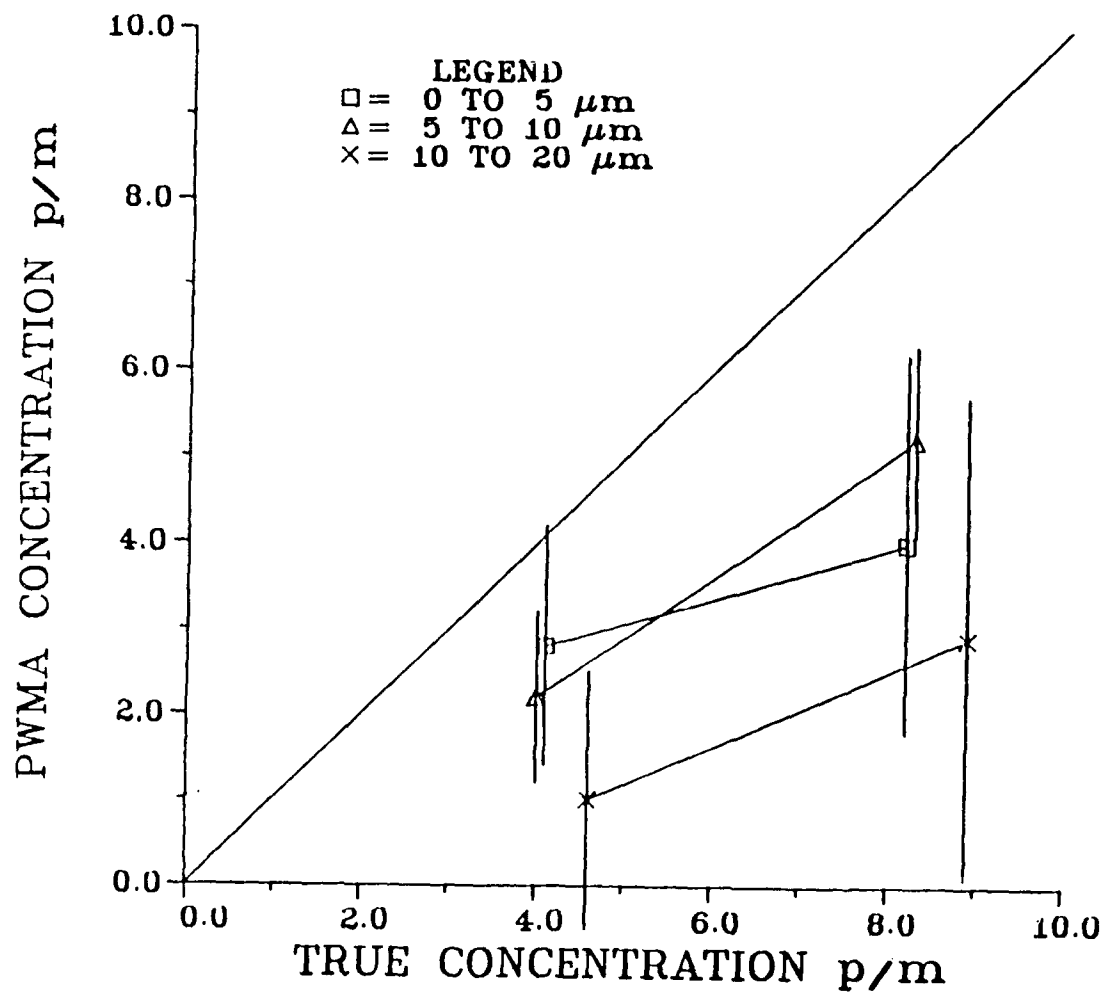Figure 7. <u>PWMA calibration - chromium particle solutions.</u>

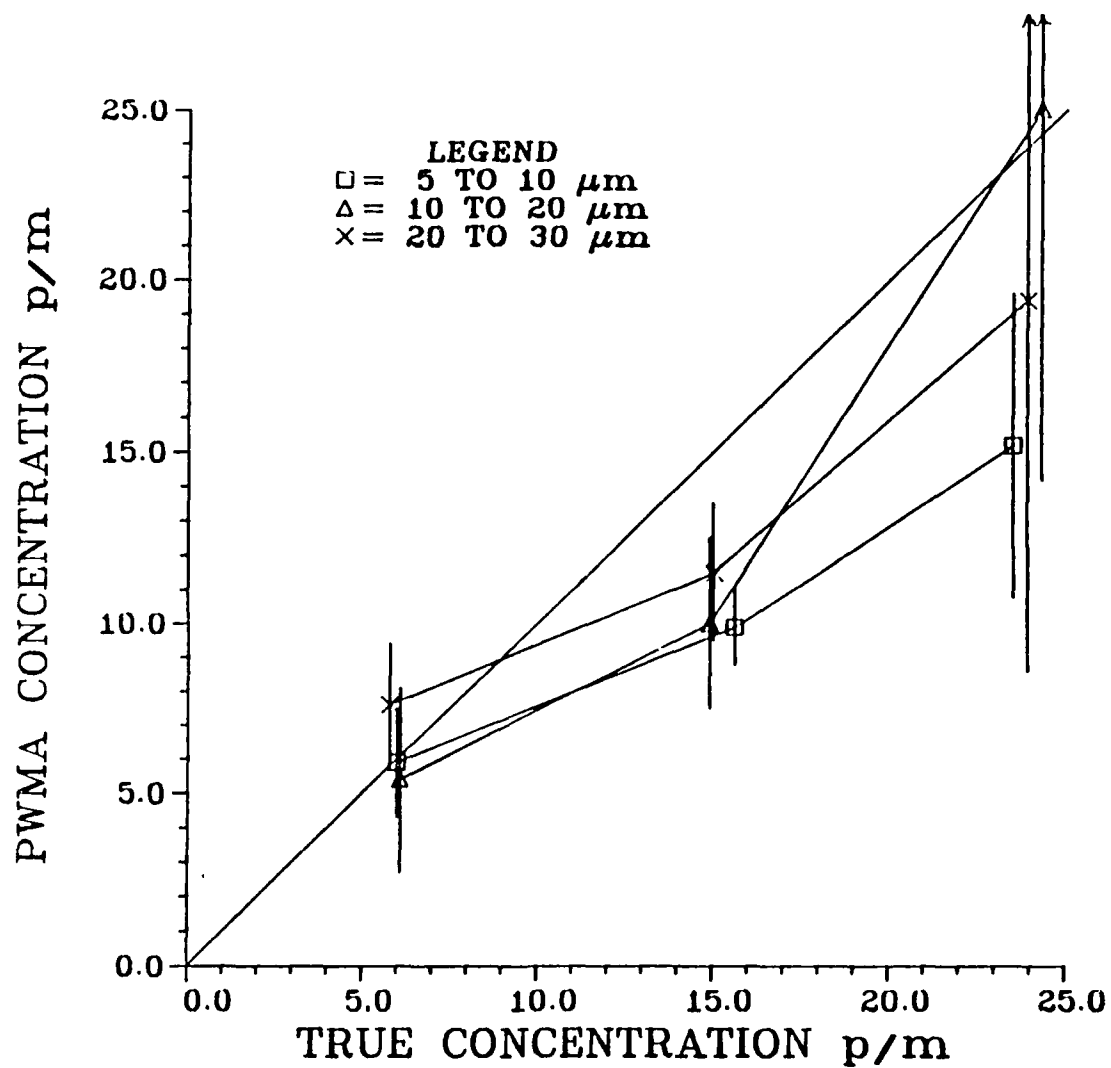Figure 8. PWMA calibration - silver particle solutions.

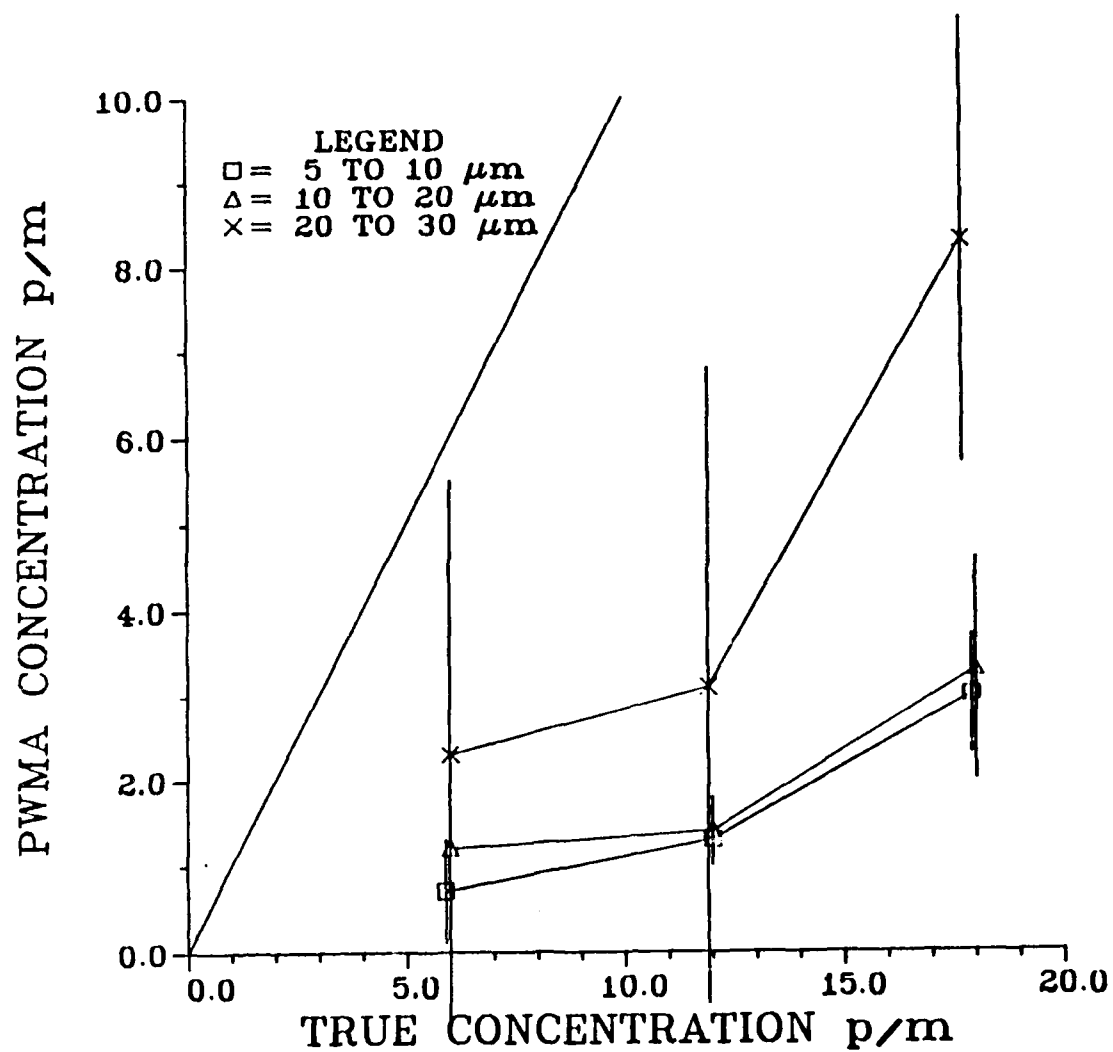Figure 9.   PWMA calibration - magnesium particle solutions.

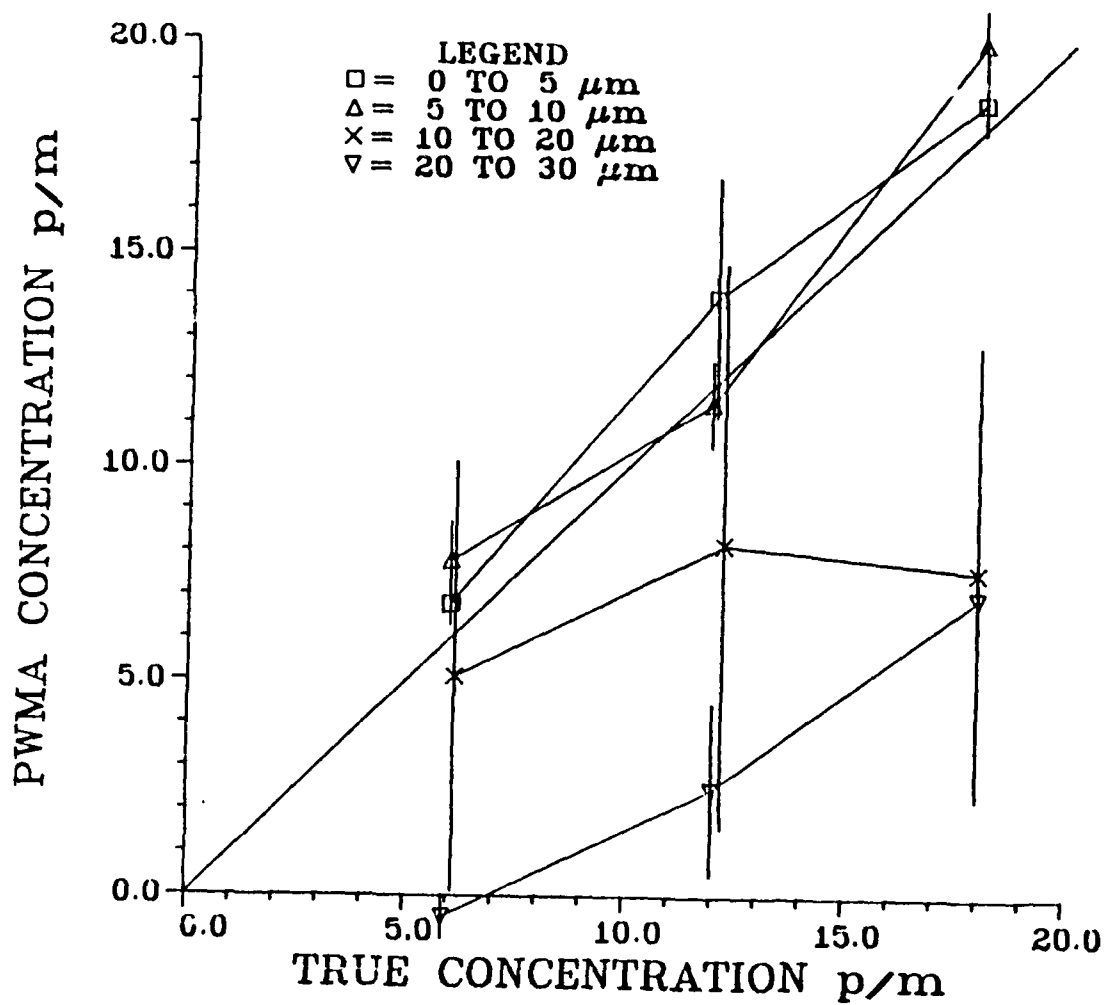Figure 10. PWMA calibration - silicon particle solutions.

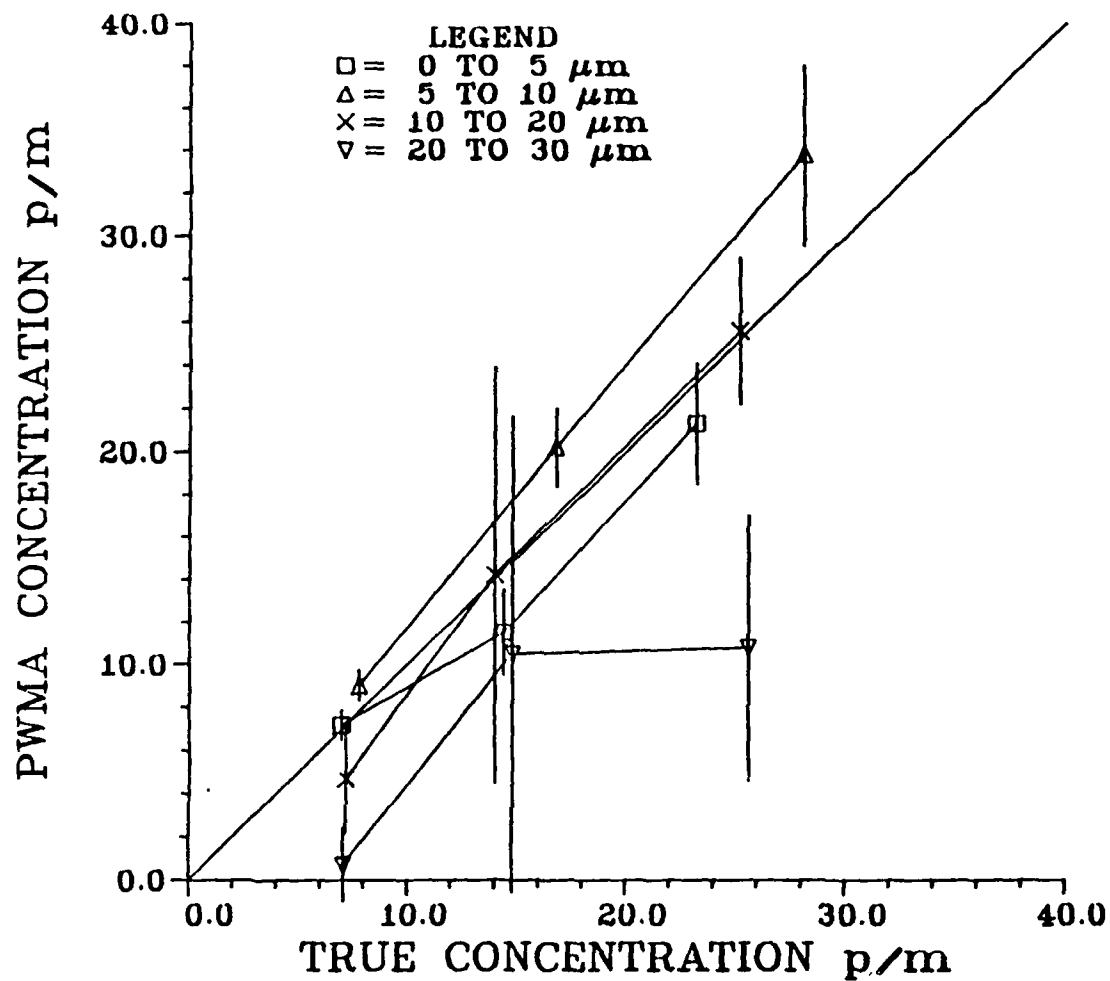Figure 11. PWMA calibration - titanium particle solutions.

Figure 12. PWMA calibration - aluminum particle solutions.

Figure 4 shows the calibration of the PWMA against solutions of nickel metal powders. As in all the following figures, the straight line through the origin represents an ideal response. The four calibration curves connect the mean values of metal powder solutions of the same size (all derived from the same stock solution by different dilutions) at concentrations across the PWMA designed concentration range. The vertical bars represent the n-1 weighted standard deviation. The lines trend in the direction which indicates decreasing response to larger particles, and the standards deviations trend toward greater variation with larger particles. The former effect can be explained by a description of the analysis cycle. During each analysis, several temperature plateaus were reached very quickly and held for several seconds. During the atomization of the sample, one of the two multielement hollow cathode lamps illuminate the appropriate element for a few milliseconds; all of this is timed to coincide with the sequential vaporization of the desired element. In the design phase, the physical size limitation of the polychrometer forced the selection of the wavelengths viewed, this coupled with the range of concentrations required, forced certain tradeoffs. One primary tradeoff was to view the element for only a portion of its atomization period so as to avoid detector saturation and obtain the best signal-to-noise ratio. Herein lies the explanation for the observed results: If the evolution of material represented by a Gaussian curve (time the abscissa, mass rate of vaporization the ordinate) and the machine is set to "look" at only a fraction of that curve (window), and the curve shifts to the right (i.e., later in time); then the window located originally to the left of the maximum will show a lesser value (see Figure 13). The PWMA was calibrated initially with soluable organometallic standards. Since their kinetics of atomization are faster than those of particles (and the larger the particle, the slower its atomization), the effective curve will be to the right of the standard curve. The second effect previously mentioned, that of the standard deviation growth with increasing particle size, is related to the small sample error factor of the injected sample.

One of the most significant aspects of the PWMA is that much larger particles are "seen" now than ever before; particles up to 10 μm exhibit excellent analytical results, while particles as large as 30 μm show at least some response. To provide the best correction factor will require a different factor for each engine. For field use a complicated formula or plot to reference is not reasonable. Therefore, the maximum acceptable concentration should set the factor chosen. If, for example,
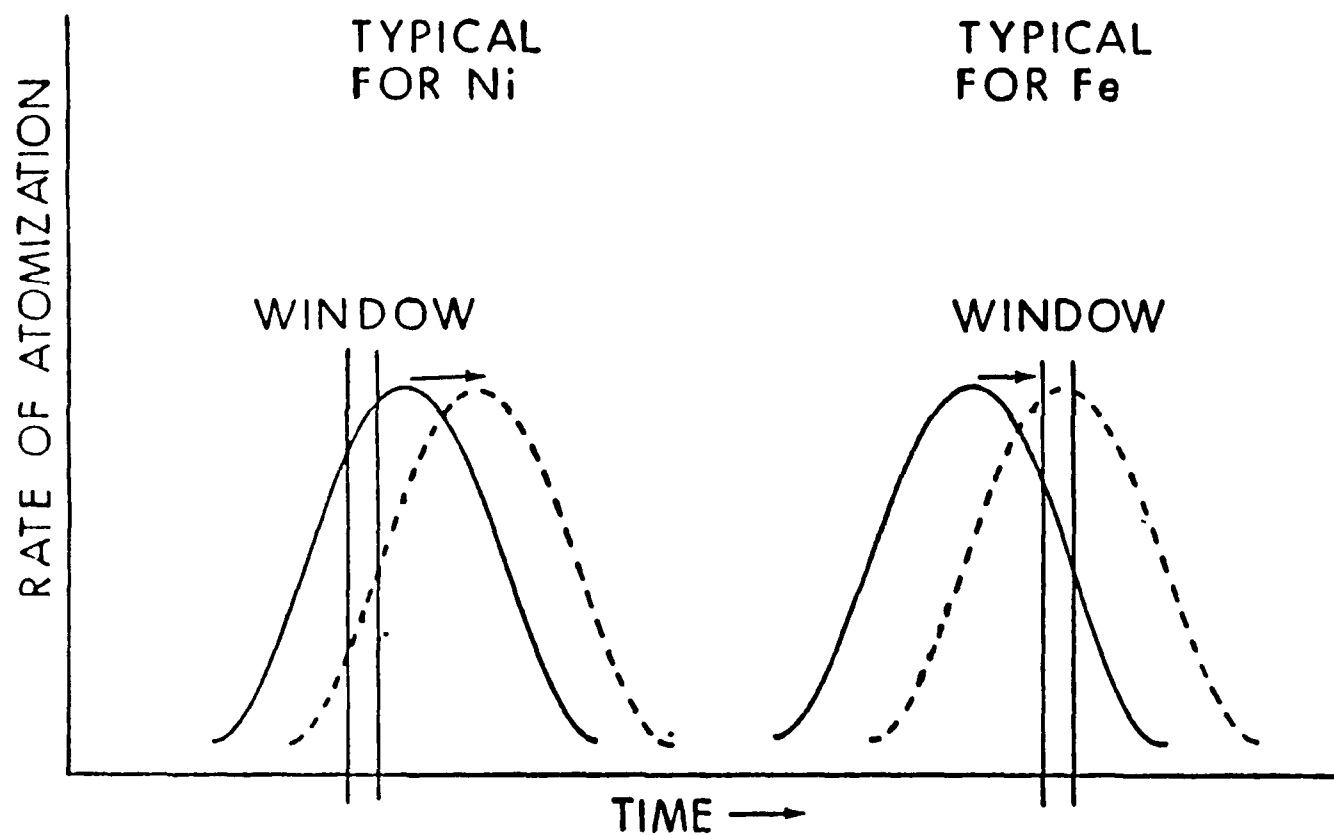
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Figure 13. Comparison of vaporization of solutions containing organometallic standards (——) versus particles (----).

the maximum acceptable nickel concentration was 10 p/m, the correction factor we could apply to all PWMA nickel results might be 1.33, i.e., if the PWMA result is 6 p/m, the true value recorded is 8 p/m. We can reach this same result by adjusting the critical concentration for PWMA analysis to 7.5 p/m. This practical solution was based on an average of the 0- to 5- and 5- to 10- μm particle curves.

Figure 5 shows the calibration curve for iron particle solutions. This element exhibits excellent and analytical results in the most important concentration range, for particles less than 20 μm. Greater than ideal response can be explained by the kinetics model presented above. In this case, we chose the window on the leading slope of the atomization curve so that the slower evolution of vapor from the increasing particle sizes could cause the viewed portion to pass through the peak and down the trailing edge. The vapor reached the peak with the 5- to 10- μm particles. The curves, drawn with a smooth splined curve fit, clearly show the high concentration roll-off response. This response may be a saturation-related phenomenon. A good correction factor valid up to 40 p/m is 0.66. This weights the response of the 0- to 5- μm sample most, and averages the low-concentration response of the 5- to 10- and 10- to 20- μm particle solutions. Again, note that no one single correction factor will best fit all needs.

Copper particles, Figure 6, show an overall decreased sensitivity compared to the organometallic standards and are rated as good with respect to their analytical performance. The ordinate is half the full-scale range to better show the calibration data. A factor of 2.66 will correct samples of 20 p/m with particles of 0 to 20 μm. Although the correction factor is large, the response to particles up to 20 μm shows a strong clustering nature. Note that the expanded verticle scale exaggerates the spread of the data and lengthens the standard deviation bars. The high concentration roll-off is apparent, whereas the calibration curves' slopes are much smaller than the ideal response line's slope. At the maximum concentration of 40 p/m, the response would be about one-fourth the value obtained from organometallic standards.

Chromium, Figure 7, is rated overall as fair. The anomalous result for the 0- to 5- μm particles is caused by large particle contamination in the sample. The

material tends to agglomerate when the size reaches about 5 μm, and this sample was not processed through the sieve stack. Size specifications of samples by vendors is usually suspect. The low absolute analytical resolution of samples adds to the problem of large standard deviations. One p/m is a minimum threshold of sensitivity for the PWMA and the standard deviation bars show wide variance in a relative sense. A correction factor for a 5-p/m target might be 3.33, with much depending on the actual size distribution of the wear debris of concern.

Silver, Figure 8, shows good response to particle solutions with sizes up to 10 μm, but larger particles show much scatter and low resolution. Due to the small sample error factor, 20- to 30-μm particles were not tested. The midrange correction factor, 5 p/m true concentration, would be 1.66. The relatively large standard deviation bars are the result of analysis at the concentration detection threshold as well as the small sample factor.

Magnesium, Figure 9, shows excellent response to all particles up to 15-p/m concentration. The average correction factor for this region would be 1.25. The results at high concentration are suspect. From the working curve, saturation effects predominate and small variations in absorbance cause large changes in calculated concentration. The standard deviation bars (capped at the top for drawing purposes but equal above and below the mean) are the largest of all the samples. Particles in the 0- to 5-μm range were not available, due primarily to their pyrophoric nature. The standard deviation bars on the largest particles are no larger than those of the small particles. The low density of magnesium appears to decrease/eliminate the small sample statistical errors.

Silicon, Figure 10, shows fair response and represents the worst case for the PWMA. Although, we can find probably no native silicon in a lubricant, its boiling point (and melting point and associated vapor pressure) is close to the predominant source of contamination, SiO_2. Secondary sources of contamination are as SiC from bearing surfaces and silicones. Since large variations from the ideal response, i.e., organometallic solution, occur the correction factor is less reliable than the other elements. A correction factor of 5.0 is reasonable. Due to agglomeration during separation, we did not test any 0- to 5-μm samples.

Titanium, Figure 11, shows excellent response over the entire concentration range for particles up to 10 μm. The correction factor should be 0.9. From this result, and the very linear working curve, titanium's concentration range could be extended with little chance of significant adverse effects.

Aluminum, Figure 12, like titanium, shows excellent response over the entire concentration range for particles up to 20 μm. The response shows the effect of the analysis "window" to the right of the peak, providing maximum sensitivity to 5- to 10-μm particles. No correction factor should be used. And like magnesium, small sample errors were noticeably reduced.

SECTION V

CONCLUSIONS

The PWMA is capable of good-to-excellent analysis of turbine engine oils containing particles of those elements studied in the size range of 0 to 10 μm, with the exception of silicon. Statistically significant response is possible on solutions with particles up to 30 μm. Seven of the nine elements show significant deviation from the ideal response of organometallic standards, but in all cases correction factors can be calculated which will correct the results to an acceptable level for the spectrometric oil analysis program. The large standard deviations associated with large particle solutions will likely cause more random high readings in real samples than with current, limited sensitivity, instruments. As with other avionics support equipment with microprocessor-controlled functions, configuration control will be of considerable importance. To maintain field operations, and recognizing the inherent problems of implementing cross sample controls, units must have reliable unit-to-unit repeatability. Unit-to-unit repeatability is even more important than absolute response accuracy which can be fixed with correction factors. If the time windows used for looking at the atomized sample are changed in any manner, ensure new correction factors are obtained. Make sure the production units are tested in this manner to establish their baseline performance. I recommend magnesium's concentration range be reduced or some change made to improve the working curve. Titanium and aluminum may offer potential for concentration range expansion. Silicon's response is useable, but significant improvement is required to match the performance of the other elements.

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A P P E N D I X   A

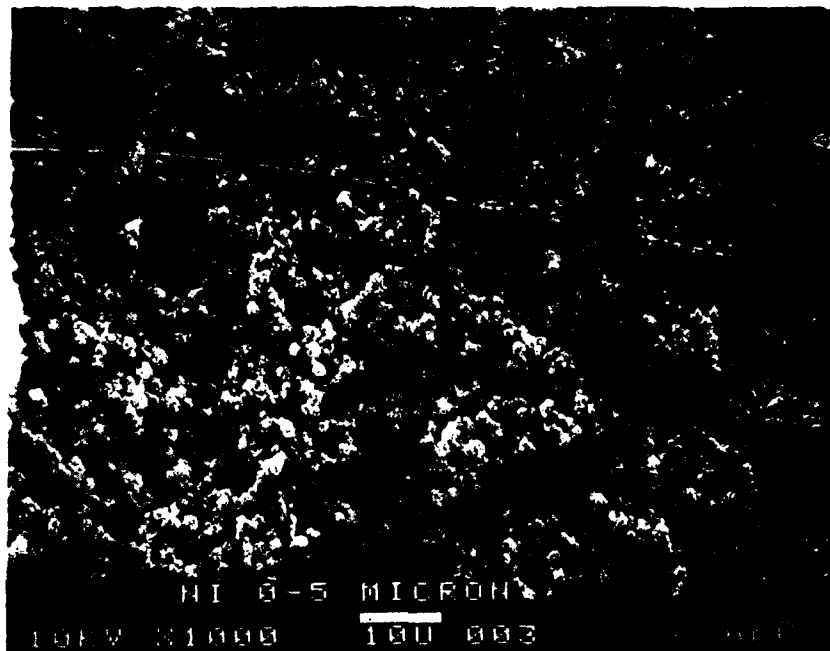ELECTRON MICROSCOPY OF PARTICLES

Figure A-1.   Nickel particles, 0 to 5 µm
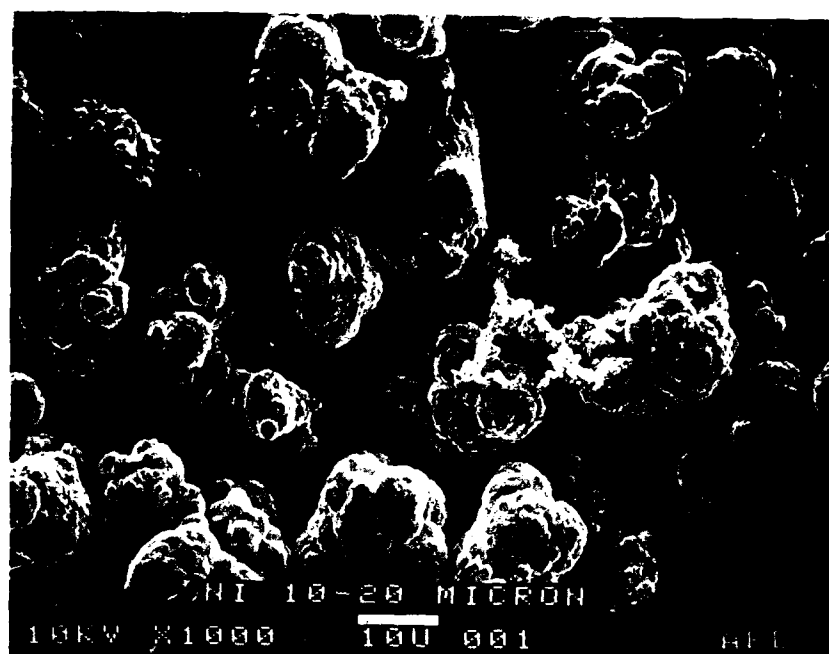

Figure A-2.   Nickel particles, 5 to 10 µm
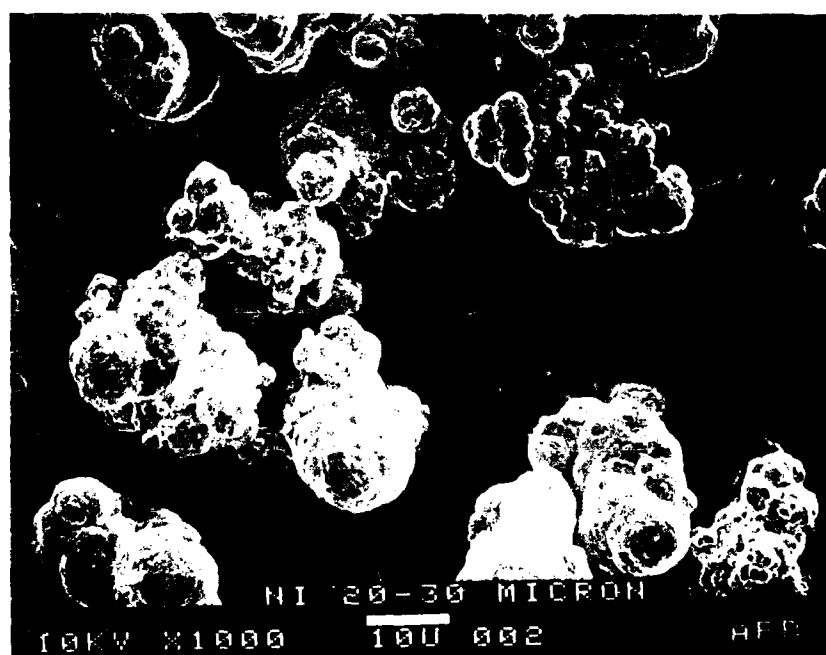
Figure A-3. Nickel particles, 10 to 20 μm

Figure A-4. Nickel particles, 20 to 30 μm

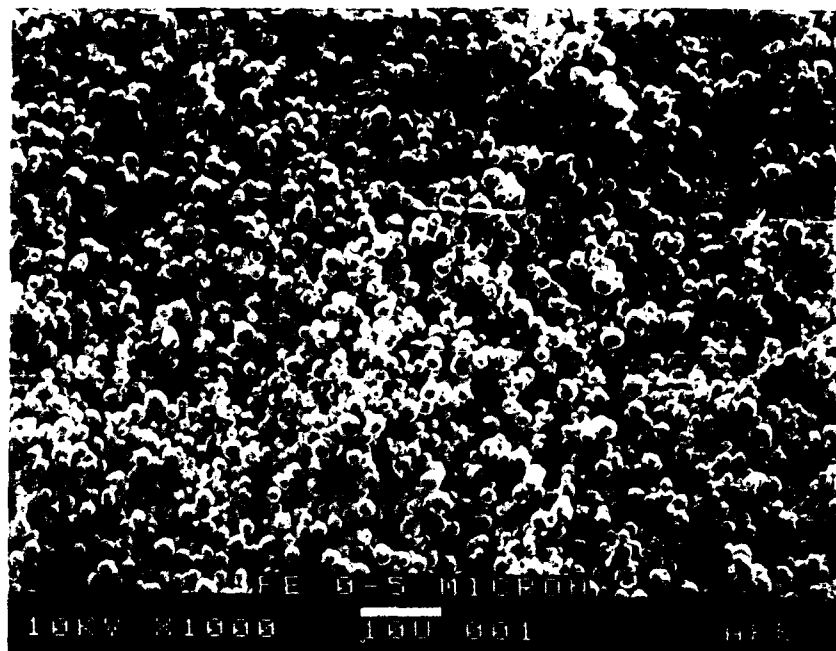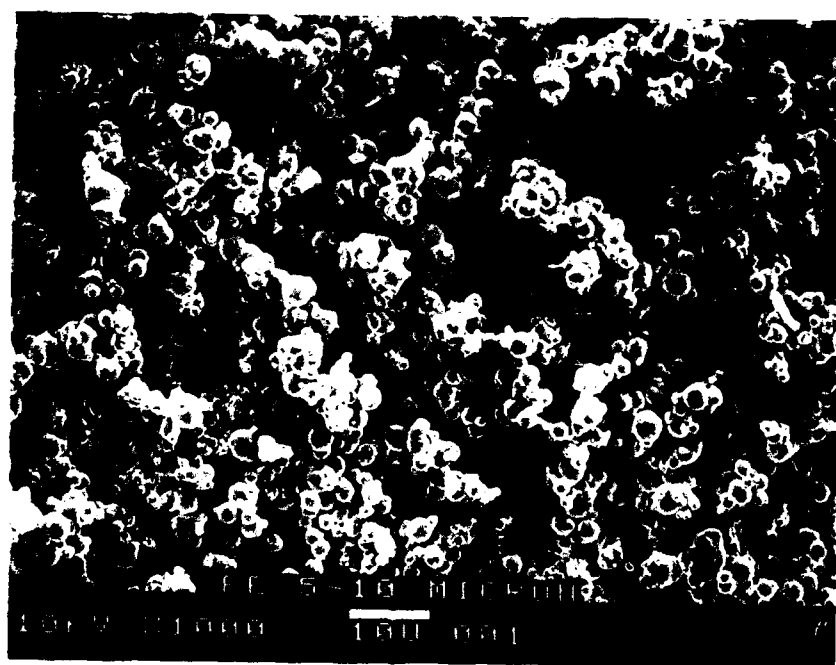Figure A-5. Iron particles, 0 to 5 µm

Figure A-6. Iron particles, 5 to 10 µm
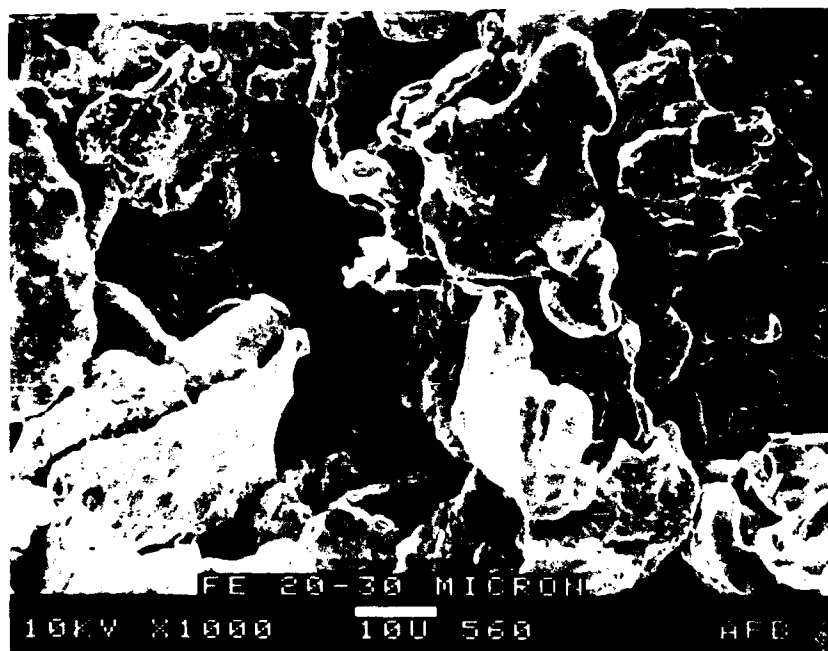
Figure A-7.   Iron particles, 10 to 20 μm
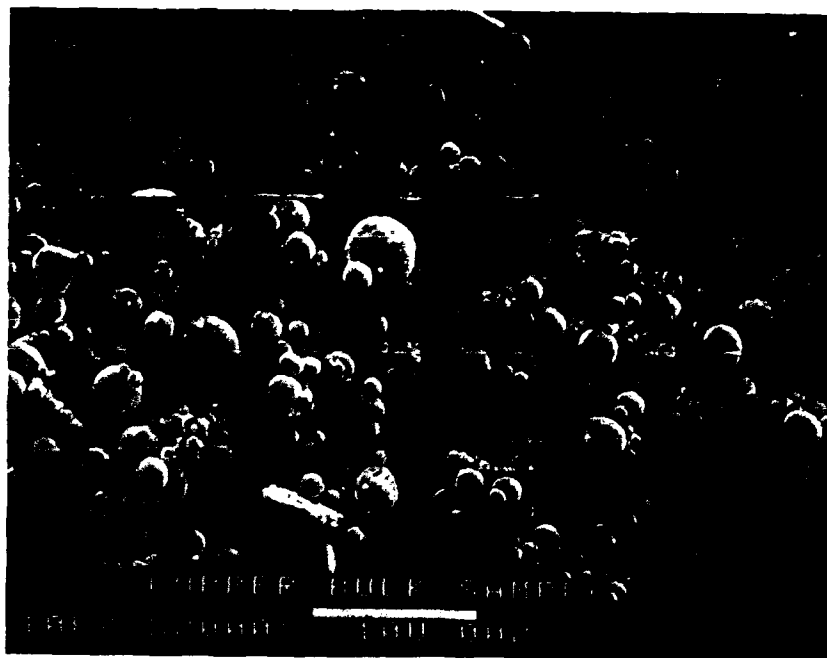

Figure A-8.   Iron particles, 20 to 30 μm

Figure A-9. Copper particles, 0 to 5 μm

Figure A-10. Copper particles, 5 to 10 μm
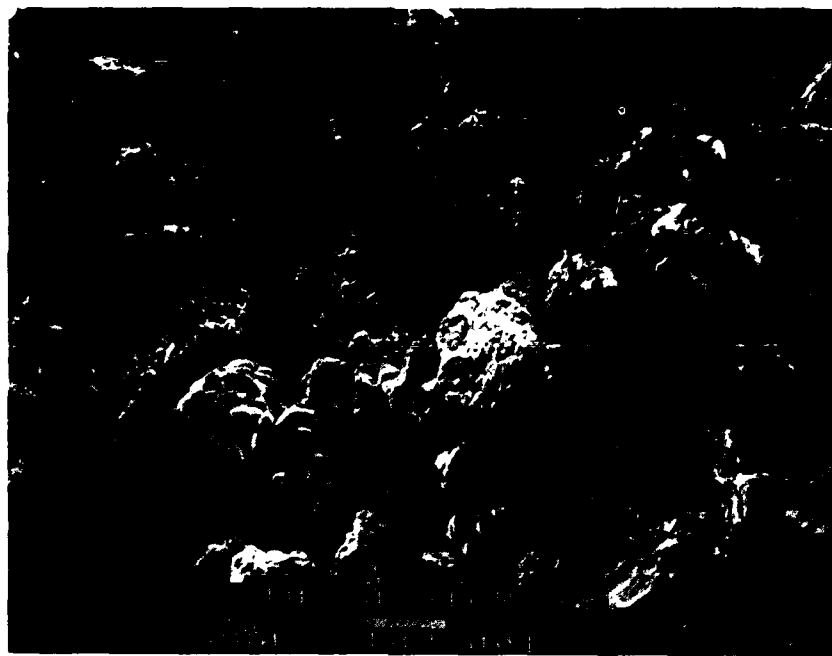
Figure A-11. Copper particles, 10 to 20 µm

Figure A-12. Copper particles, 20 to 30 µm
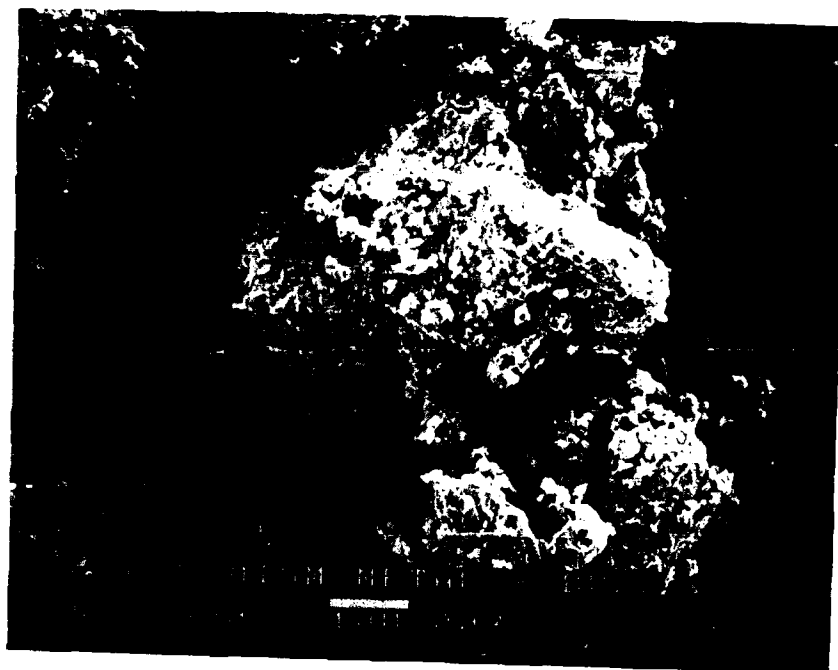
Figure A-13.   Chromium particles, 0 to 5 μm

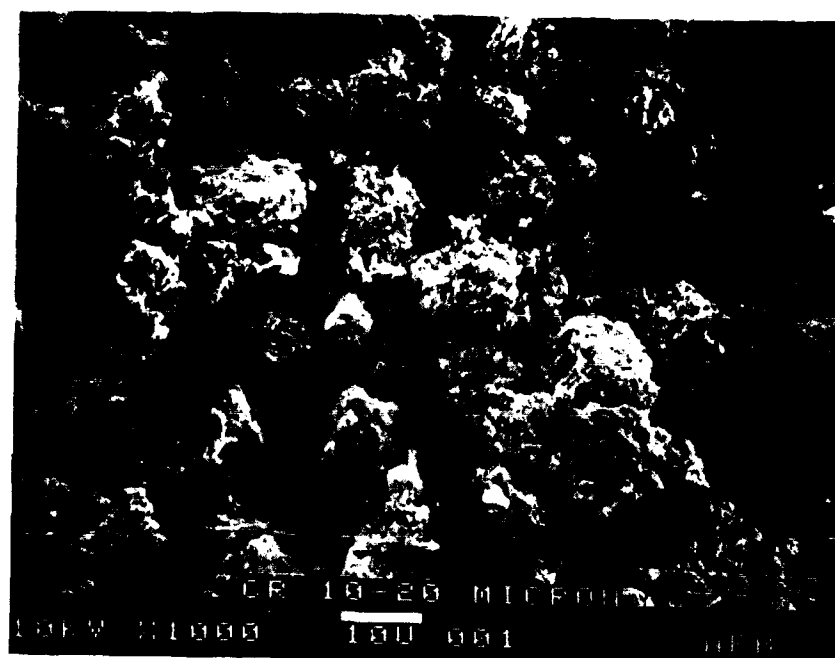
Figure A-14.   Chromium particles, 5 to 10 μm

Figure A-15. Chromium particles, 10 to 20 μm
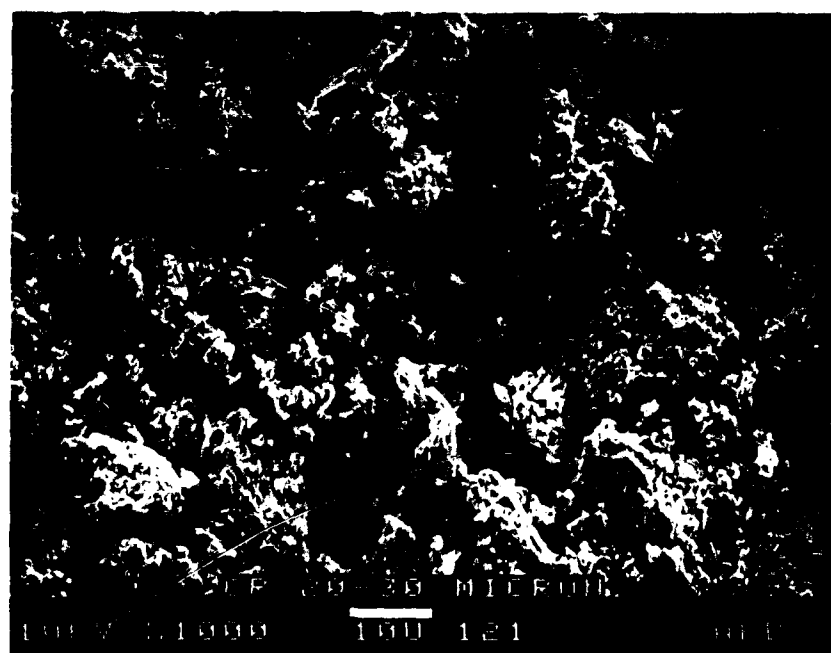
Figure A-16. Chromium particles, 20 to 30 μm

Figure A-17.   Silver particles, 0 to 5 μm
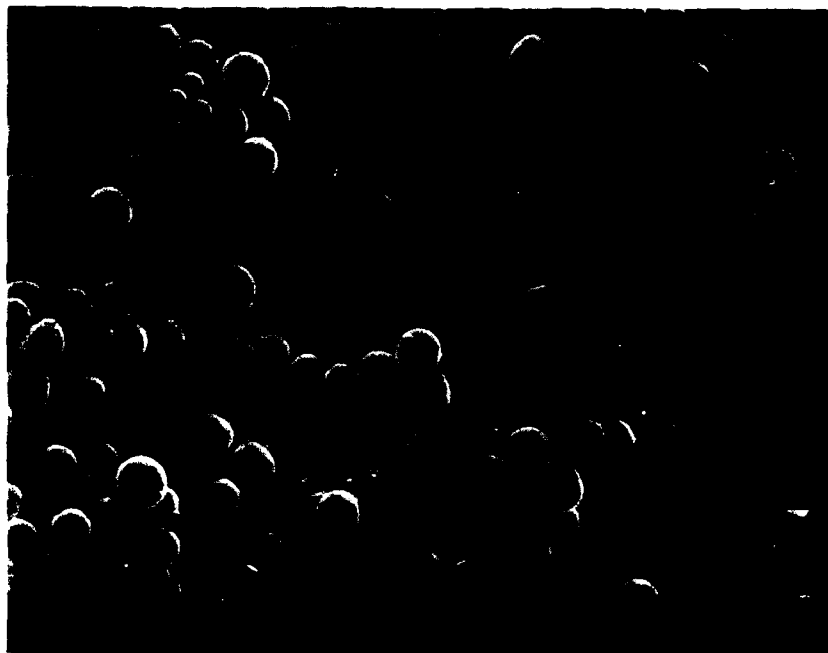
Figure A-18.   Silver particles, 5 to 10 μm
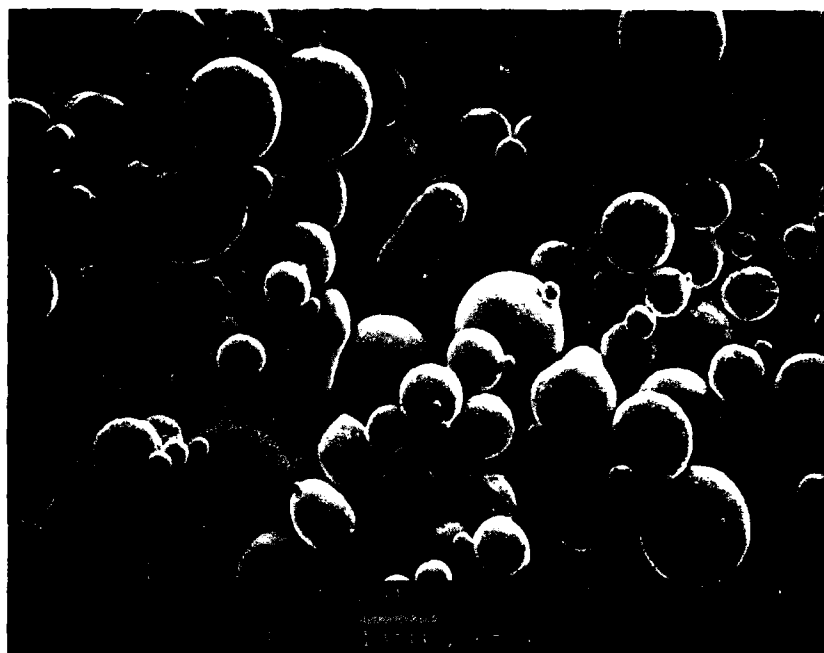
Figure A-19.   Silver particles, 10 to 20 μm
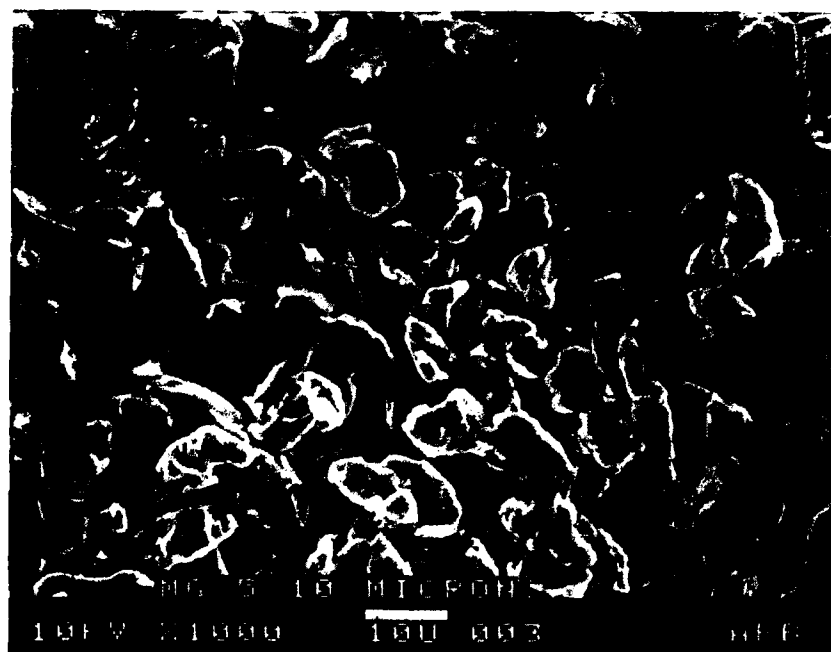
Figure A-20.   Magnesium particles, 5 to 10 μm

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Figure A-21.   Magnesium particles, 10 to 20 µm

Figure A-22.   Magnesium particles, 20 to 30 µm

Figure A-23.   Silicon particles, 5 to 10 μm

Figure A-24.   Silicon particles, 10 to 20 μm

Figure A-25.   Silicon particles, 20 to 30 μm

Figure A-26.   Titanium particles, 0 to 5 μm

Figure A-27.   Titanium particles, 5 to 10 μm

Figure A-28.   Titanium particles, 10 to 20 μm

Figure A-29. Titanium particles, 20 to 30 μm

Figure A-30. Aluminum particles, 0 to 5 μm
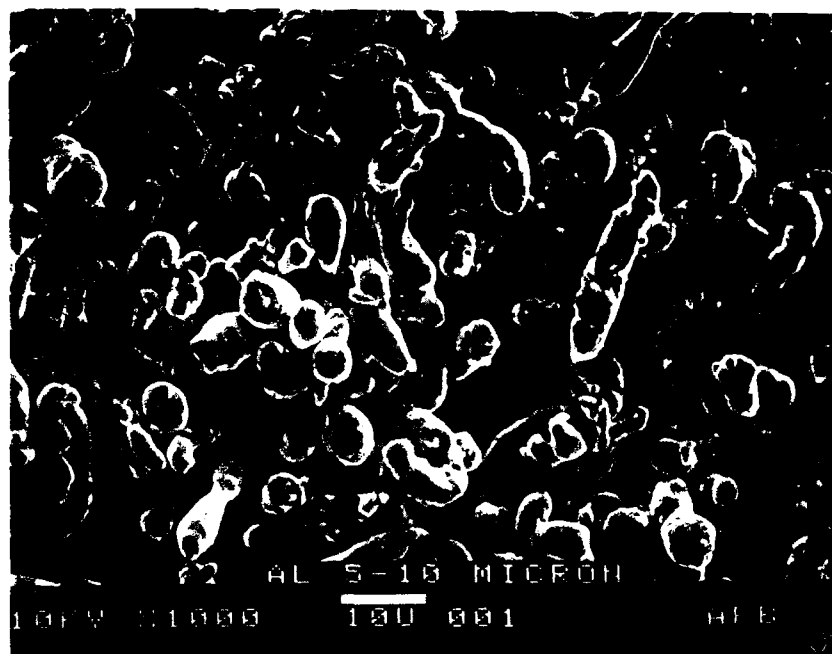
Figure A-31. Aluminum particles, 5 to 10 μm
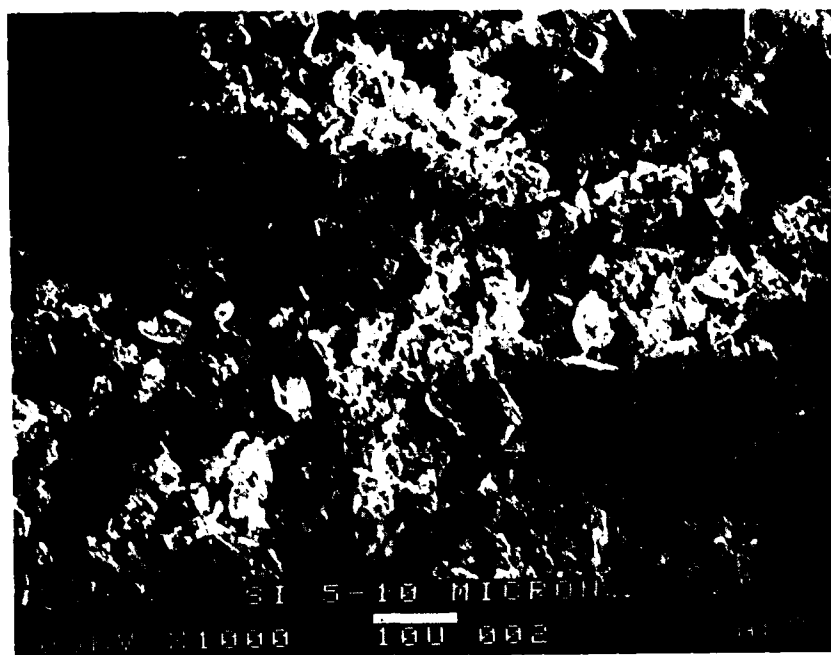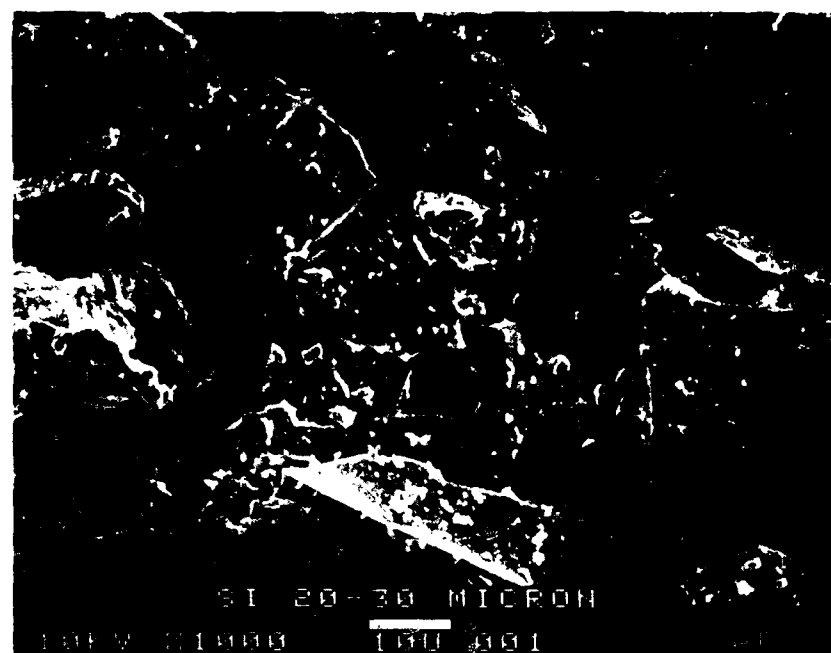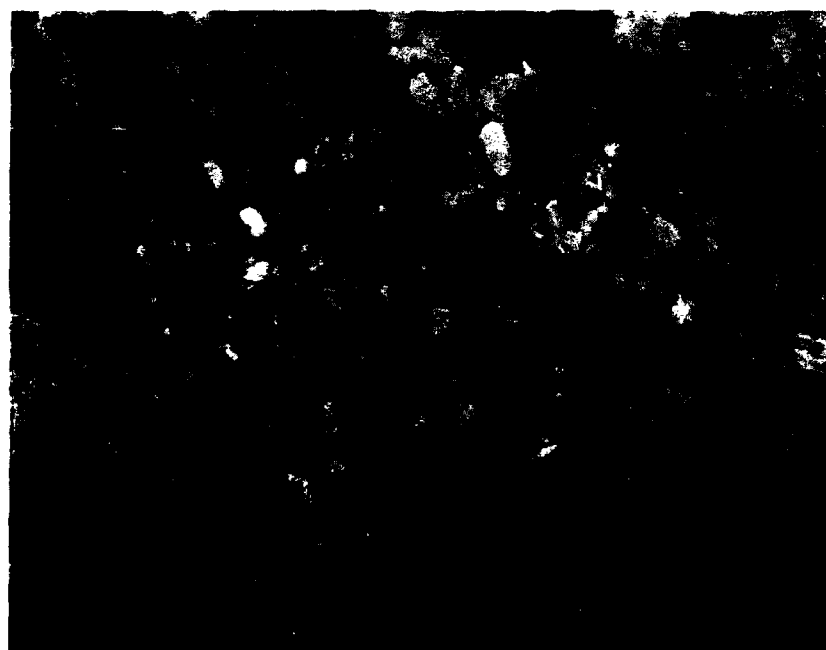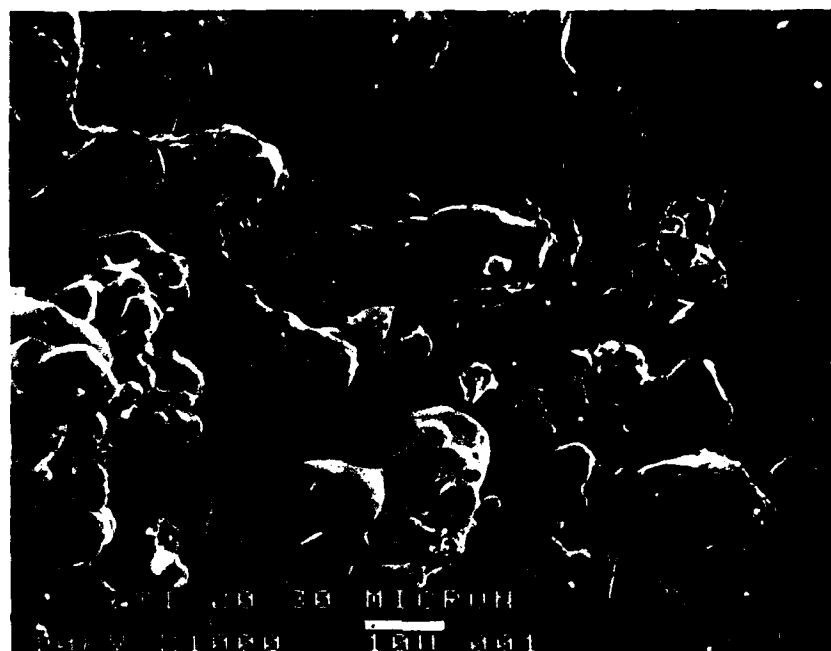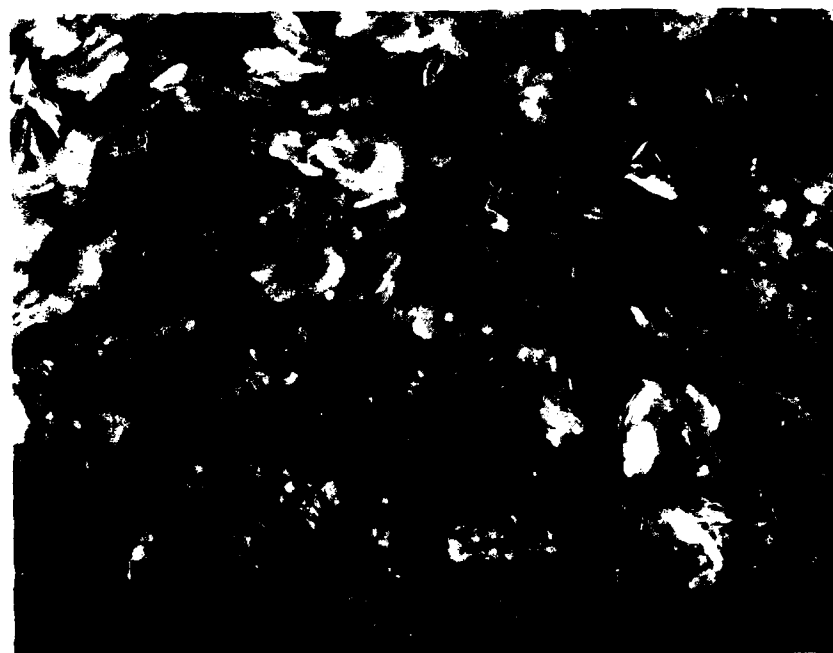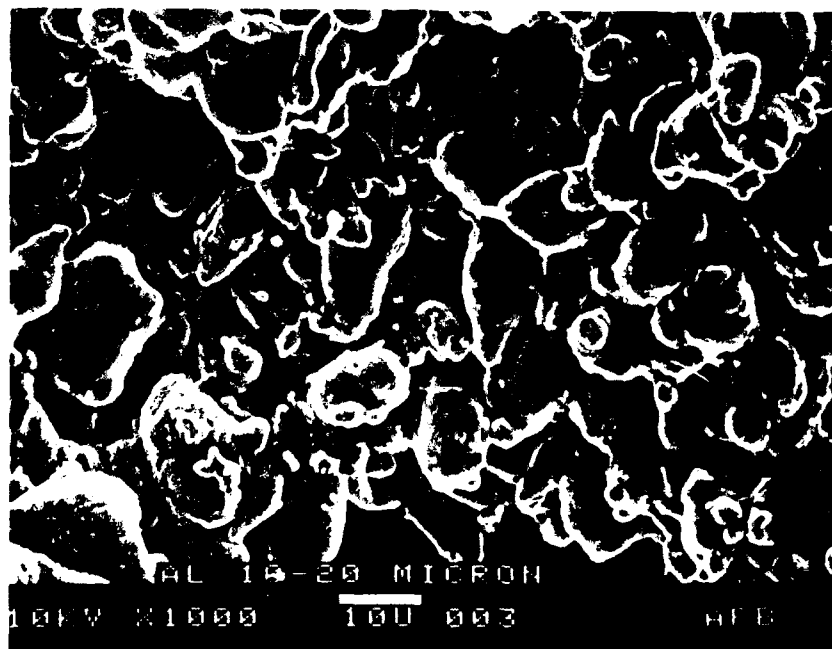

Figure A-32. Aluminum particles, 10 to 20 μm

Figure A-33.   Aluminum particles, 20 to 30 μm

APPENDIX B

ACID DISSOLUTION METHOD ANALYSES

TABLE B-1. True versus ADM Analysis - Nickel

Ni Sample	True Concentration (p/m)	Particle Size Micrometer	ADM Concentration (p/m)
2	7.3	0-5	7.44±0.06
3	14.1	0-5	14.92±0.42
4	27.8	0-5	29.17±0.60
6	6.6	5-10	6.01±0.02
7	18.6	5-10	16.40±0.37
8	29.2	5-10	24.55±0.23
10	7.3	10-20	5.21±0.02
11	13.8	10-20	11.16±0.41
12	29.0	10-20	22.9 ±1.0
14	7.0	20-30	5.5 ±0.1
15	14.0	20-30	13.4 ±0.2
16	28.0	20-30	17.0 ±0.4

TABLE B-2. True versus ADM Analysis - Iron

Fe Sample	True Concentration (p/m)	Particle Size Micrometer	ADM Concentration (p/m)
2	9.2	0-5	8.11±0.00
3	17.1	0-5	17.79±0.07
4	24.7	0-5	25.17±0.42
5	38.7	0-5	38.31±0.28
21	94.9	0-5	91.6 ±1.4
7	4.9	5-10	5.05±0.26
9	44.2	5-10	37.72±0.15
10	82.8	5-10	87.0 ±1.5
12	7.2	10-20	8.56±0.10
13	16.5	10-20	18.26±0.36
14	45.0	10-20	51.12±0.31
15	91.5	10-20	86.4 ±1.7
17	7.6	20-30	8.63±0.22
18	15.3	20-30	16.84±0.08
19	40.3	20-30	41.41±0.26
20	95.0	20-30	88.24±0.52

TABLE B-3. True versus ADM Analysis - Copper

Cu Sample	True Concentration (p/m)	Particle Size Micrometer	ADM Concentration (p/m)
5	5.9	0-5	5.26±0.04
6	18.9	0-5	16.60±0.04
7	36.9	0-5	33.23±0.10
8	6.3	5-10	5.07±0.01
9	16.3	5-10	13.41±0.18
10	36.6	5-10	31.38±0.03
11	6.9	10-20	5.72±0.03
12	16.8	10-20	14.20±0.02
13	36.9	10-20	32.46±0.17
14	6.0	20-30	5.03±0.02
15	17.3	20-30	14.98±0.02
16	36.7	20-30	31.83±0.08

TABLE B-4. True versus ADM Analysis - Chromium

Cr Sample	True Concentration (p/m)	Particle Size Micrometer	ADM Concentration (p/m)
5	4.5	0-5	3.0±0.1
6	7.4	0-5	3.0±0.1
7	3.4	5-10	0.3±0.0
8	8.7	5-10	0.9±0.0
9	4.2	10-20	3.1±0.1
10	9.4	10-20	6.3±0.1
11	4.6	20-30	2.1±0.1
12	7.9	20-30	3.7±0.0

TABLE B-5. True versus ADM Analysis - Silver

Ag Sample	True Concentration (p/m)	Particle Size Micrometer	ADM Concentration (p/m)
2	4.1	0-5	2.95±0.03
3	8.2	0-5	6.43±0.03
5	4.0	5-10	3.63±0.03
6	8.3	5-10	8.14±0.06
8	4.6	10-20	3.47±0.03
9	8.9	10-20	7.74±0.01

TABLE B-6. True versus ADM Analysis - Magnesium

Mg Sample	True Concentration (p/m)	Particle Size Micrometer	ADM Concentration (p/m)
5	6.0	5-10	3.74±0.03
6	15.6	5-10	10.40±0.52
7	23.5	5-10	15.82±0.05
8	6.1	10-20	5.66±0.06
9	14.9	10-20	14.47±0.03
10	24.3	10-20	23.29±0.08
11	5.8	20-30	5.60±0.01
12	15.0	20-30	14.26±0.28
13	23.9	20-30	22.93±0.11

TABLE B-7.   True versus ADM Analysis - Silicon

Si Sample	True Concentration (p/m)	Particle Size Micrometer	ADM Concentration (p/m)
5	5.9	5-10	5.2±0.2
6	12.0	5-10	7.0±2.0
7	17.9	5-10	10.1±2.2
8	6.0	10-20	6.3±0.8
10	18.0	10-20	13.4±2.1
11	6.0	20-30	5.9±1.2
12	11.9	20-30	10.8±1.4
13	17.7	20-30	15.1±2.3

TABLE B-8.   True versus ADM Analysis - Titanium

Ti Sample	True Concentration (p/m)	Particle Size Micrometer	ADM Concentration (p/m)
2	6.0	0-5	4.92±0.14
3	12.0	0-5	9.6 ±0.7
4	18.0	0-5	14.6 ±0.4
5	6.0	5-10	4.48±0.01
6	11.9	5-10	8.94±0.10
7	18.0	5-10	13.16±0.44
8	6.1	10-20	4.92±0.01
9	12.2	10-20	10.91±0.01
10	18.0	10-20	16.13±0.27
11	5.9	20-30	4.78±0.11
12	12.0	20-30	11.56±0.04
13	18.0	20-30	15.62±0.16

TABLE B-9. True versus ADM Analysis - Aluminum

Al Sample	True Concentration (p/m)	Particle Size Micrometer	ADM Concentration (p/m)
5	7.0	0-5	1.84±0.06
6	14.4	0-5	7.44±0.05
7	23.2	0-5	11.92±0.11
8	7.8	5-10	8.12±0.08
9	16.8	5-10	16.02±0.01
10	28.1	5-10	25.62±0.25
11	7.2	10-20	5.42±0.12
12	14.0	10-20	9.87±0.10
13	25.2	10-20	16.80±0.20
14	7.1	20-30	6.81±0.25
15	14.8	20-30	14.05±0.05
16	25.6	20-30	22.39±0.06

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