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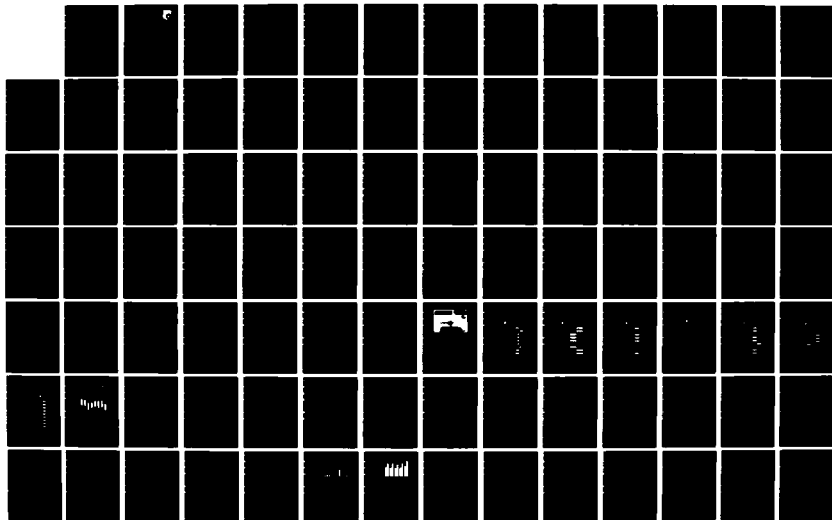
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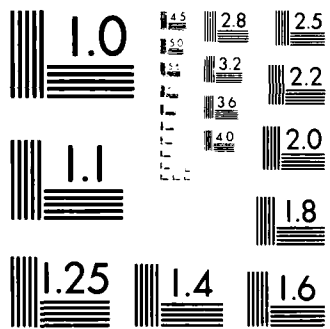
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LABORATORY SPECTROMETER FOR WEAR METAL ANALYSIS OF ENGINE LUBRICANTS

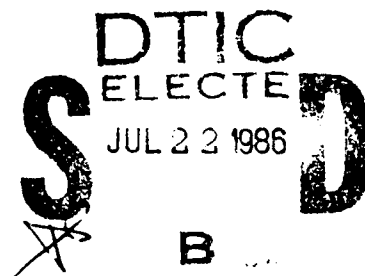
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April 1986

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

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| 19. ABSTRACT (Continue on reverse if necessary and identify by block number) A thorough technical search was conducted to define all potential spectrometric approaches for conducting wear metal analysis in engine lubricating fluids. The techniques identified were subjected to an analysis of their design and performance characteristics. The resultant data were used to determine which methods had sufficient potential for meeting the needs of the Joint Oil Analysis Program (JOAP) through the year 2000. The most promising candidate techniques were then ranked through a factorial analysis on the basis of the following criteria: (1) analysis time; (2) elemental capability range; (3) reliability/maintainability; (4) size/weight; (5) unit cost; (6) consumables requirements; (7) sample costs; (8) safety; (9) automation for sampling, calibration, and data reduction; (10) simplicity of design; (11) simplicity of operation; (12) environmental operating limits; (13) CRT, printer and data system capabilities; (14) particle size capabilities; (15) self diagnosis/modular construction; (16) reduced operator dependence; (17) data management | | | | | | |
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Engine Condition Monitoring
Inductively Coupled Plasma
Directly Coupled Plasma

Electrothermal Atomization
Mass Spectroscopy
Rotating Disk Electrode

Arc/Spark Emission
Ashing Rotrode
Continuum Source

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methods and capacity to interface with current JOAP data bases, and (18) logistics and maintenance costs. An inductively coupled plasma simultaneous atomic emission spectrometer with auto-dilution and auto sampling was found to be the best instrumental approach for supporting JOAP needs through the year 2000. Verification testing was conducted, where applicable, to confirm the capabilities of this optimum instrumental approach.

FOREWORD

This document was prepared by United Technologies Corporation, Pratt & Whitney (P&W) for Contract No. F33615-84-C-2400, "Laboratory Spectrometer for Wear Metal Analysis of Engine Lubricants." The program is sponsored by the United States Air Force Systems Command, Aeronautical Systems Division, Wright-Patterson AFB, Ohio. Ms. R. W. Newman is the Air Force Program Manager and Mr. M. Rippen is the P&W Program Manager.

The following individuals and companies were involved in the execution of this program and have contributed to this report:

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SECTION I

INTRODUCTION

1. BACKGROUND

The practice of monitoring oil-wetted component wear in engine systems has proven to be a highly successful maintenance tool, as documented by Layne B. Peiffer in his report, "Air Force Spectrometric Oil Analysis Program, 1963 - 1980" (Reference 1). To ensure effective usage of this technology, the Department of Defense (DoD) established the Joint Oil Analysis Program (JOAP) in a tri-service (Army, Air Force, and Navy) agreement that charged JOAP with the responsibility of managing all military oil analysis activities (Reference 1). The standard JOAP procedures for monitoring the wear of oil-wetted components and determining abnormal wear rates are defined in the JOAP Laboratory Manual (Reference 2). These procedures are based on determining the concentrations of wear metal elements in lubrication fluids from individual engines and monitoring any increase in the concentrations of wear metals with time of engine operation. These methods are used to support maintenance activities for a variety of engines and transmissions in aircraft and surface vehicles. The most critical JOAP mission is to monitor aircraft systems since failure of an engine component could cause the loss of the aircraft and pilot.

As documented by the JOAP Laboratory Manual, each engine has its own abnormal wear criteria which are defined by the results obtained with a particular spectrometric oil analysis method. These criteria reflect the composition of various engine components and their established wear characteristics. Wear may occur as a result of chemical or mechanical processes (Reference 3). Due to the wide variety of potential wear mechanisms, wear metals may be present in oil samples in dissolved forms or as particles ranging from sub-micrometer to millimeters in diameter.

Under current JOAP guidelines, two types of spectroscopic instruments are used for oil analyses: (1) rotating disk/arc atomic emission spectrometers (A/E35U-3's), and (2) flame atomic absorption spectrophotometers (AA's). Because of the need for rapid multielemental analyses of large numbers of samples, emission spectroscopy is usually the method of choice. Consequently there are 179 A/E35U-3 spectrometers within JOAP laboratories and only about 29 AA units. The A/E35U-3 unit was developed in 1970 as a sole-source procurement item conforming to MIL-S-83129. This instrumentation requires the use of two graphite electrodes which must be manually replaced between each sample run. The A/E35U-3 systems suffer from relatively poor precision due to the variable excitation characteristics of direct current (dc) arcs operated in air, and they may suffer from inaccuracies due to variations in sample viscosity. AA instruments provide better precision but are slow sequential multielement analytical instruments; they require hazardous gases and dilution of viscous samples, and they have limited dynamic range. Both techniques are limited in their ability to analyze particulate wear debris. The A/E35U-3 cannot effectively analyze particles larger than 10 micrometers, and the AA method is limited to quantitative determinations of particulate elements under 3 micrometers in diameter (References 4 and 5).

The present JOAP instrumentation is nearing the end of its useful life cycle. Given the technical database available and the analytical capability of presently available instrumentation, an optimum JOAP technique must be identified for the next procurement cycle.

The use of the current JOAP procedures have provided a definite history of cost savings in the diagnosis of engines by predicting potential catastrophic engine failures before their occurrence. While these techniques are very particle-size dependent, they have fulfilled their

various missions quite adequately. Although there are some specific applications which may require particle-size-independent analysis capabilities, there is no comprehensive study which has established conclusively that a spectroscopic oil analysis did not predict engine failure due to the particle-size dependency of the technique. Conversely, the data generated by a particle-size-independent technique may require a totally new approach to trend analysis to diagnose abnormal wear.

A trend toward cleaner running engines has developed as aircraft engines and their lubrication systems have evolved. This has been reflected by the lower "step change" limits set for preventive maintenance actions on the latest engines. For example, in the TF30 engine, abnormal wear is defined for iron (Fe) as an increase of 4 parts per million (ppm) or more by AA, or 8 ppm or more by the A/E35U-3 in any given 10-hour engine run. In the F100, a later generation engine, the step change for Fe indicating abnormal wear is 2 ppm or more by AA, or 4 ppm or more by the A/E35U-3, during a 10-hour engine run. This trend is now being accelerated through the development of "ultra-fine" filtration, which removes particulate wear debris as small as 3 to 5 micrometers in diameter from the lubricants in the latest generation engines. While the full impact of ultra-fine filtration on JOAP analysis has not yet been determined, it is obvious that enhanced particle-size capabilities of JOAP instrumentation cannot be justified for aircraft engine systems using such technology. There are aircraft turbine engines presently in service which employ "ultra-fine" filtration technology. In one recent incident abnormal wear was diagnosed through spectrometric oil analysis conducted with an inductively-coupled plasma atomic-emission spectrometer system (ICP-AE) (Reference 6). In this case the critical step changes for Fe and magnesium (Mg) were observed in the sub-ppm concentration range. If this one incident is a realistic reflection of the impact of "ultra-fine" filtration on spectroscopic oil analysis, then any rotrode approach (including ashing) may not offer sufficient sensitivity and/or adequate precision for measuring the critical wear element step changes for these systems.

Data collected from diesel engines and helicopter gearboxes suggest that a large number of particles in any given sample may not be seen by the current JOAP systems because they are larger than a few microns in size. Ferrography has been used in many cases where these particles are found with considerable success in predicting abnormal wear. This technique is limited to particles which can be magnetically precipitated and provides a qualitative wear-rating factor. This factor is determined through ratioing the optical wear density of larger particles (less than 5 micrometers) with smaller particles (1 to 2 micrometers) to generate a severity-of-wear index. This technique takes about 5 minutes using a direct reader ferrograph. In the area of particle-size-independent spectrometric analysis, the acid digestion technique for sample pretreatment is the best approach available to date because of its relatively large sample size (1000 microliters or more). However, this technique has two major shortcomings limiting its application: (1) it requires the use of hydrofluoric acid (a requirement deemed unacceptable for safety considerations in a military environment), and (2) its use increases sample analysis times to a point where the sample turnaround time for typical JOAP missions would be unacceptable. Methods incorporating graphite furnaces or other direct sampling modes are limited because it may be impossible to conduct trend analyses, given the typical 5- to 50-microliter samples, due to the statistical problems associated with representative sampling of particulate debris.

2. PROGRAM OBJECTIVE

The objective of this program was to identify the optimum instrument type with respect to analytical capability and cost, necessary modifications (if any), and potential sources of an advanced wear metal spectrometer system to meet Joint Oil Analysis Program (JOAP) needs through the year 2000.

SECTION II

TECHNICAL APPROACH

The technical approach was divided into five tasks. These tasks were as follows:

- ▶ Task 1 — Literature and Industry Search
- ▶ Task 2 — Instrumental Performance Evaluation
- ▶ Task 3 — Instrumental Design Evaluation
- ▶ Task 4 — Analysis of Findings
- ▶ Task 5 — Verification Testing

1. TASK 1 — LITERATURE AND INDUSTRY SEARCH

A comprehensive literature search was conducted during the first 2 months of this program. The objective was to identify any analytical instrumental methods that could be useful in the elemental analysis of wear particles in oil-wetted lubrication systems. In addition to the literature search, industrial, academic, and government research and development organizations were invited to contribute information on types of instrumentation to achieve Joint Oil Analysis Program (JOAP) goals by the year 2000. Analytical instrumentation companies were also invited to present their approaches or applicable literature on equipment that could be used for JOAP analysis.

Due to the large scope of potential approaches in addressing JOAP goals, the search for optimum JOAP instrumentation was divided into three major areas. One part of this effort was subcontracted to the University of Maryland and dealt with atomic absorption (AA)-type instrumentation. Another part was subcontracted to Northeastern University and entailed a literature search dealing with atomic emission (AE)-type instrumentation.

Pratt & Whitney (P&W) conducted a search dealing with atomic fluorescence (AF)-type instrumentation and other types of instrumentation not covered by the AA and AE searches. P&W also conducted a DIALOG™ search as well as a search set up by the Defense Documentation Center of the Defense Logistics Agency. The results of searches for reports on AA and AE techniques were forwarded to the respective subcontractor for further analysis.

2. TASK 2 — INSTRUMENTAL PERFORMANCE EVALUATION

During the second, third, and fourth months of this program, all instrumentation potentially suitable for JOAP application was evaluated on the basis of how well they could address performance requirements.

The University of Maryland evaluated performance requirements for AA instrumentation, Northeastern University evaluated performance requirements for AE instrumentation, and P&W coordinated the entire task while evaluating AF and other types of instrumentation.

The following sections detail the evaluation criteria for the various JOAP instrumentation used in the performance of this contract. Specific literature references were sought for each approach.

a. Measurements

The spectrometer should be capable of measuring at least these 19 elements important to JOAP needs: iron, aluminum, titanium, chromium, copper, magnesium, silver, nickel, silicon,

molybdenum, sodium, zinc, lead, boron, tin, barium, sulfur, phosphorus, and calcium. These elements should be measured in a simultaneous or rapid sequential mode to achieve a complete multielement analysis with a desired sample turnaround time of one per minute or less.

b. Repeatability

As defined for calibration standards and set forth as a goal for used oil samples, the precision of measurements will be $\pm 10\%$ for a 1- to 5-ppm concentration range, $\pm 5\%$ for a 5- to 100-ppm concentration range, and $\pm 2.5\%$ for a range of 100 to 1000 ppm.

c. Accuracy

As determined by gravimetric analysis of the sample, the true value or accuracy of measurements made by the spectrometer will be within the limits of $\pm 1\%$.

d. Sensitivity

Under multielement analysis conditions, the spectrometer will permit measurement of all elements with sensitivity of 1 ppm or greater for each element.

e. Dynamic Range

The linearity of working range for the spectrometer from 1 ppm up to specific full-scale levels is stated in Table 1.

TABLE 1.
ELEMENTAL DYNAMIC RANGES

| <i>Element</i> | <i>Range (ppm)</i> |
|----------------|--------------------|
| Iron | 1 to 1000 |
| Sodium | 1 to 500 |
| Aluminum | 1 to 500 |
| Zinc | 1 to 1000 |
| Titanium | 1 to 500 |
| Lead | 1 to 500 |
| Chromium | 1 to 500 |
| Boron | 1 to 500 |
| Copper | 1 to 500 |
| Tin | 1 to 500 |
| Magnesium | 1 to 500 |
| Barium | 1 to 1000 |
| Silver | 1 to 500 |
| Sulfur | 1 to 500 |
| Nickel | 1 to 500 |
| Phosphorous | 1 to 1000 |
| Silicon | 1 to 500 |
| Calcium | 1 to 1000 |
| Molybdenum | 1 to 500 |

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3. TASK 3 — INSTRUMENTAL DESIGN EVALUATION

During the second, third, and fourth months of this program, all instrumentation potentially suitable for JOAP was evaluated on the basis of design requirements. The University of Maryland conducted this evaluation on AA instrumentation, Northeastern University

conducted a similar evaluation on AE instrumentation, and P&W evaluated other instrumentation identified from the literature search.

The following design requirements were evaluated for all potential JOAP instrumentation:

1. The instrumentation should include improved, effective sample introduction systems and sample reservoir systems to achieve: (1) a complete, representative introduction of the sample and (2) adequate maximal excitation temperatures and residence times of particles for accurate analysis of metal particulates and refractory metals.
2. The instrumentation should be simple to operate, requiring no special operator skills.
3. The instrumentation should be optimized for ruggedness, durability, occasional movement, and portability. (Improvements might include shock mounting, sealed optics, and automated optical alignment equipment.)
4. Environmental constraints that influence potential JOAP instrumentation should be evaluated. A desired range is 0-to-90% humidity and 10-to-43°C (50 to 110°F).
5. Use of hazardous gases should be eliminated and requirements for consumables minimized.
6. All safety aspects should be addressed to minimize hazards to the operator and the laboratory environment.
7. High reliability should be required in daily operations and in long-term maintainability.
8. Automatic procedures for performing instrumentation calibration standardization should be implemented to eliminate dependency on operator skill, environmental conditions, and the excessive time required for repetitive manipulations. Recalibration should be required no more frequently than once per 8-hour shift.
9. Inter-element and matrix effects for various oils, both hydrocarbon and synthetic, should be evaluated and minimized by the selected instrumentation.
10. Instrumentation techniques selected should demonstrate the capability to detect large particles, i.e., demonstrating freedom from particle size discrimination.
11. Electrical power requirements should be such that the instrument demonstrates conversion capability (110/220 volts alternating current (vac), 50/60 Hertz (Hz)) and stable operation under power source fluctuations (110 vac \pm 20%, 220 vac \pm 10%).
12. The instrumentation should incorporate state-of-the-art technology including: printed circuit boards, integrated circuit/chip technology, solid-state electronics, and modular maintenance, such that internal diagnostics may be used by the operator for detection of instrument malfunction and subsequent module replacement.

13. State-of-the-art laboratory microprocessor capability for an automated spectrometer operation is as follows:

- Capability for expandable memory
- Automatic data storage for subsequent reformat
- Provision for additional communication ports
- Printer with graphics capability
- Large cathode-ray tube (CRT) with graphics capability
- Software for system self diagnostics
- CRT with roll capability for multiple-page data display
- Software for spectrometer standardization
- Software to compensate for instrument drift
- Provision for Interfacing with central data bank; output of results compatible with entry into JOAP data management systems.

4. TASK 4 — ANALYSIS OF FINDINGS

The results of Tasks 1 through 3 were the basis for an analysis of findings conducted during the fifth and sixth months of this program. The data generated in Tasks 1 through 3 were reviewed by senior investigators from the University of Maryland, Northeastern University and P&W during a meeting at the P&W West Palm Beach, Florida facility. Evaluation criteria were reviewed and a weighting system was devised to rank the candidate instruments. Through this analysis the spectroscopic techniques best meeting the design and performance criteria contained in Solicitation No. F33615-84-R-2400 were identified. At the end of Task 4 a conference of the senior investigators and representatives of the three services was held to discuss the results.

P&W subsequently selected for additional testing and evaluation the spectroscopic technique best meeting the design and performance criteria. This selection was made on the basis of an evaluation of the findings presented at the meeting and additional input from the AFWAI/POSL Project Engineer.

The following factors were considered in the selection process:

- The accuracy, sensitivity, and linearity at full-scale dynamic range and repeatability (precision) attainable for each element and technique
- Interferences in detectability of any element by spectral, physical, and chemical (interelement and matrix effects) techniques and effects of viscosity differences
- The ability of candidate instrumentation to conduct rapid multielement analysis

- Special provisions enhancing particle-size independence such as special sample introduction systems, nebulizers, or high-intensity sources
- The applicability to nondilution of oil samples
- Compatibility with use of present JOAP Conostan standards
- The applicability toward trending analysis of data
- The feasibility of microcomputer automation of analysis cycle, optical alignment, calibration, standardization, output of results, and interface with central data bank
- The suitability to internal-diagnostic modular repair
- The requirements for consumables and electrical power
- The operability under required environmental conditions
- Safety considerations for instrument operations
- The cost per sample for the current and proposed methods
- Cost benefit analysis.

5. TASK 5 — VERIFICATION TESTING

Task 5 was initiated in the seventh month of the program and was concluded in the eleventh month. Three subtasks were completed during this phase of the contract.

a. Instrument Optimization

This subtask involved establishing optimal operating conditions for the candidate instrument in accordance with the selection factors listed in Task 4. Northeastern University was responsible for this effort.

b. Synthesis of Standards and Collection of Used Engine Samples

This subtask involved research efforts at P&W and at Northeastern University. P&W provided used engine samples with help from the JOAP Technical Service Center. These samples included MIL-L-7808, MIL-L-87100, MIL-L-23699, and mineral-base used-oil samples provided by Army JOAP management. The group at Northeastern University generated particulate metal standards and acquired organometallic standards from the National Bureau of Standards and from Conoco, Ponca City, OK.

c. Verification Testing

This subtask was accomplished by Northeastern University and involved an evaluation of the performance characteristics of the target instrument identified in Task 4. Design characteristics were evaluated on the basis of the manufacturer's literature and an analysis of the spectrometer's features.

SECTION III

RESULTS

1. GENERAL SEARCH RESULTS

During the literature search, 718 abstracts were reviewed from the Defense Documentation Center of the Defense Logistics Agency (DDCDLA). Of these, 79 papers were studied in detail. Fifty-three abstracts were reviewed from the DIALOG™ search and 25 reports were further analyzed in detail. Additional searches of the technical literature in analytical chemistry and applied spectroscopy produced hundreds of references.

Manufacturers of potential JOAP instrumentation were also contacted and asked to provide information on currently available instrumentation and products under development. The following are synopses of the information provided.

Allied Analytical Systems, Waltham, MA

Allied Analytical Systems provided data on their inductively-coupled plasma atomic emission (ICP-AE) and atomic absorption (AA) systems. The former included two simultaneous multielement spectrometers, the "ICAP 9000" and the "ICAP 1100". Both are based on 0.75 m Rowland circle optics in a sealed chassis for measurements in the vacuum ultraviolet region. The ICAP 1100 incorporates a 2400 groove/mm grating and provides greater linear dispersion and resolution for wavelengths up to 500 nm than does the ICAP 9000. The former spectrometer also has greater data handling capacity through the use of a minicomputer-based work station. Allied Analytical Systems has recently developed an electrothermal vaporization (ETV) cell for sample introduction to the ICP sources. This combination may eliminate particle-size dependency from among the disadvantages of ICP atomic emission spectrometry. While an ETV-ICP system was shown at the Pittsburgh Conference in March 1985, the system will probably not be available until mid- or late-1986.

Applied Research Laboratories (ARL), Sunnland, CA

ARL supplied documentation of the Model 34000, a 0.75-meter simultaneous ICP emission spectrometer, and the Model 3520, a 1-m scanning instrument. The latter features a stationary concave grating in a Paschen-Runge mount and an array of 225 exit slits in the focal plane. A wavelength is selected by driving a photomultiplier tube to a position behind one of the exit slits and then moving the entrance slit slightly to align the desired wavelength on the selected exit slit. Both spectrometers may be evacuated for measurements at wavelengths shorter than 190 nm. Data were also provided on the ARL line of x-ray fluorescence spectrometers.

Baird Corporation, Bedford, MA

Baird demonstrated three spectroscopic instruments including an updated version of the A/E35U-3 rotode system (the FAS-2C) which was introduced in 1979. The FAS-2C features modified power distribution and venting systems for the source, a new control panel layout and readout displays, and considerably simplified signal processing and data reduction hardware. Electronic modifications have reduced the number of circuit boards from 89 to 8 and eliminated the mechanical relays of the A/E35U integrator circuits.

Analyses of used oil samples were conducted by Baird applications chemists using the "Spectrovac" multichannel ICP atomic emission spectrometer and the "AFS 200" 12-channel atomic fluorescence spectrometer. The former instrument featured an automatic on-line sample

dilution system in which the oil samples were mixed with kerosene in a volume ratio of about 1:4 as they were introduced to the ICP.

Buck Scientific, East Norwalk, CT

Buck Scientific provided data on an AA spectrometer. The instrument is simple, compact, and inexpensive.

EDAX International, Prairie View, IL

EDAX provided data on x-ray analysis techniques which were considered to be suitable for wear particle analysis in lubricating oils. EDAX markets the Philips line of x-ray spectrometers which are highly automated and are available in simultaneous configurations.

Instruments SA (ISA), Metuchen, NJ

ISA provided data on their simultaneous ICP-AE systems, which are used for routine wear metal analysis of oils by the French Air Force. According to the manufacturer, use of this technique has allowed the French Air Force to identify alloy metals from wearing components in oil samples at sub-ppm levels. This has presumably been made possible by the lower detection limits obtained with the ICP than with rotrode atomic emission systems.

Keve Corporation, Foster City, CA

Keve provided information on its x-ray spectrometers. Technical briefs on wear particle analysis of lubricating oils by x-ray techniques were included in their correspondence.

Leeman Labs, Lowell, MA

Leeman Labs provided information on a prototype direct current plasma (DCP) called the graphite filament plasma which incorporates a moving graphite braid as the anode of the plasma arc and as the conveyor of sample to the arc. The source is not available commercially and is under study and development in a research program supported by Leeman Labs at Northeastern University.

Leeman manufactures ICP AE spectrometers based on an echelle grating and a prism which serves to separate wavelengths in overlapping orders and to focus dispersed radiation on the focal plane. Both the grating and prism are stationary; wavelength selection is achieved in the sequential mode of operation by driving a photomultiplier tube to a position behind one of approximately 300 exits slits which have been etched at positions corresponding to the focal plane locations of prominent emission lines of 62 elements. A simultaneous multichannel version of the spectrometer can be configured with up to 48 photo tubes.

The Leeman Labs ICP uses free-running circuitry and direct coupling to provide power to the plasma. The radio frequency (RF) feedback antenna used in most ICPs is replaced by circuitry that maintains constant plate current by continuously adjusting power to the oscillator. Because the RF generator is directly coupled to the induction coil surrounding the plasma discharge, there are no power losses in the impedance-matching network, and the source is relatively compact and less susceptible to shock damage.

Perkin-Elmer Corporation, Norwalk, CT

Perkin-Elmer provided data on their ICP atomic emission and atomic absorption instruments. The emission spectrometers are designed for sequential multielemental analyses only.

Photochemical Research Associates (PRA), London, Ontario, Canada

PRA provided data on an ICP AE spectrometer in the advanced stages of development. The spectrometer features a low-resolution preliminary dispersing element, elimination of unwanted spectral regions using filters, recombination of the optical beam and final dispersion using an echelle grating. The detector is a single 1024-pixel photodiode array for simultaneous multielemental analyses.

SCIEX, Thornhill, Ontario, Canada

SCIEX provided information on the "ELAN" ICP/ mass spectroscopy elemental analysis system. The use of a mass spectrometer as a detector provides greater freedom from spectral interferences and detection limits that are one to two orders of magnitude lower than those obtained with ICP optical emission. The interface between the ICP and the quadrupole mass spectrometer features a cryostatic vacuum pump.

Spectro, Fitchburg, MA

Spectro furnished data on the "Spectroil Model W" pulsed dc arc/spark rotrode AE system. The arc is struck using a high voltage spark at the rate of 120 per second. In the prototype data acquisition mode, the emission produced by each arc/spark is recorded. These data are used to generate histograms of frequency of occurrence versus intensity which provide an indication of particle size. The excitation source may be coupled to one or two 24-channel polychromators using quartz optical fibers. Each polychromator is based on 0.75-m optics in a Paschen-Runge mounting. Information was provided on an ashing rotrode source in which 30- μ l volumes of oil samples are dispensed directly on rotating disk electrodes. The samples are ashed by resistively heating the disks prior to striking the arc. Spectro also offers an ICP source coupled to the above polychromator.

Beckman Instruments (Spectrametrics), Fullerton, CA

Spectrametrics provided literature on the "Spectraspan V" 20-channel polychromator coupled to either a DCP or an ICP. The performance of the three-electrode dc plasma is well documented by past research (References 3, 68, and 69). The polychromator is basically the same echelle grating instrument introduced as the Spectraspan III in the early 1970s. It features movable grating and prism components and manual optical alignment.

VG Instruments, Stamford, CT

VG Instruments provided technical data on the "PlasmaQuad" ICP/mass spectrometer for elemental analysis. The major distinction between the VG instrument and the SCIEX ICP/MS described above is in the pumping system which allows the coupling of an argon plasma operating at atmospheric pressure with a quadrupole mass spectrometer operating at 10^{-6} torr. The VG system includes tandem diffusion pumps following a 1st-stage mechanical pump to produce this pressure differential. The SCIEX instrument uses a single cryo-pump instead of the tandem diffusion pumps.

Varian Instruments Group, Palo Alto, CA

Varian provided data on AA instrumentation.

Academic research teams, including those headed by Dr. Ramon Barnes at the University of Massachusetts, Dr. Joseph A. Caruso at the University of Cincinnati, and Dr. James Winefordner at the University of Florida, also provided information and advice in

personal interviews and through correspondence. Additional data and accounts of analytical experiences were collected from the Army, Navy and Air Force technical specialists assigned to the JOAP Technical Support Center in Pensacola, Florida.

As a result of the general literature search and the above fact-finding activities, the following spectroscopic techniques in the configurations indicated were identified as having potential use in the JOAP.

a. Atomic Absorption Spectroscopy (AAS)

- Hollow cathode source with flame atomization
- Hollow cathode source with electrothermal atomization
- Continuum source simultaneous multielement analysis with flame atomization
- Continuum source simultaneous multielement analysis with graphite furnace atomization.

b. Atomic Emission Spectroscopy (AES)

- Arc/spark excitation source incorporating the rotating disk electrode
- ICP excitation source with aerosol sample introduction
- ICP excitation source with graphite furnace sample introduction
- ICP excitation source with laser ablation
- Laser induced breakdown spectroscopy
- Graphite furnace excitation source with direct sampling
- DCP excitation source with aerosol sample introduction
- DCP excitation source with graphite braid sample introduction.

c. Other Instrumental Techniques

- ICP atomic fluorescence with aerosol sample introduction, and cathode lamp excitation
- X-ray fluorescence with direct sampling
- ICP with aerosol sample introduction as an ionization device for mass spectroscopy
- X-ray fluorescence with prefiltration of samples prior to analysis.

2. PERFORMANCE REQUIREMENT EVALUATION

a. Measurements

All of these potential methods may be used to determine most, or all, of the following elements in lubricating oils: iron, aluminum, titanium, chromium, copper, magnesium, silver, nickel, silicon, molybdenum, sodium, zinc, lead, boron, tin, barium, sulfur, phosphorous, and calcium. The time required for one sample to be analyzed for all of these elements can vary from 1 minute to several hours. An important consideration is whether the instrument is sequential or simultaneous in its multielement mode of operation. For this study, only polychromators providing simultaneous multielement analysis were considered to be capable of providing 1-minute analyses by atomic spectroscopy with the requisite precision and accuracy. Sample preparation including filtration or acid digestion may increase analysis times by 20 minutes or more.

b. Repeatability

In the analysis of used oil samples, the precision of analytical measurements depends on several factors including (1) analytic concentration versus analytical detection limit, (2) the stability of the source/atom reservoir, (3) the reproducibility with which the sample is introduced to the source/atom reservoir, (4) the signal acquisition interval, and (5) the particle-size dependence of the technique.

For the purposes of this study, precision was evaluated from measurements of the short-term relative standard deviations in analytical signals produced as oil samples containing dissolved analytic species were introduced. In this context, precision provides an estimate of the random error one may associate with a particular instrumental technique rather than with overall analytical uncertainty. Other factors, such as variability in sample viscosity or the size of wear particles or spectral or chemical interferences, may affect both precision and accuracy. These are assessed in the next section in an evaluation of the systematic errors which degrade accuracy.

Argon plasmas are exceptionally stable atom reservoirs and excitation sources. Short-term variations in emission intensity are typically 1% or less for ICPs and 1 to 2% for DCPs. Much of the variability that is encountered does not appear to come from variations in the source, but rather from the sample introduction system. It was found, for example, that when an ICP was coupled to a high-pressure cross-flow nebulizer that provided a more uniform sample aerosol than the commercially available nebulizers, the relative standard deviation in emission intensities fell into the 0.1 to 0.3% range (Reference 8). Similarly with the DCP, introduction of a sample matrix (hexane), which was completely vaporized in the sample introduction system, yielded relative standard deviation (RSD) values less than 1% (Reference 9) because variability in the size of aerosol particles reaching the DCP ceased to be a source of analytical variability.

While the literature contains many papers describing the analysis of organic samples with ICPs and DCPs, plasma instability resulting in decreased precision has been reported with these samples. ICP stability can be degraded by volatile sample matrices that increase the rate of vapor delivery to the plasma. If this rate is too high, the plasma is partially quenched, reflected power levels increase, and the plasma becomes less stable. To overcome these problems, analysts typically: (1) use higher applied power to the ICP, i.e. 1.75 kw versus 1.0 kw for aqueous samples, and (2) select solvents of moderate volatility such as xylenes or kerosene (Reference 10) rather than acetone or hexane to dilute viscous oil samples. Improved stability has also been achieved by decreasing the rate of sample delivery to the nebulizer and by using an aerosol/vapor delivery tube of narrower bore to increase back pressure in the spray chamber and so decrease solvent vaporization (Reference 11).

The precision of atomic absorption measurements with combustion flames approaches that of atomic emission measurements using the ICP. In both techniques samples are converted into aerosols that are fed continuously into the atomization cell. Such steady state atom populations tend to produce the most precise measurements. The use of *electrothermal vaporization* increases the sensitivity of AA (and AE) measurements, but the transient atom populations that produce the analytical signal do so with less precision; RSD values for graphite furnace AA are typically 5%. This is about the precision obtained with arc/spark emission sources and with the graphite filament plasma (GFP). The unique sample delivery system of GFP sets it apart from those that rely on aerosol generation. The conveyor belt approach to sample delivery in the GFP enhances the efficiency of sample transfer, but produces a transient emission signal.

c. Accuracy

The particle size distribution of wear debris and the particle-size dependency of the analytical technique are believed to be the most critical factors limiting the accuracy of spectroscopic methods for wear metal analysis. The data plotted in Figure 1 were obtained when several particle-size-dependent and independent methods were used to analyze a set of used-engine oils. Accuracy to within 1% of the true value may not be achieved even with a particle-size-independent technique incorporating acid digestion and/or dry ashing in sample pretreatment; previous investigations have documented incomplete recoveries of particulate wear metals (References 12 and 13).

The accuracy (and precision) of analytical results obtained with the direct introduction of small sample volumes may be adversely affected by low-number densities of wear particles. For example, the volumes taken for analysis in graphite furnace techniques are typically 10 — 20 μ l. If the wear process produces few relatively large particles, the probability of one of these particles being present in so small a sample volume may be significantly less than unity. Overcoming this problem in sampling statistics may involve replicate (n) analyses to increase the volume of sample analyzed. This approach would have the undesirable effect of lengthening analysis time by a factor of n.

Differences in the viscosity of oil samples may affect analytical accuracies when the rotating disk arc/spark is used for emission spectroscopy. The rate of sample delivery to the arc depends on the viscosity of the sample. Therefore, the standards used for calibration and the samples to be analyzed must have the same viscosity or inaccurate measurements will result.

d. Sensitivity

Detection limits of 1 ppm or less can be achieved for a majority of the 19 elements of interest with most of the candidate techniques. X-ray fluorescence is generally the least sensitive of the candidate techniques particularly for the low-atomic number elements. To determine sulfur by atomic spectroscopy, evacuated or purged optics are required since the prominent sulfur lines are located at wavelengths below 185 nm. For most elements the required dynamic ranges can be achieved by plasma emission and fluorescence techniques. However, only limited ranges are achieved with AA using hollow cathode lamps and with carbon furnace atomic emission.

e. Ranking and Elimination of Potential JOAP Techniques Using Performance Criteria

Based on the performance requirements established for a spectrometer to support JOAP through the year 2000, and based on discussions with JOAP personnel, contract monitors, and engine lubrication system specialists at P&W, the following were set as minimum performance standards for candidate JOAP instrumentation:

1. The instrumental technique must be capable of determining iron, aluminum, titanium, chromium, copper, magnesium, silver, nickel, and silicon
2. The technique must be capable of conducting an analysis in under 4 minutes. This interval includes sample preparation, introduction, and quantitation of the target elements
3. The technique must be capable of a precision of $\pm 10\%$ for analyte concentrations of 1 to 5 ppm and $\pm 5\%$ for all concentrations above 5 ppm as established by analyzing organometallic standards
4. The technique must be capable of analytical accuracy within 5% of the true value for organometallic standards
5. The technique must have a linear dynamic range from 1 to 100 ppm for all elements listed in criterion No. 1.

The above standards were set as the minimum performance requirements for the most critical mission of JOAP: the monitoring of aircraft engines. However, JOAP has other missions which require a greater dynamic range for the target elements and the inclusion of a greater number of elements. The instrument to be designated the optimum JOAP instrument would be the one meeting the above standards and the greatest number of the performance criteria listed below. A grading system was developed allocating credits for performance beyond the previously listed requirements. Credits were awarded as follows:

1. *Elements*

- Five credits were awarded for their ability to monitor the following elements (on a per element basis): molybdenum, sodium, zinc, lead, boron, tin, and barium.
- Two credits were awarded for their ability to monitor each of the following elements (on a per element basis): sulfur, phosphorus, and calcium.

2. *Simultaneous Analysis/Total Analysis Time*

- Twenty credits were awarded for an analysis time of under 1 minute.
- Ten credits were awarded for an analysis time of under 2 minutes.
- Five credits were awarded for an analysis time of under 3 minutes.

3. *Repeatability*

- Five credits were awarded for achieving precision of measurements within $\pm 5\%$ for 1-to-5-ppm concentrations.
- Five credits were awarded for achieving precision of measurements within $\pm 2.5\%$ for 5-to-100-ppm concentrations.

- Five credits were awarded for achieving precision of measurements within $\pm 2.5\%$ for 100-to-1000-ppm concentrations.

4. *Accuracy*

- Two credits were awarded for accuracy of measurements of $\pm 7.5\%$
- Two credits were awarded for accuracy of measurements of $\pm 1.0\%$.

5. *Sensitivity/Dynamic Range*

- As was previously shown in Table 1, a credit of 2 points per element will be allowed to achieve the full dynamic ranges for each of the various elements.

Upon evaluation of potential JOAP instrumentation approaches, the following techniques were found *not* to meet minimum performance requirements:

1. Hollow Cathode Source Flame Atomization

- Multielement analysis time exceeded 5 minutes.
- Detection limit for aluminum, titanium, silicon, molybdenum, and boron cannot be achieved with required sample dilution within the minimum precision requirements at 1-ppm concentrations.

2. Hollow Cathode Source Electrothermal Atomization

- Multielement analysis time exceeded 5 minutes.

3. Continuum Source Flame Atomization

- Detection limits for aluminum, titanium, silicon, molybdenum, and boron cannot be achieved with required sample dilution within the minimum precision requirements at 1-ppm concentrations.

4. ICP Excitation Source With Laser Ablation Sample Atomization and Graphite Braid Sample Introduction

- Minimum detection limits of 1 ppm cannot be achieved.

5. Laser Ablation Excitation Source with Direct Sampling

- Minimum detection limits of 1 ppm cannot be achieved.

6. X-Ray Excitation Source, Direct Sampling, and AF Spectroscopy

- Minimum detection limits for aluminum, magnesium, sodium, and boron of 1 ppm cannot be achieved.

7. X-Ray Excitation Source, Prefiltration of Sample Prior to Analysis, and AF Spectroscopy

- Minimum analysis time of 5 minutes cannot be achieved.

The ranking of these techniques are presented in this report with the results of the Analysis of Findings.

3. DESIGN REQUIREMENT EVALUATION

The design requirement evaluation for potential JOAP instrumentation was broken down into different areas and is presented as follows.

a. Sample Introduction

There are various techniques in sample transport and introduction used in AA, AE, AF, and other potential JOAP techniques. These include aerosol generation, laser ablation, high-voltage sparking, electrothermal, graphitic braid, and direct injection.

(1) *Pneumatic Nebulization*

Aerosol generation systems typically consist of a nebulizer, spray chamber, and a torch or burner excitation/atomization component. These sample introduction systems function well with homogeneous liquids, but may not quantitatively deliver representative fractions of heterogeneous liquids, such as suspensions of engine or transmission fragments in oil. There is a maximum size for particles of a given density which will pass through a nebulizer and spray chamber; above this size, particles are lost as a result of inertial impaction and gravitational settling. Even larger particles may clog the nebulizer. This is a problem particularly with fine bore concentric nebulizers used with many ICP's (Reference 14).

According to Stokes Law, gravitational settling velocities of particles are related to their size and density. The particle transportation limits for sample delivery systems can be evaluated empirically or calculated as shown in the following equation.

$$V_s = 4.5 \rho_p g r_p^2 / N$$

where:

- ρ_p = The density of the particles
- g = The gravitational constant
- r_p = The radius of the particle
- N = The viscosity of the nebulizer gas (argon)

The mean residence time, t , of particles in a spray chamber is determined by measuring the time it takes for a pulse of liquid aerosol to pass through it. The product $t \times V_s$ defines the distance through which a particle settles. This distance can be compared to the vertical dimensions of the chamber to derive a settling velocity for the particle which will be removed from the gas stream. Using the Stokes Law equation, the maximum size of particles of a given density that will just pass through the chamber can be calculated from this V_s value.

A second factor limiting the transport of particles is inertial impaction.

Impaction occurs when:

$$\rho_p r_p L = 4.5 N V_g$$

where:

L = The radius of curvature through which the particle must travel to avoid impaction

V_g = The velocity of the gas stream in which the particle is entrained

The region of a spray chamber with the smallest L/v(g) ratio will be the one which limits the size of the transported particles based on inertial impaction.

In an analysis of several spray chamber designs, Skogerboe and Olson demonstrated that the cutoff diameters for aqueous aerosols and particles of NaNO_3 and $\text{Pb}(\text{NO}_3)_2$ were three-to-six times smaller due to gravitational settling than to inertial impaction.

In contrast, Browner et al. (Reference 10) determined that, as a result of relatively high gas flow rates and extensive baffling in AA spray chambers, inertial impaction was more critical to aerosol loss. They also found that neither mechanism adequately predicted the low transport efficiencies and cutoff diameters of ICP sample introduction systems.

Additional losses can be induced by the turbulent mixing of aerosol and nebulizer gas within the spray chamber. Circumstantial evidence for this mechanism comes from the visual observation that aerosol deposition occurs throughout a spray chamber and not just on the bottom surface (as a result of gravitational settling) or at the end of the chamber opposite the nebulizer (as a result of inertial impaction). The fractional transport (T) of particles of diameter d through a tubular spray chamber is given by

$$T = \exp(-kd^1 L/Q)$$

where

k = A constant whose value is relative to the degree of turbulence

L = The length of the chamber

Q = The volumetric gas flowrate.

All three models predict that the transport of dense particles larger than a few microns will occur only when volumetric gas flow rates are relatively high. Unfortunately, the pneumatic nebulizers used with ICPs are designed to function efficiently at gas flow rates of only 0.5 to 0.8 liters per minute. Most ICP spray chambers contain baffles to limit the passage of large aerosols. The commercial DCP jet uses nebulizer gas flow rates of 4 to 5 liters per minute and a spray chamber of simple design. Not surprisingly, the DCP has been successfully used to quantitatively determine iron particles in oils up to 14 microns in diameter, while in the same study, an ICP was found to give less than nonquantitative results for particles greater than 7 microns in diameter (Reference 4).

Large particles, which do pass through the sample introduction systems and into an argon plasma, may still not contribute quantitatively to the analytical signal. During its flight through the central channel of the ICP discharge or toward the analytical zone of a DCP arc, a large particle may not be totally dissociated. This phenomenon has been documented in inverted ICPs in which large metal particles were allowed to enter the plasma by literally falling out of the spray chamber. Incandescent particles were observed in the region in which analytic emission normally occurs (Reference 17). Similarly, the zone of maximum AE produced by iron particles up to 28-micrometers in diameter was above the normal viewing zone and closer to the arc continuum of the three-electrode DCP (Reference 4). This pattern suggests that dislocation and excitation of these particles requires longer residence times and greater temperatures than may be provided by ICPs or DCPs.

(2) Rotating Disk Electrode

In addition to being an excitation source for emission spectroscopy, the rotating disk electrode (rotrode) represents a unique sample delivery technique. Studies of the particle transport capabilities of the rotating disk have revealed that large particles (5 to 10 μm or more in diameter) are not effectively vaporized and excited in the arc gap. This limitation may be the result of the particles settling in the sample container from which the portion analyzed is drawn, or it may be due to the lack of sufficient electrical power in the arc to vaporize particles larger than a few μm in diameter. Incomplete recoveries of metal particles suspended in low-viscosity oils may be due to settling in the sample container while suppressed emission from metal particles in high-viscosity oils is believed to be due to a thick layer of sample on the disk. If more arc power is consumed vaporizing the sample matrix, less is available for vaporizing analytic particles and emission intensities decrease (Reference 4).

(3) Direct Injection

A modification of the rotrode in which viscous samples are applied directly to an array of rotating graphite disks is under development at Spectro, Inc. (as discussed above). After deposition the samples are ashed and the residues are analyzed by arc/spark emission spectroscopy. The goal of this approach is to decrease the particle size dependency of the rotrode technique by delivering the sample direct to the surface of the electrode and to increase sensitivity by removing the organic matrix and concentrating the sample on the electrode surface. To reduce analysis time, a cylindrical electrode containing 10 disk-shaped lobes has been developed which allows for the deposition and ashing of up to 10 samples at a time. An automatic sample dispensing system is under development.

Atomic absorption spectrophotometry with electrothermal vaporization (ETV) has been shown to give quantitative results for particulate metals in oils (Reference 7). Unfortunately commercial AA systems can be used to determine only one or two elements at a time and so do not meet the rapid multielemental analysis requirements of the proposed JOAP instrument. However, ETV cells have recently been coupled to ICPs (References 18-38). This approach provides for simultaneous multielemental analyses with the particle-size independence of furnace AA. It also offers the advantage of isolating sample desolvation, ashing, vaporization and partial atomization in the furnace from atomization, excitation, and ionization in the ICP. More of the plasma's RF power is then available for the latter processes and the need to vaporize the solvent and particulate analytcs in the rapidly moving central channel of the ICP is eliminated. ETV/ICP has been shown to provide greater linear dynamic range than a graphite furnace AA. It should not be susceptible to many of the matrix problems encountered in AA since there is no requirement that a free atom population be reproducibly formed within the ETV cell during each atomization cycle.

A potential problem with electrothermal vaporization is the need to take a representative 10 to 20 μl aliquot of a used oil sample. The number density of wear-metal particles may be such that a larger volume will be required as noted above in the discussion of analytical accuracy. Sampling considerations may require the use of modified atomization cells, perhaps with removable sample boats upon which successive volumes of sample could be deposited, desolvated, and ashed.

Direct sample insertion into an argon plasma has been developed as an alternative way to use the power of the plasma to sequentially desolvate, ash, and vaporize samples. Usually milligram quantities of sample are introduced to the plasma in a graphite cup supported on a non-conducting rod. This assembly is inserted into the plasma torch or jet in place of the conventional aerosol delivery tube.

This approach was first described in 1979 (Reference 39). Since then various investigators have developed and applied the technique (References 40-46). Systems to automatically deliver the sample to the plasma have been developed (Reference 43) and improvements in sample holder design have been made (References 45-46). Automatic delivery has resulted in improved analytical precision: from 5-to-10% relative standard deviation (RSD) in emission intensity measurements with manual insertion to 2% with a microprocessor-controlled stepper motor to drive the sample insertion rod. Both precision and sensitivity are enhanced as the diameter of the graphite holder is decreased, thereby reducing its thermal mass and increasing the rate of sample vaporization (Reference 46). Precision is also improved by adding a lid to the sample compartment which has the effect of delaying sample vaporization until the sample holder has reached a higher temperature (Reference 45).

The temperatures of the sample holders inserted into ICPs vary between 1800 (Reference 46) and 3000°C (Reference 40). At these relatively low temperatures some elements, especially those that form refractory carbides, may not be completely vaporized. For the elements that are, absolute detection limits in the picogram range and calibration curves that are linear over 10^3 to 10^4 have been reported (Reference 39).

(4) Moving Graphite Braid

A DCP arc with a unique configuration that allows the direct delivery of desolvated sample to the plasma has recently been developed. This graphite filament plasma (GFP) gets its name from its anode, which consists of graphite fibers doubly woven into a braid approximately 2.5 mm in diameter. To remove contaminants, large batches of the filament are pyrolyzed in a halogen atmosphere during the manufacturing process. The braid may be additionally purified prior to analysis by passing it through the plasma arc as shown in Figure 2.

In the GFP, the filament is fed from a spool into graphite clips attached to a transport system which resembles a miniature conveyor belt. The belt, which is driven by a stepper motor, conveys the filament to positions where sample is first deposited using an automatic pipette. The sample residue is desolvated and then introduced into the plasma. As the sample is dispensed, low level heating, produced by applying a dc voltage across bracketing clips, may be used to control the spread of the sample along the filament.

After desolvation, the leading clip of the bracketing pair is positioned above a cathode assembly block. The block has a center orifice in which a thoriated tungsten electrode is positioned. This electrode serves as a cathode when the plasma arc is struck. Argon flows upward through the orifice at a rate of about 1 liter per minute.

To strike the arc, an automatic sequence is started in which argon flow turns on, the cathode is driven up through the assembly block, and 170 volts dc (open circuit) is applied

between the cathode and the clip above it. When the cathode contacts the clip and current flows between them, the cathode is withdrawn into the block. Electrical continuity between the electrodes is maintained through ionization of argon in the plasma arc. Once the arc is struck, the conveyor belt moves the clip away from the area of the block so that the filament, rather than the clip, serves as the anode. During the following analyte interval, the filament passes through the plasma and analyte deposited on it is vaporized and excited by the plasma.

(5) Electrical Discharge/Argon Plasma

The use of electrical discharges as vaporization and aerosol generation devices for argon plasmas has met with some success particularly for analyses of conductive solids (References 47, 49-52). At least one commercial spark source/ICP is available. The sample usually consists of a solid machined into an appropriate shape so that it may become one of the electrodes of the discharge. Erosion of the electrode produces a highly dispersed aerosol of sample fragments which are swept into the plasma source by a stream of argon gas.

In a variation of the widely used approach in which tandem discharges are coupled together (one for sampling and one for vaporization and excitation), Farnsworth and Hieftje (Reference 53) modified an ICP torch so that a portion of the incident RF power was directed downward toward a grounded conductive plate. This secondary discharge had the form of a thin arc with a power of 100 to 200 watts. Samples placed on the plate were sputtered off by the arc and were swept into the ICP. Initial results were only semiquantitative.

More reliable results were obtained using a dc micro arc in which 0.5 to 2.0 μ l of liquid samples were placed on a tungsten loop. After a desolvation step the loop became the cathode of a 100-watt arc. Sample sputtered from the loop was carried into an ICP. Absolute detection limits ranging from 0.06 Picograms (pg) for Ca to 280 pg for Pb and a precision of 5% RSD were reported (Reference 51).

(6) Laser Vaporization/Argon Plasma

A laser is an attractive, although expensive, alternative to electrical discharges for vaporizing oil samples because neither the sample or its residue need be conductive nor must the sample be applied to a conductive metal substrate. Impingement of the laser beam results in vaporization and ablation of the sample; the latter process gives a dispersed aerosol much of which is small enough to be entrained in a stream of argon gas flowing into the sample delivery tube of an ICP.

Ruby lasers in both normal and Q-switched modes have been used to ablate and vaporize metal and geological samples (References 53-55). Cells similar to those for ETV/ICP are used to transport sample aerosol and vapor to the ICP. The precision of emission intensity measurements is in the 3-to-10%-RSD range with 5% being a typical value provided the sample is homogeneous. Given the potentially heterogeneous distribution of particulate-wear debris in used oils, considerable short term variability in laser/ICP measurements is anticipated. Reliable quantitative results may require complete destruction of the sample target. Absolute detection limits are in the picogram range (Reference 56), but calibration curves are sometimes linear only over 1-to-2 orders of magnitude (Reference 55).

b. Simple Operation

The ease of operation for a candidate spectrometer is defined by the level of automation and computer control incorporated into the instrument's design. Many atomic absorption and emission systems have auto-sampling and/or auto-dilution accessories which can be programmed either individually or through a system controller. The best documented auto-dilution/auto-

sampling technique for use with viscous liquids is the automatic injection dilution system (AIDS) developed by Baird Corporation (Reference 57).

No automatic sampling ability has been developed for the rotrode which requires that both of the electrodes and the sample carrier be manually replaced between runs. Prior to each analysis, the counter electrode must be sharpened and the arc gap reset to achieve an arc of reproducible geometry and power. This level of sample and source manipulation has deterred automation of the analytical cycle.

Most of the candidate techniques are commercially available in configurations that allow for automatic generation and updating of analytical signal versus concentration curves. Usually a dedicated microcomputer is programmed with calibration subroutines that allow the instrument to be calibrated and recalibrated at selected intervals by signaling the sample changer to deliver the appropriate standard solutions to the source. Calibration curves are automatically fitted to the signals produced by the standard solutions using linear or nonlinear regression algorithms. Popular software features include the flagging of unusual values for the calibration curve, parameters based on previously calculated values, and the flagging of samples which produce signals outside the range of those produced by the standard solutions.

Some of the above features are available on the FAS-2C, Baird's current commercial version of the A/E 35U-3, but none are available on the military version. In the latter configuration, manual adjustment is required for each analytical channel during calibration. The calibration procedure can take hours of manual effort to record and calculate calibration data, adjust the gain for each channel, make any needed adjustments for burn time, and adjust the arc/spark generator system. These steps must be carried out in the proper sequence and, if an error is made during one step of the calibration, the entire procedure must be repeated from the beginning.

Automated data entry is a common standard feature of most spectrometric systems. This is another software function in which the operator is prompted to identify each sample and to select the elements to be determined. A data set is created from the results obtained with the sample and from whatever descriptors were entered by the operator. These data can then be displayed immediately through a printer or a cathode ray tube (CRT) output device and/or they can be compared with the results for previous samples for trend analysis. These features are available as options for the FAS-2C. The standard readout system requires manual interrogation and recording of the analytical results, as with the A/E35U-3 unless an optional printer and driver board have been added to the unit or unless a computer is integrated into the system.

Other operator conveniences, such as a level of internal diagnosis and performance assessment, are included in the software which supports most new spectroscopic systems. Most optical spectrometers include an internal optical reference to check on optical alignment.

c. Durability/Maintainability/Reliability/Simplicity of Design/Environmental Restraints

JOAP instruments used in the field and at some bases will be subjected to occasional relocation. Ruggedness and durability factors were considered in this evaluation. The modular approach offered by some potential JOAP units allows for easy disassembly, transport, and maintenance and sets the stage for multiple part sourcing. Most of these spectrometers consist of the following modules:

- Sample delivery
- Atomization/excitation cell
- Spectrometer
- Signal acquisition and data reduction.

The sample delivery module includes an automatic sample changer and, in the optimal configuration, a device to provide for any needed sample pretreatment, such as an automatic dilutor. The atomization/excitation cell module is online with the sample delivery module. Typically, these cells rely on direct or aerosol atomization using an energy source to atomize and excite the analytes to a suitable state for quantification by emission or absorption techniques.

The most reliable and durable spectrometers are those with the fewest moving components and with the most rugged mounts. On this basis optical spectrometers operating in the rapid sequential mode are less desirable than those providing sequential multielemental analysis, and those that achieve wavelength selection by precisely moving the dispersing element are the least desirable of all. Rugged simultaneous spectrometers in which optical adjustment is achieved automatically by slightly moving the entrance slit or exit slit array are available from several manufacturers. Most of them are based on an auto-focusing grating used in the first or second order of diffraction and incorporated in a Paschen-Runge optical mount. One of them uses an immobilized echelle grating and quartz prism to achieve comparable durability but with considerably higher resolution. Both designs can be made more durable by incorporating a shock-absorbing system that would be activated at times when the instrument was to be moved.

The system control and data reduction modules offered with many systems consist of internal microprocessors or external dedicated computers. The dedicated computer is the preferred approach since it is likely to be more easily upgraded by revised software or hardware.

Temperature and humidity are the environmental constraints of most concern. According to the JOAP Laboratory Manual, "temperature and humidity controls should be exercised in any laboratory to $75 \pm 3^\circ\text{F}$ and less than 50% relative humidity" (Reference 2). However, as defined by the program objective, the desired operating ranges for JOAP instruments are 0-to-90% relative humidity and 10 to 43°C (50 to 110°F). To minimize the possible effects of temperature and relative humidity on JOAP instrumentation, it was necessary to evaluate each of the modules separately. Optical and data modules are most sensitive to temperature and humidity. Humidity affects the optics and data modules by providing a source of water condensation. Moisture directly affects the performance of the optics and electronics and promotes the corrosion of optical coatings and electronic components. Two approaches that could be used in any potential instrumentation are: (1) sealing the optical and data modules, and (2) incorporating the use of coatings or moisture-resistant materials.

Temperature directly affects the performance of the optical and data modules. The JOAP Laboratory Manual indicates that with the A/E35U-3 "frequent restandardization is required where significant changes of 10°F or more occur or when rapid changes in temperature occur" (Reference 2). In the optical module, thermal expansion or contraction in or around the grating slits or photomultipliers can alter wavelength alignment and so diminish analytical performance. A JOAP spectrometer should incorporate a temperature stabilization system including, for example, heating elements and associated thermostats. Some of the commercial optical spectrometers have such devices.

The data module is also sensitive to operating temperature since the resistance of some electronic components and the life expectancy of others are a function of temperature. Electronic systems generate heat during use, so most are equipped with air circulation and cooling systems. The capacities of these systems may need to be expanded to accommodate extended operation in the upper end of the specified temperature range.

The reliability of an instrument should be a function of the simplicity of its design. The designs of the candidate instruments vary considerably. Some, such as energy-dispersive x-ray spectrometers and graphite furnace atomic emission spectrometers are compact and include few modules and few moving parts. At the other extreme are the ICP/mass spectrometers which are

much larger than the present rotrode AE spectrometer and which incorporate multistage vacuum pumps with heavy duty use cycles.

Among the argon plasma sources, the DCPs feature the simplest power supplies and power transfer circuits. RF ICPs are inherently more complex, and there are different degrees of complexity among ICPs from different manufacturers. Most rely on an impedance matching network to control the power of the plasma. However, at least two manufacturers build directly-coupled, free-running ICPs in which oscillator power and, because of the direct coupling, the power of the plasma is controlled by monitoring oscillator plate current. This approach allows for simplified and more compact power supplies and source modules.

d. Hazardous Gases/Consumables

Each method was evaluated for gas consumption. AE spectrometers which use a plasma source require argon gas to sustain the plasma and, in the ICP, to cool the walls of the outer quartz tube of the torch. The 3-electrode DCP consumes about 8 liters (l) of argon per minute; most ICPs need about 15 to 20 l.

Several approaches have been taken to reduce the high rate of argon consumption in ICPs. These include redesigning the torch to provide more efficient cooling and use of alternate coolants. Miniaturized versions of the plasma torches in common use have been shown to operate at reduced RF power levels and much lower gas flowrates (References 58-60). More recently, Rezaaikyaan et al. (Reference 61) showed that the entire torch did not need to be miniaturized to operate more efficiently, only several key dimensions had to be reduced: (1) the annular spacing between the middle (tulip-shaped) and outer tubes (from 1.0 to 0.5 mm), (2) the inner diameter of the aerosol injection tube (from 2.0 to 0.75 mm), and (3) the diameter of the coolant inlet port (4.0 to 1.0 mm). The result was a torch requiring 500 watts (W) of RF power and 10 l per minute of argon for ignition. The plasma could be sustained with only 3-to-5 l per minute of argon and 100 to 200 W of power.

Montaser et al. (Reference 62) evaluated the analytical performance of this low-flow torch design and found its performance to be comparable to conventional ICP torches. It was observed, however, that the precision of emission intensity measurements was somewhat poorer, with RSDs typically in the 3% range. Lower electron densities were observed in the analytical zone of the torch indicating that this plasma would be more susceptible to ionization-related matrix effects.

Other approaches to reduce argon consumption have included cooling the plasma torch externally with water or compressed air (References 63-66). Water-cooled designs may still require 4 l per minute of coolant argon flow and 1.5 kW of RF power to maximize sensitivity. Much of this power is dissipated through the outer tube to keep its skin temperature at 373°K. De Galen and co-workers used compressed air at 62 l per minute as a plasma coolant (References 64-66). This allowed the skin of the outer quartz tube to reach approximately 1000°K. Under these conditions, a stable plasma was formed in a 16-mm inner diameter (ID) tube using 400 W of RF power and 1 l per minute of argon flow. The emission intensity measurements made over a 3-hour period had a precision of 1.5% RSD. These measurements were made using a 0.48-mm ID injector tip and a carrier argon flow of only 120 milliliters (ml) per minute. To analyze organics, the carrier flow was reduced to 75 ml per minute and the power was adjusted to 300 watts. Calibration curves were linear over five orders of magnitude. Users of both water and aircooled systems have observed occasional cracking of the outer tube at shutdown, apparently as a result of rapid cooling of torch components.

Other types of instrumentation have unique requirements for consumables. Some solid-state detectors used in x-ray spectroscopy require liquid nitrogen. Small amounts of oxygen are

added to the sample carrier argon in the low power ICP used in atomic solvent vapor. Several techniques require small amounts (1 l per minute or less) of inert gas: graphite furnace AA and AE and the graphite filament plasma. The rotrode arc requires no inert gas.

Organic solvents may be needed to dilute oil samples thereby reducing their viscosity or to clean the sample boats used with the rotrode. For most techniques requiring sample dilution, kerosene, xylene, or toluene may be used. These solvents or Freon may be used to clean aluminum sample boats. The JOAP Technical Support Center has recommended the use of disposable sample boats to eliminate this cleaning requirement.

Many high-temperature sources, including graphite furnaces and argon plasmas, require external cooling. Where water supplies are limited, this can often be accomplished most economically by recirculating liquid coolant through an air heat exchanger.

e. Safety

Each spectrometric technique was evaluated on its basis of the safety features commonly incorporated into commercially available instruments. For atomic spectroscopy systems these features included interlocks to shut off power to high-temperature sources in the event of over heating or loss of coolant flow. Protection from the intense UV radiation and electrical fields of the argon plasmas and arc/spark sources included interlocks on access panels and welder's glass in the viewing ports. Only one of the candidate techniques, flame AA, used explosive gas mixtures.

f. Matrix Effects

Four types of matrix-related interferences were considered: spectral, chemical, viscosity-related, and particle-size dependent. Freedom from spectral interferences was evaluated using the performance of the A/E35U-3 system as a reference point. The optical system of the A/E35U-3 uses the optical layout found in most polychromators for emission spectroscopy. The resolving power of these instruments is closely matched with reciprocal linear dispersion values of about 0.5 nm/mm in the first order for almost all of them. Exceptions to this rule are the echelle grating instruments built by Spectrametrics and Leeman Labs. The resolving power of these instruments is approximately a factor of 5 to 10 greater in the 200 to 400 nm wavelength region.

The severity of spectral interferences is also a function of the complexity of the background emission spectrum of the excitation source. Because of the inert argon atmosphere and the relatively long residence times of sample aerosols and vapors in the central channel of an ICP, there is little molecular band emission and the background spectrum of this source is simpler than that produced by atmospheric arcs and sparks and by the DCP. The spectrum of the excitation zone of the DCP contains more molecular band emission than does that of the ICP because of air entrainment and because of incomplete atomization of molecular fragments. When organic samples are introduced to the DCP, intense band emission is observed due to the presence of C, CN, and NO species (Reference 7).

Line source AA spectrophotometry is less susceptible to spectral interferences than any of the AE techniques because of the narrow widths of the emission lines produced by hollow cathode lamps and electrodeless discharge lamps, the two most popular sources of radiation in AA instruments. Continuum source AA requires a high resolution spectrometer to avoid spectral interferences. For this reason the SIMAAC system designed at the University of Maryland includes an echelle grating polychromator.

Freedom from chemical interference was evaluated by comparison with flame atomic absorption spectrophotometry. Among the high-temperature sources used in atomic spectroscopy, the argon ICP enjoys the greatest freedom from chemical interferences. Several factors contribute to this performance: (1) sample aerosol and vapor passes through the plasma and not around it as with the DCP of the 3-electrode jet, (2) the temperature of the central channel of the ICP is 6000K or about twice as hot as the hottest combustion flame, (3) the residence time of analytic species is longer than in the DCP or in dc arcs so the atomization process is more complete, and (4) the atmosphere in the induction and observation zones of the argon ICP is chemically inert so there is much less chance of recombination reactions such as oxide formation which could affect atomic emission intensities.

The maximum temperatures of the graphite furnaces used in AA and AE techniques inert are in the 3000 to 3300°K range which brackets the temperature of a nitrous oxide/acetylene flame. Consequently, electrothermal AA and AE techniques suffer from some of the chemical interferences encountered in flames. Chemical interferences which are unique to graphite furnace techniques include carbide formation, variable rates of atomization due to the presence of inorganic sample residues, and recombination reactions in the furnace. Carbide formation has been greatly reduced with the use of impervious, chemically-inert coatings of the graphite heating element. The other two effects have been reduced with the development of the L'vov platform and modified heating element geometries which promote more uniform and rapid atomization of sample residue into an atmosphere at a higher temperature than the element itself (Reference 38).

Changes in analytical sensitivity caused by variable sample viscosity have been well documented for the rotrode source as discussed in Section III.3.a. One solution to this problem is to dilute oil samples with a less viscous solvent. This approach is used in those atomic spectroscopy techniques incorporating a pneumatic nebulizer in the sample introduction system. Sample delivery in *direct methods of analysis* usually consists of injection with a micropipet. Expulsion of viscous samples from the pipet tip by air displacement may not be quantitative. One solution to this problem is to use a positive displacement pipet in which a solid, usually Teflon, plunger draws up and expels the sample.

A detailed discussion of the particle size dependencies of the candidate techniques is contained in Section III.3.a. which addresses different modes of sample introduction. The results of technique comparisons made by analyzing used oil samples indicate that particle-size-independent analyses can only be achieved by those methods which incorporate direct sample injection, such as graphite furnace AA. When samples are diluted and then sprayed into a high-temperature atomization/excitation cell, as in plasma emission and flame AA, analytical results for particulate wear metals do not appear to be "quantitative" (Reference 5). The results obtained with two other techniques incorporating direct sample introduction, the graphite filament plasma and the ashing rotrode, are presented in the section on Verification and Testing.

g. Electronics

The electronics of commercial configurations of the candidate instrumental techniques were evaluated in terms of the degree to which their design and components represent the state of the art. Many of the commercial instruments feature computer control of most operating functions and so most techniques were rated equally. The rotrode AE and the DCP were rated lower than the rest. The model rotrode system was the FAS-2C which, although it features major circuitry design changes from its 1969-vintage predecessor, still incorporates many of the same approaches to signal acquisition and data reduction. Features which are standard on most spectrometers, such as an automatic printer providing a hardcopy of the analytical results, are options on the FAS-2C. Others such as menu-driven software to guide the operator are not available at all.

The DCP was not rated highly for some of the same reasons as the FAS-2C. Functionally the commercial multichannel DCP system, the Spectraspan V, is the same as its predecessor introduced in the early 1970s. More options, such as dynamic background correction, are now available, but the standard features and operations, including calibration and wavelength alignment, are unchanged.

h. Data Station

All the candidate techniques are available commercially with micro- or mini-computer-based work stations. In many systems these computers are an integral part of spectrometer design and function. For some others, including the FAS-2C and the Spectraspan V, the work station is an optional component. Almost all feature expandable memory, data storage, communication ports, CRT with graphics, graphics printer, diagnostic software, and trend analysis capabilities.

i. Ranking of Potential JOAP Techniques by Design Evaluation Criteria

Based upon the initial program guidelines and discussions with JOAP personnel, the contract monitors, and technical experts, the following design rating criteria were used:

Minimum Design Requirements

- The instrumentation must operate within following power parameters: 110/220 volts alternating current (vac) and 50/60 hertz (Hz), and stable under power source fluctuations of $\pm 20\%$ for 110 vac and $\pm 10\%$ for 220 vac.
- The instrumentation must operate within a laboratory environment as defined in the *JOAP Laboratory Manual* ($75 \pm 3^\circ\text{F}$ and less than 50% relative humidity).
- Instrumentation restandardization is required no more frequently than once per 8-hour shift.
- The instrumentation must be capable of using JOAP Conostan Standards for calibration.

Desired Design Criteria

Credits were awarded as follows to achieve desirable design criteria:

1. Sample introduction systems

- Ten credits were awarded for nondilution of samples and standards prior to analysis.
- Ten credits were awarded for the elimination of graphite electrode requirement.
- Ten credits were awarded for an automatic sample agitation mechanism in system.
- Ten credits were awarded for the ability to atomize and excite particles in the zone of analysis.

- Ten credits were awarded for an automatic sample dilution system.
- Five credits were awarded for the capability to analyze particles to 5 microns in size.

2. Simplistic Operation/Calibration

- Ten credits were awarded for an automated sample introduction systems.
- Ten credits were awarded for an automated optical alignment and electronics systems.
- Ten credits were awarded for an automated analysis routine which prompts the operator for necessary sample and standard data, either through a CRT display or printout.
- Ten credits were awarded for an automated calibration routine which prompts the operator through any required calibration routine.
- Ten credits were awarded for an automated sample "flagging" routine which alerts an operator if the JOAP results indicate abnormal wear since data on JOAP analysis is accumulated on every engine.
- Ten credits were awarded for an automated internal diagnostic system which notifies the operator if any components are not operating properly.

3. Durability/Reliability/Maintainability

- One credit was awarded for a reduction of 10% in total instrumentation volume as compared to the present rotrode system.
- One credit was awarded for a reduction of 10% in total instrumentation weight as compared to the present rotrode system.
- Ten credits were awarded to candidate instrumentation that were specifically ruggedized for military applications.
- Ten credits were awarded for modular construction for easy assembly/disassembly of critical components, both for ease of transport and maintenance.

4. Environmental Constraints

- Ten credits will be awarded for each 25% increase in relative humidity with the 0-to-50% relative humidity as a baseline.

- Ten credits will be awarded for each 10°F increase in operating temperature range starting with a baseline of 70 to 80 F up to 50 to 110°F.

5. Hazardous Gases/Consumables

- Five credits were awarded for analysis without replacement of electrodes or furnace tubes on a routine basis.
- Twenty credits were awarded to operate the instrumentation without any consumable gas.
- Ten credits were awarded to operate the instrumentation without solvents (for dilution).
- Ten credits were awarded to operate the instrumentation without graphite electrodes.
- Ten credits were awarded for operation without cooling water.

6. Safety

- Ten credits were awarded for the incorporation of safety interlocks to control the flow of combustible gas, the ignition of a plasma source in a nonshielded mode, and other critical parameters directly or indirectly affecting the health of the operator.
- Ten credits were awarded for the ability not to use **hazardous gases**.
- Ten credits were awarded for not using or requiring dilution of samples with organic solvents.

7. Matrix Effects

- Ten credits were awarded for dramatic improvement of freedom from spectral interferences as compared to the present A/E35U-3 system.
- Ten credits were awarded for dramatic improvement of freedom from chemical interferences as compared to the present JOAP AA technique.
- Ten credits were awarded for the ability to compensate for, in an analytically reproducible manner, differences in sample viscosities.
- Ten credits will be awarded to any instrumentation that shows a dramatic improvement over the A/E35U-3 system in particle-size independency of analysis.

8. Simplicity of Instrumentation Design

The consensus of the participants in the Analysis of Findings conference awarded 0-to-20 credits for simplicity of instrumentation design. This was an objective comparative rating based upon experience with analytical instrumentation and included the following factors: durability, reliability, maintainability, environment, and weight.

9. State-of-the-Art Technology

- Ten credits were awarded for solid-state electronics in the form of printed circuit boards and integrated circuit/chip technology.
- Ten credits were awarded for modular arrangement of electronic components for ease of maintenance and repair.

10. Data Station

- Ten credits will be awarded for the capacity for expandable memory.
- Ten credits will be awarded for automatic data storage for subsequent reformat.
- Ten credits will be awarded for the provision for additional communication ports.
- Ten credits will be awarded for a printer with graphics capability.
- Ten credits will be awarded for a large CRT with graphics capability.
- Ten credits will be awarded for software for system diagnostics.
- Ten credits will be awarded for software for instrumentation drift compensation.
- Ten credits will be awarded for JOAP interface capacity.
- Ten credits will be awarded for providing data consistent with the present JOAP data.

The results of the design evaluation are illustrated by data presented in the Analysis of Findings results.

4. ANALYSIS OF FINDINGS

a. Types of JOAP Instrumentation

Instrumentation that could achieve minimum performance and design requirements were considered to be candidate JOAP instrumentation. These include AE, AA, and other types of instrumentation.

(1) AE Instrumentation

AE instrumentation includes:

- ICP with sample dilution and aerosol nebulization. This type of system was evaluated with auto dilution and auto sampling accessories
- ICP with graphite furnace and auto-sampling accessory
- DCP with auto-sampling, auto-dilution, and aerosol nebulization
- Graphite filament DCP with auto-sampling
- A new and improved rotrode system with a computer option
- Graphite furnace AE with auto-sampling capabilities.

(2) AA Instrumentation

- SIMAAC with graphite furnace and auto-sampling.

(3) All Other Instrumentation

Other JOAP instrumentation includes:

- ICP AF with autodilution, auto-sampling, and aerosol nebulization
- ICP mass spectrometer with auto-sampling, auto-dilution, and aerosol nebulization.

Figures 3 through 9 are plots of the ratings for each technique for their performance and design criteria evaluation. Weighting values have also been introduced. These values were determined by discussions between the contract monitor and program manager to reflect the relative importance of the various design and performance requirements for an optimum JOAP instrument. The values which are multiplied against the total ratings for each factor, are shown in Table 2. A simplistic generic evaluation of all methods can be found in Appendix A.

TABLE 2.
WEIGHTING VALUES FOR JOAP INSTRUMENTATION

| <i>Factor</i> | <i>Weighting Value</i> |
|---|------------------------|
| All performance factors | 10 |
| Durability, reliability, maintainability, environmental, and simplicity of design | 9 |
| Simplistic operation | 8 |
| Data station capability | 7 |
| All other factors | 5 |

The total rating for each technique is presented in Figure 10. As defined by the Analysis of Findings, the ICP-AE technique was the optimum JOAP approach.

b. Cost Analysis

Based upon the input of JOAP personnel, a cost analysis was performed using the following assumptions:

1. The present JOAP instrumentation must be replaced either with an updated version of the A/E35U-3 or the optimum ICP system.
2. The unit price for each proposed instrument must reflect a 19-element unit including all available automation accessories.
3. Other assumptions include:
 - A life cycle span of 12 years
 - A one-shift operation
 - An average work load of 300 samples a day, 250 days per year
 - An initial purchase of 200 units
 - A potential trade-in allowance toward a modernized version of the A/E35U-3
 - No incorporation of volume discounts
 - A \$11,400 per year average manpower cost (based upon E1-E4 basic pay and allowances)
 - The same maintenance and training costs
 - 10% of initial total unit purchase cost for spare parts
 - Identical JOAP manual revision costs.

The following costs were identified in this study:

1. Cost per sample based upon use of consumables
 - \$0.38 per sample using the rotrode
 - \$0.10 per sample using the ICP with argon tanks (this can be reduced to \$0.05 cents per sample if a liquid argon tank is used).
2. Unit cost
 - \$109,657 - \$19,500 (trade-in of A/E35U-3) = \$90,157 for a 19-element advanced type of A/E35U-3 with a computer system. This does not include a vacuum system required for sulfur analysis.

- The following are quoted prices for a 19-element simultaneous ICP with auto-dilution and auto-sampling. This does not include a vacuum system required for sulfur analysis:

\$ 83,005 Manufacturer A

\$ 88,160 Manufacturer B

\$ 70,710 Manufacturer C

\$ 96,620.00 Manufacturer D

\$156,750.00 Manufacturer E -- This price does include a vacuum system. (For other instruments, the upgrade to vacuum is anywhere from \$3,600 to \$10,000 in addition to the price quoted.)

\$ 55,000.00 Manufacturer F -- 18 elements with no sulfur channel and no vacuum system.

The typical multiple unit purchase discount ranges are stated in Table 3.

TABLE 3.
MULTIPLE UNIT PURCHASE DISCOUNTS

| <i>No. of Units</i> | <i>Discount Range (%)</i> |
|---------------------|---------------------------|
| 1 to 24 | 0.0 to 8.0 |
| 50 to 99 | 10.0 to 20.0 |
| 25 to 49 | 8.0 to 12.0 |
| 100 to 200 | 10.0 to 20.0 |

The typical delivery for all defined quantities of systems ranges from 30 days to 6 months after receipt of order. Typically, transportation, installation, and training costs are included with the instrument. System warranties range from 3 months to 1 year after installation or delivery.

c. Manpower Determination

As defined in the JOAP Laboratory Manual, the number of full-time personnel required for spectrometric analysis may be computed with the following formula (assuming an A/E 35U-3 spectrometer):

$$P = \frac{W}{1000} \text{ with automatic recording}$$

$$P = \frac{W}{865} \text{ with manual recording}$$

Where:

- P = Number of full-time personnel required
- W = Estimated work load in samples per month.

Using this formula, and with the assumption that 300 samples a day, 20 days each month are run, $W = 6000$ samples a month. This means six full-time personnel with automatic reading and seven full-time personnel with manual data entry would be required. In addition, where separate keypunching is required for data reduction, the manual calls out one additional person per 6000 samples per month, giving a total of seven or eight persons, respectively.

Based upon input from various JOAP personnel, the incorporation of the new advanced A/E35U-3 with computer option could reduce the number of personnel required for the assumed sample load to three or four people. According to the data, as well as literature from manufacturers of analytical instrumentation, this sample load can be readily achieved by one operator on an ICP-AE system. At a technical presentation by a manufacturer of ICP instrumentation, at the JOAP International Symposium, held on the 17th and 18th of May 1983, an effective labor of 1.5 hours was defined based upon 250 samples per day using an ICP/AIDS system, with a required operator skill level equivalent to that required for the A/E35U-3.

d. Cost Benefit Analysis

Using all of the data and assumptions defined previously in the Cost Analysis discussion, the projections of life cycle cost differences between the upgraded rotrode A/E35U-3 and the ICP-AE systems are as follows:

Initial Unit Purchase Costs

- The total cost for 200 units of the upgraded rotrode A/E 35U-3 system is \$18,440,900.
- Using the average price of an ICP-AE system, 200 units at \$91,708 each cost a total of \$18,341,600.

Initial spare parts inventory cost

- 10% level of initial unit purchase total cost for an upgraded rotrode is \$1,844,090.
- 10% level of initial unit purchase total cost for ICP AE is \$1,834,150.

Manpower costs over life cycle of the instrument

- With sample load of 6000 per month, the upgraded retrode A/E35U-3 system requires three people assuming that the FASCOMP feature will cut manpower requirements by more than 50% over the present A/E35U-3 system. Automatic recording should do away with key punching requirements for data entry. The manpower costs are determined by the following formula: $p \times c \times s \times l = t$, where p = number of people per system, c = cost per person per year, s = number of systems, l = the life expectancy of the system, and t = total manpower cost over life cycle. For this instrument, $t = 3 \times \$11,400 \times 200 \times 12 = \$82,080,000$.

- With a sample load of 6000 a month, an ICP-AE requires one person. For this instrument, $t = 1 \times \$11,400 \times 200 \times 12 = \$27,360,000$.
- With a sample load of 6000 a month, using the JOAP guidelines, the manpower cost for running the A/E35U-3 should be $7.5 \times \$11,400 \times 179 \times 12$ (assuming half the systems have automatic recording) = \$183,654,000.

Cost per sample for consumables

- For the updated rotrode system, given 300 samples per day, 250 operational days per year and a cost per sample of \$0.38 for 12 years for 200 units, the cost is \$68,400,000. This cost should be identical to retaining the A/E35U-3 for the next 12 years.
- For the ICP-AE given 300 samples per day, 250 operational days per year and a cost per sample of \$0.10 for 12 years for 200 units, the cost is \$18,000,000. An additional \$9,000,000 could be saved through the use of liquid nitrogen in bulk tanks.

Total of life cycle costs

- For the updated rotrode, the cost is \$170,760,000.
- For the ICP, the cost is \$ 65,535,650.
- For retaining the A/E35U-3, the cost is \$252,050,000.

The level of funding for maintenance, training and other cost factors not scrutinized intensively in this report, should be about the same as currently experienced, based upon the input from JOAP managers. An exception would be the A/E 35U-3, which, due to its age and the lack of spare parts, will be subjected to ever-rising maintenance costs.

Figure 11 shows a visual comparison for the life-cycle costs of the various options as presented.

5 VERIFICATION TESTING

a. Candidate Instrumentation Evaluated

Section 4, Analysis of Findings, identified plasma emission spectroscopy as the technique best suited to JOAP (as shown in Table 4.). The excitation source best meeting most of the performance criteria including precision, sensitivity, freedom from chemical interferences, linearity of response, stability, and rapid analysis time was inductively-coupled plasma atomic emission (ICP-AE). This evaluation assumed the plasma would be coupled to a multichannel emission spectrometer and would have a conventional sample introduction system. Such instruments are available from at least seven American manufacturers: Allied Analytical

Systems. ARL, Baird Corporation, Beckman, Labtest, Leeman Labs and PT Analytical, and from several foreign instrument builders.

TABLE 4.
WORKSHEET OF DESIGN AND PERFORMANCE CRITERIA

| Criteria | Potential JOAP Instrumental Techniques | | | | | | | | |
|---|--|-----|------|-----|-------|-----|--------|----|-------|
| | ICP | DCP | CFAE | RDE | CFICP | GFP | SIMAAC | AF | ICPMS |
| <i>Performance</i> | | | | | | | | | |
| 1. All elements | 41 | 39 | 27 | 39 | 41 | 39 | 39 | 15 | 41 |
| 2. Analysis time | 20 | 20 | 10 | 10 | 10 | 10 | 10 | 20 | 20 |
| 3. Precision | 15 | 15 | 10 | 5 | 10 | 5 | 5 | 15 | 15 |
| 4. Accuracy | 4 | 4 | 2 | 0 | 2 | 2 | 2 | 2 | 4 |
| 5. Dynamic Range | 38 | 34 | 12 | 34 | 38 | 34 | 36 | 4 | 38 |
| Subtotals | 118 | 112 | 61 | 88 | 101 | 90 | 97 | 58 | 118 |
| <i>Design</i> | | | | | | | | | |
| <i>Sample Introduction</i> | | | | | | | | | |
| 1. Non-dilution | 0 | 0 | 10 | 10 | 10 | 10 | 10 | 0 | 0 |
| 2. No Electrodes replacement per sample | 10 | 10 | 10 | 0 | 10 | 10 | 10 | 10 | 10 |
| 3. Sample agitation | 10 | 10 | 0 | 0 | 0 | 0 | 0 | 10 | 10 |
| 4. Particulate Capability | 0 | 5 | 10 | 5 | 10 | 10 | 10 | 0 | 0 |
| 5. Auto-Dilution | 10 | 10 | 10 | 0 | 10 | 10 | 10 | 10 | 10 |
| Subtotals | 30 | 35 | 40 | 15 | 40 | 40 | 40 | 30 | 30 |
| <i>Simple Operation</i> | | | | | | | | | |
| 1. Auto-dilution | 10 | 10 | 10 | 0 | 10 | 10 | 10 | 10 | 10 |
| 2. Auto-alignment | 10 | 0 | 0 | 0 | 10 | 10 | 10 | 0 | 10 |
| 3. Auto-analysis | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| 4. Auto-calibration | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| 5. Flagging of unusual data | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| 6. Internal Diagnostics | 10 | 0 | 0 | 0 | 10 | 10 | 0 | 0 | 10 |
| Subtotals | 60 | 40 | 40 | 30 | 60 | 60 | 50 | 40 | 60 |
| <i>Durability/Reliability/Maintainability</i> | | | | | | | | | |
| 1. Modular Construction | 10 | 10 | 10 | 0 | 10 | 10 | 10 | 10 | 10 |
| 2. Reduced Size | 2 | 3 | 3 | 0 | 2 | 3 | 3 | 3 | 0 |
| 3. Reduced Weight | 6 | 7 | 7 | 0 | 5 | 7 | 7 | 7 | 0 |
| 4. Ruggedness | 10 | 0 | 10 | 10 | 10 | 10 | 0 | 10 | 0 |
| 5. Environmental Constraints | 50 | 50 | 50 | 50 | 50 | 50 | 50 | 50 | 0 |
| 6. Simplicity of Design | 12 | 15 | 20 | 13 | 6 | 13 | 18 | 10 | 0 |
| Subtotals | 90 | 85 | 100 | 73 | 83 | 83 | 88 | 90 | 10 |
| <i>Hazardous Gases/Consumables/Safety</i> | | | | | | | | | |
| 1. No Gas Consumption | 0 | 0 | 0 | 20 | 0 | 0 | 0 | 0 | 0 |
| 2. No Solvents | 0 | 0 | 10 | 10 | 10 | 10 | 10 | 0 | 0 |
| 3. No Cooling Water | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 4. No Graphitic Consumables | 5 | 0 | 0 | 0 | 0 | 0 | 0 | 5 | 5 |
| 5. No Rotrode Electrodes | 10 | 10 | 10 | 0 | 10 | 10 | 10 | 10 | 10 |
| 6. Safety Interlocks | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| 7. No Hazardous Gases | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 0 | 10 |
| Subtotals | 35 | 30 | 40 | 50 | 40 | 0 | 40 | 25 | 35 |

TABLE 4.
WORKSHEET OF DESIGN AND PERFORMANCE CRITERIA (Continued)

| <i>Criteria</i> | <i>Potential JOAP Instrumental Techniques</i> | | | | | | | | |
|-----------------------------------|---|------------|-------------|------------|--------------|------------|----------------|-----------|--------------|
| | <i>ICP</i> | <i>DCP</i> | <i>CFAE</i> | <i>RDE</i> | <i>CFICP</i> | <i>GFP</i> | <i>SIMAAAC</i> | <i>AF</i> | <i>ICPMS</i> |
| <i>Matrix Effects Electronics</i> | | | | | | | | | |
| 1. Spectral | 10 | 10 | 10 | 0 | 10 | 10 | 10 | 10 | 10 |
| 2. Chemical | 10 | 10 | 0 | 10 | 10 | 10 | 0 | 10 | 10 |
| 3. Viscosity | 10 | 10 | 0 | 0 | 10 | 0 | 0 | 10 | 10 |
| 4. Particle Size | 0 | 0 | 10 | 0 | 10 | 10 | 10 | 0 | 0 |
| 5. State of the art electronics | 10 | 0 | 10 | 0 | 10 | 10 | 10 | 10 | 10 |
| 6. Modular electronics | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| Subtotals | 50 | 40 | 40 | 20 | 60 | 50 | 40 | 50 | 50 |
| <i>Data Station Capabilities</i> | | | | | | | | | |
| 1. Expandable Memory | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| 2. Data Storage | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| 3. Communication Ports | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| 4. CRT w/graphics | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| 5. Graphics printer | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| 6. Diagnostics Software | 10 | 0 | 10 | 0 | 10 | 10 | 0 | 0 | 10 |
| 7. Drift Calibration | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 0 | 10 |
| 8. JOAP Interface | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| 9. Trend Analysis | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| Subtotals | 90 | 80 | 90 | 80 | 90 | 90 | 80 | 70 | 90 |
| <i>Weighting (Factor)</i> | | | | | | | | | |
| Performance (10) | 1180 | 1120 | 610 | 880 | 1010 | 900 | 970 | 580 | 1180 |
| Dur/Maintain/Reliability (9) | 810 | 765 | 900 | 657 | 747 | 747 | 792 | 810 | 90 |
| Simple Operation (8) | 480 | 320 | 320 | 240 | 480 | 480 | 400 | 320 | 480 |
| Data Station Capabilities (7) | 630 | 560 | 630 | 560 | 630 | 630 | 560 | 490 | 630 |
| Total of all Other Criteria (5) | 575 | 525 | 600 | 475 | 700 | 650 | 600 | 525 | 575 |
| Grand Total | 3675 | 3290 | 3060 | 2812 | 3567 | 3407 | 3322 | 2725 | 2955 |

List of Abbreviations

| | |
|---------|---|
| ICP | Inductively Coupled Plasma Atomic Emission Spectrometer |
| DCP | Directly Coupled Plasma Atomic Emission Spectrometer |
| CFAE | Carbon Furnace Atomic Emission Spectrometer |
| RDE | New Improved A/E35U-3 with Computer, Rotating Disk Spark/Arc Atomic Emission Spectrometer |
| CFICP | Carbon Furnace Atomization Inductively Coupled Plasma Atomic Emission Spectrometer |
| GFP | Graphite Filament Plasma Atomic Emission Spectrometer |
| SIMAAAC | Simultaneous Continuum Source Atomic Absorption Spectrometer with a Graphite Furnace Atomizer |
| AF | Inductively Coupled Plasma Atomic Fluorescence with Hollow Cathode Source Spectrometer |
| ICPMS | Inductively Coupled Plasma Mass Spectrometer |

Because the ICP with conventional sample introduction does not provide particle-size-independent measures of wear metals, two other emission sources were also evaluated experimentally: the graphite filament plasma and a rotating disk electrode arc source in which oil

samples are deposited directly on the disk. Since both of the alternative sources incorporate direct sample introduction to the excitation source, they were considered more capable of detecting particulate wear debris than the ICP.

A preliminary evaluation of a prototype electrothermal vaporization/ICP system under development by Allied Analytical Systems, Waltham, MA, was made to determine whether this technique could be used to analyze oils for particulate wear metals. Additional testing included evaluations of precision and sensitivity for the 3-electrode direct current plasma (DCP) when optically coupled to the same echelle grating monochromator used for most of the ICP testing.

(1) ICP Emission Spectrometers

Three commercial ICP-AE spectrometers were used in the verification testing program. The majority of testing was done with a Plasma-Spec emission spectrometer (Leeman Labs, Lowell, MA). The power supply for the ICP is a free-running tuned cavity design and uses an antenna to sense fluctuations in power levels within the torch box caused by the introduction of different sample matrices. The source is coupled to an automated echelle grating spectrometer featuring immobilized dispersion and order-sorting optics. Wavelength selection and scanning is under computer control. Stepper motors are used to adjust the position of an aperture plate and the photodetector. The plate contains an array of exit slits which are aligned to the prominent emission lines of over 60 elements. The optical path of the spectrometer is not purgable; therefore, emission lines in the vacuum ultraviolet region, including the prominent lines of sulfur, were not available for this study.

The Baird automatic dilution system was evaluated using a Baird Spectrovac plasma emission spectrometer. The ICP source incorporates an impedance-matching network to maintain uniform forward power in the induction zone. The spectrometer is a 1-m focal length vacuum polychromator of conventional Rowland circle design. Most of the wavelengths in the ultraviolet region were detected in the second order of diffraction. Seventeen channels were monitored. As with the Leeman spectrometer, background subtraction was not used in any of the measurements of emission intensity.

Used oil samples were also analyzed using an ARL 3520 rapid sequential ICP atomic emission spectrometer. Like the Leeman instrument, the ARL 3520 features immobilized dispersion optics, and wavelength selection is achieved by moving the detector behind the appropriate exit slit. Additional alignment of the ARL spectrometer is done by moving the entrance slit slightly. The ARL ICP source uses power control circuitry similar in design to that of the Baird system. The optics are in a Paschen-Runge mounting.

(2) Graphite Filament Plasma

Because the graphite filament plasma (GFP) scored almost as highly as the ICP systems in the Analysis of Findings and because it features direct sample introduction to the excitation source, it was evaluated along with the ICP in this portion of the study. The GFP used in the verification testing program is a modified version of an excitation source first developed by Leeman Labs. Its construction and operational characteristics were discussed in detail in Section III.3.a.

(3) Ashing Rotrode

A modified rotating disk electrode in which the oil sample is deposited directly on the surface of the disk was provided by Spectro, Inc., Fitchburg, MA for evaluation. The cathode of this source consists of a row of 10 disks machined from graphite rod stock 10-cm long by 1.2-cm in diameter. Each disk lobe is 0.5-cm wide. The rod is mounted between horizontal chucks that

rotate the rod and supply electrical contact to the arc power supply. A graphite rod, 0.6 cm in diameter and sharpened to a point with a pencil sharpener, is mounted on a slide assembly which allows it to be positioned above any one of the 10 disk lobes. As the disks are turning, a 30- μ l aliquot of oil sample is dispensed on each one. After 10 samples (or standards) have been dispensed, an electrical current is passed through the rod for 2 minutes and the samples are desolvated and ashed.

After the samples are ashed, the counter electrode is positioned above one of the lobes, and as the rod is rotated, the sample residue is vaporized and analyte species are excited by a direct current (dc) arc struck between the tapered electrode and the rod. The vaporization interval is typically 20 seconds. The counter electrode is positioned above the next lobe; the arc is struck and emission intensity data are collected for that sample. This process is repeated for the other lobes on the rod. A new rod is mounted in the arc stand and the analytical cycle is repeated for the next 10 samples.

For verification and testing the arc stand was coupled through an optical fiber to a 0.75-m focal length 16-channel polychromator with fixed optics in a Paschen-Runge mounting. The detector for one of the channels was aligned to the carbon line at 387.1 nm and was available for use as an internal standard to compensate for changes in the rate of analyte vaporization. Two of the channels were aligned to strontium emission lines: Sr(I) 460.7 nm and Sr(II) 407.8 nm. These lines were also used for internal standardization.

b. Performance Validation

(1) Rapid Multielement Analysis

Verification testing confirmed that the total time for a simultaneous analysis of the 19 elements of interest is under 1 minute for a multichannel ICP-AE spectrometer with an auto-sampler and auto-diluter accessory. Analysis times with the GFP were found to be just under a minute if the segment of filament on which the sample was deposited was not precleaned by passage through the plasma arc. The cleaning step added approximately 25 seconds to the analytical cycle. The ashing rotrode and the electrothermal ICP systems were found to take between two and three minutes for each sample.

(2) Repeatability

Conventional sample introduction into argon plasmas produces steady-state signals which are much more precise than those produced by dc arc or dc spark sources. Inductively coupled plasma was the most precise of the sources investigated.

Analytical precision for the ICP was evaluated by introducing 10-ppm Conostan S-21 standard previously diluted 9 to 1 with xylene. The relative standard deviation in 9 replicate measurements of net analytical signal (the difference in emission intensities produced by the diluted standard and by a solvent blank) are presented in Figure 12 along with comparable data obtained with a 3-electrode DCP coupled to the same spectrometer. The results show that most of the elements of interest can be determined by ICP emission spectroscopy with RSD values in the 1.0 to 2.0% range. Exceptions are sodium (Na) and phosphorous (P), which are elements with high detection limits. The diluted 10-ppm standard did not contain concentrations of Na and P sufficiently above their detection limits to provide optimum precision.

The degradation of precision at analyte concentrations approaching the limit of detection is shown in Figure 13 for the ICP and DCP. The latter set of data are based on typical precision of emission measurements at high analyte concentrations of 3% rather than 1.5% for the ICP. Typical detection limit values were assumed to be 0.1 ppm for most of the elements of interest in

the ICP and 0.25 ppm in the DCP, as shown in Figure 14. Because the ICP affords better detection limits, precision, and better long-term stability than the DCP, no further testing of the latter source was undertaken.

Measurements made with the Graphite Filament Plasma (GFP) and the ashing rotrode were considerably less precise than those made with the ICP and DCP. The GFP was the more precise of the two, yielding RSD values that averaged 5% for several of the elements of interest at the 10-ppm level. Replicate measurements of emission for the 11 elements shown in Figure 15 using the ashing rotrode, had an average RSD of 26%. Apparently, this high value was the result of the uneven distribution of sample residue along the surface of each lobe and to irreproducible applied power level to the arc. Subsequent modifications to the electrical contacts in the arc electrodes have yielded measurements with RSD values in the 5-to-8% range.

To further improve the precision of measurements with the ashing rotrode, the method of internal standardization was investigated. A 1.00-milliliter aliquot of 100-ppm Conostan S-21 standard was spiked with 30 microns of 5000 ppm Conostan strontium standard. After blending, the mixture was applied in 30-micron aliquots to 10 lobes of an electrode rod. Emission intensities for the 11 analyte lines were divided by the intensity of the appropriate strontium line. Ionized emission lines were compared to the strontium (II) 407.8 nm line and neutral atom lines were compared to the strontium (I) 460.7 nm line. The resulting normalized emission intensities had an average RSD of 8%, or about three times better precision than without internal standardization as shown in Figure 16. After the electrical contacts in the source described above had been modified, the precision of measurements was typically 5% RSD and was not significantly enhanced by the use of internal standards.

(3) Sensitivity

Detection limits (DL), as indirect measures of sensitivity, were calculated from the net emission intensities (NEI) produced by 10-ppm Conostan standards introduced either directly to the source (the method used with the ashing rotrode and GFP) or following a 9-to-1 dilution with xylene. The minimum detectable signal was taken to be that equal to three times the standard deviation in emission intensities produced by a reagent blank. For the two direct methods of analysis, emission intensity for the blank was measured as either the bare graphite filament or the bare graphite disk passed through the arc. Blank emission intensities for the argon plasmas consisted of 3-second integrations of detector signal as xylene was introduced to the sample delivery system. In all cases, the square root of the variance in nine consecutive measurements of blank emission was taken as the standard deviation value. The detection limit values were then calculated as follows:

$$DL = 3 \times \text{Standard Deviation} \cdot 10 \text{ ppm/NEI}$$

Detection limits for the excitation sources studied are shown in Figures 14, 17, and 18. The values for the ICP and for the DCP (Figure 14) are relatively high compared to published data for these techniques due in part to a 9-to-1 dilution of the samples prior to analysis. As may be seen, detection limits for most wear metals by ICP are in the 0.1-to-0.3-ppm range. Exceptions include phosphorous, lead, sodium and tin. Phosphorous is added to some lubricating oils and therefore should be present at concentrations well above 1 ppm. Sodium would probably be present as a result of contamination of lubricating oil by engine coolant rather than by engine wear.

Detection limits for the DCP are generally higher than for the ICP. This appears to be the result of: (1) the greater efficiency with which the ICP destroys the organic sample matrix, and (2) the exclusion of air from the excitation zone of the ICP. As a result, molecular band emission contributes less to the background of the ICP than it does to the DCP. Moreover, analyte passing through the ICP is more efficiently atomized and excited than in the DCP.

Figure 17 shows detection limits obtained with the direct introduction of 50 μ l samples into the GFP. As with the ICP, detection limits are generally in the sub-ppm range. The notable exception is phosphorous. Other studies have shown that the GFP provides relatively low limits of detection compared to the ICP because of two factors: (1) the sample is not diluted prior to analysis, and (2) the entire sample residue is introduced directly into the plasma discharge. The ICP is a much more efficient excitation source for the analyte which does pass through it, and its greater stability gives less variation in blank emission signals than does the GFP. The net effect of all these factors is a set of detection limits for the GFP comparable to or slightly lower than those of the ICP and apparently well below those of the conventional rotrode source.

Detection limits for 11 of the elements of interest in the ashing rotrode are shown in Figure 18. The elements in the figure were the only ones available in the polychromator to which the rotrode was optically coupled. Detection limits with the ashing rotrode are mostly in the 0.2 to 0.5-ppm range with silicon and molybdenum values considerably higher. For several elements, including iron, copper, magnesium, and silicon, the variability in blank emission was affected by contamination of the electrode lobes with these metals. Alternate machining procedures, or a post-machining purification step, might reduce contamination and therefore reduce the detection limit values for these and other analytes.

(4) Dynamic Range

The linearity of the working range, or the dynamic range, was determined by evaluating the concentration ranges for which the candidate instrumentation gave linear calibration curves (curves of detector response versus concentration). These were evaluated using Conostan standard solutions containing between 0.1 and 900 ppm (weight weight) of the elements of interest. For concentrations of S-12 standard below 900 ppm and for concentrations of S-21 below 10 ppm, Conostan stock solutions were diluted with the appropriate weight of Conostan base oil.

A requirement of the candidate technique was the ability to produce linear calibration curves for most of the elements of interest over the 1-to-1000-ppm concentration range. Verification of this requirement was complicated slightly by the unavailability of organo-metallic standards at 1000 ppm. Consequently, most calibration curves stop at 900 ppm. Another complication in the use of multi-element standards, such as Conostan S-21, is the presence of all the analytes at the same concentration up to 900 ppm. In the case of the S-21 standard, this upper concentration produces a total analyte concentration of 18,900 ppm plus stabilizers. Such a high inorganic loading did not appear to cause matrix-related effects in the ICP, but it did alter the excitation characteristics of the direct analysis sources, usually producing nonlinear calibration curves above 300 ppm.

As shown in Figures 19 through 22, calibration curves for the ICP were linear over three and, in some cases, four orders of magnitude (0.1-to-900 ppm). The only exception to this rule was the curve for silicon which exhibited nontheoretical behavior below 100 ppm. This is due to a misadjustment in the argon gas flowrates in the ICP torch. As a result, sample vapor flowed around and through the discharge transferring the plasma's energy to the outer wall of the quartz torch. Erosion of the torch wall results in a high level of silicon emission in the cone of the ICP. Subsequent adjustment in the plasma gas flowrate appeared to cure the problem, but this result suggests that coolant gas flow rates in ICPs must be carefully controlled to avoid erratic results for silicon.

The lower limits in the calibration curves in Figures 19 through 22 were established by calculating the ratio of the average net intensity ($n = 9$) produced by 0.1 ppm of the analyte to the standard deviation in net intensity. If the ratio was less than three, the datapoint was considered imprecise and not plotted. Some of the points just meeting this criterion are off the

calibration curve as defined by the higher intensity measurements. As previously discussed, this is due to the lack of precision in measurements made near the limits of detection.

Calibration curves for the GFP (Figures 23 through 27) and the ashing rotrode are linear up to 300 ppm. However, they generally curve toward the concentration axis between 300 and 900 ppm. The reason for the non-linear response at high concentrations is not spectroscopic; it appears to be due to the large amount of residue left after the 900-ppm standard is ashed on the graphite filament or disk electrode. The power required to vaporize this residue diminishes the power available for atomizing and exciting analyte species. The discharges of both sources become noticeably more diffuse when residue from a 900-ppm standard is present in the arc gap. It should be noted that growth curves prepared from single-element aqueous standards of iron and magnesium are linear through 1000 ppm in the GFP. It is unlikely that a sample of used lubricating oil will produce the amount of inorganic residue left by either the S-12 or S-21 900-ppm Conostan standard.

(5) Accuracy

The accuracy of wear metal analyses using the candidate techniques was evaluated as described in Section III.3.c. Initially a subset of seven samples including at least one of each type of oil were analyzed by all the candidate techniques under consideration. The results of these analyses are presented in Table 5.

TABLE 5.

COMPARISON OF EMISSION TECHNIQUES FOR WEAR METALS IN USED OILS

| <i>Oil Type</i> | <i>Sample No</i> | <i>ICP/AES</i> | <i>ICP/AES</i> | <i>Ash/RDE</i> | <i>RDE</i> | <i>GFP</i> | <i>ETV/ICP</i> |
|-------------------|------------------|----------------|----------------|----------------|------------|------------|----------------|
| <i>Magnesium</i> | | | | | | | |
| 7808 | 1 | 0.05 | | 0.5 | ND | < 0.2 | |
| 7808 | 4 | 0.05 | | 0.19 | ND | < 0.2 | |
| 7808 | 6 | 0.06 | | 0.45 | ND | < 0.2 | |
| 524 | 15 | 0.02 | | 0.26 | ND | < 0.2 | |
| 23699 | 24 | 0.88 | | 1.52 | 1 | 0.9 | |
| Army | 1436 | >35.5 | | 536 | 370 | 330 | |
| Army | 1491 | >35.5 | | 640 | 840 | 470 | |
| <i>Molybdenum</i> | | | | | | | |
| 7808 | 1 | 0.16 | | 1.5 | ND | | 1 |
| 7808 | 4 | 0.31 | | 1.1 | ND | | 1 |
| 7808 | 6 | 0.39 | | 2.3 | ND | | 1 |
| 524 | 15 | 0.27 | | 0.4 | ND | | |
| 23699 | 24 | 0.14 | | 0.3 | ND | | |
| Army | 1436 | 1.1 | | 20 | ND | | |
| Army | 1491 | 0.7 | | 25 | 1 | | |
| | | | | | | | (0.1) |
| <i>Sodium</i> | | | | | | | |
| 7808 | 1 | 2.47 | 2.7 | | | | 2.4 |
| 7808 | 4 | 3.07 | 3.4 | | | | 2.8 |
| 7808 | 6 | 3.4 | 3.8 | | | | 3.5 |
| 524 | 15 | 0.53 | 0.3 | | | | |
| 23699 | 24 | 3.05 | 2.5 | | | | |
| Army | 1436 | 16.8 | 21 | | | | |
| Army | 1491 | 21.9 | 27.1 | | | | |
| <i>Nickel</i> | | | | | | | |
| 7808 | 1 | 0.4 | 0.2 | 1.2 | 1 | | 2.8 |
| 7808 | 4 | 1.5 | 0.7 | 5.8 | 2 | | 2.8 |
| 7808 | 6 | 2.06 | 1.1 | 8.4 | 2 | | 3.7 |
| 524 | 15 | 1.11 | 0.1 | 6.2 | 1 | | |
| 23699 | 24 | 0.47 | 0.2 | 2.1 | ND | | |
| Army | 1436 | 2.2 | 1.1 | 17.8 | 2 | | |
| Army | 1491 | 1.1 | 1.2 | 10.1 | ND | | |
| <i>Aluminum</i> | | | | | | | |
| 7808 | 1 | 0.43 | 0.9 | 3.8 | ND | | |
| 7808 | 4 | 0.96 | 1.1 | 1.3 | ND | | |
| 7808 | 6 | 1.07 | 0.9 | 4.3 | ND | | |
| 524 | 15 | 0.76 | 1.4 | 1.4 | ND | | |
| 23699 | 24 | 1.31 | 0.9 | 0.9 | ND | | |
| Army | 1436 | 46.1 | 10.8 | 660 | 43 | | |
| Army | 1491 | 8.52 | 8.8 | 123 | 7 | | |
| <i>Chromium</i> | | | | | | | |
| 7808 | 1 | 0.42 | 0.2 | 1.5 | 1 | 0.3 | < 0.2 |
| 7808 | 4 | 1.13 | 0.5 | 1.7 | 1 | 1.4 | 1.2 |
| 7808 | 6 | 1.4 | 0.7 | 4.3 | 2 | 1.9 | 2.8 |
| 524 | 15 | 0.79 | 0.3 | 1.3 | 1 | 0.7 | |
| 23699 | 24 | 0.55 | 0.2 | 0.6 | ND | 0.5 | |
| Army | 1436 | 5.3 | 3.4 | 47 | 6 | 4.9 | |
| Army | 1491 | 7.91 | 6.8 | 74 | 6 | 7.5 | |

TABLE 5.

COMPARISON OF EMISSION TECHNIQUES FOR WEAR METALS IN USED OILS
(Continued)

| <i>Oil Type</i> | <i>Sample No.</i> | <i>ICP/AES</i> | <i>ICP/AFS</i> | <i>Ash/RDE</i> | <i>RDE</i> | <i>GFP</i> | <i>ETV/ICP</i> |
|-----------------|-------------------|----------------|----------------|----------------|------------|------------|----------------|
| <i>Copper</i> | | | | | | | |
| 7808 | 1 | 0.12 | <0.2 | 0.6 | ND | <0.2 | 0.1 |
| 7808 | 4 | 0.12 | <0.2 | <0.5 | ND | <0.2 | 0.1 |
| 7808 | 6 | 0.21 | <0.2 | 2.2 | 0.1 | <0.2 | 0.3 |
| 524 | 15 | 0.13 | <0.2 | <0.5 | ND | <0.2 | |
| 23699 | 24 | 0.26 | <0.2 | <0.5 | 0.1 | 0.4 | |
| Army | 1436 | 121 | 104 | 348 | 97 | 130 | |
| Army | 1491 | 19.1 | 17.5 | 77 | 15 | 24 | |
| <i>Iron</i> | | | | | | | |
| 7808 | 1 | 0.98 | 0.6 | 3.2 | 1.1 | 1.1 | 1.1 |
| 7808 | 4 | 3.74 | 2.2 | 7.1 | 3.9 | 3.3 | 9.9 |
| 7808 | 6 | 4.98 | 2.7 | 7.4 | 5 | 4.6 | 13.3 |
| 524 | 15 | 8.91 | 0.6 | 15.9 | 6.6 | 7.8 | |
| 23699 | 24 | 2.57 | 1.8 | 2.5 | 2 | 2.6 | |
| Army | 1436 | >400 | 182 | 548 | 490 | 590 | |
| Army | 1491 | 61.7 | 53.1 | 229 | 49 | 60 | |
| <i>Silicon</i> | | | | | | | |
| 7808 | 1 | 1.1 | 1.2 | 1.2 | 1 | | |
| 7808 | 4 | 1.2 | 0.8 | 2.4 | 2 | | |
| 7808 | 6 | 1.6 | 1.3 | 2.7 | 1 | | |
| 524 | 15 | 0.8 | 0.7 | 1.9 | 2 | | |
| 23699 | 24 | 3.4 | 3.4 | 0.6 | 1 | | |
| Army | 1436 | 126 | 67.9 | 472 | 130 | | |
| Army | 1491 | 17.8 | 10.7 | 30.6 | 11 | | |
| <i>Titanium</i> | | | | | | | |
| 7808 | 1 | 0.34 | <2 | 0.8 | ND | | |
| 7808 | 4 | 0.49 | <2 | 0.6 | 1 | | |
| 7808 | 6 | 0.3 | <2 | 0.8 | 1 | | |
| 524 | 15 | 0.27 | <2 | 0.7 | ND | | |
| 23699 | 24 | 0.3 | <2 | 0.2 | ND | | |
| Army | 1436 | 1.64 | 11.3 | 4.4 | 1 | | |
| Army | 1491 | 0.13 | 10.1 | 0.8 | 1 | | |

Analyses by ICP atomic emission spectroscopy (ICP-AES) were carried out with a Baird Spectrovac spectrometer connected to an automatic sample dilution system. Additional analyses were run with four direct methods designated in Table 5 as GFP, Ash/RDE (ashing rotrode), RDE (conventional rotrode), and electrothermal vaporization (ETV)-ICP and by ICP atomic fluorescence spectroscopy (ICP-AFS) using a Baird AFS-2000 12-channel fluorescence spectrometer. While ICP-AFS did not score well in the Analysis of Findings and so was not of primary interest in the verification program, data obtained with the technique are presented for comparison purposes. The ETV-ICP data are the results of preliminary measurements made with the electrothermal vaporization ICP system under development at Allied Analytical Systems.

The results obtained with the different techniques appear to correlate well, although the agreement for individual samples is not always close. When major differences occur, there is a

discernible trend in them. The ICP-AES data appear to be the most precise and are almost always greater than those obtained by ICP-AFS. However, the ICP-AES data are generally less than those obtained with the direct methods of analysis. Among the direct methods, the ashing rotrode usually gives the highest results. The GFP and RDE results more closely agree with those obtained by ICP-AES. In the case of iron, the agreement between these three techniques is surprisingly good, given the differences in their abilities to detect particles greater than a few micrometers in diameter. The two samples obtained from the Army contained particles that formed a visible deposit in the bottom of the containers. Considerable difficulty was encountered in bringing these particles into suspension, and uncertainties in subsampling may have contributed to some of the differences between techniques.

To provide a larger data base on which to evaluate the primary candidate technique, ICP-AES, and to examine the quantitative capabilities of the technique, additional samples were analyzed by ICP-AES following dilution with kerosene (the standard method) and following an acid digestion procedure developed to dissolve particulate wear metals and so provide a particle-size-independent method (PSIM) of analysis (Reference 13). The results of analyses of 18 jet engine oil samples for iron, which was the most commonly detected wear metal, are shown in Figure 32. The reference line has a slope of 1.0. The results obtained by ICP-AES consistently fall below this line; the slope of the best fitting straight line to the data is 0.86. These results suggest that a portion of the Fe present in these samples is not detected. However, the correlation between these sets of data ($r = 0.990$) is much better than in a comparison of the results obtained with the conventional rotrode and the PSIM shown in Figure 33. The greater scatter in the latter data from analyses of 19 jet engine oil samples reflects the poorer precision of the rotrode technique at Fe concentrations approaching 1 ppm. In fact, if the highest data point is disregarded from the data set, the correlation coefficient is only 0.70.

The results of these measurements indicate that an ICP with conventional sample introduction does not give "quantitative analytical" results for wear metals in lubricating oils. This result is not surprising given the particle-size dependence of the technique which has been confirmed in other portions of this study (Section III.5.c.1.). On the other hand, the high degree of correlation between the ICP results and those obtained by the reference procedure (PSIM) indicate that an ICP is well suited to trend analysis particularly if step changes in the low-ppm or sub-ppm range are to be detected.

c. Design Validation

(1) Sample Introduction

Both synthetic and petroleum-based oils are used by the military as lubricants with synthetic oils most widely used in high-speed turbine engines. The viscosities of these oils differ considerably. MIL-L-7808 and MIL-L-23699 are low-viscosity (13 and 26 centistokes respectively) synthetic lubricants while MIL-L-87100 oil, used in some high-performance aircraft, is highly viscous (330 centistokes). Used oils of all three types were obtained from test engines at P&W Government Products Division, West Palm Beach, Florida. Samples of used petroleum-based oils were obtained from the U. S. Army.

The samples were analyzed using ICP, GFP, ashing rotrode, ferrography, and a AFE5U-3 unit. Conventional sample introduction to the ICP with pneumatic nebulization requires that the samples be of low and uniform viscosity. While oils may be heated to decrease their viscosity, the most common pretreatment of lubricating oils prior to analysis by ICP is dilution with a nonpolar solvent of moderate volatility such as kerosene or xylene. Typical dilution factors are 1 to 4 and 1 to 9 sample to solvent. Both solvents and dilution factors were investigated in the testing program.

Samples are usually diluted prior to analysis as are the calibrating standards. Predilution adds to analysis time and increases the chances for loss of analyte due to the settling of particles in the less viscous diluted samples. An automatic online dilutor for lubricating oils which reproducibly dilutes oil samples with a predetermined ratio of solvent was evaluated in this study. Dilution occurs as the sample is pumped to the pneumatic nebulizer of an ICP. The device was evaluated in the testing program and was found to provide reproducible dilution, and its use did not add significantly to analysis time.

For studying the particle-size capability of the sample introduction systems, the starting materials for preparing particulate standards were Conostan-type 75-base oil and single-element powders obtained from Research Organic/Inorganic Corporation, Bellvue, New Jersey. Powdered iron, titanium, nickel, and silver were of nominal mesh size 325. A nickel dust with a specified size range of 0.05 to 0.5 μms was also obtained from the same supplier.

The 325-mesh powders were dry sieved using an ATM model LT-3-p sonic sifter (ATM Corporation, Milwaukee, Wisconsin) with screen sizes of 5, 10, 15, 20, 25, 32, and 38 μms . Suspensions of the particles were prepared in base oil at concentrations of 1000 and 100 ppm (weight/weight) using ultrasonication and manual shaking.

To determine how effectively the sieving process produced a true particle-size distribution, a portion of the 1000-ppm suspension of iron particles, which passed through the 10- μm sieve but not the 5- μm sieve, was taken for particle-size analysis. The particles in suspension were agglomerated by adding several drops of the suspension to water. The particles were removed by pipet and transferred to a small vial containing 10 ml of 3% sodium chloride in water. A drop of Triton X surfactant was added and the mixture was ultrasonicated for 10 minutes. Several drops of the mixture were analyzed using a Tracor Northern particle size analyzer equipped with a 38- μm orifice tube (Serial No. 886).

As discussed in the Analysis of Findings, argon plasmas with conventional sample introduction systems do not provide quantitative analyses of particulate metals due to: (1) losses of these analytes in the sample introduction systems, and (2) incomplete atomization in the plasmas. These findings were confirmed in the verification program for the ICP as shown in Figure 28. Concentrations of particulate silver, iron, and titanium as small as 5-to-10- μm in diameter were not determined quantitatively based on calibration curves produced with Conostan standards (the signal produced by an equivalent concentration of organometallic standard is represented by a particle size of zero).

The two excitation sources incorporating direct sample introduction detected greater proportions of metal particles greater than 10 μm in diameter (Figures 29 and 30) than did the ICP. Particles of nickel and iron from less than 0.5-to-10- μm in diameter produced signals that were greater than 60 percent of those produced by soluble forms of the metals. Particulate iron in the 20-to-25- μm range and less than 38 μm in diameter and particulate nickel less than 38 μm in diameter produced slightly lower signals than did the smaller particles of these metals. The reason for this decrease in signal is not clear. Repeated introduction of the same segment of graphite braid through the GFP and repeated burns of the same rotrode disk gave data indicating that the proportion of analyte vaporized in the first pass was not a function of particle size. In the case of the GFP, analyte vaporization was quantitative in the first pass of the sample residue through the plasma when a plasma current of 14 amperes was applied regardless of whether the analyte was in a soluble or particulate form.

One likely reason why the direct analysis techniques give less than quantitative results for particulate metals may be incomplete and/or heterogeneous suspension of the metal particles in base oil. It was observed that extensive sample agitation was necessary to suspend even the smaller diameter particles. In the process, air bubbles were entrained in the samples. Subsequent

subsampling could have produced an aliquot with less than the theoretical volume of sample. Aggregation of the particles was also a concern particularly in light of the results obtained by a particle size analysis of the fraction of iron powder passing through a 10- μm , but not a 5 μm sieve (Figure 31). The data indicated that the dry powder forms aggregates or clusters during sieving. While these may be broken up by suspension in an aqueous medium containing surfactant, they may not be disrupted when suspended in oil. In fact, the formation of even larger clusters might occur making uniform suspension that much more difficult to achieve. The preparation of uniform suspensions of particulate metals in oil substrates is an area in need for considerable investigation.

(2) *Simplicity of Operation*

The operation of the ICP spectrometers evaluated in this study was aided by several factors including automatic sample delivery, automatic sample dilution, computer-controlled spectrometers and software that presented analytical results automatically in the desired concentration units. Operation of the GFP was aided by most of these features (except automatic dilution none being required). The ashing rotrode required more operator involvement since the source has yet to be automated. Electrode insertion, gap adjustment and sample delivery are manual operations.

(3) *Durability/Reliability/Simplicity of Design/Environmental Restraints*

These criteria were evaluated using specifications and warranties supplied by instrument manufacturers and by personal observation and experience. The results of this evaluation are shown in Figure 6.

(4) *Hazardous Gases/Consumable Requirements*

The results of the Analysis of Findings (Figure 8) were confirmed experimentally. Argon gas is the major consumable commodity for the ICP; the average consumption rate for the three sources used in this study was 18 liters per minute. The graphite filament plasma consumes about 1.5 l of argon per minute of operation, but the source is not operated continuously. The overall rate of argon consumption is approximately 0.3 l per minute reflecting a single plasma burn of 10 seconds during each minute of analysis. The braided graphite filament is consumed at the rate of 8 cm per sample. The major consumable in the ashing rotrode source is the 10-lobe cylindrical array of sample disks.

(5) *Safety*

All of the ICP spectrometers used in the verification program had the appropriate interlocks and other safety features described in Section III. Similar features were incorporated into the design of the GFP and ashing rotrode sources. Figure 8 shows the safety ratings for the candidate methods.

(6) *Matrix Effects*

As noted in Section III.3.f., four types of matrix-related interferences may be encountered in the analysis of lubricating oils for wear metals: spectral, chemical, viscosity-related, and particle size dependent. Spectral interferences in emission spectroscopy are related to the resolution of the spectrometer and the complexity of the spectrum produced by the source. Based on these factors one would predict that an argon ICP coupled to a high-resolution spectrometer, such as the echelle grating spectrometer used in this study, would produce fewer spectral interferences than an arc operating in air and coupled to a medium-resolution spectrometer such as the 0.75 m polychromator used with the ashing rotrode. Experimental results confirm this prediction.

The intensity of background emission was evaluated and used to calculate background equivalent concentrations (BECs) for the ashing rotrode and the ICP. BEC values were calculated for the dry rotrode and for the ICP when xylenes, the solvent used to dilute the samples, were introduced. Shifts in BEC values due to the introduction of 1000 ppm Fe, Ca, or Mg were also calculated for each source. The results are presented in Table 6 and in Figures 34 and 35.

Figure 34 provides a graphic comparison of the contributions background emission makes to the analytical signals in the argon ICP and the ashing rotrode. To make the comparison more meaningful the same emission lines were used with both sources even though some of the lines are neutral atom lines that are not very sensitive in the ICP. Moreover the calculations took into account a 10-fold dilution factor which further reduced the sensitivity of the ICP measurements and contributed to greater BEC values. Despite these negative factors BEC values for the ICP/echelle spectrometer are consistently lower than those observed with the ashing rotrode coupled to a medium-resolution (reciprocal linear dispersion = 0.5 nm/mm) polychromator.

Spectral interferences produced by concomitant Fe and Mg at 1000 ppm are shown for the ICP/echelle spectrometer for 18 of the elements of interest in Figure 35. For most elements background shifts expressed as equivalent concentrations were below 1 ppm and in many cases were not detectable. Those emission lines for which shifts greater than 1 ppm were observed included the B (I) 249.68 nm and Cr (II) 283.56 nm lines which are not completely resolved from neighboring Fe emission lines. An alternative chromium line at 205.55 nm appears to be free of significant Fe interference. No useful alternative B line was found in this study. Major Mg interferences were encountered at Mo (II) 281.61 and Sn (I) 284.00 nm. These lines occur in the same spectral orders as prominent neutral atom and ionized Mg lines. An alternative Sn line at 317.50 nm has a Mg-induced shift in background corresponding to only 1.17 ppm (Table 6). An alternative Mo line at 202.03 nm appears to be resolved from Fe and Mg emission lines.

Chemical interferences caused by incomplete dissociation of molecular analyte species were not detected in this study; however shifts in sensitivity and background emission resulting from changes in sample viscosity, sample dilution, and the diluent solvent were observed. Two solvents were evaluated: purified kerosene marketed by Shell Oil Co. as "Shell-Sol," and reagent grade xylenes. Use of the different solvents produced major changes in both background emission and sensitivity as shown in the results for Cr (II) 283.56 nm (Figures 36 and 37). Dilution of standards with Shell-Sol yielded greater sensitivity than dilution with xylenes, but background emission intensity was also higher with the former samples.

The net effect of the above two factors was a slight enhancement in signal-to-background with the use of Shell-Sol as shown in Figure 38. The data in this figure represent the ratios of net emission from organometallic standards and of signal-to-backgrounds obtained by dividing the results obtained with Shell-Sol with those obtained with xylenes for 18 of the elements of interest. Values greater than 1.0 indicate that the use of Shell-Sol enhanced sensitivity and signal to background for most elements.

Standards and blank solutions were prepared using MIL-L-7808, a low viscosity (19 centistokes at 100°F) di-2-ethylhexyl azelate oil, and with more viscous Conostan (75) Base Oil at two dilution factors 4-to-1 and 9-to-1, giving solutions that were 20% and 10% (weight/weight) oil. The effects of oil viscosity and dilution factor on background emission and sensitivity were small as may be seen in the results shown in Figures 36 to 38. Usually the less diluted samples gave somewhat less sensitivity, presumably due to lower nebulization efficiency, but the slight decreases that were observed were more than compensated for by the factor of two increase in effective analyte concentration with less dilution. On this basis, 4-to-1 dilution with Shell-Sol or equally pure kerosene is recommended for routine oil analysis by ICP.

TABLE 6.
BACKGROUND EQUIVALENT CONCENTRATIONS

| <i>Inductively Coupled Plasma Echelle Grating Spectrometer</i> | | | | | | | | | | | | | |
|--|-------------------|---------------------------|------------|----------------|----------------|----------------|---------------------------|-----------|-----------|----------------------|-----------|-----------|--------------|
| <i>Element</i> | <i>Wavelength</i> | <i>Emission Intensity</i> | | | | | <i>Matrix Blank Ratio</i> | | | <i>B.E.C. Values</i> | | | |
| | | <i>Blank</i> | <i>Std</i> | <i>1000 Fe</i> | <i>1000 Ca</i> | <i>1000 Mg</i> | <i>Fe</i> | <i>Ca</i> | <i>Mg</i> | <i>Fe</i> | <i>Ca</i> | <i>Mg</i> | <i>Blank</i> |
| Cr | 425.43 | 1900 | 9,240 | 2,092 | 2231 | 1,935 | 3.02 | 4.48 | 1.37 | 2.62 | 4.51 | 0.48 | 1.28 |
| Al | 396.15 | 2575 | 40,480 | 2,507 | 5656 | 2,705 | 0.91 | 5.00 | 1.17 | 0.00 | 8.13 | 0.34 | 1.99 |
| Ni | 341.48 | 2730 | 53,120 | 3,169 | 3140 | 3,049 | 1.47 | 1.44 | 1.34 | 0.87 | 0.81 | 0.63 | 1.80 |
| Ti | 334.94 | 2980 | 561,664 | 3,081 | 3160 | 3,344 | 1.09 | 1.15 | 1.31 | 0.02 | 0.03 | 0.07 | 0.21 |
| Ag | 328.07 | 2710 | 265,664 | 3,592 | 3436 | 3,120 | 1.97 | 1.80 | 1.45 | 0.34 | 0.28 | 0.16 | 0.34 |
| Cu | 324.75 | 3200 | 592,908 | 7,368 | 6816 | 4,252 | 3.99 | 3.59 | 1.75 | 0.71 | 0.61 | 0.18 | 0.24 |
| Sn | 317.5 | 4560 | 43,230 | 4,680 | 5636 | 5,028 | 1.04 | 1.39 | 1.17 | 0.31 | 2.78 | 1.21 | 6.65 |
| Mo | 281.61 | 2862 | 313,636 | 3,512 | 2879 | 17,152 | 1.61 | 1.02 | 14.52 | 0.21 | 0.01 | 4.60 | 0.34 |
| Fe | 259.94 | 2060 | 298,752 | 2,574,120 | 2168 | 2,906 | 0.00 | 1.42 | 4.32 | 0.00 | 0.04 | 0.29 | 0.09 |
| Si | 251.61 | 2485 | 50,000 | 2,736 | 2581 | 2,728 | 1.37 | 1.14 | 1.36 | 0.53 | 0.20 | 0.51 | 1.41 |

| <i>Element</i> | <i>Wavelength</i> | <i>Emission Intensity</i> | | | | <i>B.E.C. Values</i> | | |
|----------------|-------------------|---------------------------|---------------|----------------|----------------|----------------------|-----------|--------------|
| | | <i>Blank</i> | <i>20 ppm</i> | <i>1000 Fe</i> | <i>1000 Mg</i> | <i>Fe</i> | <i>Mg</i> | <i>Blank</i> |
| Ag | 328.07 | 17,146 | 265,664 | 17,444 | 19,066 | 0.02 | 0.15 | 1.16 |
| Al | 308.22 | 33,258 | 138,069 | 36,096 | 35,237 | 0.54 | 0.38 | 4.62 |
| B | 249.68 | 9,857 | 50,000 | 13,803 | 10,785 | 1.97 | 0.46 | 3.34 |
| Ba | 455.4 | 6,672 | 570,000 | 6,449 | 6,722 | 0.00 | 0.00 | 0.17 |
| Ca | 393.37 | 19,685 | 9,924,930 | 22,256 | 30,090 | 0.01 | 0.02 | 0.04 |
| Cr | 283.56 | 20,853 | 1,212,440 | 94,122 | 62,442 | 1.23 | 0.70 | 0.31 |
| Cu | 324.75 | 24,256 | 585,000 | 25,888 | 25,808 | 0.06 | 0.06 | 0.77 |
| Fe | 238.2 | 4,924 | 237,000 | 10,305,400 | 6,612 | 0.15 | 0.15 | 0.27 |
| Mg | 279.55 | 11,632 | 20,163,300 | 16,656 | | 0.00 | | 0.01 |
| Mo | 281.61 | 22,042 | 300,000 | 24,421 | 117,909 | 0.17 | 6.90 | 1.36 |
| Na | 589.59 | 3,352 | 20,000 | 3,354 | 3,472 | 0.00 | 0.14 | 1.70 |
| Ni | 231.6 | 5,959 | 169,000 | 10,352 | 6,342 | 0.54 | 0.05 | 0.50 |
| P | 214.91 | 3,309 | 35,000 | 3,508 | 3,464 | 0.13 | 0.10 | 0.91 |
| Pb | 220.35 | 4,022 | 21,322 | 3,980 | 3,981 | 0.00 | 0.00 | 2.27 |
| Si | 251.61 | 9,219 | 130,000 | 13,205 | 10,976 | 0.66 | 0.29 | 1.16 |
| Sn | 284 | 19,845 | 80,000 | 21,088 | 67,712 | 0.41 | 15.91 | 4.61 |
| Ti | 337.28 | 26,661 | 400,000 | 27,237 | 26,661 | 0.03 | 0.00 | 1.25 |
| Zn | 213.86 | 3,418 | 154,000 | 4,367 | 4,277 | 0.13 | 0.11 | 0.21 |

| <i>Ashing Rotrode Spectro Spectrometer</i> | | | | | | | | | | |
|--|-------------------|---------------------------|----------------|----------------|----------------|----------------|----------------------|-----------|-----------|--------------|
| <i>Element</i> | <i>Wavelength</i> | <i>Emission Intensity</i> | | | | | <i>B.E.C. Values</i> | | | |
| | | <i>Blank</i> | <i>900 ppm</i> | <i>1000 Fe</i> | <i>1000 Mg</i> | <i>1000 CA</i> | <i>Fe</i> | <i>Mg</i> | <i>Ca</i> | <i>Blank</i> |
| Cr | 425.43 | 337 | 50,842 | 299 | 304 | 300 | 1.69 | 1.47 | 1.65 | 5.97 |
| Al | 396.15 | 221 | 38,822 | 207 | 214 | 366 | 0.82 | 0.41 | 8.45 | 5.12 |
| Ni | 341.48 | 131 | 11,264 | 126 | 123 | 119 | 1.01 | 1.62 | 2.43 | 10.47 |
| Ti | 334.94 | 158 | 26,262 | 153 | 155 | 170 | 0.43 | -0.26 | 1.03 | 5.41 |
| Ag | 328.07 | 122 | 36,925 | 117 | 115 | 118 | 0.31 | 0.43 | 0.24 | 2.97 |
| Cu | 324.75 | 172 | 50,940 | 114 | 120 | 150 | 2.57 | 2.30 | 0.98 | 3.04 |
| Sn | 317.50 | 113 | 11,851 | 104 | 102 | 307 | 1.73 | 2.11 | 37.19 | 8.58 |
| Mo | 281.61 | 82 | 8,000 | 85 | 214 | 78 | 0.85 | 37.51 | 1.14 | 9.23 |
| Fe | 259.94 | 96 | 15,776 | 7,312 | 69 | 98 | | 3.87 | 0.29 | 5.48 |
| Si | 251.61 | 66 | 3,823 | 60 | 72 | 77 | 3.59 | 3.59 | 6.59 | 15.54 |
| Mg | 280.27 | 93 | 260,000 | 393 | 112,616 | 506 | 2.60 | | 3.58 | 0.32 |

(7) **Electronics**

Vendor specifications served to validate electronics criteria established for this study. Figure 7 shows the capability of candidate systems. (Further details can be found in Section III.)

(8) Data Station

Vendor specification and physical inspection of systems available for JOAP-type analysis confirmed data for this design area. Figure 9 shows the capabilities of candidate units. (Further details are given in Section III.)

d. Verification Summary

The results of the verification program confirm that emission spectroscopy with ICP meets or exceeds most of the design and performance criteria established by the Department of Defense for JOAP candidate instrumentation. The single-performance criterion not met by the ICP is the ability to detect and quantify large metal particles. The significance of this defect is not clear given the agreement between the results obtained with the ICP and the rotrode for used oil samples containing particulate wear metals. Graphite filament plasma and ashing rotrode sources, which allow for the direct analysis of used oils by emission spectroscopy provide enhanced capabilities to detect large wear particles, but lack the precision of the ICP.

SECTION IV

CONCLUSIONS

This study has defined inductively-coupled plasma atomic emission (ICP-AE) spectrometry as the optimum Joint Oil Analysis Program (JOAP) method through the year 2000. In addition to superior analytical performance over the present improved rotrodes available, this choice also provides a major cost savings in reduced manpower requirements and lower sampling costs in the amount of 100 million dollars or more. These savings can be achieved over the options of either maintaining the present instrumentation or going with a modernized version of A/E35U-3. The ICP will provide the most cost-effective and automated approach for JOAP application at a unit price competitive with that of any new rotrode configuration.

The JOAP ICP AE spectrometer should be equipped with automatic dilution and sampling capability. This optimum ICP AE instrument uses an aerosol generation sample introduction system which is geared toward eliminating particulate clogging potential by the sample, as well as efficiency of aerosol droplet generation (for precision) and transport into the ICP source. Such auto-sampling and auto-dilution systems are readily available from a variety of commercial sources. This system should employ a user-friendly, dedicated computer which operates by prompting the user for any required sample and standard data. This computer is capable of controlling the automatic sampling and dilution accessories as well as collecting and storing JOAP data for archiving and trend analysis applications. While most manufacturers offer systems with data stations that have the capacity to perform these functions, the software is designed for general analytical applications. The manufacturer, whose instrument is chosen for JOAP analysis, must make necessary and specific software changes to optimize its usage for JOAP applications.

Although there are many manufacturers of ICP AE spectrometers, the system components may not be interchangeable except for certain parts, for example, any JOAP instrumentation not developed under Government funding.

Given the criteria defined by this study, the ICP system is the optimum JOAP instrument. However, the system has two major shortcomings. It consumes argon gas and is particle-size dependent. Because ~~welding~~-grade argon is frequently used, the logistics problem of stocking argon cylinders can be minimized by using the present system which supports welding operations on military bases. By installing liquid argon storage tanks at engine maintenance and repair stations or at JOAP laboratories, a major cost savings can be realized for both welding and ICP applications. If particle-size independence becomes a critical requirement for the desired multiservice JOAP analysis unit, then the use of a graphite furnace sample introduction system to an ICP source can be considered. This system is commercially available at a reasonable cost.

SECTION V

RECOMMENDATIONS

It is recommended that the number of elements required of a common Joint Oil Analysis Program (JOAP) laboratory system be reduced to 15. This reflects the number of elements currently offered for JOAP calibration in the 14-element standard and the single-element boron standard. This action would decrease the unit price of any potential JOAP spectrometer by about \$4,000. An additional cost savings of approximately \$10,000 could also be realized if the requirement for sulphur and the purged or required evacuated optics was eliminated.

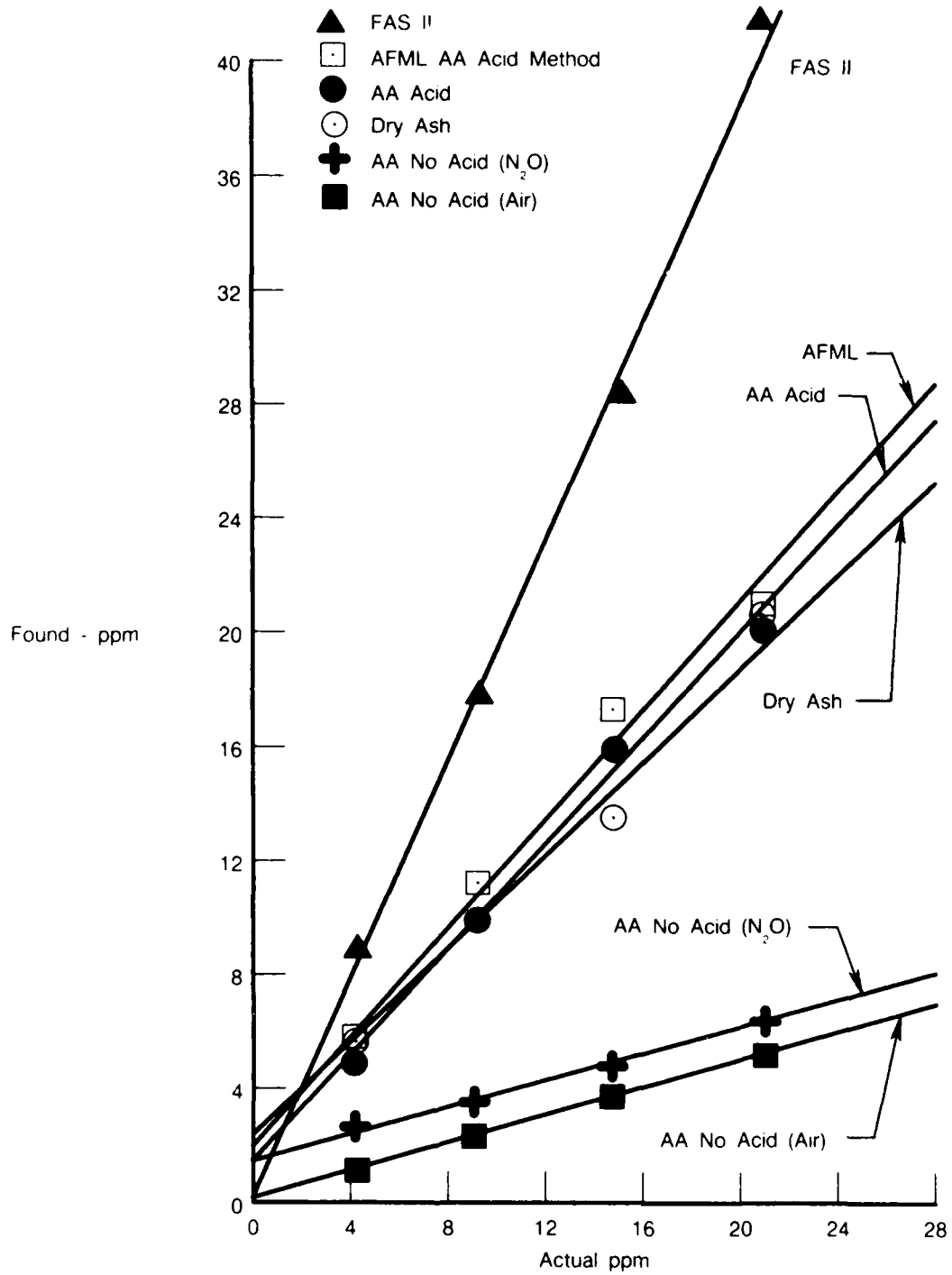
A program is recommended to subject any instrumentation selected for JOAP laboratory-based support to a realistic field test. This field test would indicate if any instrumentation design options need further improvements. This study indicates that one critical area for the ICP AE system is the improvement of the system software for JOAP trending applications. Software must be more user-friendly for simplicity of operation.

A study should be conducted to establish the impact of particle size in JOAP analysis and applications. Programs supporting the development of particle-size independent methods of JOAP analysis should also be conducted. These techniques will be essential to evaluate the effects of particle-size wear on trending analysis.

The impact of fine filtration (3-to-5 microns) should be investigated to determine what impact this technology will have on the JOAP program. Initial data indicates that the dilutory effect of this type of filtration will push the required sensitivity of JOAP instrumentation below the 1-ppm level with the requirement of high precision at those levels.

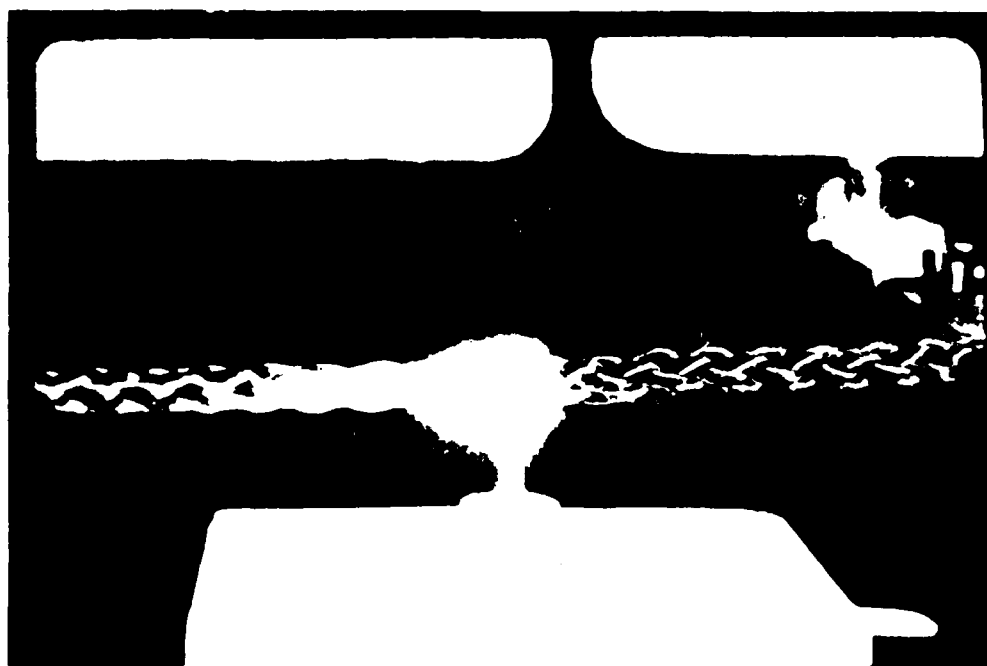
SECTION VI

FIGURES



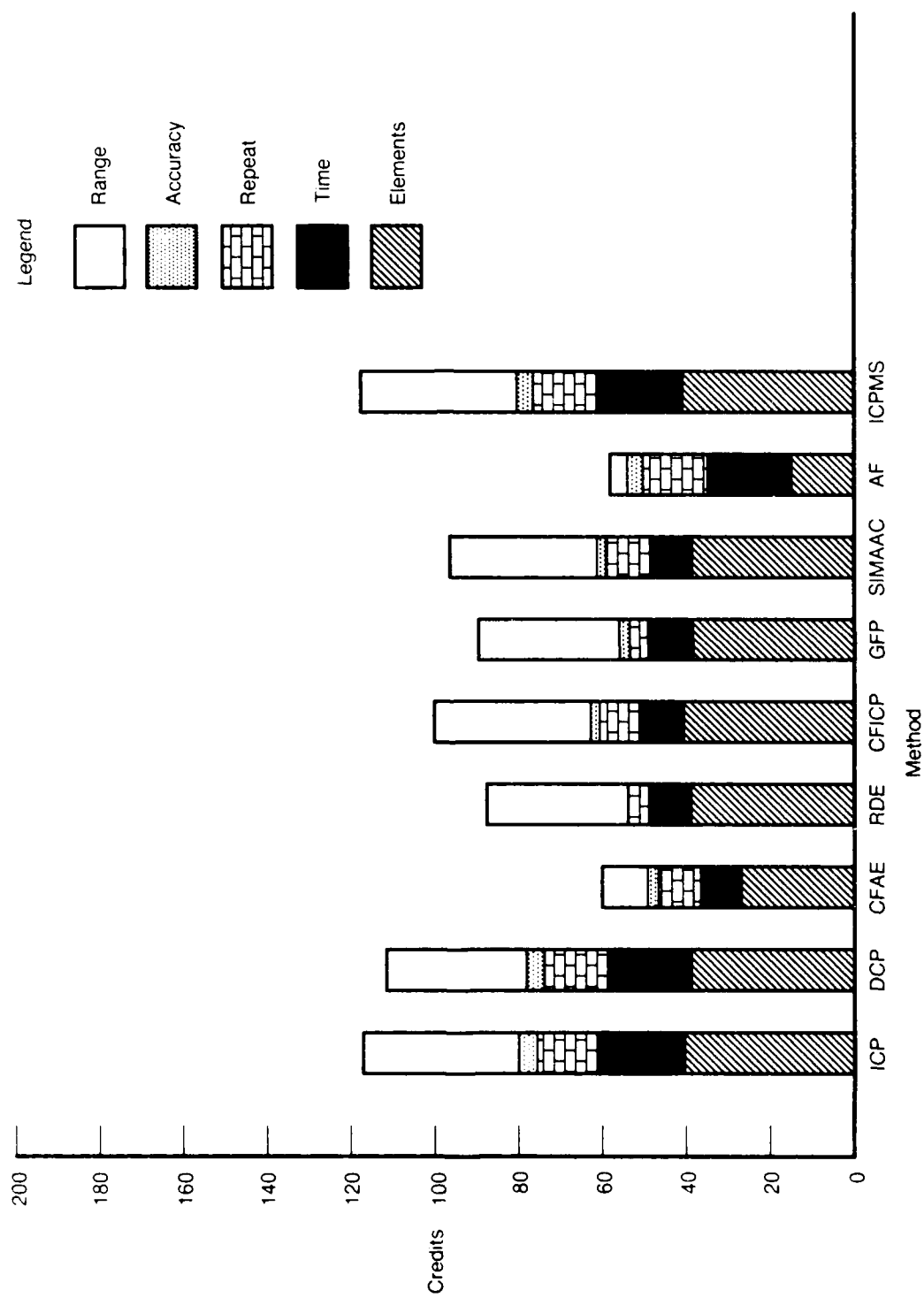
FDA 299395

Figure 1. Comparison of Particle Size Dependent and Independent Methods



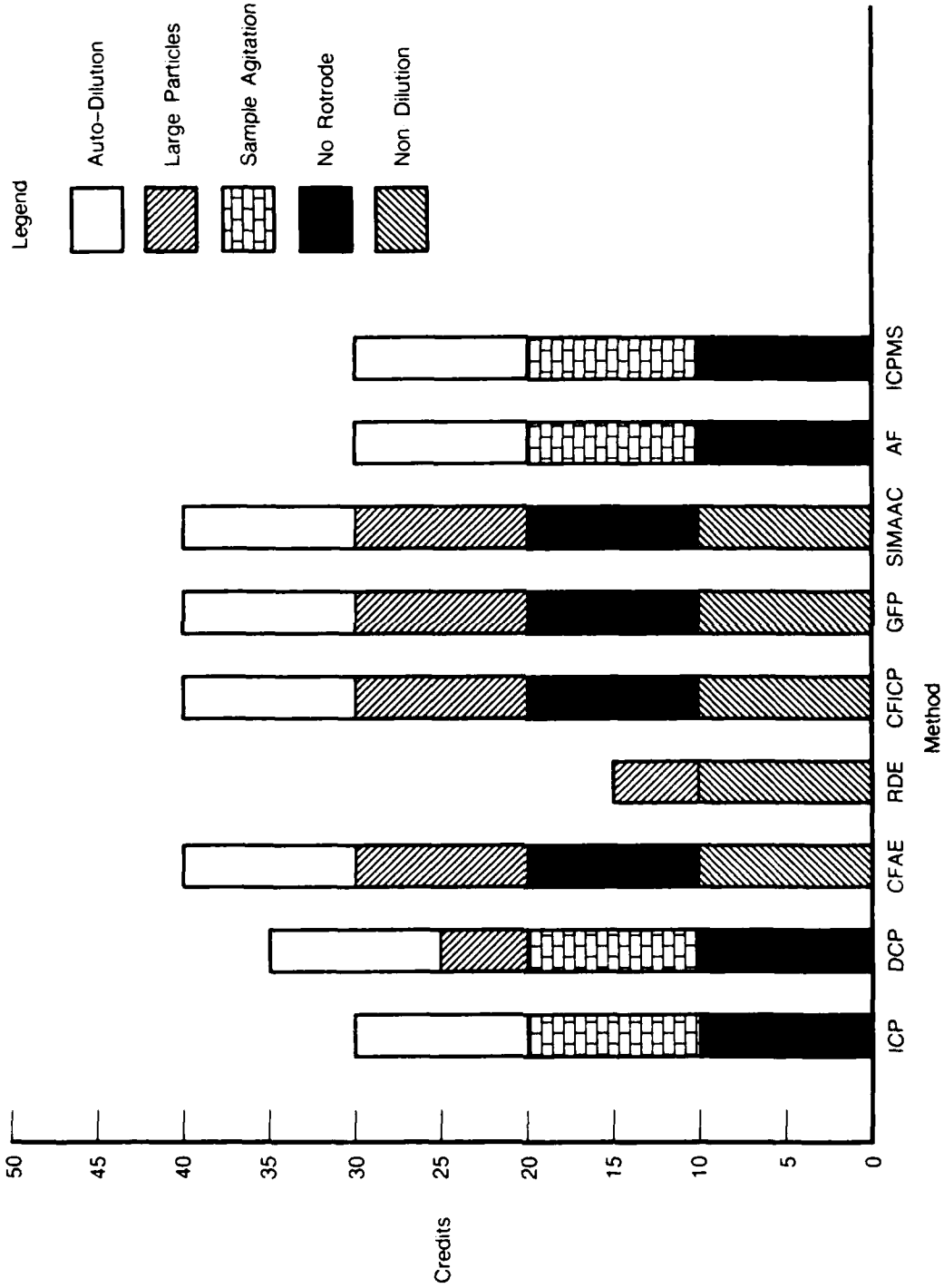
FC 90266

Figure 2. — Graphite Filament Plasma Excitation



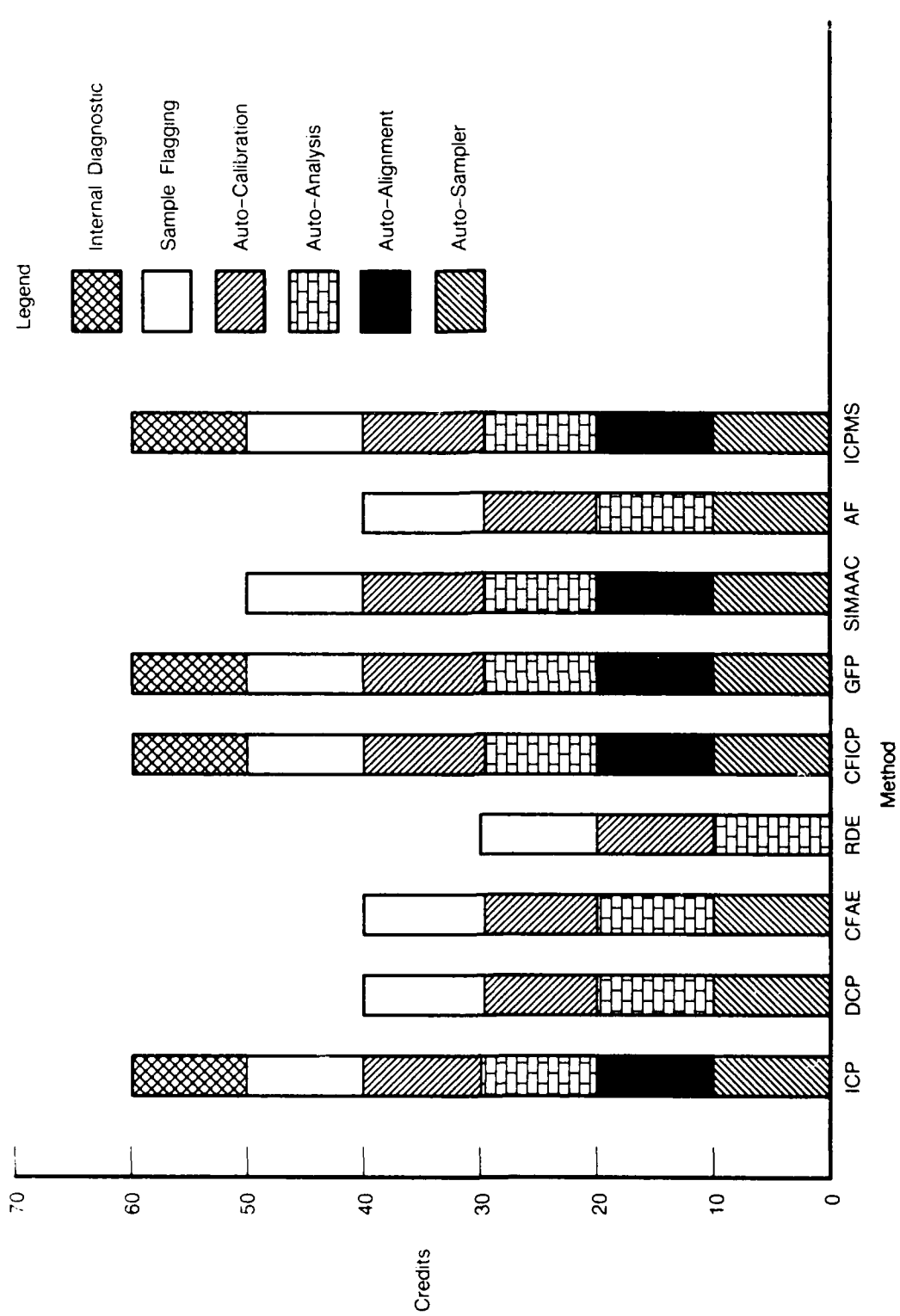
FDA 299394

Figure 3. — Performance Comparison



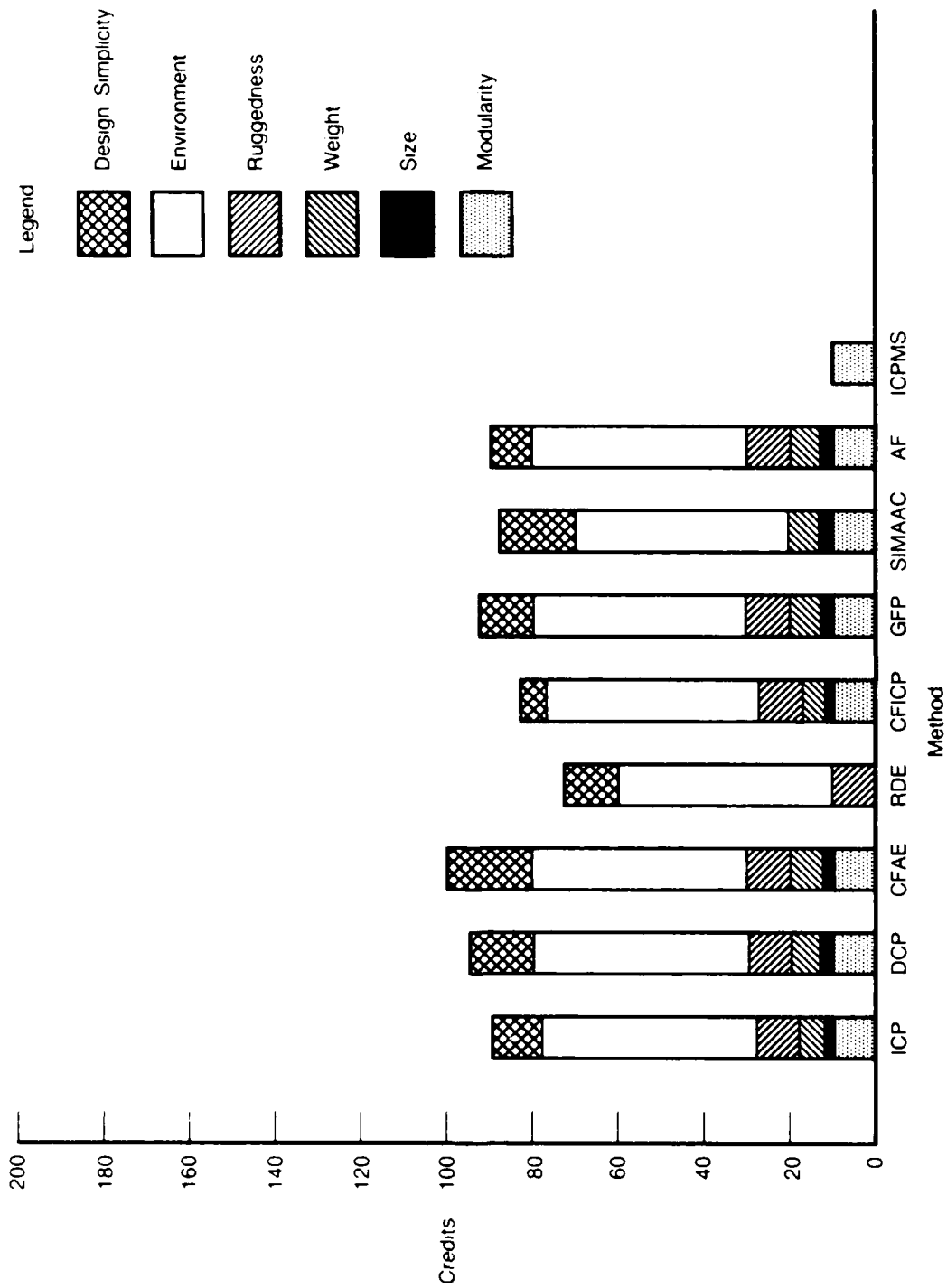
FDA 299393

Figure 4. — Sample Introduction Comparison



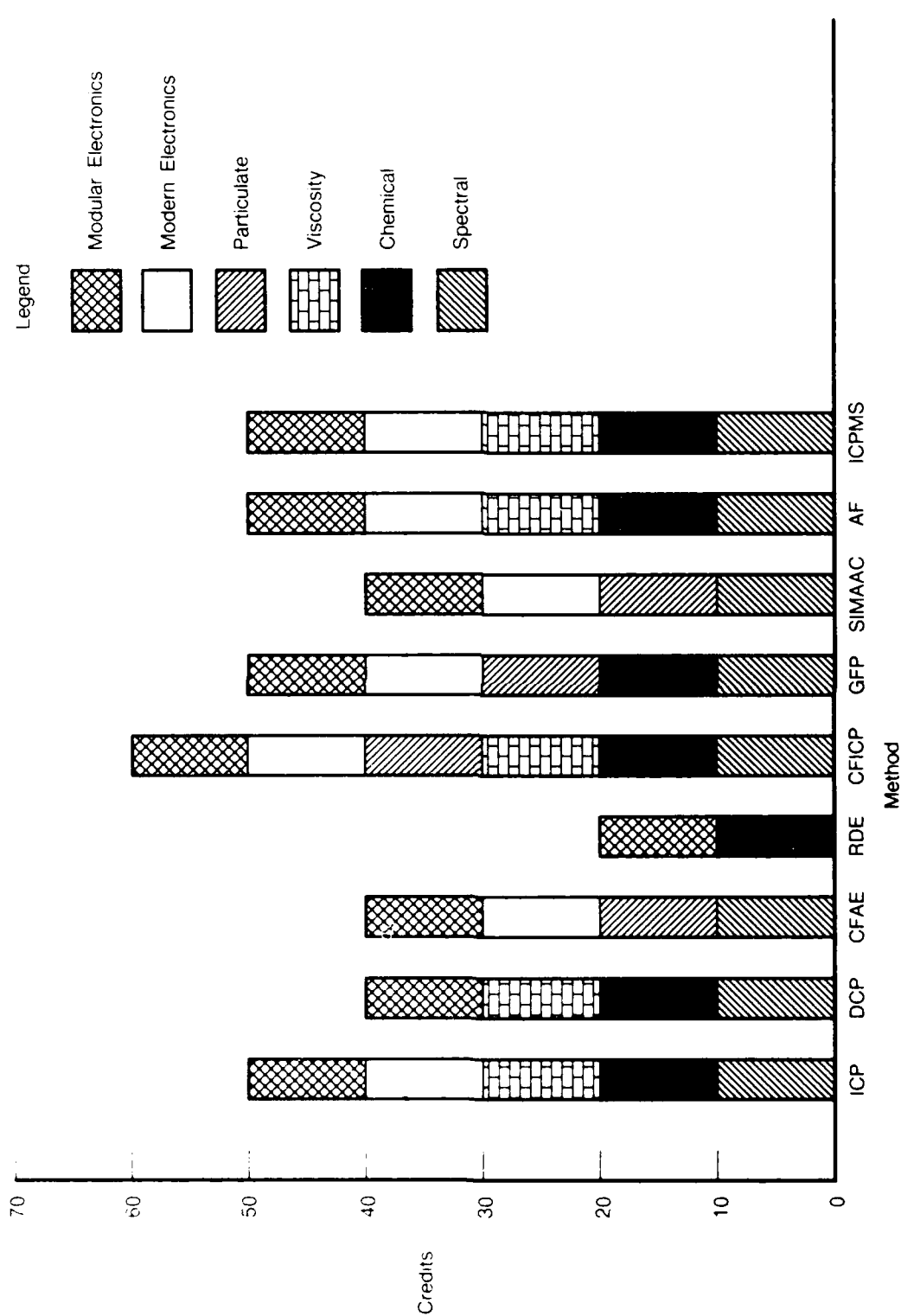
FDA 299392

Figure 5. — Simple Operation Comparison



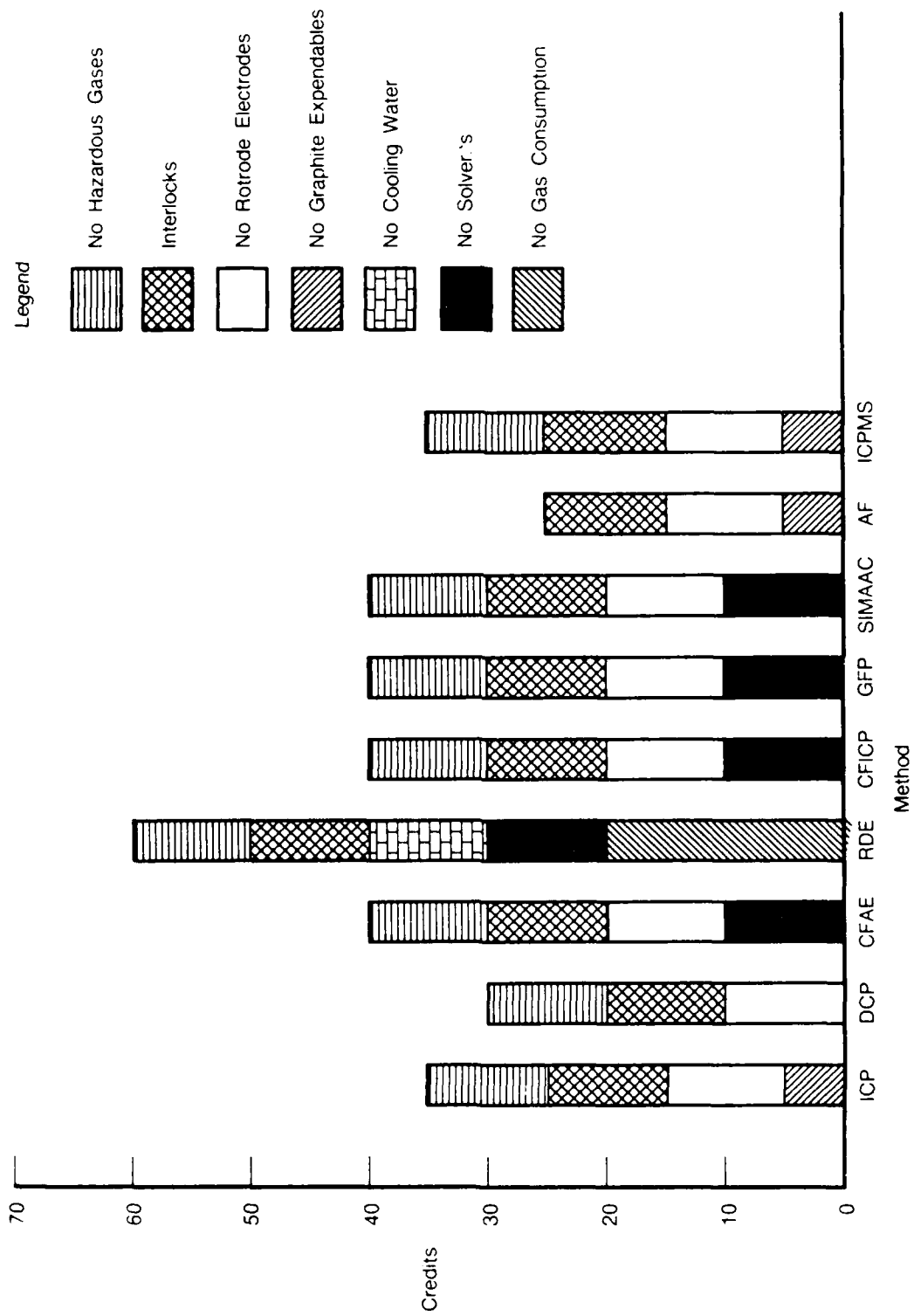
FDA 299391

Figure 6. — Durability/Reliability/Maintainability Comparison



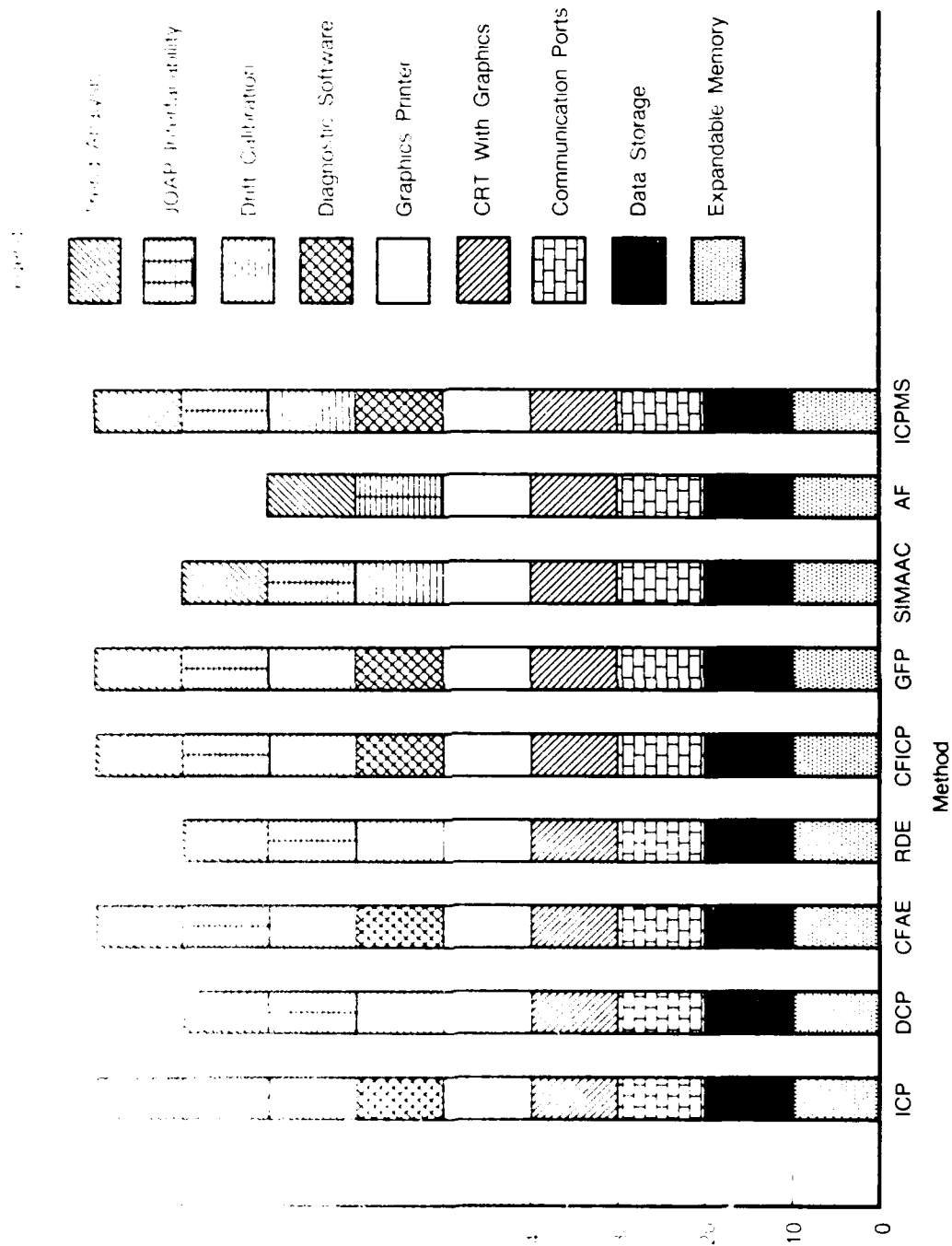
FDA 299390

Figure 7 — Matrix and Electronics Comparison



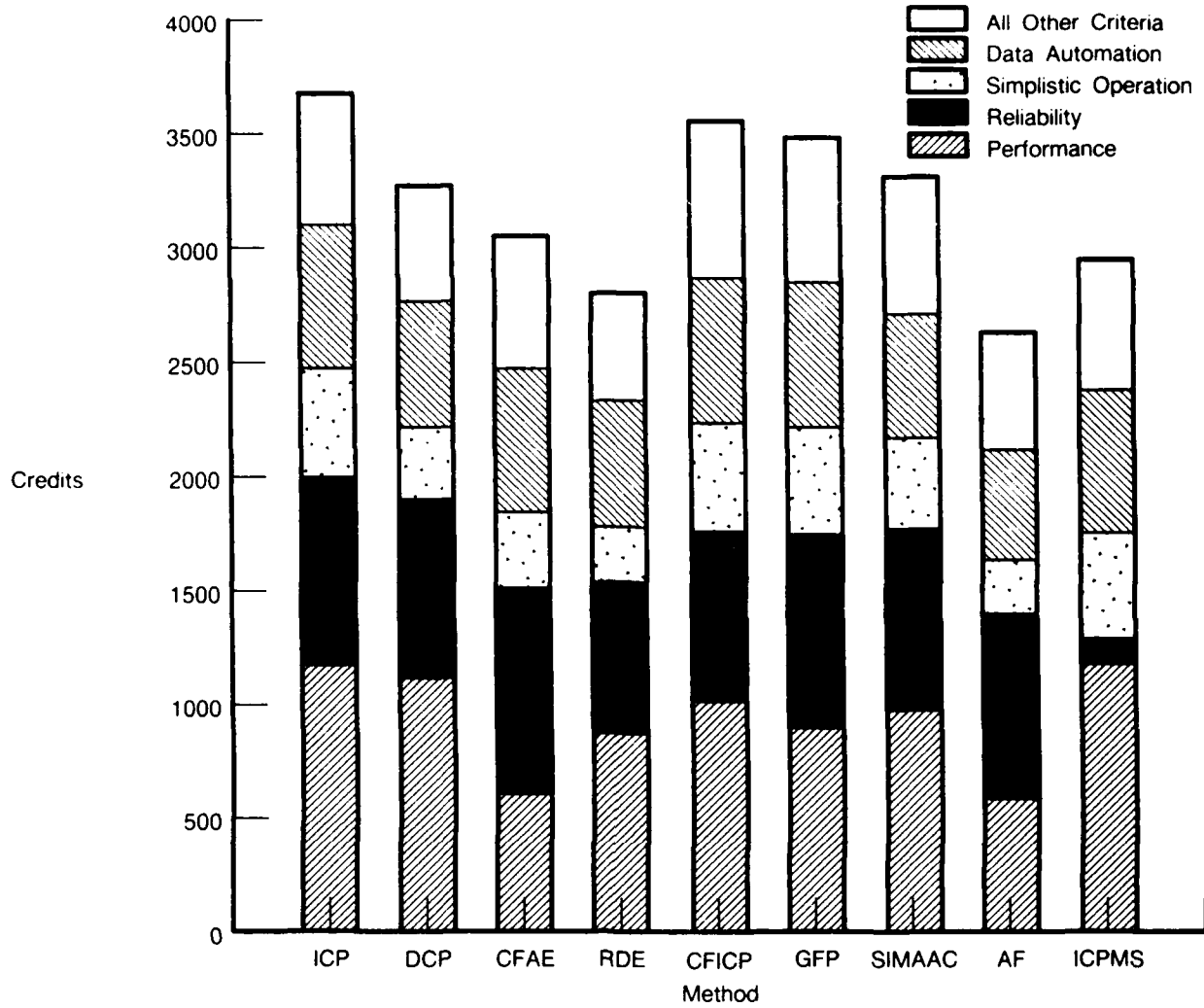
FDA 295389

Figure 8. — Consumables and Safety Comparisons



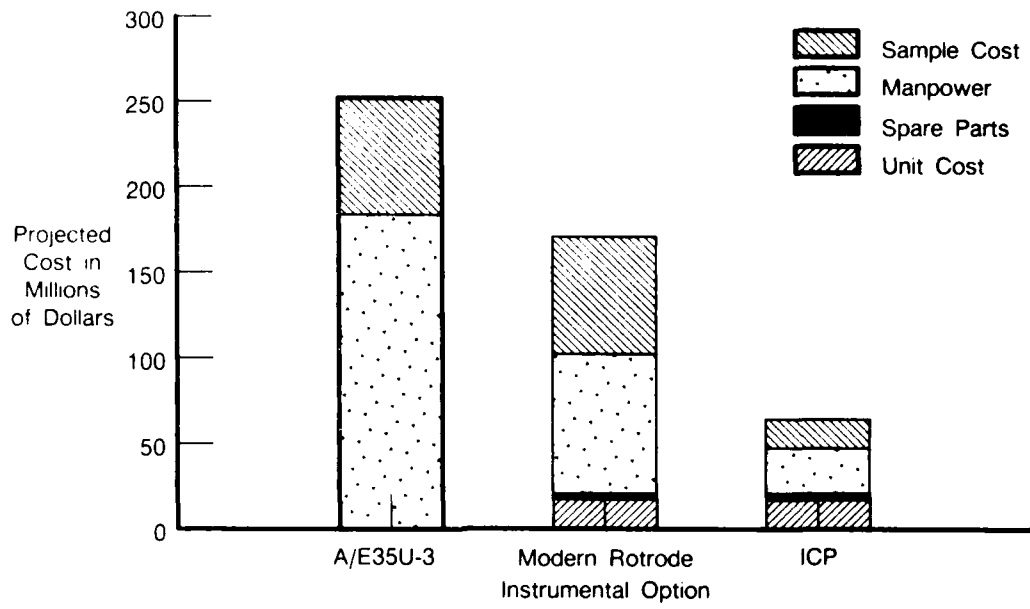
FDA 299388

Figure 9. Data Station Comparison



FDA 299387

Figure 10. — Weighted Design and Performance Ranking



FDA 299386

Figure 11. — Cost Analysis

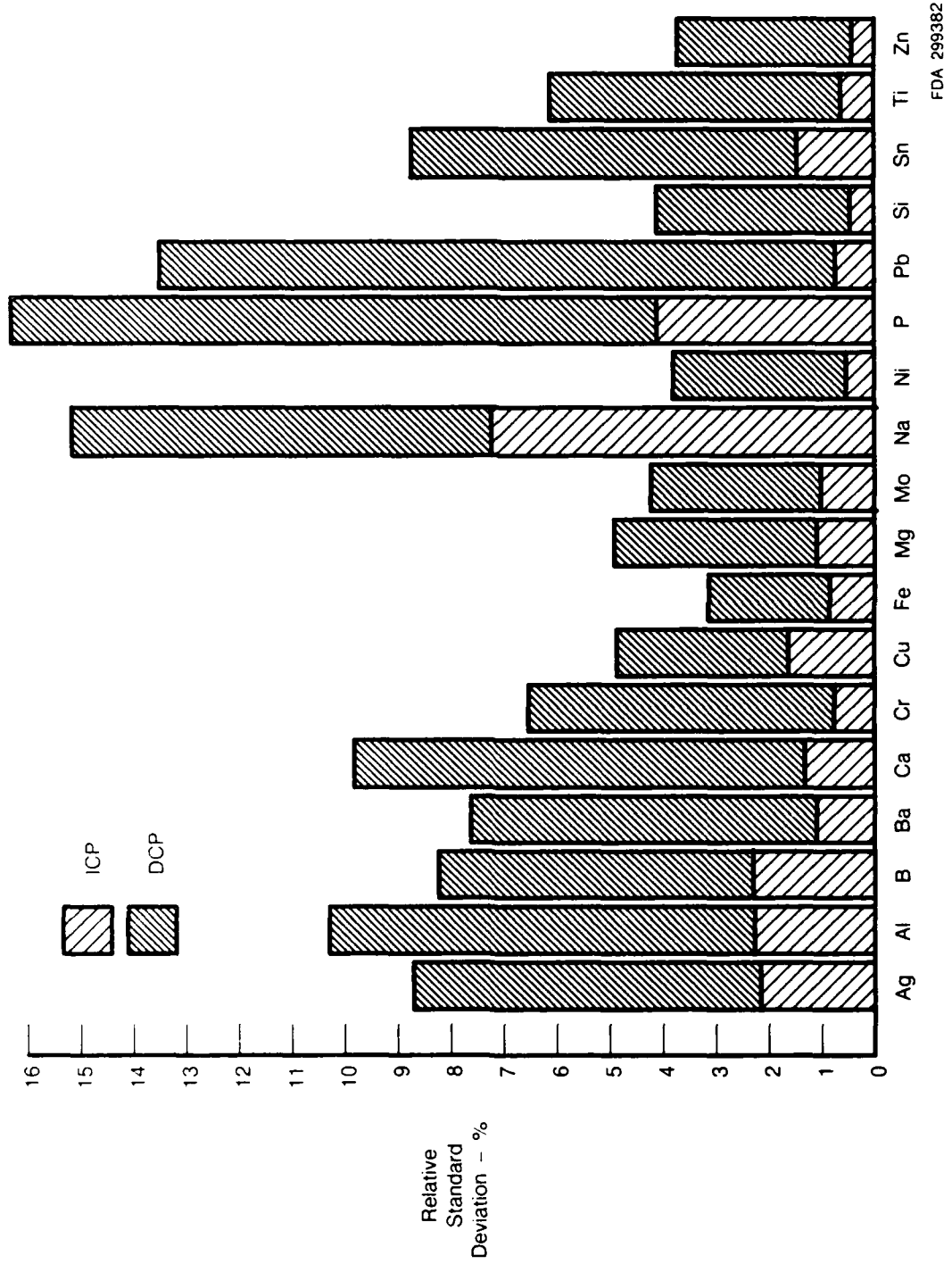
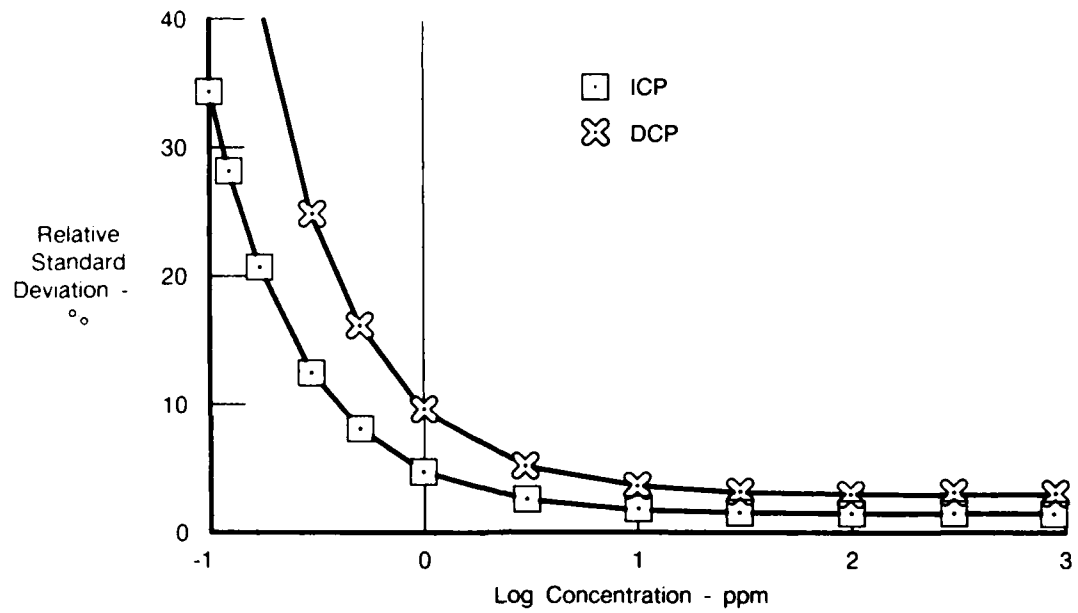


Figure 12. -- Precision of Emission Measurements -- 10 ppm Conostan ESS-21, Dilution Factor 1-9



FDA 299381

Figure 13. — Precision of Analysis With ICP and DCP for Most Wear Metals in Oil

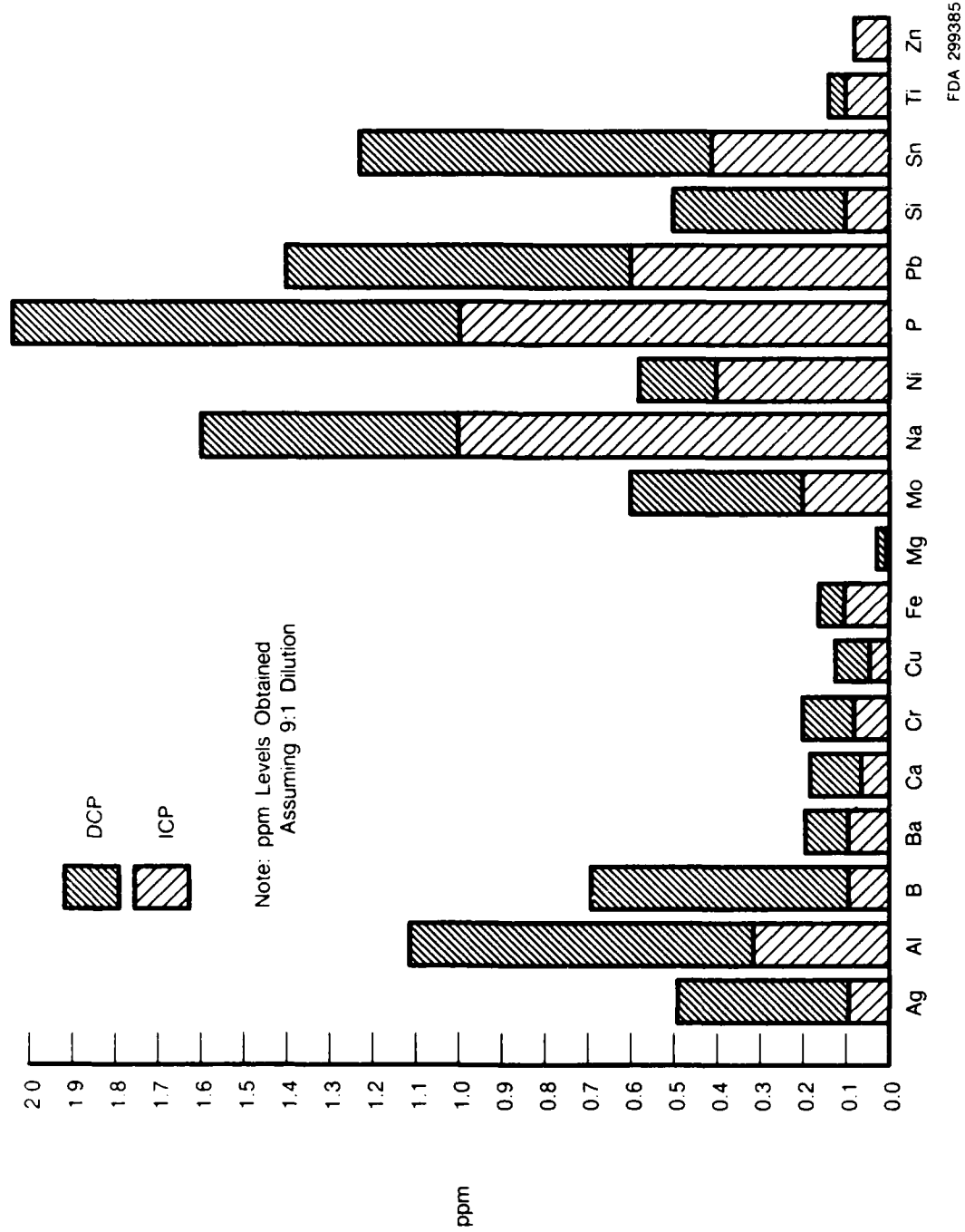
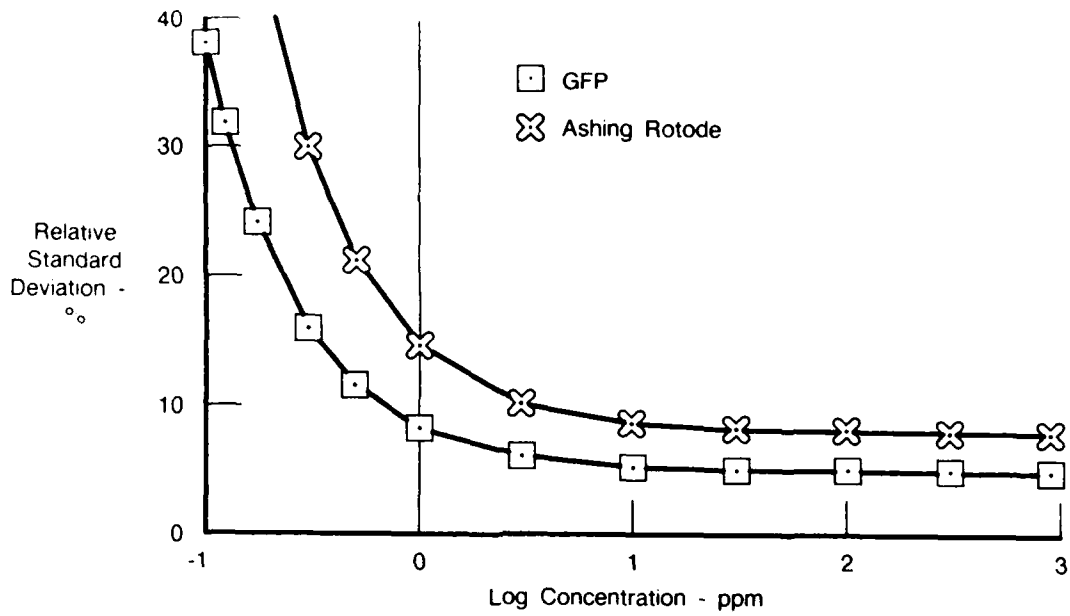
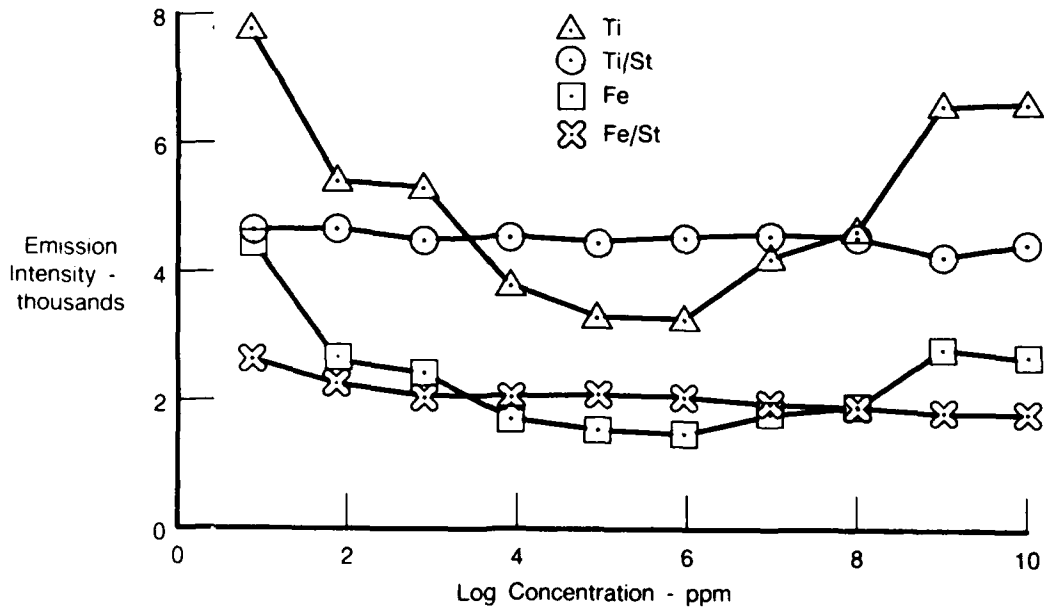


Figure 14. — Deflection Limits by Plasma Emission



FDA 299379

Figure 15. — Precision of Analysis: GFP and Ash-RDE for Most Wear Metals in Oil



FDA 299380

Figure 16. — Effect of Internal Standardization — 100 ppm S-21 With 150 ppm Sr

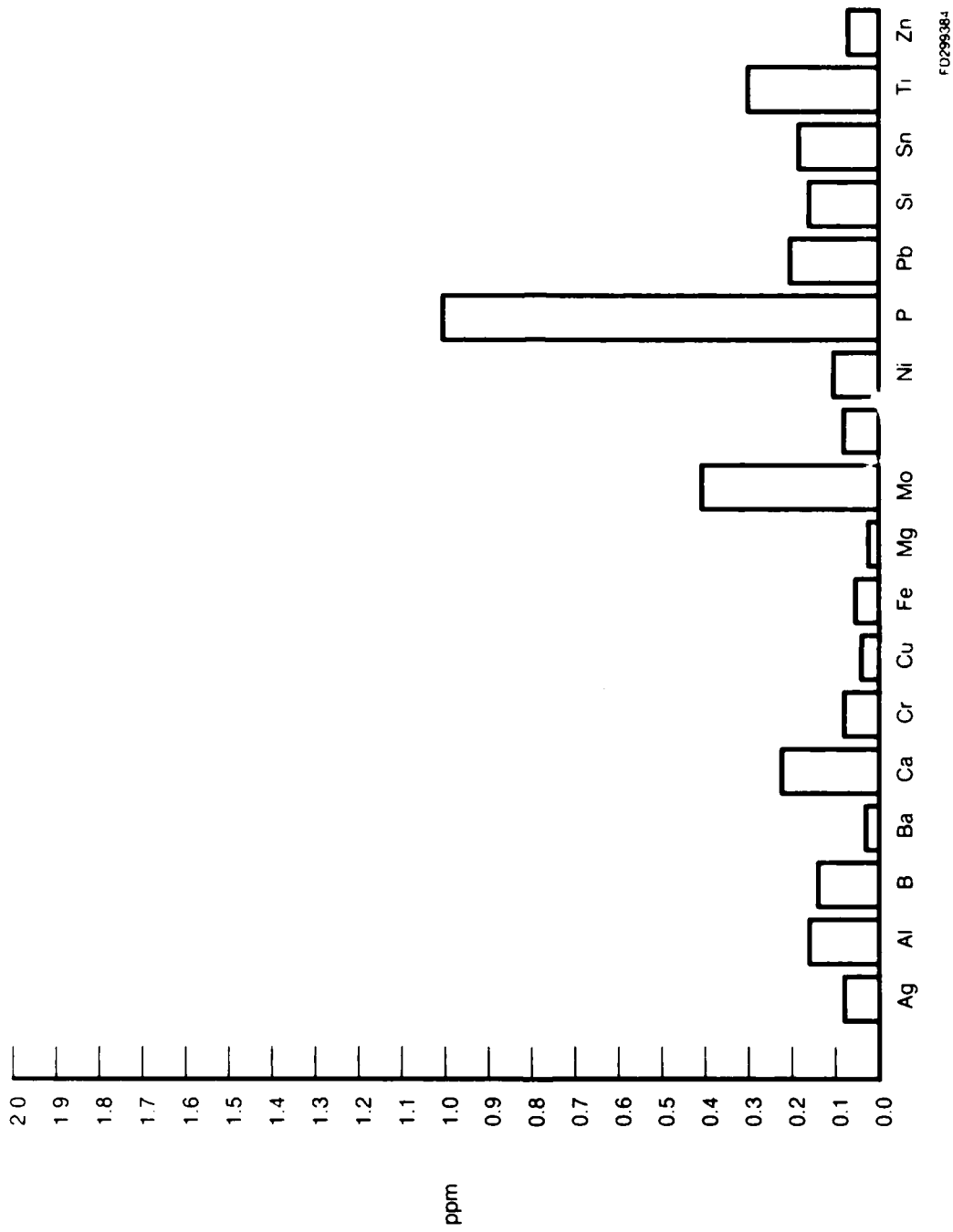


Figure 17. — Detection Limits With the GFP (Based on 50 µl Samples)

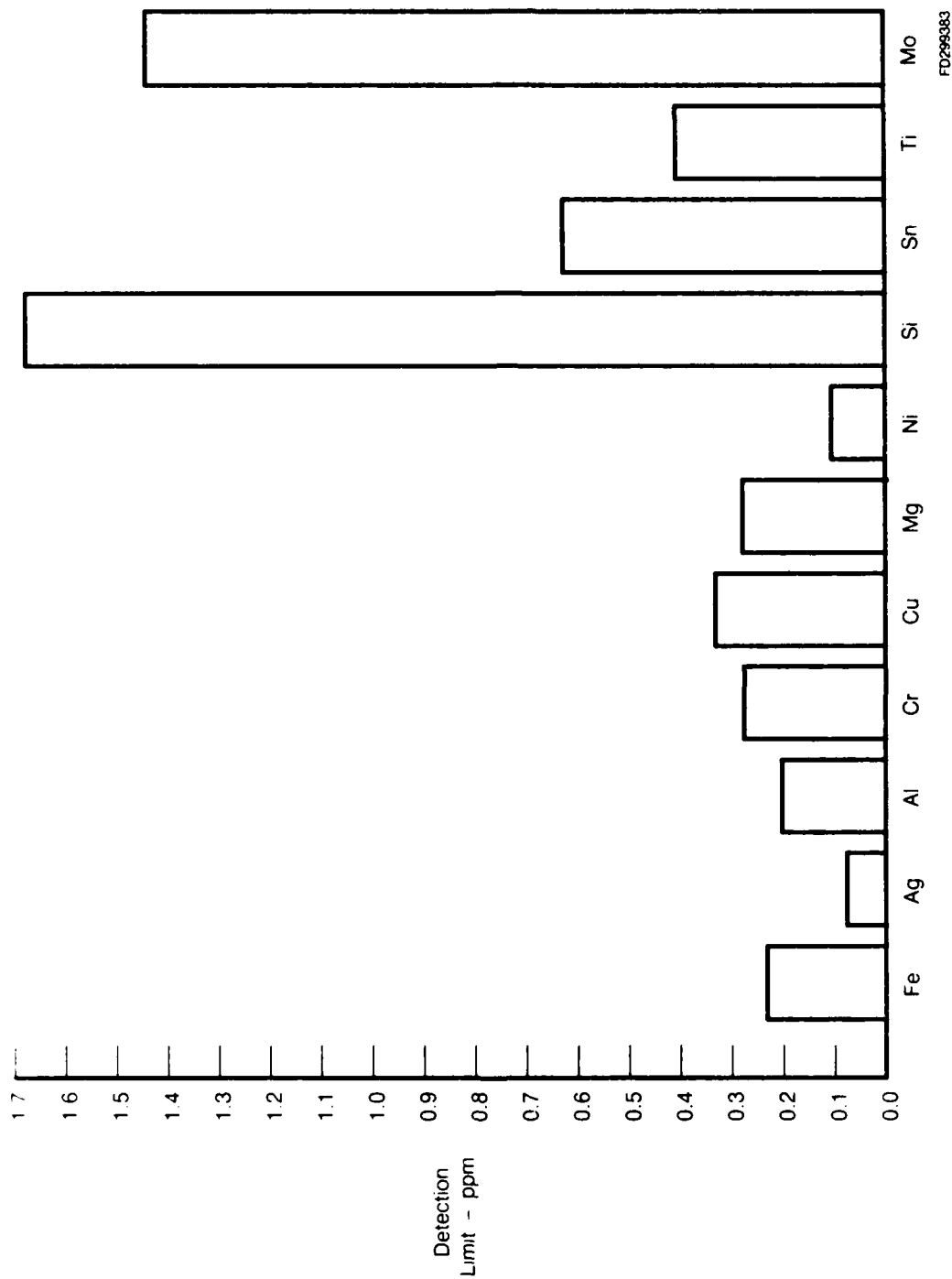
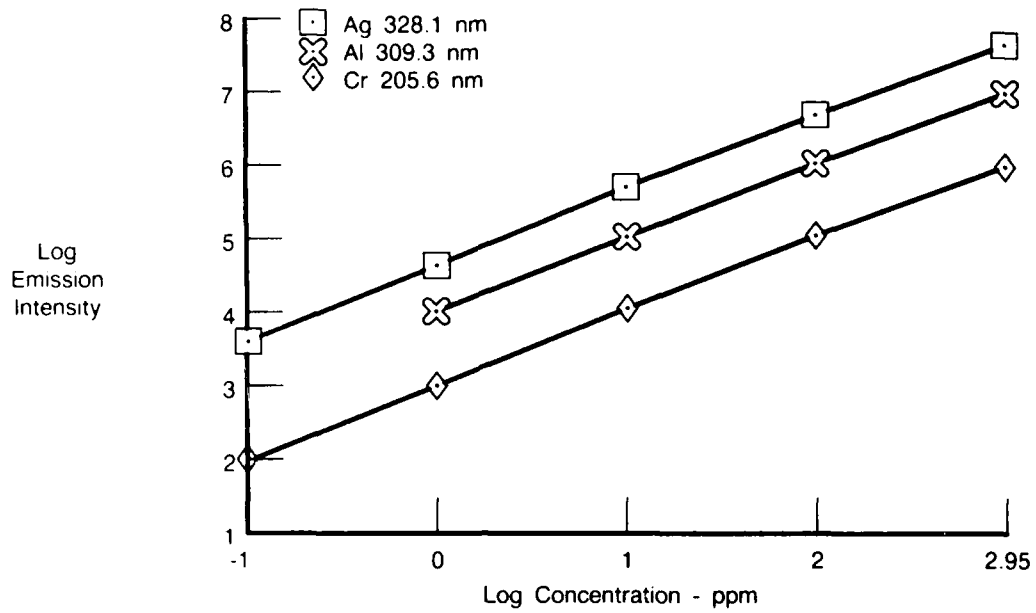
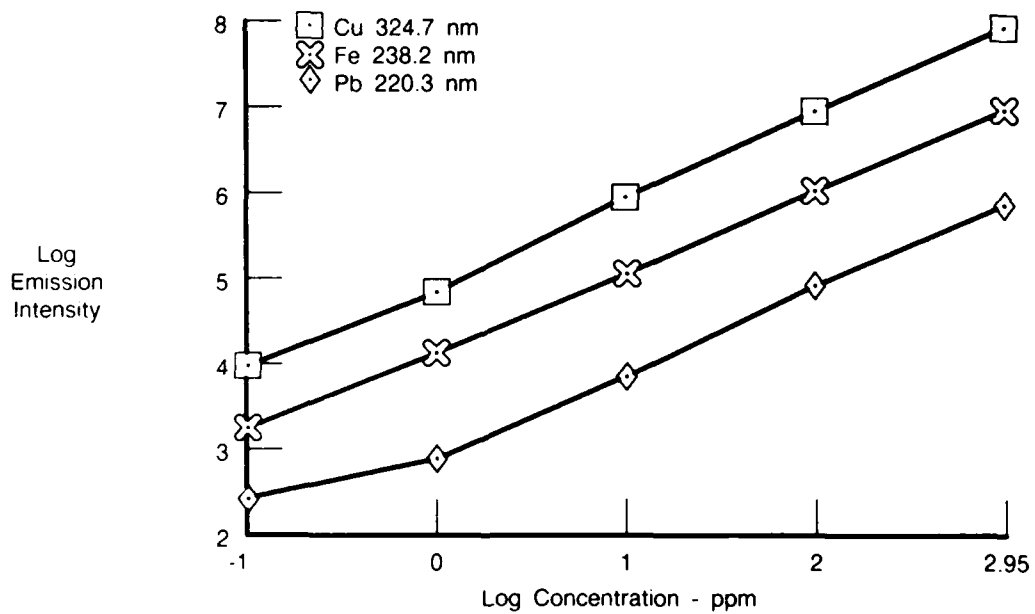


Figure 18. — Detection Limits With Ashing Rotrode



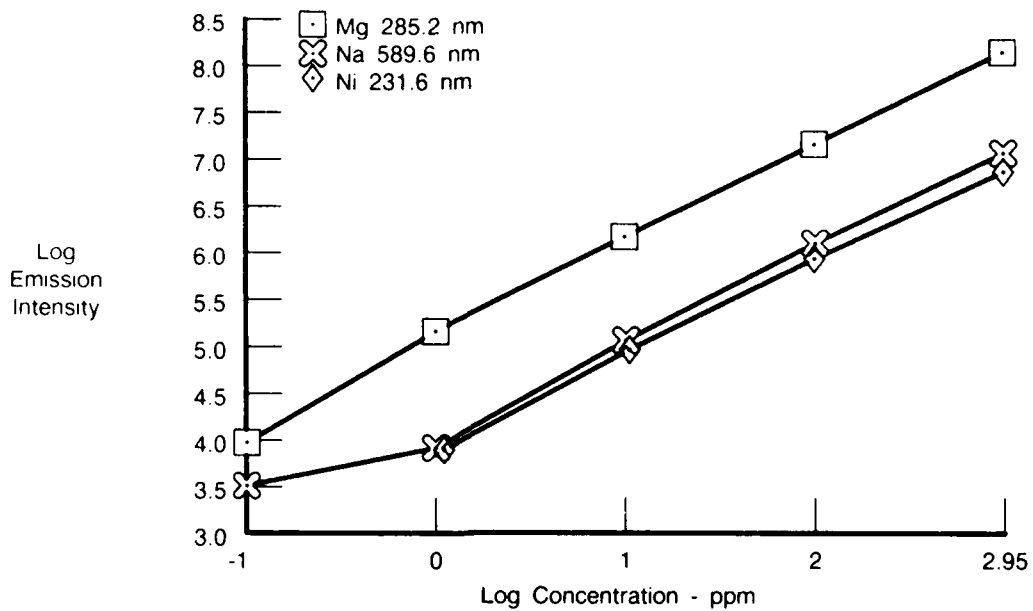
FDA 299378

Figure 19. — ICP Calibration Curves for Ag, Al, and Cr — Conostan S-12 Diluted 1 to 4 With Kerosene



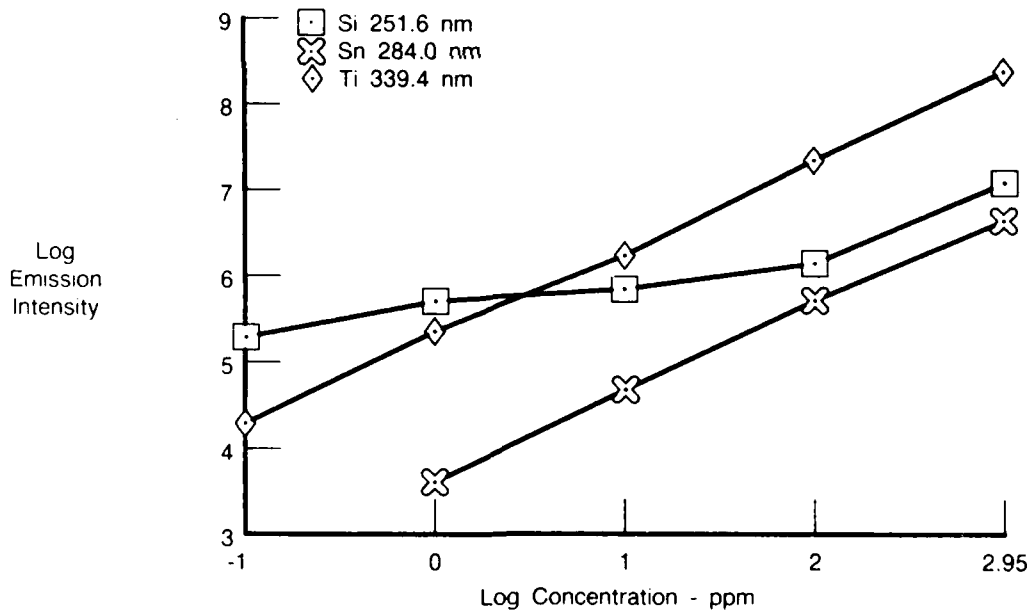
FDA 299377

Figure 20. — ICP Calibration Curves for Cu, Fe, and Pb — Conostan S-12 Diluted 1 to 4 With Kerosene



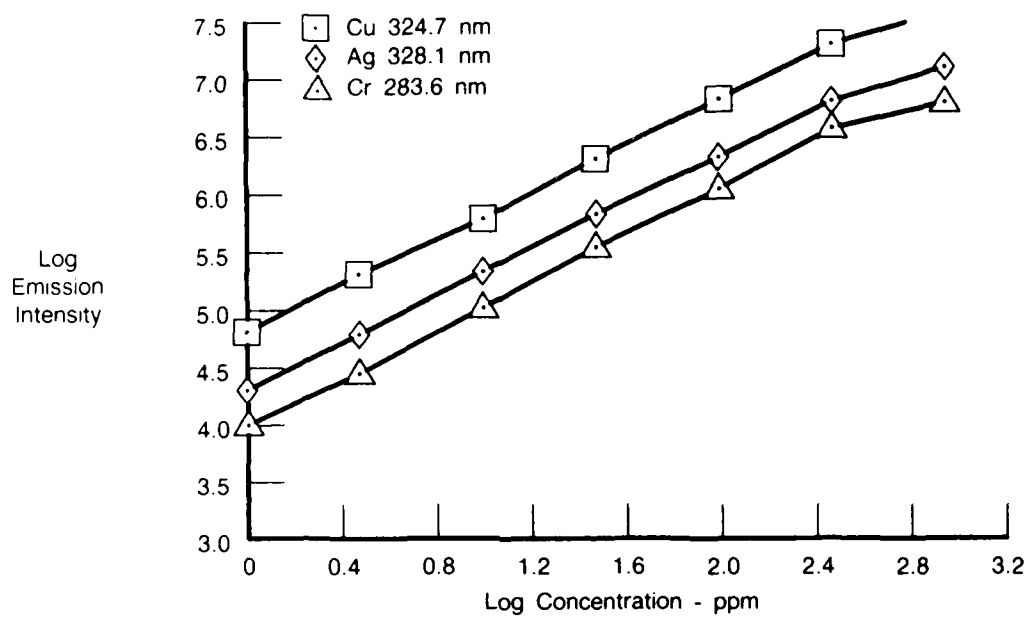
FDA 299376

Figure 21. — ICP Calibration Curves for Mg, Na, and Ni — Conostan S-12 Diluted 1 to 4 With Kerosene



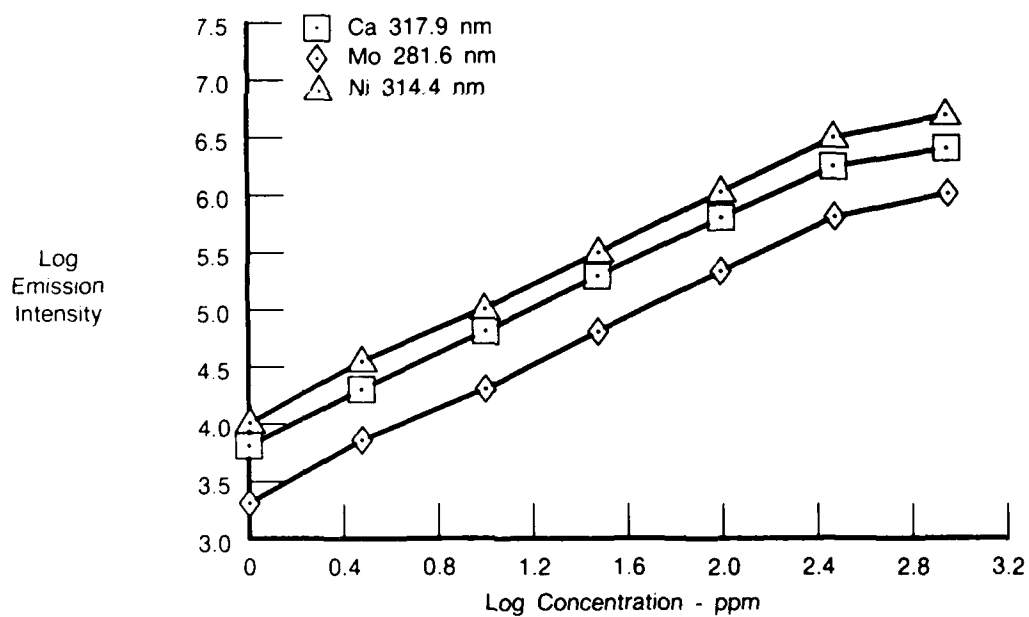
FDA 299375

Figure 22. — ICP Calibration Curves for Si, Sn, and Ti — Conostan S-12 Diluted 1 to 4 With Kerosene



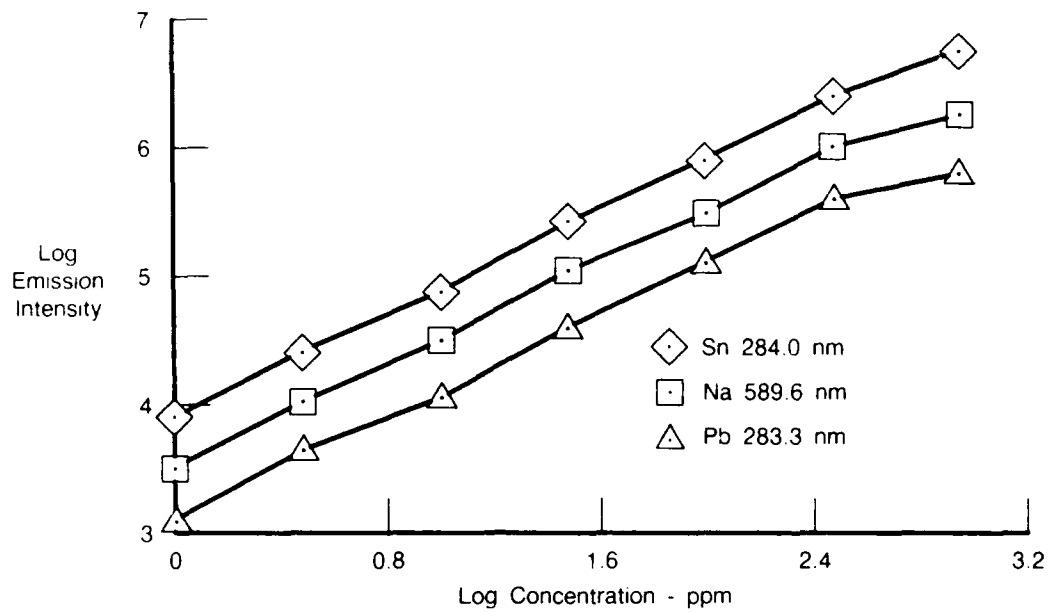
FDA 299374

Figure 23. — GFP Calibration Curves for Cu, Ag, and Cr



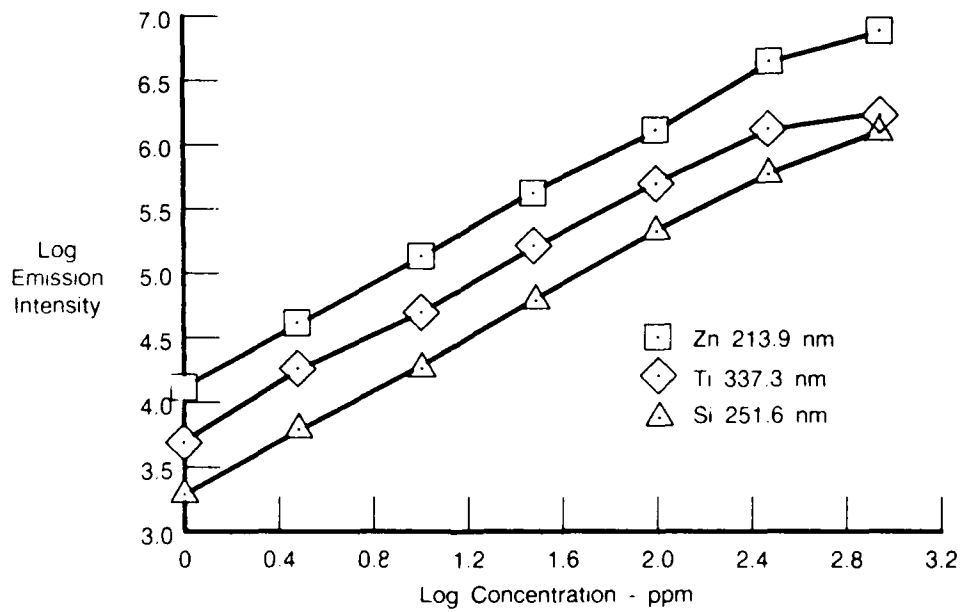
FDA 299373

Figure 24. — GFP Calibration Curves for Ca, Mo, and Ni



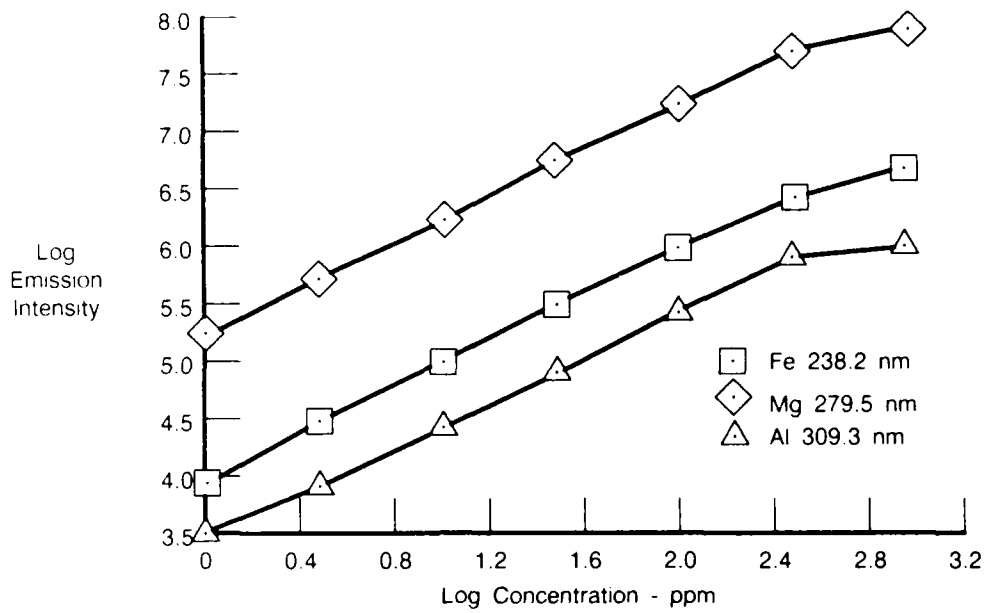
FDA 299372

Figure 25. — GFP Calibration Curves for Na, Pb, and Sn



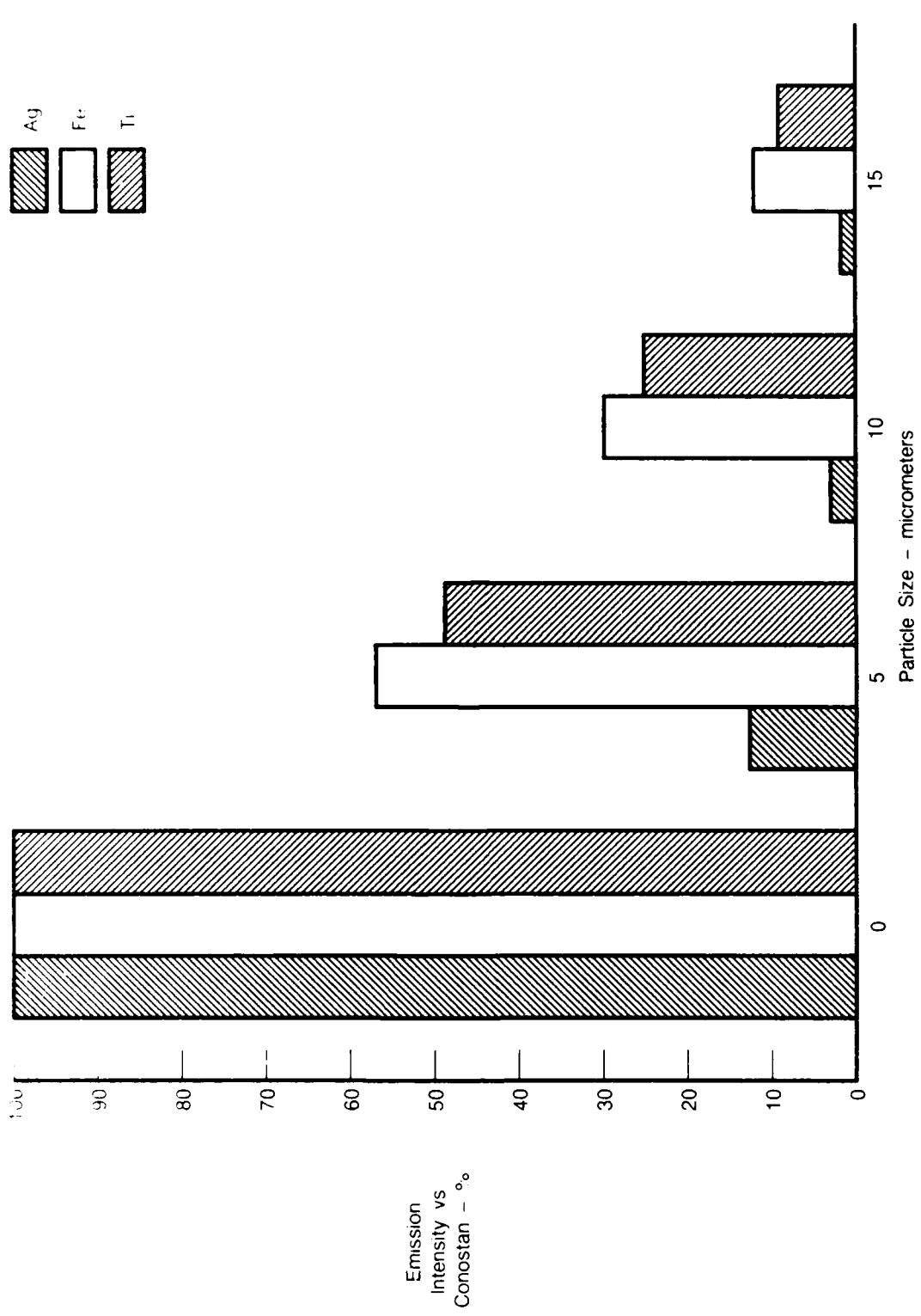
FDA 299371

Figure 26. — GFP Calibration Curves for Si, Ti, and Zn



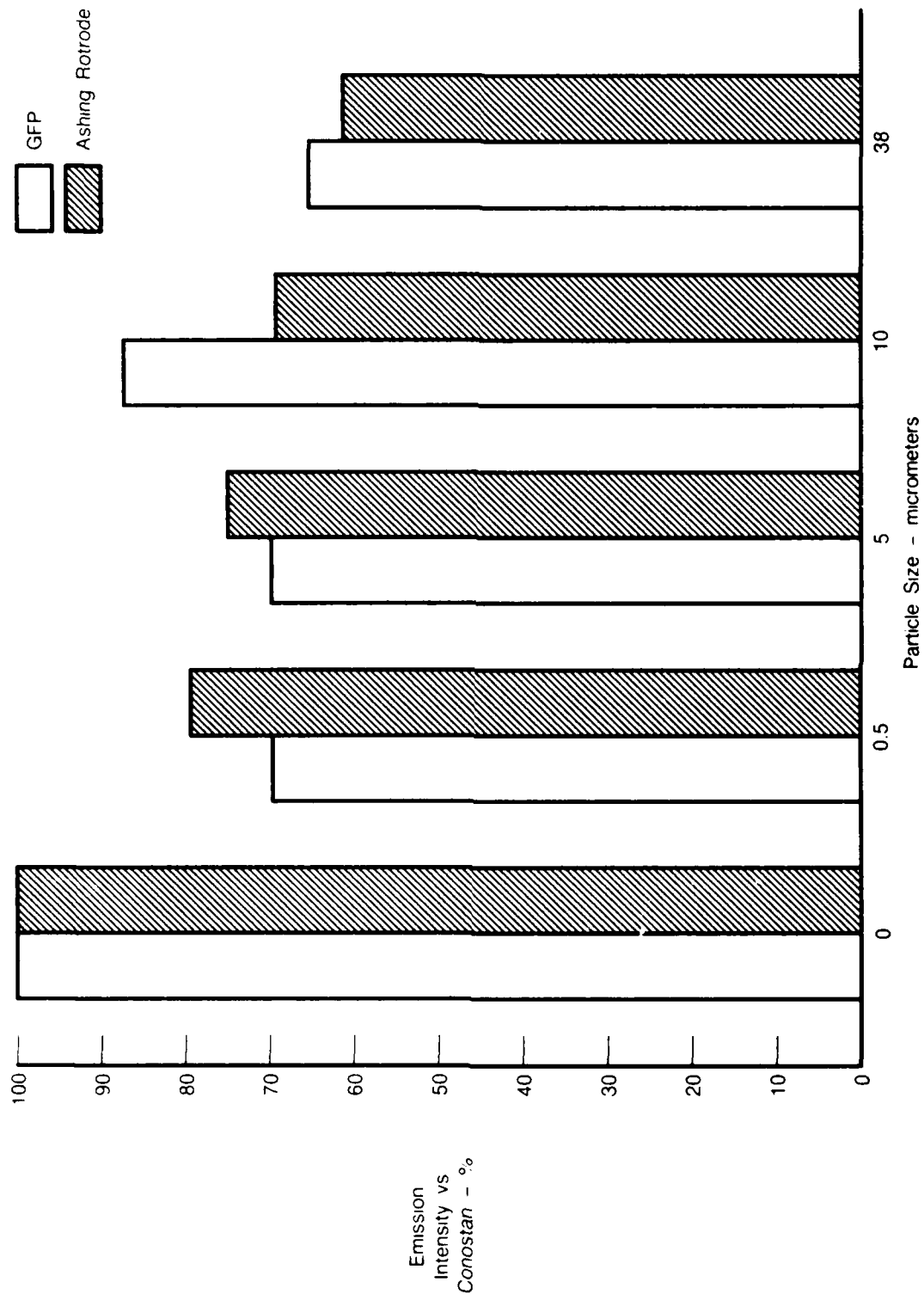
FDA 299370

Figure 27. — GFP Calibration Curves for Fe, Mg, and Al



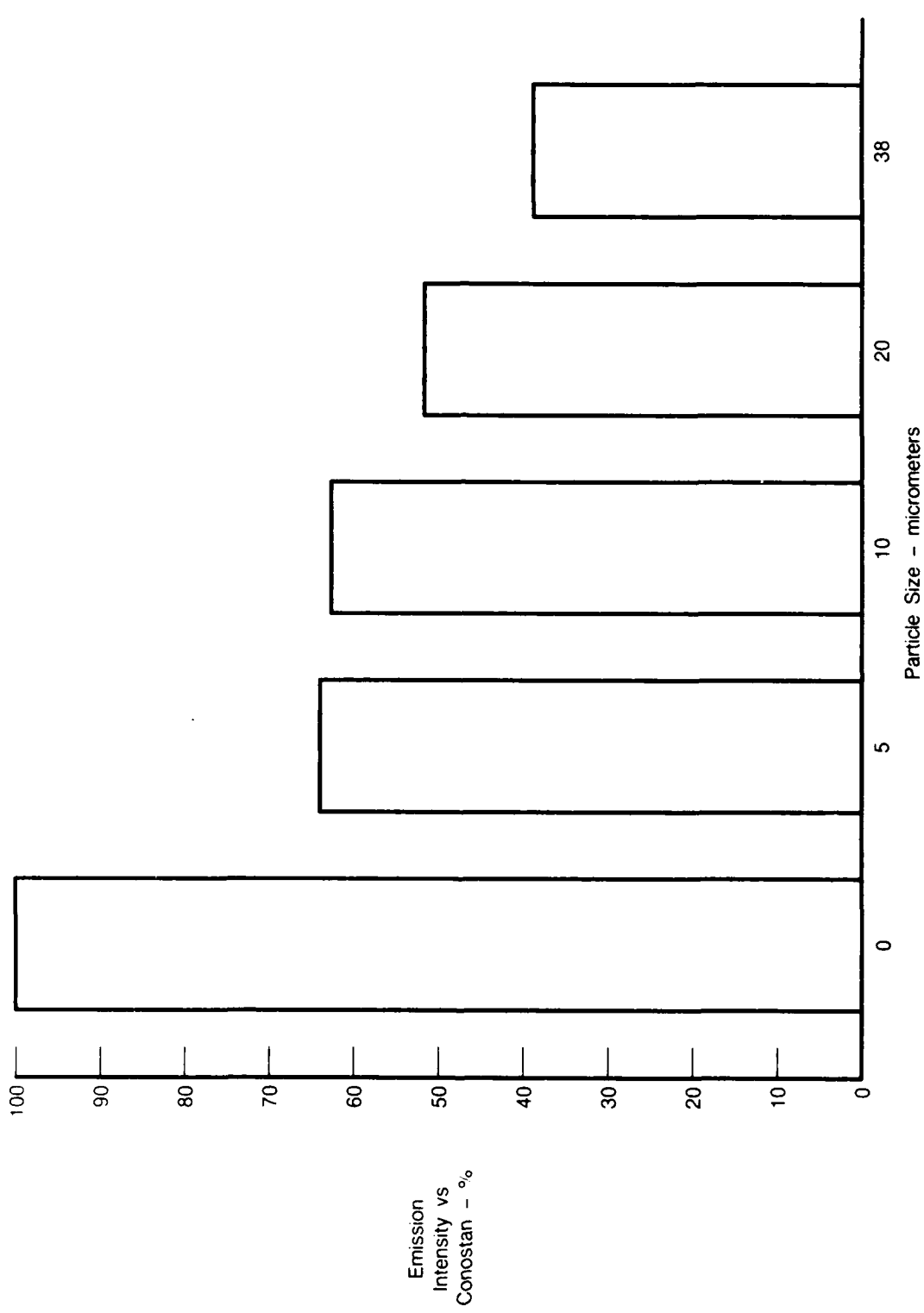
FDA 299366

Figure 28. — Detection of Particulate Metals



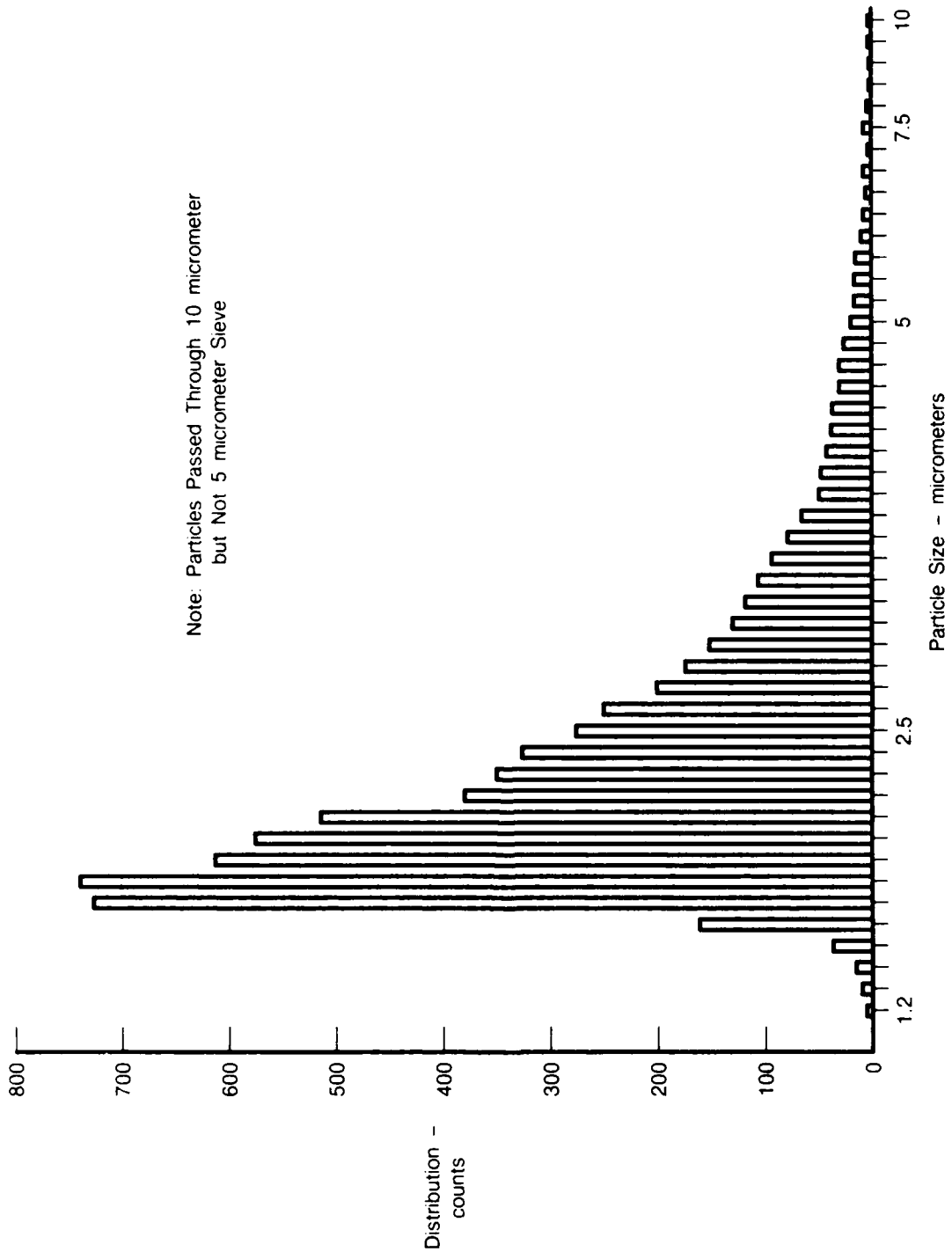
FDA 299365

Figure 29. — Detection of Particulate Nickel With GFP and Ashing Rotrode



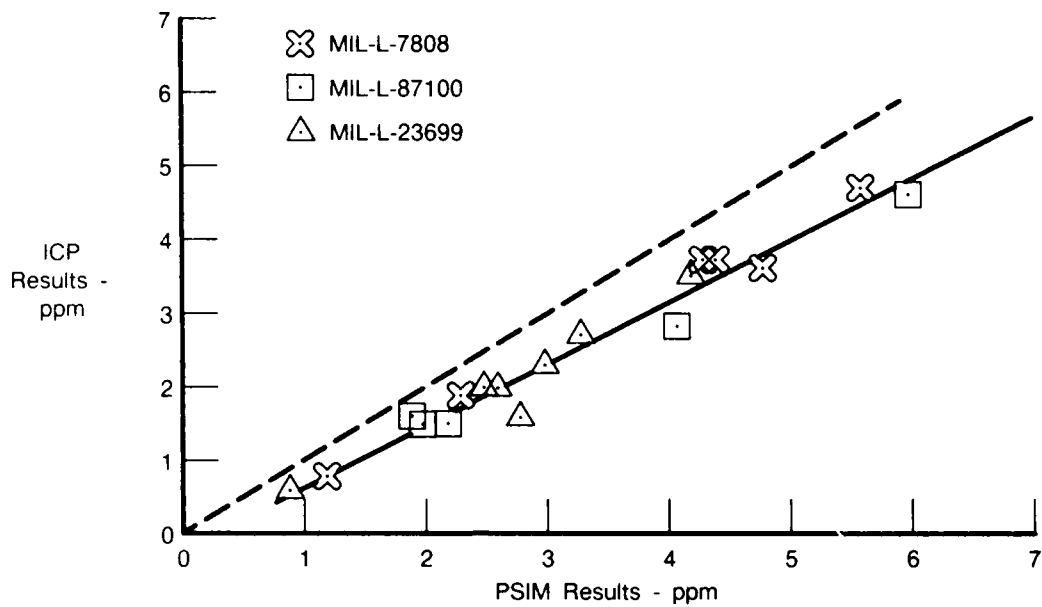
FDA 299364

Figure 30. — Detection of Particulate Iron With the Graphite Filament Plasma



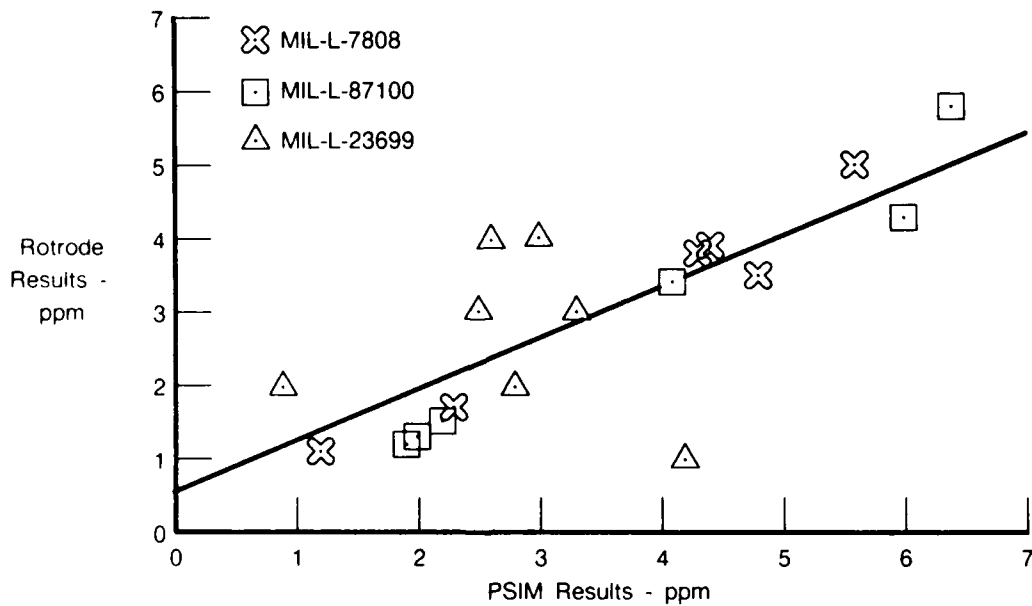
FD299363

Figure 31. — Size Distribution of Iron Powder



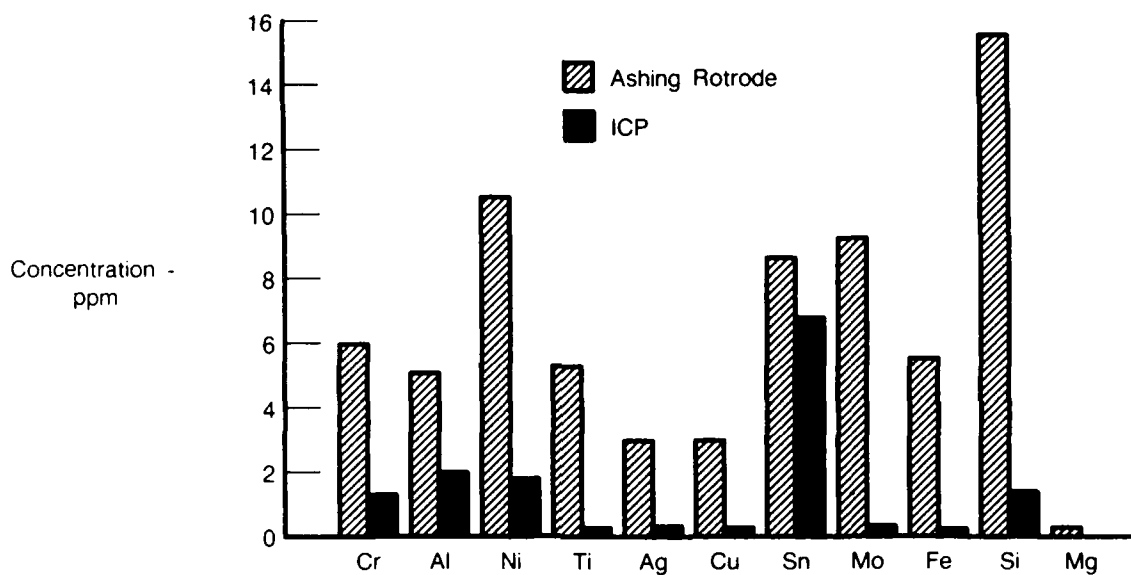
FDA 312611

Figure 32. — Comparison of Analyses of Used Jet Engine Oils for Iron by ICP-AES and by a Particle-Size-Independent Method (PSIM)



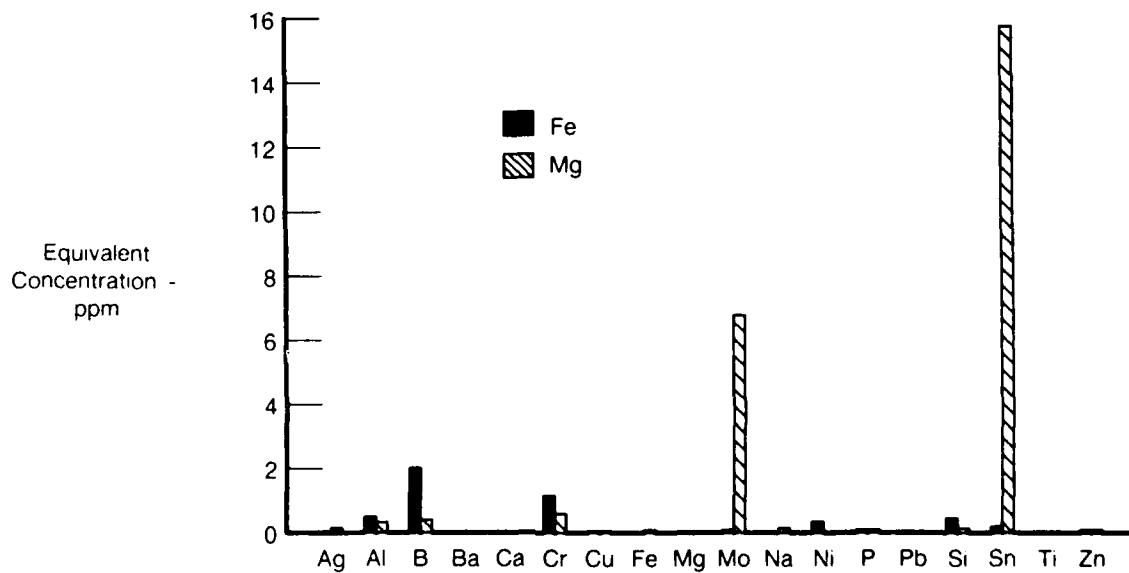
FDA 312612

Figure 33. Comparison of Analyses of Used Jet Engine Oils for Iron by Rotrode AES and by a Particle-Size-Independent Method (PSIM)



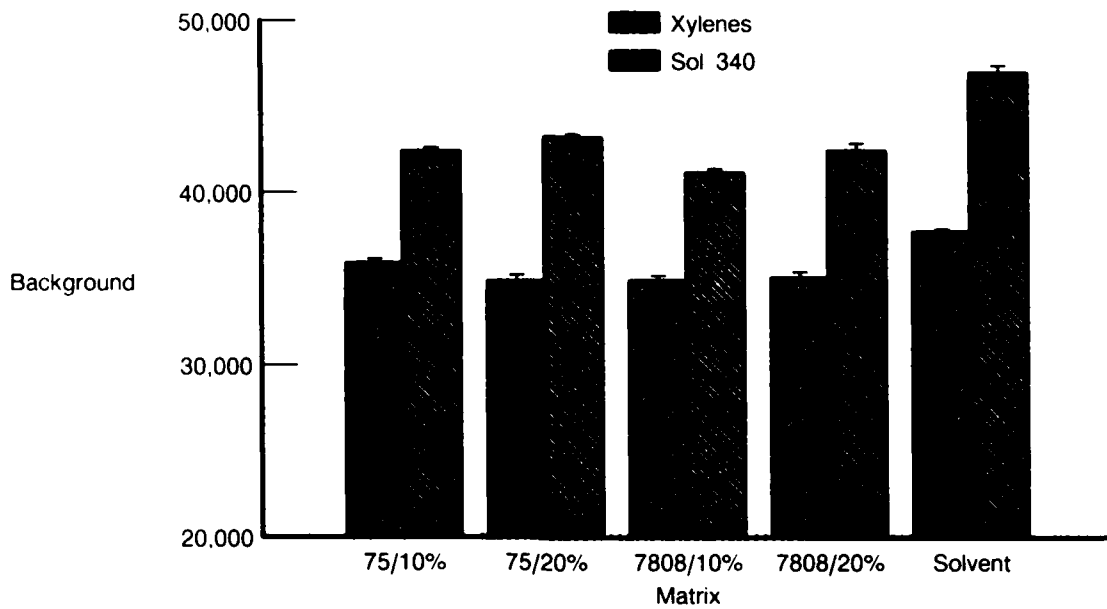
FDA 312613

Figure 34. — Background Equivalent Concentrations for Wavelengths of Spectro Polychrometer



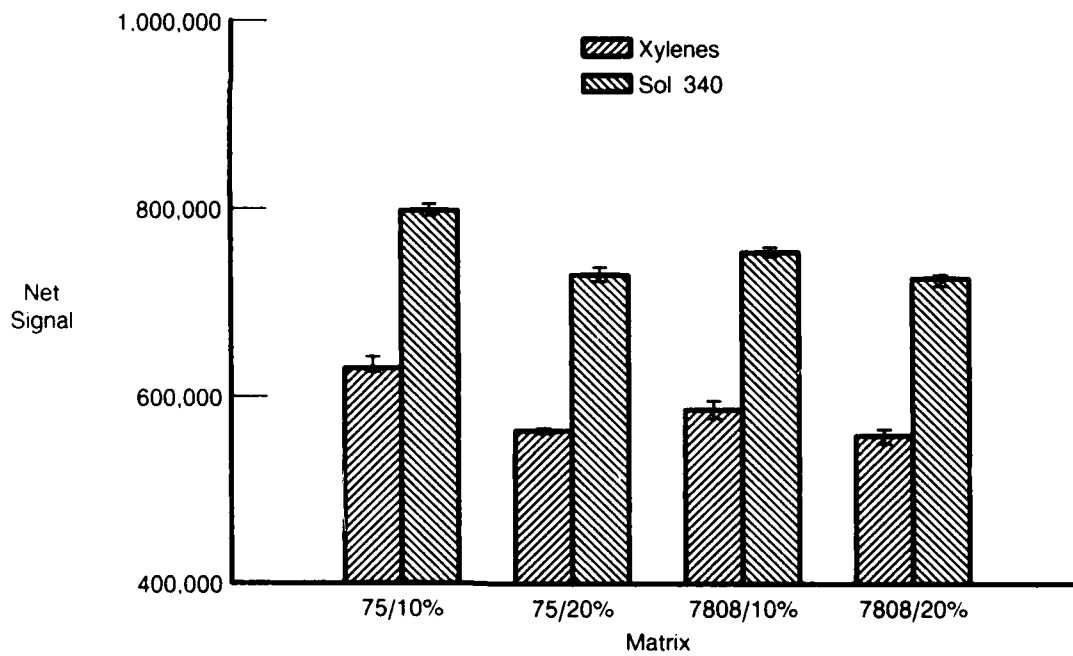
FDA 312614

Figure 35. — Spectral interferences from 1000 ppm Fe or Mg on 18 Analytical Emission Lines



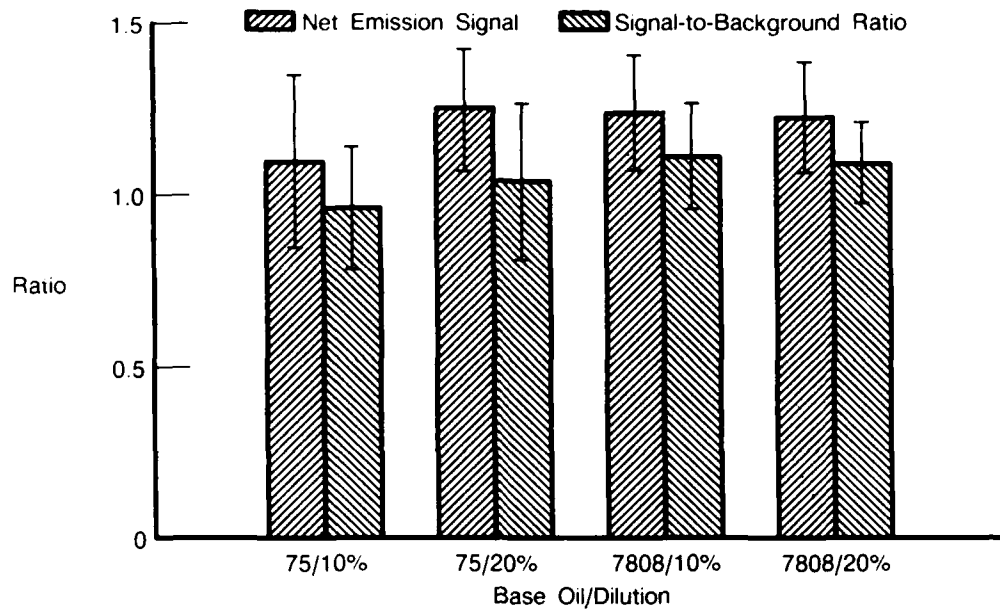
FDA 312615

Figure 36. — Gross Background vs Matrix Effect of Solvent Cr II 283.58 nm



FDA 312616

Figure 37. — Net Emission Signal vs Matrix Effect of Solvent Cr II 283.58 nm



FDA 312617

Figure 38. — Ratio and Effect of Solvent on Net Emission Signal and Signal-to-Background Ratio Solvent 340: Xylenes

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APPENDIX A

SAMPLING TECHNIQUES

ATOMIC ABSORPTION TECHNIQUES

Flame Atomization

- Combustible gases
- N_2O flame required for Ti, Si, Mo, B
- Particle-size dependent
- Poor detection limits for Al, Ti, Si, Mo, B, P
- Dilution required

Graphite Furnace Atomization

- Particle-size independent
- Very good detection limits
- Very small gas consumption
- Direct sampling possible

however

- Less precise
- Problems at high concentrations

ATOMIC ABSORPTION TECHNIQUES

Line Source

- Compact, rugged design

however:

- Limited dynamic range (2-3 decades)
- Unsuitable for 19 elements
- Background correction problems

Continuum Source

- Up to 20 elements simultaneously
- Extremely wide dynamic range (4-6 decades)
- Excellent inherent background correction

however:

- No commercially available system
- Larger, less rugged than line-source system

COMPARISON OF THE ICP AND SIMAAC TECHNIQUES

ICP

- Commercially available
- Precision \approx 1%
- Dilution with organic solvent required
- High argon consumption
- Measures only very small particles
- Steady-state signal
- Complex spectra
- Better at high concentrations
- Very well studied (100's of papers)

SIMAAAC

- Not currently commercially available
- Precision \approx 2-3%
- Direct sampling possible
- Very low argon consumption
- Particle-size independent
- Transient signal
- Simple spectra
- Better at low concentrations
- Limited experience (\approx 30 papers)

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LABORATORY SPECTROMETER FOR WEAR METAL ANALYSIS OF
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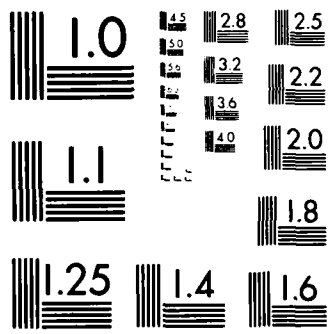
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ATOMIC EMISSION TECHNIQUES

Spark source rotating disk sample introduction

ICP source aerosol sample introduction

ICP source electrothermal sample introduction

ICP source laser ablation sample introduction

Laser ablation source direct sampling

Electrothermal source direct sampling

DCP source aerosol sample introduction

DCP source graphite braid sample introduction

SPARK SOURCE ROTATING DISK SAMPLE INTRODUCTION

Advantages

- Mature system

Disadvantages

- Poor precision
- High cost per analysis
- Highly manual sampling
- Matrix dependent
- Expensive
- Obsolete

ICP SOURCE AEROSOL SAMPLE INTRODUCTION

Advantages

- State of the art technology
- Highly automated
- Superior analytical capability
- Low cost per sample

Disadvantages

- Requires argon
- Particle size dependent

ICP SOURCE ELECTROTHERMAL SAMPLE INTRODUCTION

Advantages

- Better particle size capability
- Lower detection limits
- No sample dilution

Disadvantages

- Increased time per analysis
- Increased argon consumption
- Increased system complexity

ICP SOURCE LASER ABLATION SAMPLE INTRODUCTION

This technique could not meet minimum performance criteria for:

- Sensitivity
- Precision

LASER ABLATION SOURCE DIRECT SAMPLING

This technique could not meet minimum performance criteria for:

- Sensitivity
- Precision

ELECTROTHERMAL SOURCE DIRECT SAMPLING

Advantages

- No dilution
- Improved particle size capability
- Simplistic design

Disadvantages

- Poor analytical performance
- Increased sample analysis time
- Requires argon

DCP SOURCE GRAPHITE BRAID SAMPLE INTRODUCTION

Advantages

- No dilution
- Greater particle size capability
- Robust source

Disadvantages

- Poor precision
- Argon consumption
- Requirement for graphite braid

DCP SOURCE AEROSOL SAMPLE INTRODUCTION

Advantages

- Greater particle size capability
- Robust source

Disadvantages

- Poor stability of source
- Poor analytical performance

ATOMIC FLUORESCENCE ICP

Advantages

- Simplistic optics
- Medium argon consumption
- Low acquisition cost

Disadvantages

- Limited number of elements
- Requires use of oxygen and/or propane
- Lower RF power

X-RAY FLUORESCENCE

- Could not meet minimum JOAP requirements

ICP — MASS SPECTROSCOPY

Advantages:

- No spectral interferences

Disadvantages:

- High cost
- Very complex

END

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