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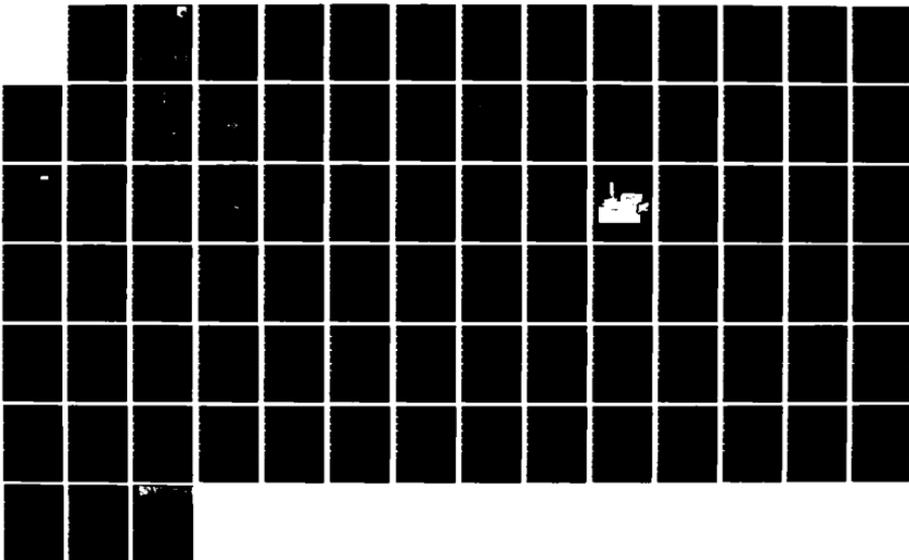
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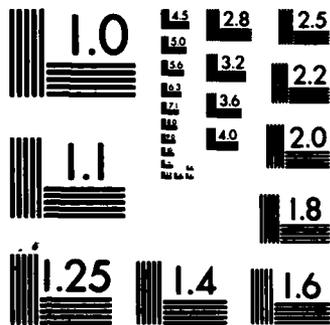
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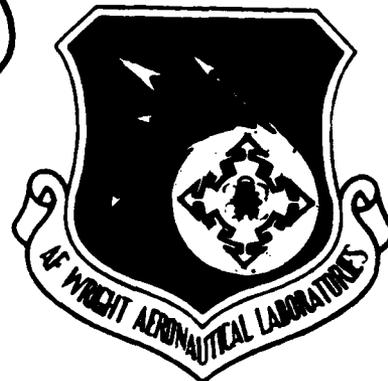




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**DEVELOPMENT OF A PORTABLE  
WEAR METAL ANALYZER FOR  
FIELD USE**

PERKIN-ELMER CORPORATION  
APPLIED SCIENCE DIVISION  
2771 NORTH GAREY AVENUE  
POMONA, CALIFORNIA 91769

DECEMBER 1983

INTERIM REPORT FOR PERIOD AUGUST 1982 - AUGUST 1983

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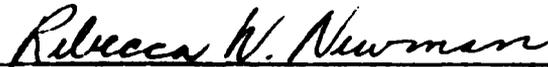
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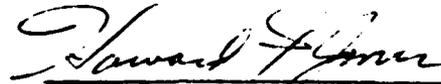
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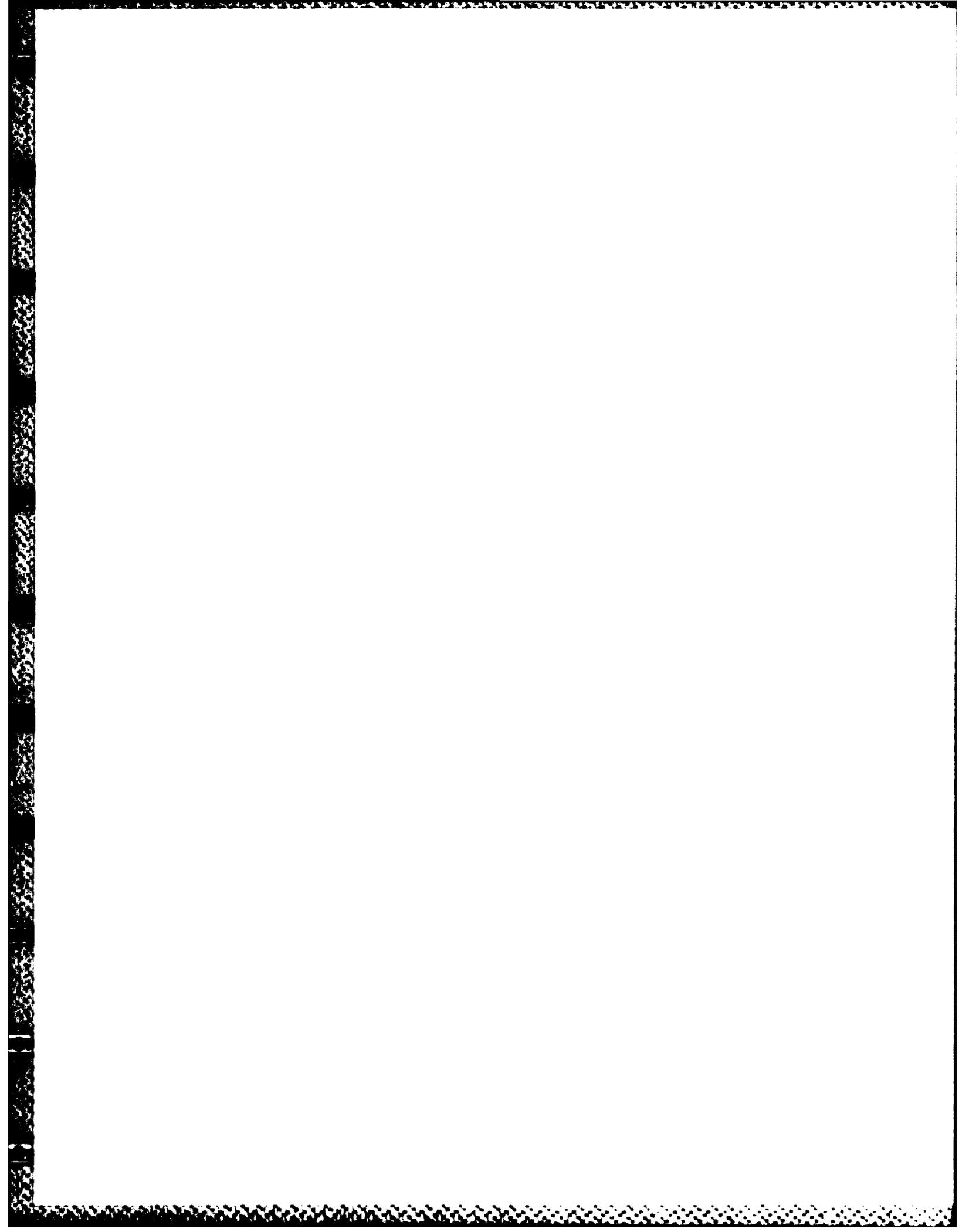
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analysis, the two containers will be electrically connected and operated from either 115 or 230 VAC. Simultaneous element analyses are accomplished by introducing an undiluted oil sample into the graphite furnace and pushing a start button. The generated atomic absorption signals are received by the detectors through a polychromator and the wear metal concentrations are printed in approximately 1.5 minutes. A brassboard, including a nine channel spectrometer, an air/water cooled graphite furnace, a miniaturized high-current furnace power supply, and a microcomputer was constructed to test the feasibility of this approach. Data obtained through the brassboard indicates that the design can achieve the requirements of the portable wear metal analyzer. Areas of improvement identified by brassboard testing will be incorporated into the preproduction design.

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SECTION I  
INTRODUCTION

1.1 SCOPE

This interim report describes Perkin-Elmer Corporation design efforts on the Portable Wear Metal Analyzer (PWMA) and the performance of the brassboard. The report covers the period from August 1982 to August 1983.

1.2 BACKGROUND

1.2.1 SPECTROMETRIC OIL ANALYSIS PROGRAM

Modern spectrometric methods have been routinely used to detect trace metals in aircraft engine lubricating oil as an indication of service condition. Wear metal particles are generated by relative motion between the contact area of metallic parts. The metal particles entering the surrounding lubricant can be detected and quantified by spectrometric methods. A large amount of wear metal data has been collected and wearing trends have been used to predict engine conditions. An abnormal wear rate can be related to the probable source within the engine and appropriate maintenance action can be taken before failure occurs. The value of the Department of Defense (DoD) Joint Oil Analysis Program (JOAP) has been proven over the past two decades. Presently, the United States Air Force has over 100 JOAP laboratories throughout the world, and over 1.5 million samples are analyzed yearly.

1.2.2 THE PORTABLE WEAR METAL ANALYZER

When USAF aircraft are deployed away from their home bases, the requirement for engine oil analysis still exists. Some aircraft are required to have engine oil analyzed after each flight due to the critical nature of aircraft turbine engines. Laboratory-type Flame Atomic Absorption (FAA) spectrometers have been used for deployment support with limited success. The requirement for using nitrous oxide/acetylene gases and methyl isobutyl ketone solvent makes the FAA technique undesirable for field use. The logistics involved in moving the various supplies associated with this technique are extremely difficult and costly. Furthermore, the FAA spectrometer is operated on a one element at-a-time basis; thus, the measuring of nine elements is cumbersome and time consuming. It is critical, therefore, that a portable, easy to operate, and reliable system be developed to perform oil analyses during aircraft deployment.

1.2.3 PORTABLE WEAR METAL ANALYZER DEVELOPMENT

In October 1981 the USAF funded a feasibility study to determine the techniques suitable for a PWMA. Techniques under consideration included atomic emission spectroscopy, atomic absorption spectroscopy, X-ray fluorescence spectroscopy, colorimetry, and radioactive tagging. The study concluded that Graphite Furnace Atomic Absorption (GFAA) spectroscopy is the best technique for a PWMA application.

Based on this study, the USAF funded a contract to Perkin-Elmer Corporation to develop a PWMA using graphite furnace AA technology. The PWMA design objectives are described below.

- a. Multi-element Analysis. The PWMA shall be capable of analyzing engine lubricating oil for Silver (Ag), Aluminum (Al), Chromium (Cr), Copper (Cu), Iron (Fe), Magnesium (Mg), Nickel (Ni), Silicon (Si), and Titanium (Ti), within the concentration ranges listed below:

Ag (1-10 ppm)	Cu (1-40 ppm)	Ni (1-30 ppm)
Al (1-50 ppm)	Fe (1-100 ppm)	Si (1-20 ppm)
Cr (1-10 ppm)	Mg (1-50 ppm)	Ti (1-20 ppm)

Measurement repeatability should be within  $\pm 1$  ppm or  $\pm 2.5\%$  of the reading, whichever is greater.

- b. Two-Suitcase Portability. The PWMA shall be packaged in two containers balanced for one-man portability.
- c. Field Operation. The PWMA shall be capable of field setup and operation requiring only line power of 115/230 volts alternating current (VAC), 50-60 cycles per second (Hz).
- d. Environmental Protection. The PWMA shall be designed for operation under the following conditions:
1. Shock - withstand 30 gravity (g) loads
  2. Temperature  
Storage: -55 to +70° Centrigade (C)  
Operation: -18 to +57°C
  3. Humidity: 0 to 100%
- e. Simplified "One-Button" Operation. The PWMA shall be designed for operation by flight line personnel with minimum training in JOAP procedures.
- f. Self-Contained Operation and Consumables. The PWMA shall be capable of self-contained operation and provide adequate supply and storage of consumables.
- g. Correlation with JOAP Data Bases. The PWMA shall produce results consistent with existing JOAP data bases. Because of greater particle size independence, the PWMA wear metal data will be more accurate than wear metal data collected from other JOAP instruments.
- h. Calibration Standard. The PWMA shall be calibrated using organo-me allic standards in MIL-L-6082, Grade 1100 oil.
- i. Oil Sample Composition. The PWMA shall analyze wear metal samples in MIL-L-23699 and MIL-L-7808 engine lubricating oils.

### 1.3 MULTI-ELEMENT ATOMIC ABSORPTION ANALYSIS

#### 1.3.1 ATOMIC ABSORPTION

The atomic absorption analysis relies on atoms at a lower electronic state to absorb electromagnetic radiation of a specific wavelength that is emitted from a primary source and enter an excited state. By measuring the amount of radiation absorbed, a quantitative determination of the sample atom can be made. In most commercial AA instruments, a single-element Hollow Cathode Lamp (HCL) is used as the primary source. The cathode of the HCL is made of a metal which is the element to be measured. Ions bombard the cathode and dislodge atoms of the element. When the atoms collide, the spectrum of the element is emitted as spectral emission lines. In AA measurement, the metal to be measured must match the cathode material of the HCL so that the emission lines from the HCL always correspond to the electronic states of the element being analyzed. Atoms absorb light only at specific wavelengths corresponding to the energy requirements of the particular atom. A monochromator is usually employed to isolate unwanted radiation such as adjacent emission lines or the emission lines originating from the fill gas in the lamp.

The atomization process consists of taking a solution of the oil to be analyzed and heating it to a temperature that is sufficient to dissociate the compound. Two popular atomization devices, flame and graphite furnace, are briefly described. For FAA, mixtures of air-acetylene or nitrous oxide-acetylene are usually employed as fuel. The oil sample solution is aspirated through a nebulizer and atomized in the flame. The graphite furnace is a flameless atomization device. A large electric current on the order of several hundred amperes is passed through a graphite tube in which the sample is placed. The heating of the tube provides the energy to atomize the oil sample.

#### 1.3.2 MULTI-ELEMENT ANALYSIS

Commercial AA spectrometers are essentially designed for single element detection. To measure successive elements, the HCL, monochromator setting, and atomization condition must be changed. Modern instruments utilize micro-computers to control these parameters and perform sequential multielement analyses; however, a new sample must be introduced for each analysis.

To meet the multi-element requirement of the PWMA, two multi-element HCLs are used wherein one lamp contains six elements and the other lamp contains three elements. The two lamps are operated alternately. A nine channel polychromator with nine individual detectors is employed. Each channel corresponds to one spectral absorption line in order to detect each of the nine wear metals simultaneously. The atomization condition for each element was tested individually and a programmed atomization cycle was developed to accommodate all conditions. The atomization cycle will be discussed in a later section.

It is noted that with AA spectroscopy, the spectral bandwidth of the absorption line is on the order of 0.002 nm. The atom can absorb only the spectral emission line from the HCL of exactly the same wavelength so that the specific characteristic spectrum can be identified, even in the multi-element detection mode. The spectral bandwidth requirement for the polychromator ranges from 0.1 to 1 nm, which is required to isolate the adjacent lines from the HCL. Furthermore, the AA signal is derived from the ratio of the light intensities before and after atomic absorption. Thus, the signal is less susceptible to absolute spectra intensity variation caused by environmental conditions. The inherent nature of AA spectroscopy is the main reason for developing a graphite furnace AA for the PWMA.

#### 1.4 PORTABILITY

Set-up and operation of the PWMA is illustrated in Figure 1-1. Emphasis has been placed on field operation and portability since the latter are primary requirements of the PWMA. The PWMA is packaged into two military-grade containers. The containers will each weigh approximately 40 pounds, are balanced for one-person portability, and provide full environment protection for storage and transportation. The PWMA is quickly set up by placing the two containers side-by-side, making the necessary connections, and turning the instrument on. The PWMA provides self-contained operation using air cooling and a built-in argon gas supply. The only external requirement is electrical power service at 115/230 VAC, 50-60 Hz.

The PWMA has simple "one-button" operation under preprogrammed microcomputer control; thus, only minimum operator skill and training are required and the opportunity for operator error is reduced. The analyzer accepts undiluted oil samples to eliminate errors due to solvent-dilution procedures and simplify instrument operation.

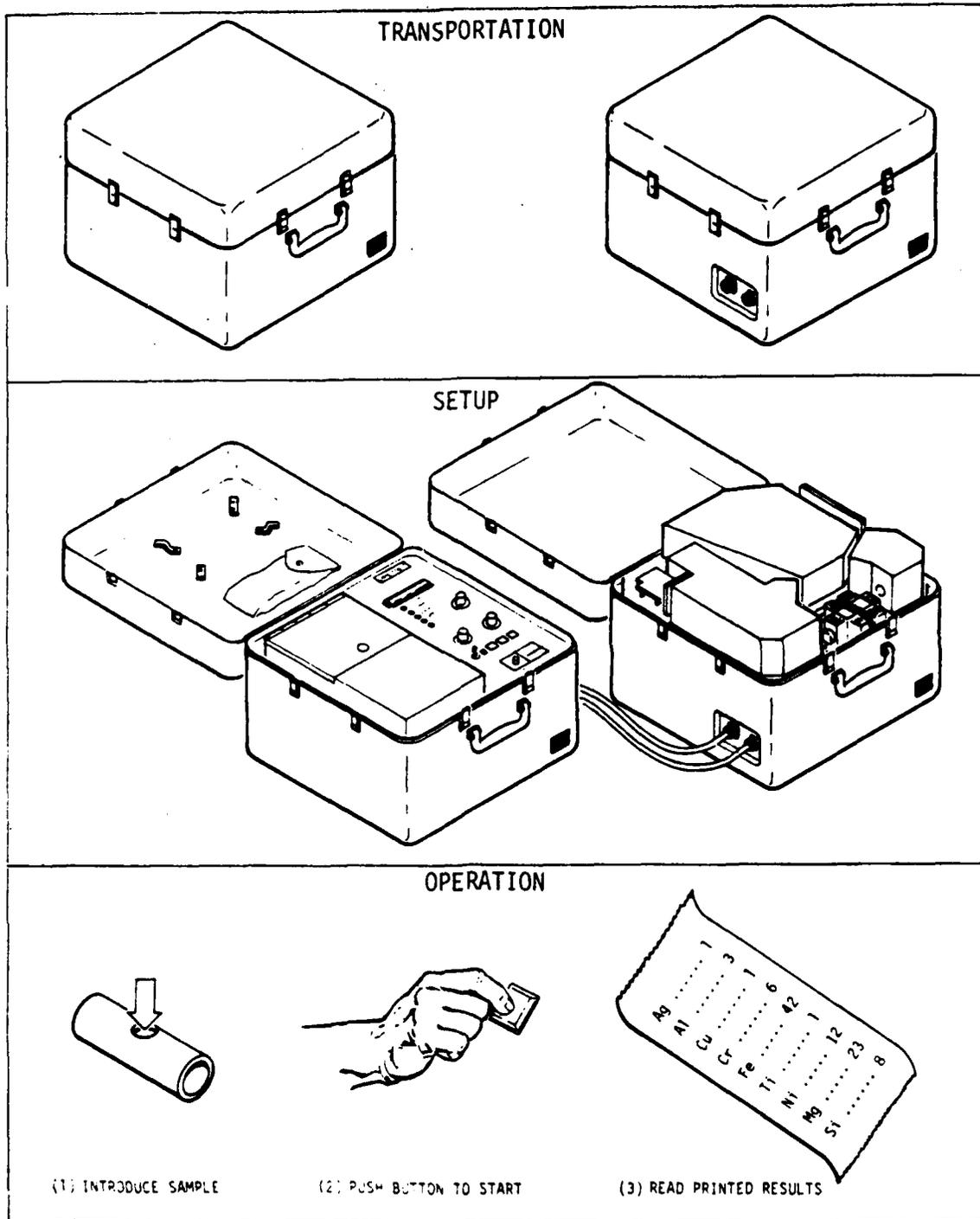


Figure 1-1. PWMA System Setup and Operation

## SECTION II

### PWMA SYSTEM

#### 2.1 SYSTEM DESCRIPTION

A block diagram representation of the PWMA oil analysis sequence is shown in Figure 2-1. The operator first introduces an oil sample into the graphite tube of the Graphite Furnace Assembly. The PWMA start button, located on the control panel is then depressed, and the entire analysis program is initiated and controlled by an "on board" microcomputer. As the graphite furnace executes the atomization cycle, the wear metals are atomized. In parallel with the atomization cycle, the emission line spectra of the wear metals are transferred to the polychromator where they are separated into individual spectral lines and further conveyed to the exit slits. The spectral lines pass through their respective exit slits where their spectral intensities are detected and measured by individual Photomultiplier Tubes (PMTs). The PMT outputs are then sampled by PWMA microcomputer algorithms. The wear metal concentrations, in ppm, are then available as hardcopy printout or as individual readings on the PWMA alphanumeric display.

#### 2.2 POLYCHROMATOR

##### 2.2.1 DIFFRACTION GRATING

A reflecting diffraction grating is a reflective surface with evenly spaced parallel grooves. Light beams which strike the grating are reflected at angular separations dependent upon their individual wavelengths. A reflecting concave grating is used in the PWMA both to separate the incident beam and focus the reflected spectrum. The spectrum is focused on a circular focal plane where nine exit slits are located. The polychromator is shown in the upper right portion of Figure 2-2. The Eagle polychromator refers to the configuration where the entrance slit and the exit slits lie on the same side of the grating normal.

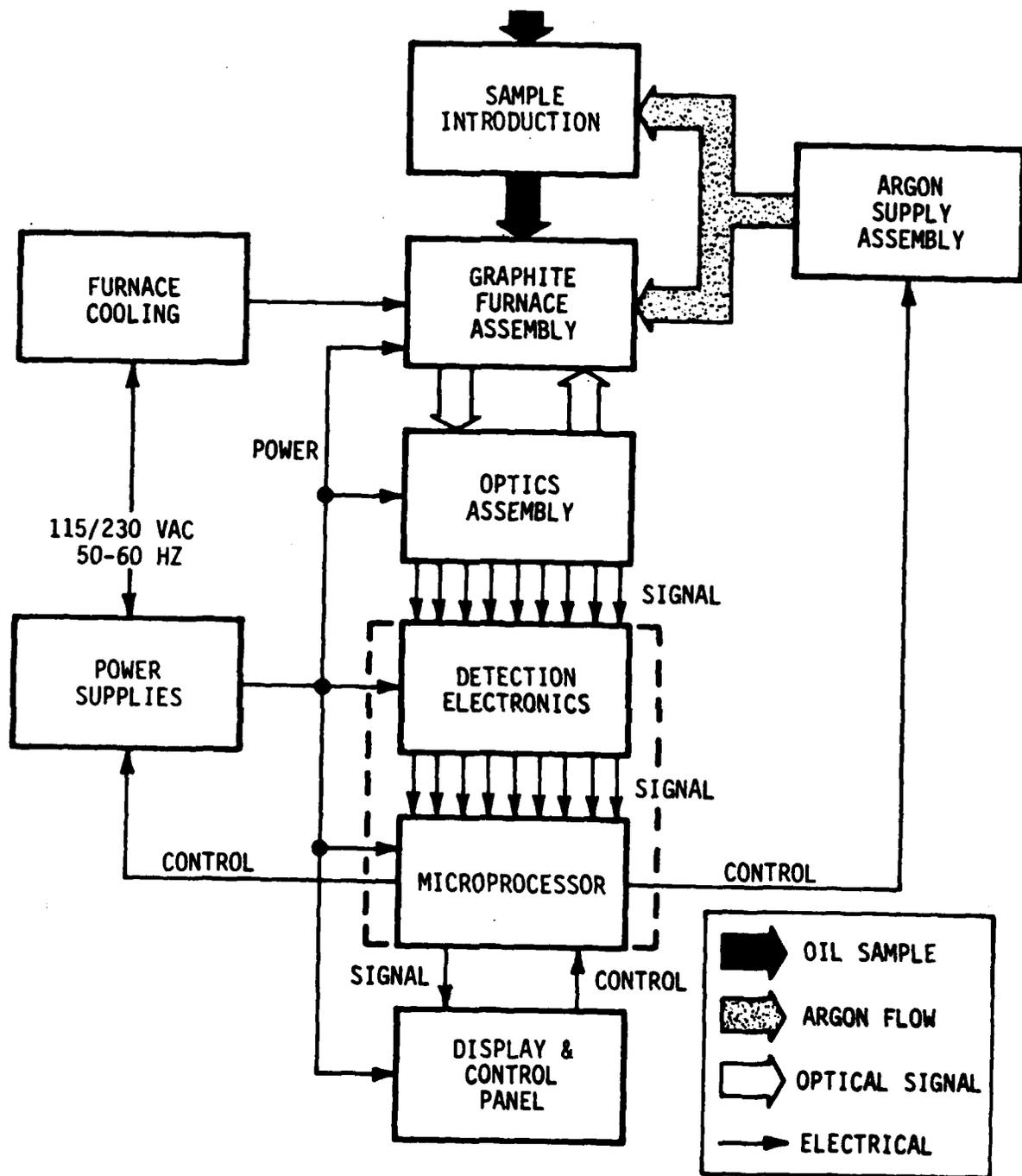
##### 2.2.2 DESIGN PARAMETERS

The general expression for a diffraction grating can be written as

$$n\lambda = d (\sin \alpha \pm \sin \beta)$$

where

- $n$  = order number
- $\lambda$  = wavelength
- $d$  = grating spacing, 1/number of grooves
- $\alpha$  = angle of incidence
- $\beta$  = angle of diffraction



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Figure 2-1. PWMA Block Diagram, Oil Analysis Sequence

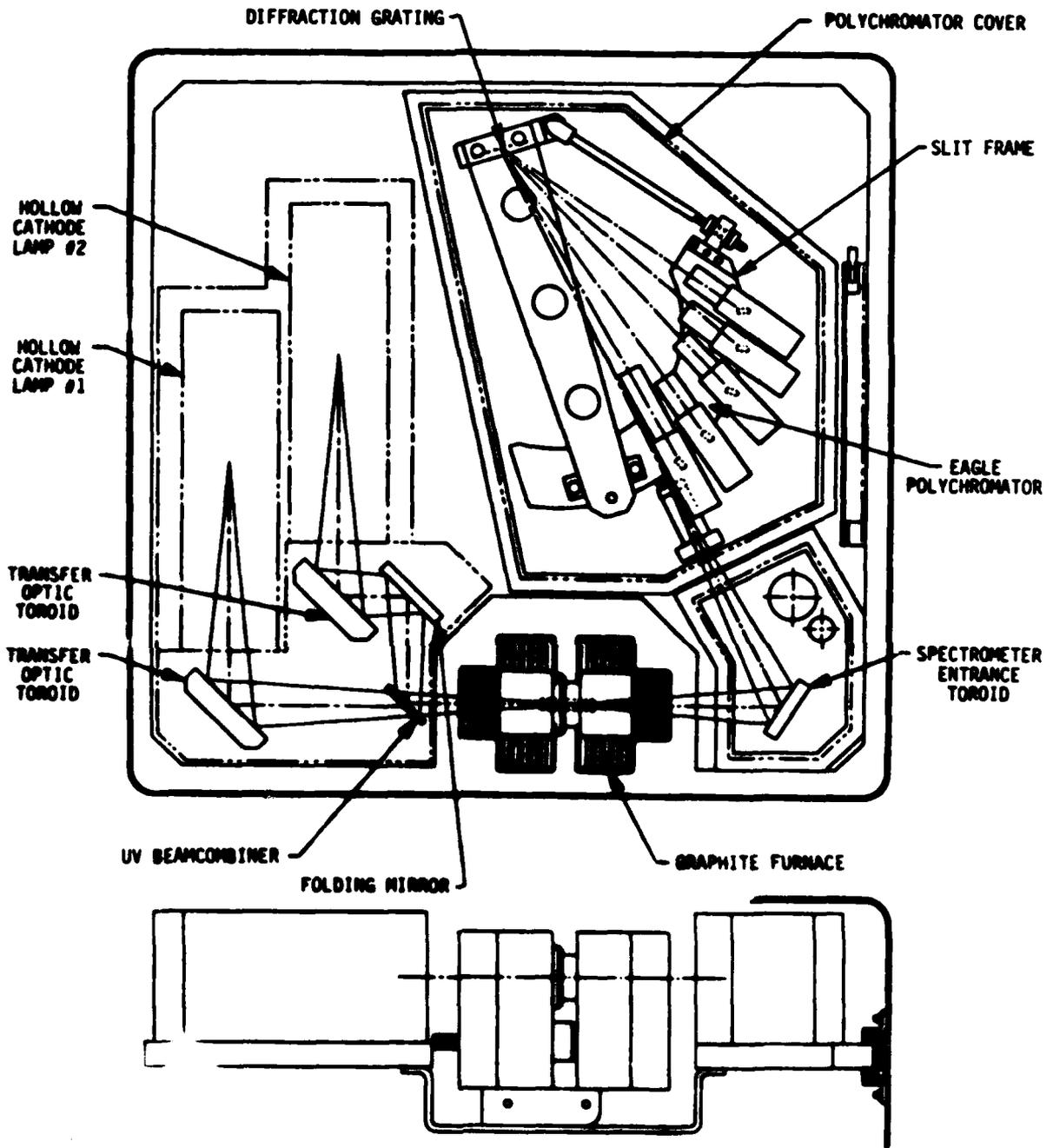


Figure 2-2. PWMA System Optical Components

The parameter of most interest is the reciprocal linear dispersion, which gives the linear separation of spectral lines along the focal plane:

$$\text{reciprocal linear dispersion} = \frac{d \cos \beta}{nf}$$

where

- d = grating spacing, 1/number of grooves
- $\beta$  = angle of diffraction
- n = order number
- f = distance between the grating and focal plane

The first order spectrum ( $n = 1$ ), is selected for PWMA. The spectral bandpass, which defines the practical resolution of the polychromator, is the product of the reciprocal linear dispersion and the slit width.

The quality of a polychromator is characterized by its resolution, optical speed, and image quality. Unfortunately, these three parameters are mutually contradictory. For example, increasing the focal length improves the resolution of a polychromator. However, a large focal length decreases the optical speed of the polychromator. A computer ray tracing program was developed to optimize these parameters. As a result, a resolution of 0.1 nm is achieved with a focal length of 20 cm where curved slits are employed to minimize aberration.

### 2.2.3 PACKAGE CONSIDERATIONS

Due to the space limitation, a polychromator of focal length less than 20 cm was first established as a design criteria. A short focal length however, limits the size of the polychromator focal plane, complicating arrangement of the detector assembly behind each exit slit. The use of fiber optic bundles to couple the exit slits to the photomultiplier detectors was considered first; however, deep ultraviolet transmission fiber optic bundles were not available at the time of the polychromator design. The package problem was finally resolved by incorporating small mirrors (13 mm O.D.) to the back of the exit slits to reflect the spectral lines to their respective PMTs. By tilting the mirrors, the spectral lines may be reflected either upward or downward. Five PMTs are mounted on top of the slit frame, as shown in Figure 2-2, and four PMTs are located at the bottom of the slit frame (not shown).

### 2.3 TRANSFER OPTICS

The transfer optics convey the emission spectra through the graphite furnace tube and onto the entrance slit of the polychromator. As shown in Figure 2-2, the emission spectra from HCL number one is focused by the toroidal mirror to the center of the graphite tube through the beam combiner. The beam is then reflected by the spectrometer entrance toroid and focused on the entrance slit of the polychromator. The emission spectra from HCL number 2 is focused to the entrance slit of the polychromator in a similar path except that a folding mirror is inserted to reflect the light path for compact packaging.

The spectral range of the PWMA extends from 200 nm to 430 nm, which is mainly in the ultraviolet region. Quartz material is used for the HCL lamp envelop, windows, and beam combiner for maximum ultraviolet transmission. Toroidal mirrors are utilized instead of spherical mirrors to minimize the astigmatism which becomes significant since relatively large off-axis angles are used in conveying the beam. The focal lengths and the angles are optimized for maximum efficiency and compactness. Finally, thermal stability, adjustability and ruggedness are considered in the design and materials of the polychromator and transfer optics.

## 2.4 HEATED GRAPHITE FURNACE

### 2.4.1 DESCRIPTION

The graphite furnace converts wear metals in the oil sample into atomic vapors. The PWMA graphite furnace is illustrated in Figure 2-3. The heating element is the graphite tube located in the center of the furnace. The tube is enclosed by two graphite end rings pressed into the metal blocks of the furnace. A pneumatic cylinder attached to the metal blocks controls the opening and closing of the furnace for tube replacement. The metal blocks are electrically connected to the Graphite Furnace Power Supply (GFPS), a large current (as high as 500 amperes) which passes through the graphite tube. With this arrangement, a temperature of 3000°C may be reached. Argon gas is provided to sheath the graphite tube to prevent incineration.

### 2.4.2 PWMA FURNACE COOLING

For logistical reasons, the use of an air cooled furnace is highly desirable. However, water cooling is more efficient and the cooling time requirement is considerably less. The PWMA incorporates both cooling modes. Approximately 500 Beryllium-copper pins, 3/32 inch of diameter, were press-fit into the metal blocks of the furnace and a cooling fan was mounted at the base of the furnace. These pins provide an efficient heat sink without obstructing the furnace open/close operation or the cooling water pipe system. This pin heat transfer design is superior to conventional heat sink design because the configuration enhances the turbulent flow of air through the pins and the press fit provides a better heat conduction than the use of thermal epoxy to bond a heat sink to the metal blocks. A computer model was developed to calculate heat dissipation of the pins. The model showed that given the designed atomization cycle, cooling time, and a 5 CFM fan, the furnace block temperature will be 20°C above the ambient temperature after repeated sample analyses. The success of this cooling design was verified by Brassboard testing.

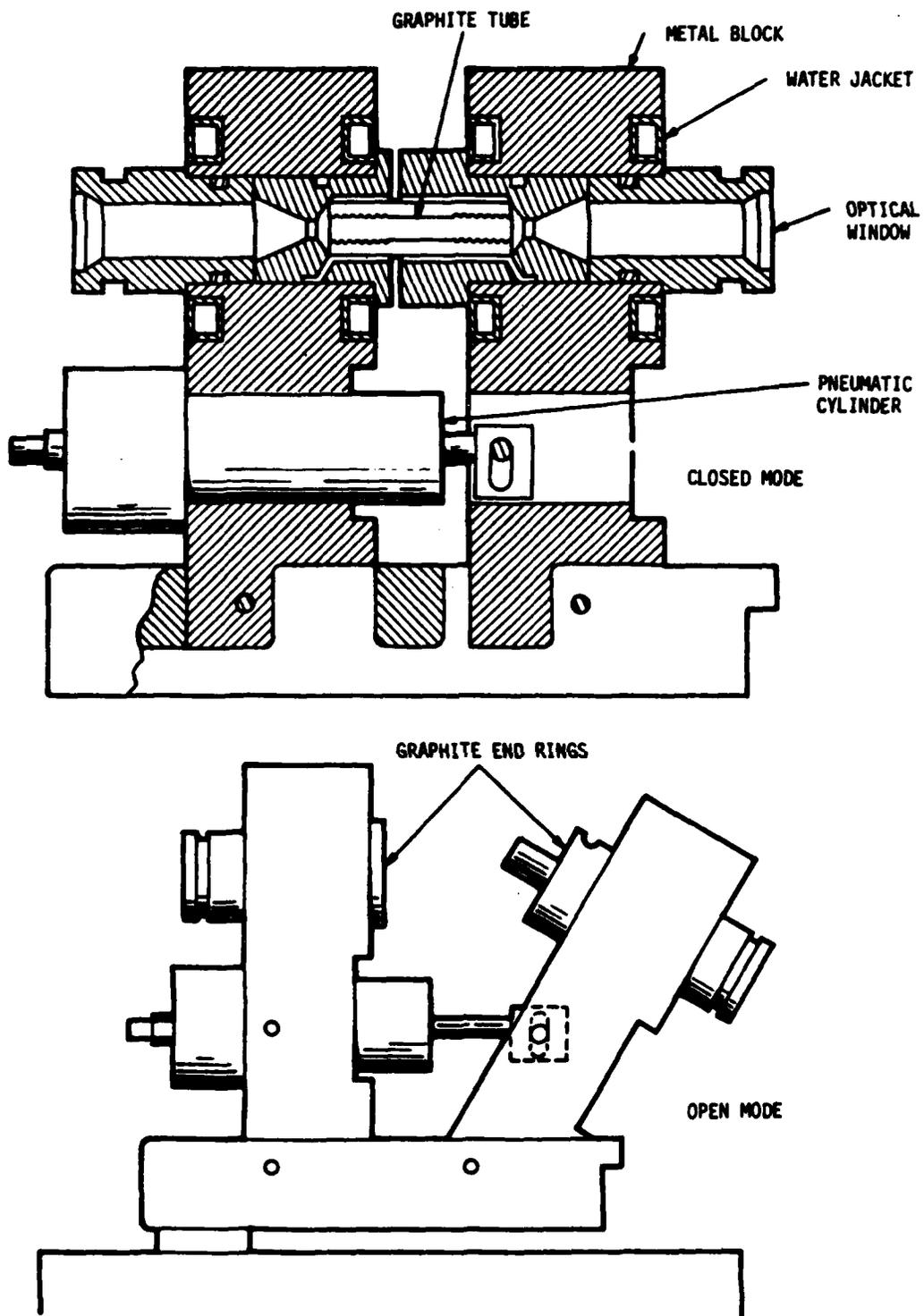


Figure 2-3a. Graphite Furnace, Cross-Sectional View

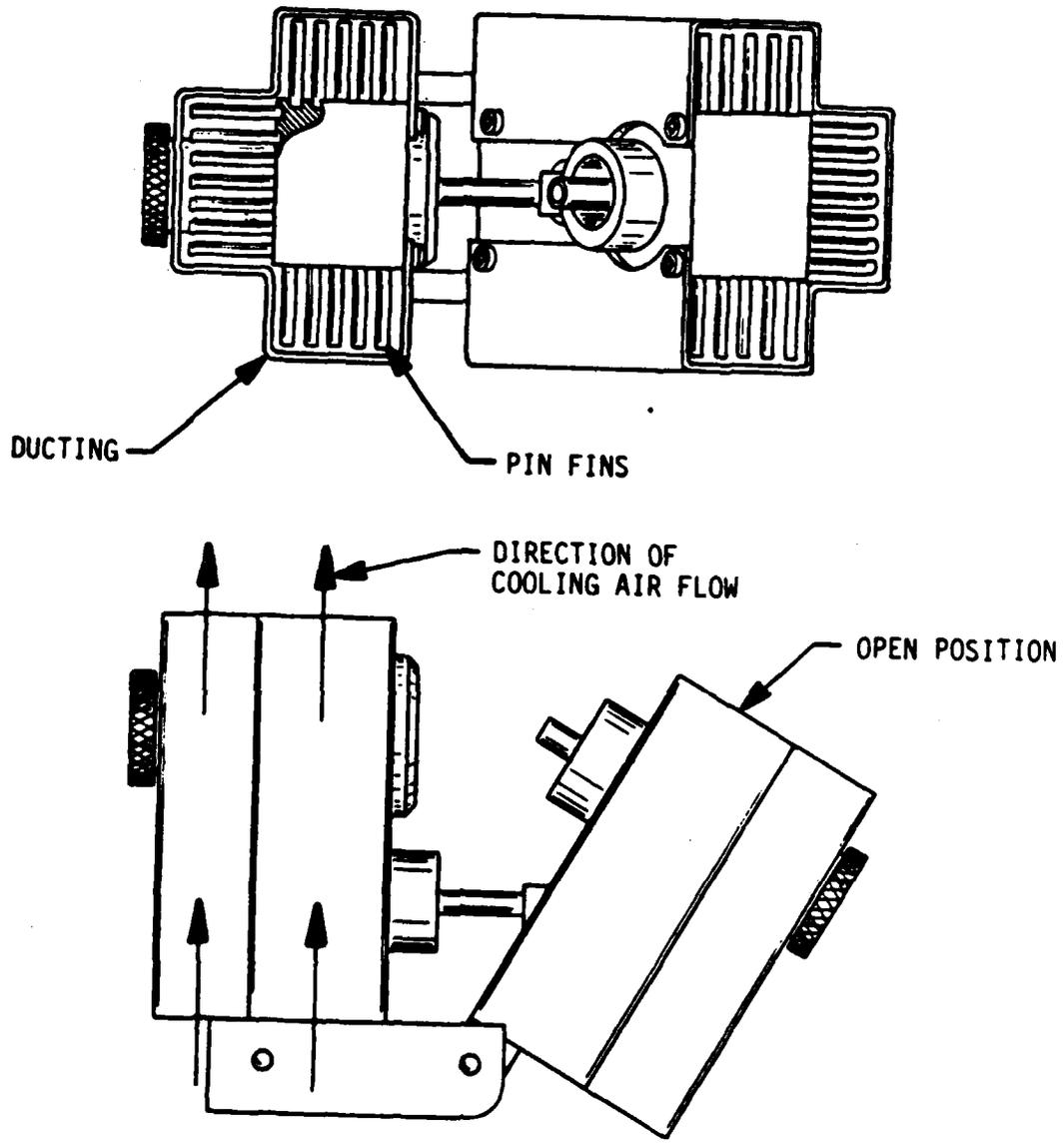


Figure 2-3b. Modified PWMA Graphite Furnace

## 2.5 GRAPHITE FURNACE POWER SUPPLY

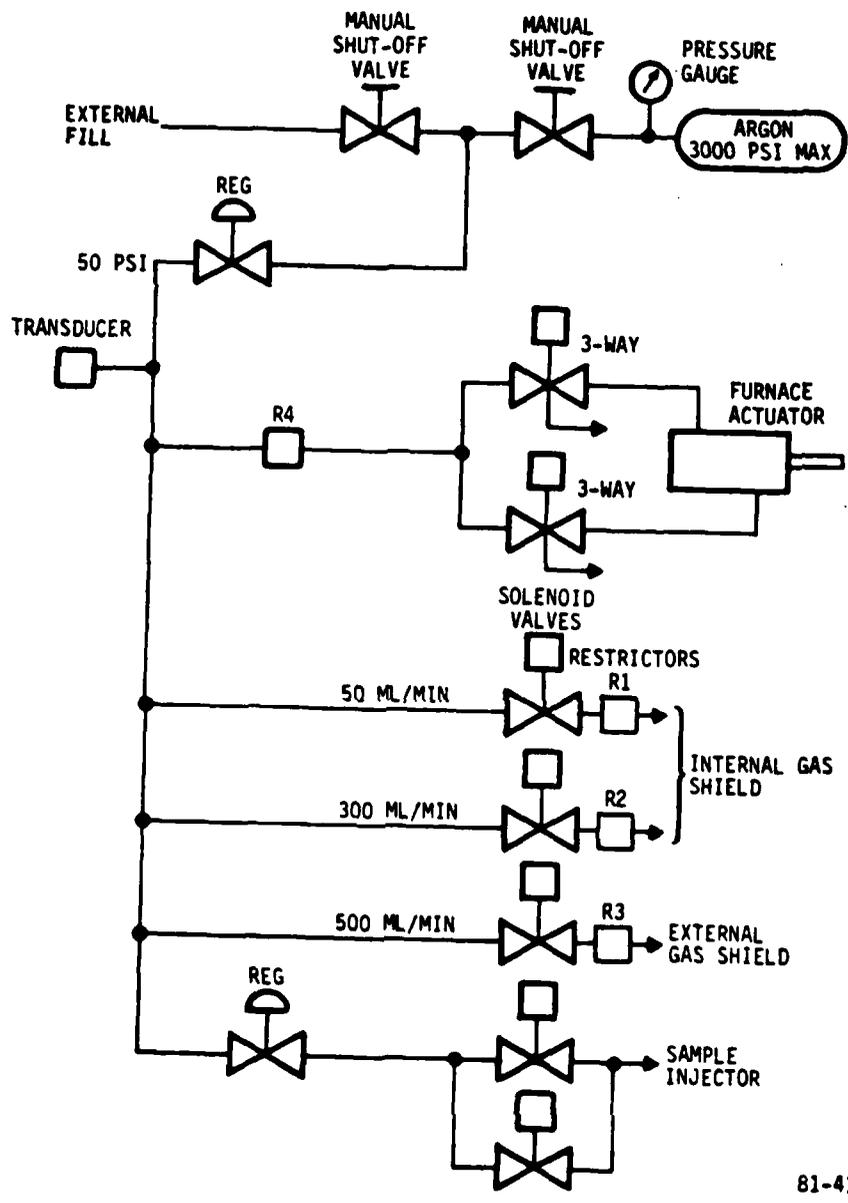
The peak current requirement of the PWMA graphite furnace is approximately 500 amperes. This requirement defines the peak capacity of the power supply. For packaging in one of the containers, the power supply must weigh less than 15 pounds and be operated at 115/230 VAC  $\pm 10\%$ , 50/60 Hz. No off-the-shelf power supply is available which meets all the above requirements; therefore, an entire new approach was initiated for the GFPS design.

Commercial GFPSs usually weigh from 50 to 100 pounds. The weight is primarily due to the heavy transformer employed since most of the commercial power supplies are operated at 60 Hz. The requirement for magnetic materials is drastically reduced when the transformer is operated at a higher frequency. The PWMA GFPS is operated at 20 kilohertz (kHz). The high current is achieved by using a series resonant type power supply which utilizes silicon controlled rectifiers (SCRs) as the switching elements. Automatic commutation of the SCRs occurs as the resonant current reverses through zero. In operation, 20 kHz current pulses are supplied to the furnace graphite tube in the form of a wave packet with a duration on the order of tenths to several milliseconds. The duration of the wave packet controls the output power and is sensed by a feedback loop. In the PWMA, current passing through the graphite tube is used to control the feedback loop. In this type of high current application, the switching losses have become a limiting factor. Thus high current asymmetrical SCRs (ASCR) with on/off time of the order of several microseconds are used in the PWMA furnace supply. An additional feature of the ASCR is that the waveform is sinusoidal, which minimizes radio frequency interference. The performance of the Brassboard GFPS is discussed in Section 3.3.

## 2.6 ARGON SUPPLY

Argon gas is used to inhibit oxidation of the external surface of the graphite tube and to remove oil residue and atomic vapor from the graphite tube. The pressurized argon also holds the furnace blocks so that the graphite tube is in close electrical contact with the two graphite end rings.

The argon supply system is shown in Figure 2-4. Gas stored in the pressure vessel flows through a regulator at 50 psi. Three solenoid valves control flowrate to the internal and external areas of the graphite tube. A second regulator reduces the gas pressure from 50 psi to that required by the sample introduction system.



81-414C

Figure 2-4. PWMA Argon Supply Schematic

The PWMA is a self contained system with stored argon gas sufficient for several hundred analyses. The Argon gas is stored in a lightweight filament-wound pressure vessel having an internal volume of 2.4 liters, a weight of 3 pounds, and an internal pressure to 3000 pounds psig. The total gas capacity is 480 liters at 3000 psig and is enough for about 500 analyses. The argon pressure vessel may be recharged.

The internal argon flow in the graphite tube purges atomic vapor during formation and therefore affects the sensitivity of wear metal detection. Depending on the wear metals being analyzed, two different internal argon flow rates are used. Flow switching is controlled by solenoid valves. Since the argon flow rate is a function of pressure, the output of the argon pressure regulator must be stable to prevent changes in sensitivity due to variation in argon flow. A compact, single-stage pressure regulator was designed for the PWMA that can maintain the argon outlet pressure at  $50 \pm 5$  psig from an inlet argon supply pressure of 3000 to 70 psig.

## 2.7 SAMPLE INTRODUCTION SYSTEM

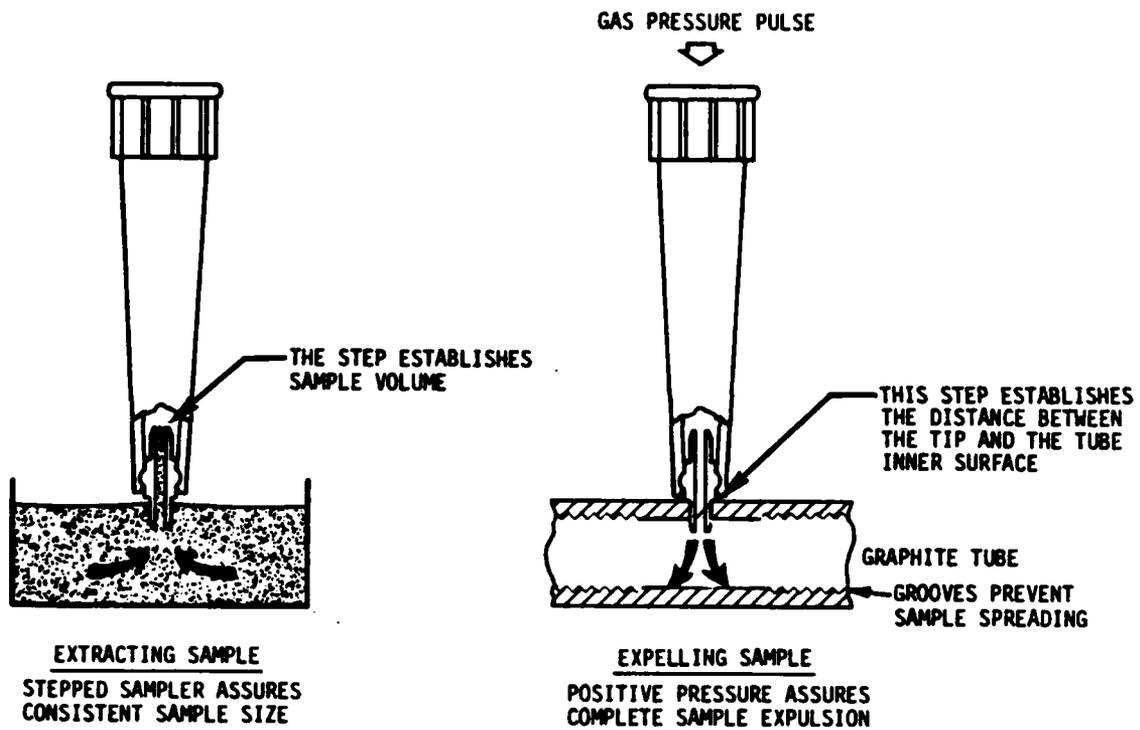
The sample introduction system is designed for simplicity to minimize operator error. Undiluted oil samples are injected directly, thus eliminating dilution solvents, the dilution step itself, and dilution errors. No commercial sample can achieve the above requirements; therefore, a sample introduction system was developed for the PWMA.

The operation of the PWMA sample introduction system is shown in Figure 2-5. The oil sample is drawn to the step or upper end of the sample tip by capillarity. The volume of the sample tip bore, then, constitutes the desired sample volume. The sample is dispensed by a pressurized argon gas pulse controlled by two solenoid valves and a sample loop housed in the "pistol" handle.

The design and material of the sample introduction tip affects the precision of the sample introduction system. Commercial disposable polypropylene tips were initially tested and the results were not satisfactory. The tapered shape of the commercial tips promoted oil sample splatter inside the graphite tube, and small beads of oil sample adhered to the tip interior. A straight-bore teflon tip was then designed to reduce the sample splatter and provide clean expelling. An additional design feature is a shoulder on the PWMA sample introduction tip. The operator places the filled sample tip onto the injection port of the graphite tube until the shoulder of the tip rests on the tube itself. This design assures that the tip is always in the same position each time, and the tip-to-tube distance selected to minimize splatter, is always the same. The handle pushbutton is then depressed, introducing the oil sample into the graphite tube.

## 2.8 ELECTRONICS

A PWMA system block diagram is illustrated in Figure 2-6. As shown in the upper left corner, the 115/230 VAC power is input to the low voltage power supplies, printer, fans, and graphite furnace power supply. The  $\pm 12$  VDC supply furnishes power for the microcomputer, alphanumeric display, and solenoid valve drivers.



83-035

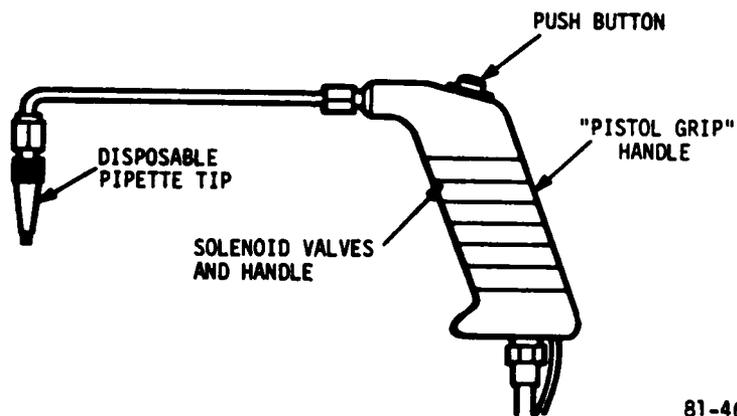


Figure 2-5. PWMA Sample Introduction System



The signal processing sequence is illustrated in the center area of Figure 2-6. Emission lines from the HCLs are conveyed by transfer optics through the graphite furnace and into the polychromator, where the signals are detected by photomultipliers and amplified by electrometers. The analog voltage output from the electrometers, representing the light intensities of the received signal, passes through a multiplexer to the analog/digital (A/D) converter. The digitized signals are stored in Random Access Memory (RAM) for absorbance calculation. Finally, the concentrations for the nine wear metals are calculated and printed out as hardcopy or optionally displayed on the front panel alpha-numeric display.

The graphite furnace control loop starts from the input/output (I/O) interface block at the lower right corner of Figure 2-6. The start button initializes the furnace controller which drives the GFPS according to a predetermined atomization cycle. In parallel, valve drivers for the argon supply are also energized following a programmed sequence. Several protection circuits are incorporated into the graphite furnace assembly and terminated into front panel alarm indicators.

The onboard microcomputer is comprised of seven circuit boards and interconnect boards. The GFPS controller, HCL current monitors, argon valve drivers, and alarm circuits are distributed among two digital circuit boards. The other five boards consist of two I/O-programmable timer boards, a 16 kbyte RAM board, a 16 channel analog input and A/O board, and a microprocessor (MPU)/40 kbyte Electrically Programmable Read Only Memory (EPROM)/serial interface port (RS232) microcomputer board. Wires extending from the interconnect board are terminated into connectors for ease of service.

All optics assemblies, i.e., source-transfer optics, HCLs, and the polychromator, are positioned on an optics baseplate. The PMT power supply and electrometers are mounted on the baseplate adjacent to the polychromator to minimize noise pickup. The HCL power supply and modulator is located adjacent to the HCLs to minimize the length of leads and modulation interferences. The GFPS is coupled directly to the graphite furnace to improve efficiency by reducing line losses.

## 2.9 SYSTEM OPERATION AND SOFTWARE

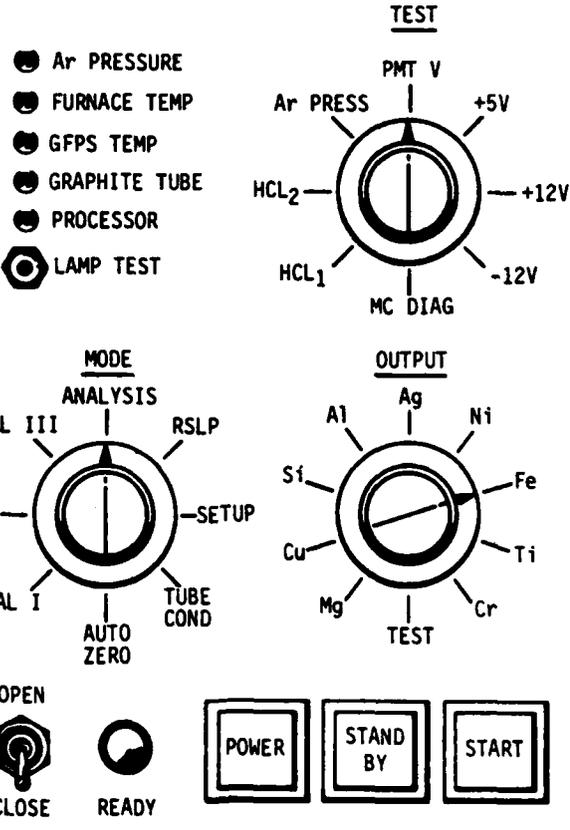
### 2.9.1 CONTROL PANEL FUNCTION

The control panel is illustrated in Figure 2-7. The POWER pushbutton switch turns on the PWMA power. The STANDBY pushbutton switch turns on the two HCLs. When the READY light is illuminated, the operator may introduce a sample and push the START button to initiate the analysis cycle. The FURNACE switch on the lower left opens and closes the furnace for graphite tube replacement, as required approximately every 200 analyses.

The concentration of the wear metals selected with the output selector may be displayed on the alpha-numeric display. When the OUTPUT selector is set at the TEST position, the test functions may be displayed for diagnostic purposes. The MODE selector allows the operator to set up and calibrate the PWMA to assure proper performance. When a new HCL is installed, the mode selector is placed at the SETUP position to properly align the lamp. TUBE COND causes a temperature

PERKIN ELMER  
 PWMA  
 PerkinElmer World  
 Model Analyzer

Fe 30 PPM



83-101

Figure 2-7. PWMA Control Panel

program to condition a new graphite tube. For routine analysis, the operator uses the AUTO ZERO position and injects a blank oil sample; he then introduces three calibration standards, using CAL I, CAL II, and CAL III positions, respectively. The PWMA now is ready for analyzing unknowns at the ANALYSIS position. The concentration of the unknown samples is measured and calculated according to the calibration curves. The RSLP (reslope) function can be periodically used to correct the sensitivity change.

Five alarm indicators are provided, and the appropriate alarm light will illuminate for the following conditions: the argon pressure is incorrect; the furnace block or the GFPS are overheated; the graphite tube is cracked; or the microcomputer has a malfunction. The LAMP TEST button is used to ensure that the lamps are functional. A sonic alarm will also alert the operator for each of these alarm conditions.

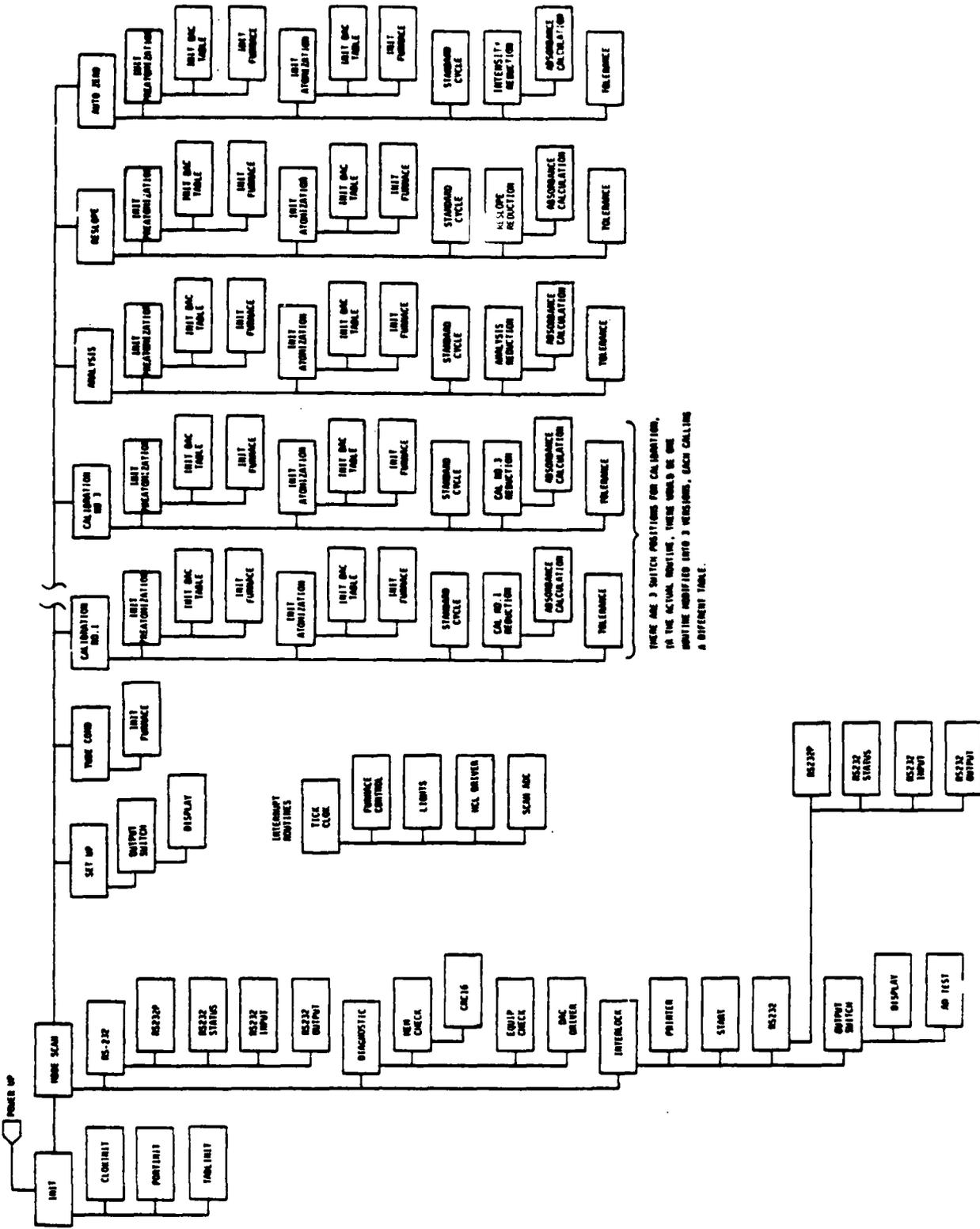
## 2.9.2 SOFTWARE ORGANIZATION

The PWMA software is primarily written in PASCAL. The entire program is subdivided into modules and linked together. The module chart is shown in Figure 2-8. The microcomputer initializes itself when the power is turned on. After the READY light illuminates and the START button is pushed, it scans the MODE selector and branches to the selected operating module. As an example, in the ANALYSIS mode, the microcomputer first initializes the preatomization and atomization cycle according to the parameters in the data acquisition table and the furnace table. The graphite furnace then goes through a predetermined standard cycle, the data collected are reduced, and the tolerance of the data is checked to ensure the proper usage of the calibration routine. Parameters such as furnace temperature, ramping time, argon flow rate, and data acquisition time are stored in EPROMs. The parameters can be changed during the development stage. With this modular programming approach, each module can be individually coded and tested.

## 2.10 SYSTEM PACKAGE

### 2.10.1 FURNACE-OPTICS CONTAINER

The PWMA is packaged into two containers; the furnace-optics container and the electronics-argon container. The furnace-optics container, illustrated in Figure 2-9, weighs approximately 40 pounds. The graphite furnace is mounted in the front of the container and is aligned with the optical path. The GFPS is mounted at the rear of the container. Argon gas for the graphite furnace is provided by a pneumatic interface located on the left side of the container. Solenoid valves, flow restrictors, and plumbing for the graphite furnace argon are also mounted in the container. The optics subassemblies (HCL, transfer optics, polychromator, etc.) are mounted on a honeycomb mounting base chosen for light weight as well as for optical stability. The optics mounting base is shock-mounted within the container for additional protection and stability. The furnace-optics container is fitted with a sealed enclosure to provide light-tight protection for the polychromator, as well as dust and humidity protection for the entire assembly.



THERE ARE 3 SWITCH POSITIONS FOR CALIBRATION. IN THE ACTUAL ROUTINE, THERE WOULD BE ONE SWITCH POSITION FOR 3 VERSIONS, EACH CALLING A DIFFERENT TABLE.

Figure 2-8. PWMA Software Module Chart

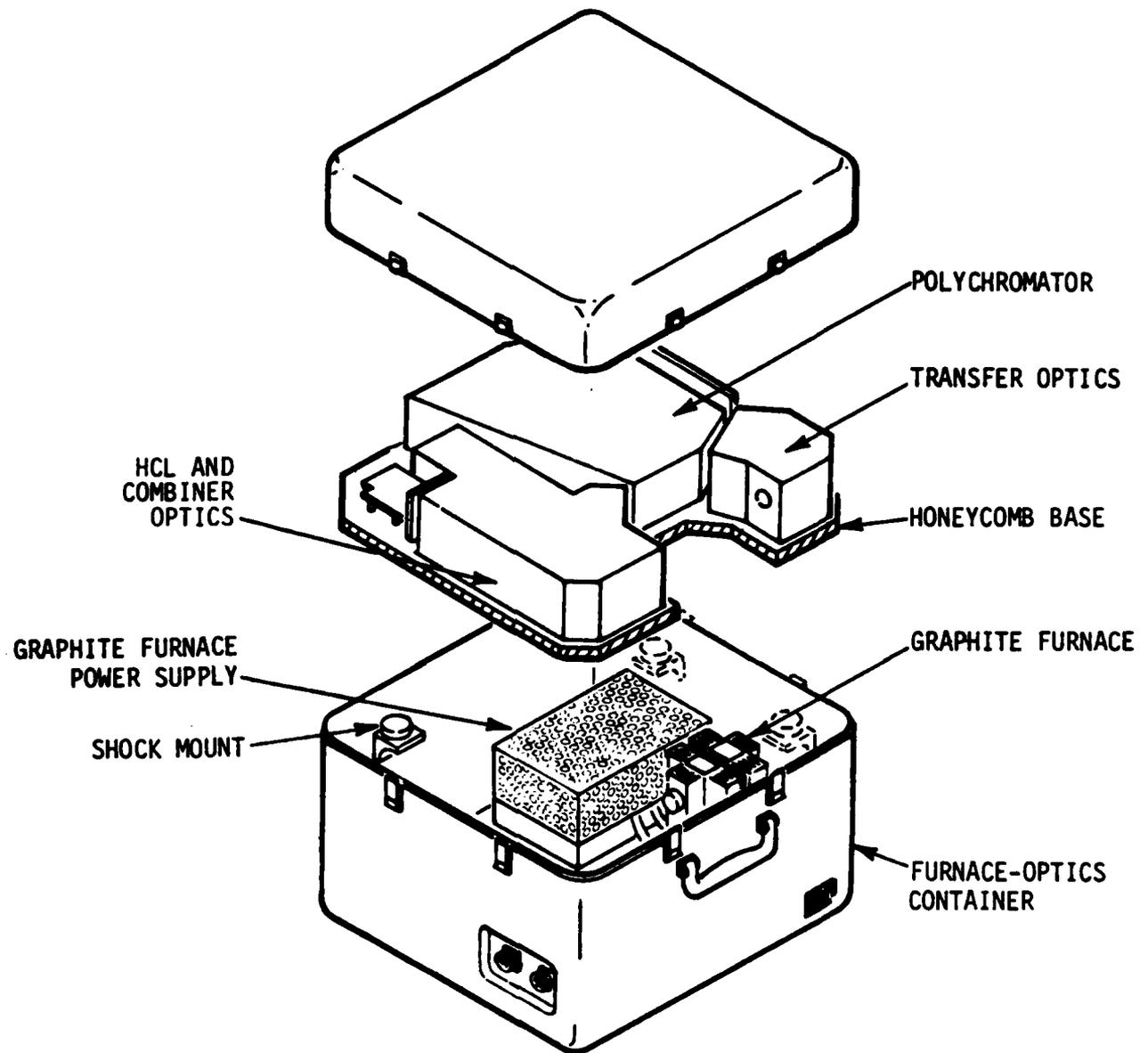


Figure 2-9. Furnace-Optics Container

## 2.10.2 ELECTRONICS-ARGON CONTAINER

The electronics-argon container, illustrated in Figure 2-10, weighs less than 40 pounds. The card cage is mounted in this container and accessed via a top cover. The argon supply tank, a lightweight filament-wound pressure vessel, is mounted at the rear of the container. The argon pressure regulator, fill-shutoff valving, and pressure gauge are mounted on a common manifold connected to the supply tank. A cover plate fits over the container. The PWMA control panel, including the controls, display, and a thermal printer are located on the right side of the cover plate. The access cover and stowage bin are on the other side. Consumables, such as sample tips and graphite tubes, are kept in the stowage bin. Interface cables (electronics and argon pneumatic line) are stored under the container cover.

## 2.11 ENVIRONMENTAL CONSIDERATIONS

### 2.11.1 TEMPERATURE

The PWMA operating temperature range is  $-18^{\circ}\text{C}$  to  $57^{\circ}\text{C}$  and the storage temperature range is  $-55^{\circ}\text{C}$  to  $70^{\circ}\text{C}$ . Considering the normal operating temperature at  $20^{\circ}\text{C}$ , the total operating temperature excursion is then  $\pm 37^{\circ}\text{C}$ . This temperature span affects the performance of optics, PMTs, and electronic components.

The polychromator is the most critical assembly in terms of temperature stability. With an increase in temperature, the grating material used in the polychromator will expand and the groove spacing will increase. According to the grating equation (Section 2.2.2), the diffraction angle will then decrease and the focal point will displace from the exit slit. Fused quartz, which has a thermal coefficient of expansion of  $0.5 \text{ ppm}/^{\circ}\text{C}$ , was selected for the grating blank. The maximum change in the groove spacing at  $\pm 37^{\circ}\text{C}$  will produce a maximum wavelength error of  $\pm 0.008 \text{ nm}$  at the chromium  $428.9 \text{ nm}$  line, and increasingly less at shorter wavelengths. By using the quartz blank, the grating expansion effect becomes insignificant with respect to the resolution requirement of the PWMA. Another important consideration is the structural material of the polychromator frame. As the frame expands, the entrance slit moves away from the grating and the object distance becomes longer. The image distance then becomes shorter and the image is focused in front of the exit slit, resulting in a defocusing effect. To minimize this effect, low expansion Invar alloy with a thermal expansion coefficient of  $1.62 \text{ ppm}/^{\circ}\text{C}$  was employed as the structural material. Given the geometry of the PWMA polychromator, the maximum increase in image width at the exit slit for the design temperature range of  $\pm 37^{\circ}\text{C}$  is less than  $0.001 \text{ nm}$ , which again is insignificant. However, if stainless steel, with a thermal expansion of  $17.3 \text{ ppm}/^{\circ}\text{C}$ , were used, the degraded performance would no longer be negligible.

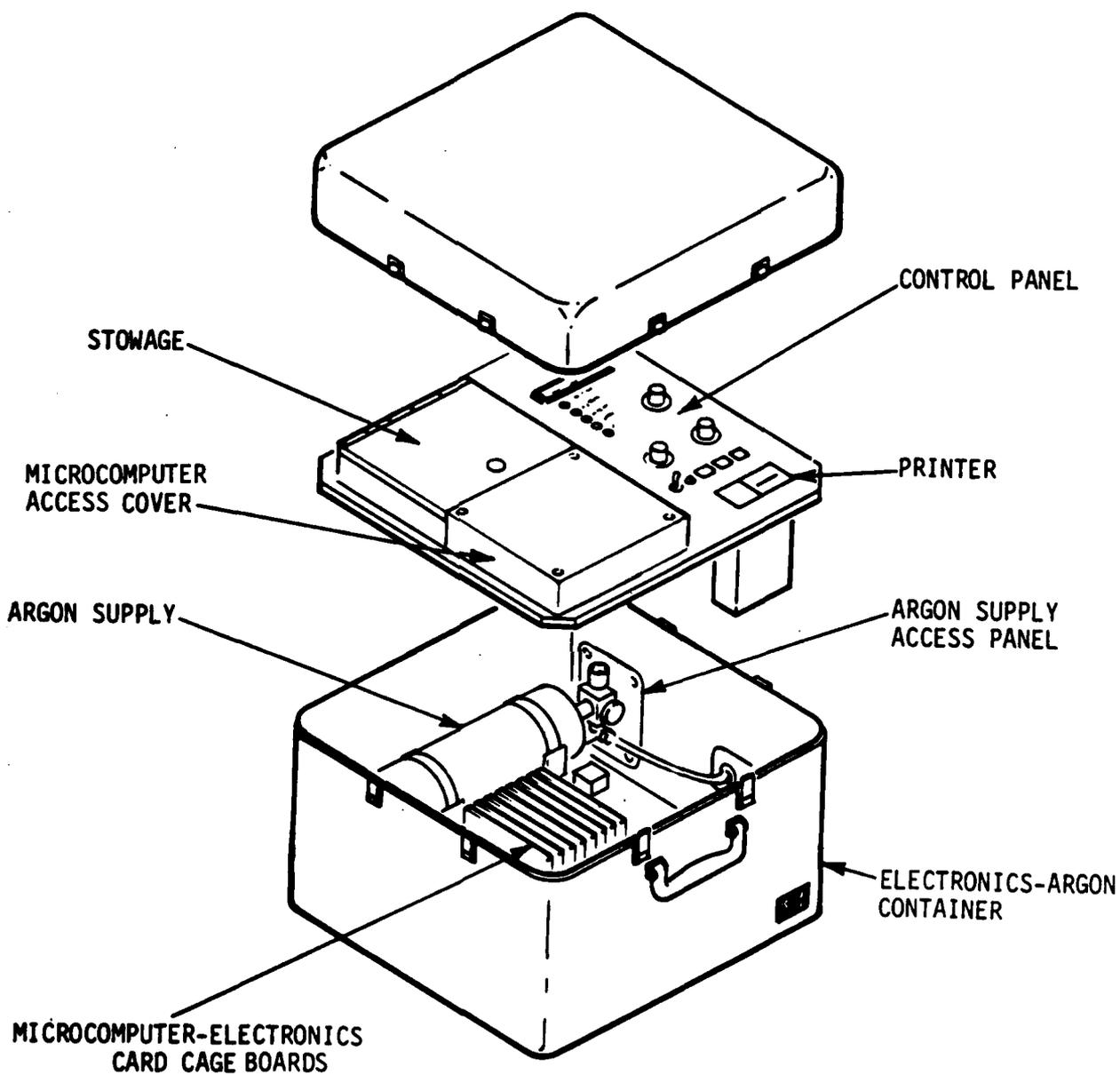


Figure 2-10. Electronics-Argon Container

The performance of the PMTs also varies with temperature. The PMTs selected for the PWMA use cesium-antimony as the cathode material. Cesium is a relatively volatile material which starts to evaporate at temperatures within the design operating temperature range. Information obtained from the PMT manufacturer shows that at 50°C the lifetime of the PMT is 5 times shorter than that at 25°C; at 60°C, the lifetime is 10 times shorter than that at 25°C. The mean time between failure (MTBF) at 25°C is quoted to be 50,000 hours. Sensitivity of the PMT also changes with temperature. At 57°C, the anode sensitivity is approximately 25% lower than that at 25°C and the dark current increases rapidly. Fortunately, in the AA measurement, the absorption signal is the ratio of the light intensities; thus, slow variations in photomultiplier tube sensitivity do not affect the result significantly.

The temperature characteristics of electronic components were also taken into consideration. In general, the leakage current, which affects the performance of a semiconductor device, becomes excessive at temperature extremes. EPROM chips are more susceptible to elevated temperatures since the leakage current may directly affect the static charge on the memory chip. Considerable efforts were made to obtain components with extended temperature rating. As an example, the commercial PMT power supply has a temperature coefficient of 100 ppm/°C over the range of 0 to 50°C. By communicating with the manufacturer, a special part with extended temperature range and a reduced temperature coefficient was developed.

#### 2.11.2 HUMIDITY

The PWMA is required to operate given 0 to 100% humidity. The polychromator is the critical assembly which is susceptible to humidity effects. The polychromator cover is sealed to the optics baseplate to provide an environmental enclosure. A dessicant cartridge is placed inside to remove any moisture when operating in highly humid environments. Electronic components and circuit boards are protected from humidity by conformal coating; in addition to the protection provided by the military-type containers.

#### 2.11.3 ELEVATION

The operating elevation requirement for the PWMA is from -250 to 15,000 feet. The storage elevation requirement is from -250 to 25,000 feet. The major effect of the elevation change is that the pressure decreases as the altitude increases. At 15,000 feet, the atmospheric pressure is approximately 9 psi. This pressure is still high enough to prevent corona discharge from occurring. Therefore, no special efforts were made to insulate electronic components. However, a breathing valve is installed on the polychromator cover to equilibrate the pressure on both sides of the polychromator cover during the elevation change.

#### 2.11.4 INCLINATION

The PWMA will operate at a 15° inclination and may be transported in any position. To meet this requirement all components in the PWMA are rigidly mounted and can be tilted in any direction. During operation, a tilting of 15° is tolerable because the graphite tube has grooves at its ends to keep the oil sample in the center of the tube.

#### 2.11.5 SHOCK

The shock requirement for the PWMA is 30g in mutually perpendicular axes. All optical components, including the polychromator and transfer optics are rigidly mounted on an aluminum honeycomb baseplate selected for lightweight and rigidity. The baseplate is shock-mounted to the container structure to protect the sensitive optical components from shock during transportation.

During operation, the baseplate is locked into a fixed position so that proper alignment with respect to the graphite furnace can be maintained. The remaining components are rigidly mounted to the container without shock absorbers. The two aluminum containers are designed to improve structural integrity.

SECTION III  
BRASSBOARD PERFORMANCE

3.1 BRASSBOARD CONFIGURATION

All PWMA components are packaged into a brassboard configuration, shown in Figure 3-1, that is the precursor to the final design. Optical components are mounted on a laboratory optical table. The polychromator is the same as the final design and is optically aligned with the other components. The transfer optics, including HCLs, toroidal mirrors, beam combiner, and folding mirror are placed at the same positions as the final design with commercial optical mounts which provide three-dimensional adjustment for optimization of focus and alignment. The optical components are enclosed in two separate covers for protection from particulates.

The air/water-cooled graphite furnace is aligned in the optical path so that the emission spectrum is focused at the center of the graphite tube. A cooling fan is mounted beneath the furnace and the whole assembly is attached to the optical table. The assembly is properly indexed to allow replacement of the furnace assembly without having to realign the optical components. The GFPS is mounted in front of the furnace and is shielded by a perforated screen cover.

A laboratory argon cylinder is connected to the PWMA regulator. The regulator, solenoid valves, and restrictors are mounted on a board and connected to the furnace using tygon tubing. It was found that the restrictors should be placed downstream from the solenoid valves to minimize gas bursts when opening valves.

The interconnect card and control panel are mounted adjacent to the furnace-spectrometer assembly. The interconnect card wiring is essentially the same as the final configuration. Laboratory power supplies are used to provide  $\pm 12$  V dc and +5 V dc power. The HCL power supply and modulator, the PMT power supply, and the electrometers are mounted adjacent to the HCLs and the polychromator, respectively.

A Motorola Exorciser is used in the brassboard for developmental use. The program is stored in the disk of the Exorciser. During operation, the Exorciser moves the program into RAM and executes the program through an emulator connected to the MPU board of the PWMA. That is, the Exorciser replaces the functions of the MPU/40 Kbyte ROM board and the 16 Kbyte RAM board of the PWMA while the two I/O boards and A/D board are still used. With this arrangement, the program can be easily modified. Eventually, the program on disk will be "burned" into the EPROM memory chips mounted on the MPU/40 Kbyte ROM board of the PWMA.



Figure 3-1. PWMA Brassboard

### 3.2 OPTICAL PERFORMANCE

Throughput and resolution are the two most important performance parameters in the optical assembly. The polychromator was assembled first and the entrance slit was aligned. A microscope mounted on a translational stage was employed to measure the width of the chromium line (428.9 nm) at the focal point. The resolution determined by this method is approximately 0.1 nm, which is close to the theoretically calculated value of .08 nm, neglecting geometrical aberrations. The chromium line at 428.9 nm was used for focusing and to check resolution because it is visible to the eye whereas other spectral lines are in the ultraviolet region.

The transfer optics were aligned with the aid of a helium-neon (He-Ne) laser. The emission lines were focused onto the entrance slit of the polychromator. The detection levels and the noise levels for all the wear metal channels were measured. The magnesium channel has the greatest noise since a weak emission line was selected for magnesium detection. The peak-to-peak noise measured was approximately 15% of the signal level which is consistent with the theoretical shot noise calculation. This noise level is relatively high; however, integrated peak areas are used for the absorbance calculation, and the noise contribution is reduced by a factor proportional to the square root of the total number of sampling points.

The magnetic field induced by the graphite furnace could affect the PMT response. A Magnetic flux probe which is sensitive at 20 kHz was employed to measure the magnetic field around the graphite furnace during operation. The highest magnetic flux found was approximately 80 gauss at the middle of the two junctions connecting the furnace and the power supply. The magnetic flux at the region where PMTs are located was less than 1 gauss. In the PWMA, the PMTs are protected with magnetic shields and the attenuation of magnetic field of the shielding material was determined to be 4:1. This low attenuation factor is mainly caused by the fact that the permeability of magnetic material decreases drastically at the design frequency. However, for the side-on type of PMT selected for the PWMA, this magnetic field would not change the tube sensitivity in any significant amount. No further improvements were made to the magnetic shield.

### 3.3 GRAPHITE FURNACE PERFORMANCE

The temperature calibration of the graphite tube was accomplished by three separate procedures because no single device can measure the entire temperature range. A Chromed-Alumel thermocouple was employed to measure temperatures up to 900°C. The thermocouple was carefully positioned inside the graphite tube. Between 900°C and 1500°C, temperatures were calibrated by a hand-held pyrometer (Pyrometer Instrument, Model 95). The meter was focused at the aperture of the graphite tube. A two-color pyrometer (Ircon 35C10) was used to measure the temperature from 1500°C and above. A calibration curve showing the tube temperature versus the current flowing through the tube is plotted in Figure 3-2. The accuracy of this calibration curve would depend on the accuracy of the three calibration instruments and the experimental conditions. However, the absolute accuracy of the temperature calibration is not critical because the temperature setting for the atomization cycle will be empirically determined.

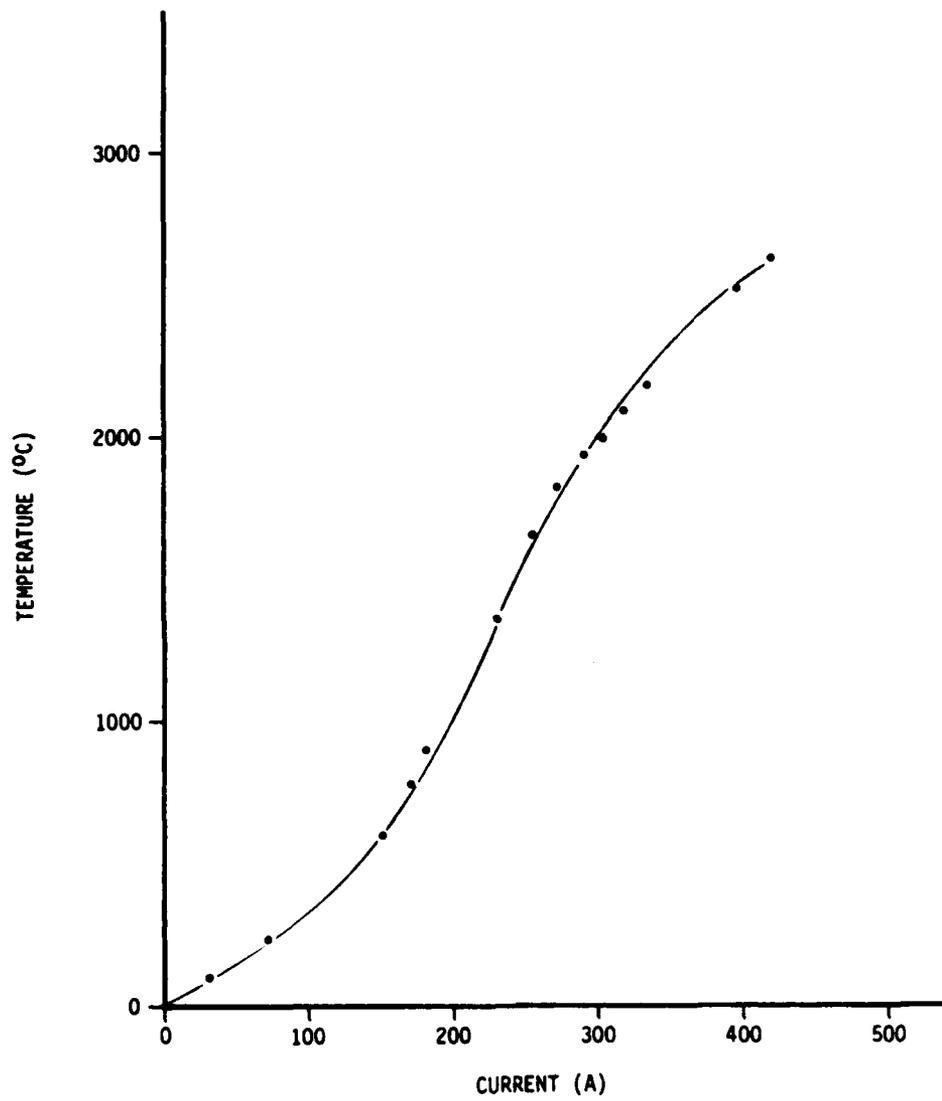


Figure 3-2. Graphite Furnace Temperature Calibration Curve

The highest temperature achieved by the present furnace is about 2650°C, while the design goal is 2900°C. Two major causes of power limitation have been identified and can be improved. For the brassboard configuration, the graphite furnace power supply is mounted in front of the optical bench. The connection between the graphite furnace and the power supply output leads is made through two pairs of connectors, which are bolted together. The resistance in each connection plus the cable is about three milliohms with a total of six milliohms in the furnace-power supply interface. The total resistance of the graphite tube and the graphite end rings is about 20 milliohms. As a result, the power loss in the furnace-power supply interface is significant. In the preproduction design, the output leads will be directly coupled to the furnace blocks. The direct coupling eliminates two connectors and approximately eight inches of cable for each lead, thus reducing the power loss considerably.

Another source of limitation was the peak current capacity and the turn off-time of the ASCRs in the GFPS. The ASCRs employed currently have a current capacity of 40 amperes and a turn-off time of 2.5 microsecond ( $\mu$ s). When operating the power supply at 20 kHz, the half cycle period is 25  $\mu$ s. The ASCRs are conducting every half cycle and the turn-off time constitutes 10 percent of the loss. This limitation can be improved by selecting ASCRs with higher current ratings or faster turn-off time. Some circuit modifications will be required to implement this change.

Air-cooling of the graphite furnace was successfully tested and was used as the primary testing mode for the brassboard testing. A thermocouple was attached to the furnace block to monitor the temperature. The peak block temperature reaches 100°C about five seconds after the end of the atomization cycle; then cools to 40°C after another three minutes. It was found experimentally that when the cooling fan was circulating, it interfered with the external argon flow. As a result, the exterior of the graphite tube was oxidized and affected the tube life. This problem was alleviated by shutting the cooling fan off at the high temperatures. The shut-off period is relatively short and does not affect the overall cooling significantly. The water cooling capability is still preserved. Preliminary tests showed that water/air cooling modes are interchangeable; however, analytical performance testing of the water-cooling mode should be considered.

#### 3.4 SAMPLE INTRODUCTION SYSTEM PERFORMANCE

The sample introduction assembly of the PWMA will introduce an oil sample into the graphite furnace without dilution. The oil sample is drawn into the sample tip primarily by capillarity and dispensed into the graphite tube by pressurized argon flow. The tip material, configuration, and argon pressure are the parameters which affect performance. After testing with different materials and configurations, the Teflon tip with a straight bore was selected for the brassboard testing. Argon pressure was optimized for best repeatability. With a higher pressure, the repeatability that was measured gravimetrically improved as a result of "clean expelling". However, the oil sample splattered inside the tube and caused nonreproducible atomization data. An optimum operating pressure of 5 psi was selected for the brassboard testing.

One hundred sample tips (see Figure 2-5) were machined from Teflon TFE. The performance of these tips were somewhat different from the performance of tips previously utilized. The tip volume cannot be totally filled by capillarity and the tip has to be partially immersed into the oil in order to fill the tip. Basically, the vertical rise of liquid in a small tube is an equilibration between the surface tension and the weight of the liquid. The relationship between them can be expressed as:

$$h = \frac{2 \sigma \cos \theta}{pgr}$$

where

- h = vertical rise of the liquid
- $\sigma$  = surface tension between liquid and gas, e.g., air
- p = mass density of liquid
- g = gravitational acceleration
- r = radius of the tube
- $\theta$  = contact angle.

The contact angle  $\theta$  is a function of the interfacial tension between the liquid and the tube wall and the surface tension between the gas and the tube wall. When the angle is less than  $90^\circ$ , the liquid is said to wet the solid and capillary rise can occur. However, the magnitude of the contact angle and the wetting ability depend on the wall material. The sample tips machined for brassboard testing are made of Teflon TFE while the tubes used for the previous test are made of Teflon FEP. The slight difference between these two materials might partially account for the difference in performance. Another factor affecting performance is that the tip bore was machined by drill bit which left marks on the interior surface of the tip. Microscopic examination of the tip bore surface showed light annular tracks. Since the final configuration of the sample tip will be injection-molded, this interior surface problem will be eliminated. However, a minimum amount of additional testing is required to determine the optimum molding material.

The sampling performance of MIL-L-7808 and MIL-L-6082 oil are also different. The MIL-L-6082 oil is used for the calibration standards and has a viscosity of about 230 centistokes at  $37^\circ\text{C}$ . This "thick" oil tends to cling to the sample tip wall and requires a higher pressure for expelling. The MIL-L-7808 jet engine oil has a viscosity of 13 centistoke at  $37^\circ\text{C}$  and requires a reduced expelling pressure. To optimize the pressure for either type of oil sample would cause a degraded performance for the other. The best method is to use the same type of oil for both calibration standards and test samples. An alternative method is to use two different pressures for the two different types of oils; however, doing so would complicate the design as well as the operation of the PWMA.

### 3.5 SYSTEM PERFORMANCE

#### 3.5.1 ATOMIZATION CYCLE

The basic graphite furnace AA process involves three steps. The furnace temperature is first brought to 100°C to remove water from the sample. The furnace temperature is then raised to an intermediate temperature to ash the sample matrix, e.g. oil. Finally, a very high temperature is reached to atomize the sample. As a general rule, the dry and char temperatures should be ramped slowly to avoid sample bumping. The atomization temperature should be stepped as fast as possible to obtain maximum efficiency and minimize any chemical interaction within the sample or between the sample and the graphite tube wall. The char temperature is usually set as high as possible in order to completely ash the sample matrix without losing the elements to be measured. Instrument manufacturers usually publish "cookbooks" which list the standard instrument measurement conditions for each element. The analyst can then use the cookbook as a guide to procedure development. Again, the standard conditions listed are for single element analyses.

The atomization cycle for the PWMA must accommodate the atomization conditions for all nine elements, thus requiring a totally new development approach. Graphite furnace AA is a very sensitive measuring instrument and the sensitivities are too high for most of the elements on the PWMA list. Secondary lines with reduced sensitivities are used for these elements. As an example, the primary line for Fe at 248.33 nm is too sensitive. Selection of the secondary line at 385.99 nm reduces the sensitivity by a factor of 15, resulting in a relatively linear working curve for concentrations from 1 ppm to 100 ppm. The secondary lines originate from the non-ground state transitions in the HCL, e.g., photons emitted by atom transitions from excited state to excited state. Because most of the atoms formed in the graphite furnace are in the ground state and fewer atoms are in the excited states, the absorption sensitivities for these secondary lines are lower. The absorption lines selected for the brassboard are listed in Table 3-1. The physical locations of the lines on the focal plane must also be taken into account. For example, Ti is an insensitive element, and the primary line should be used. However, the primary line is at 3564.27 nm, which is difficult to accommodate for the present polychromator design. The absorption line at 398.98 nm was then selected at the expense of reduced sensitivity. Furthermore, not all elements have adequate secondary lines. An element such as silver has only two absorption lines, and both have very high sensitivities. Accordingly, a different means of sensitivity reduction was sought, and it is discussed in the next paragraph.

A commercial instrument, the Perkin-Elmer Model 5000, was employed for developing the PWMA atomization cycle. All wear metals on the design list were tested individually and their atomization conditions were characterized. An atomization cycle which accommodates all the conditions was developed and tested. The atomization cycle is as follows.

- a. Ramp the temperature from ambient to 100°C in 5 seconds and hold for 5 seconds.
- b. Ramp the temperature from 100°C to 700°C in 10 seconds and hold for 10 seconds.

Table 3-1. Analytical Lines for the PWMA Brassboard

Element	Wavelength (nm)	Sensitivity Reduction*
Ag	328.07	1
Al	256.80	12
Cr	428.97	5
Cu	218.17	11
Fe	385.99	15
Mg	202.58	30
Ni	341.47	4
Si	251.61	1
Ti	398.97	2

\*Estimated from Flame AA data published by AA Manufacturers

- c. Ramp the temperature from 700°C to 1300°C in 12 seconds and hold for 0 seconds.
- d. Step the temperature from 1300°C to 2100°C in 1 second and hold for 5 seconds.
- e. Step the temperature from 2100°C to 2900°C in .3 second and hold for 5 seconds.

Step a removes water from the oil sample. Traces of water may originate from the oil or from contamination of the sample during rainy weather. The temperature is then raised to 700°C to completely ash the oil matrix. Silver is analyzed in the temperature ramp from 1300°C to 2100°C. As discussed in the proceeding paragraph, silver is a very sensitive element and no adequate secondary line is available. Analyzing silver on this long temperature ramp tends to atomize it slowly, thus resulting in a broad peak without saturating the absorbance signal. Although analyzing an element on a ramp is not recommended, the peak area measurement of silver has been proven to be repeatable. After the silver analysis, the temperature is stepped to 2100°C where copper, magnesium, iron, nickel, and chromium are measured. The optimum atomization temperatures for the above five metals are somewhat different from 2100°C. The 2100°C is chosen because all five metals can be appropriately atomized at this temperature without atomization of the remaining metals. Finally, the temperature is quickly stepped to 2900°C where silicon, aluminum, and titanium are atomized. The quick temperature stepping is achieved by a special feature in the Perkin-Elmer instrument, the "maximum power" burn. Using this maximum power burn, the temperature increase from 2100°C to 2900°C is accomplished in about 300 milliseconds and maximum atomization efficiency is achieved.

The internal argon gas flow rate is another parameter that affects performance and sensitivity of analyses. From Step a through Step d, argon flow rate is maintained at 300 ml/min to effectively purge the "smoke" from the oil matrix and to reduce the sensitivities for the six sensitive elements. At Step e, the argon flow rate is changed to 50 ml/min to promote the sensitivities of the remaining three less sensitive elements.

### 3.5.2 ANALYTICAL PERFORMANCE

After the temperature characteristics of the brassboard furnace were determined on the P-E 5000, the atomization cycle was duplicated on the brassboard. However, reproduction of the same temperature profile was difficult due to the differences in performance and control between the P-E 5000 GFPS and the brassboard GFPS. The final atomization cycle settings were determined by examining the individual absorption peak curves for each element. A software program was written to input absorbance data to an analog recorder.

Multi-element samples were diluted from individual Conostan standards prepared in hydrocarbon oil at 5000 ppm concentration. Since each wear metal has a different working range, the sample concentrations are expressed as a percent of the full scale. For example, a 100% full scale standard contains 100 ppm iron, 50 ppm magnesium and aluminum, 40 ppm copper, 30 ppm nickel, 20 ppm silicon and titanium, and 10 ppm silver and chromium. Different concentrations were prepared in both MIL-L-6082 grade 1100 reciprocating engine oil and MIL-L-7808 oil. Analytical curves for metals in MIL-L-6082 oil are shown in Figure 3-3. Analytical curves for metals in MIL-L-7808 oil are shown in Figure 3-4.

Ideally, the analytical curve should be linear to obtain maximum accuracy. However, the linear working range for AA is relatively small and, in most cases, the analytical curve tends to bend toward the concentration axis at higher concentrations. In the PWMA, the analysis is further complicated by measuring nine elements in one analysis sequence. Thus, the atomization condition of an element cannot be adjusted individually to shift the work range of that element into a linear region. In Figures 3-3 and 3-4, the analytical curves for magnesium bend heavily toward the concentration axis. This is primarily because magnesium is a very sensitive element and saturation occurs at higher concentrations. The causes and possible improvements are detailed in Appendix B. Aluminum and silicon are very insensitive with the brassboard test scheme. The causes and improvements are also discussed in Appendix B.

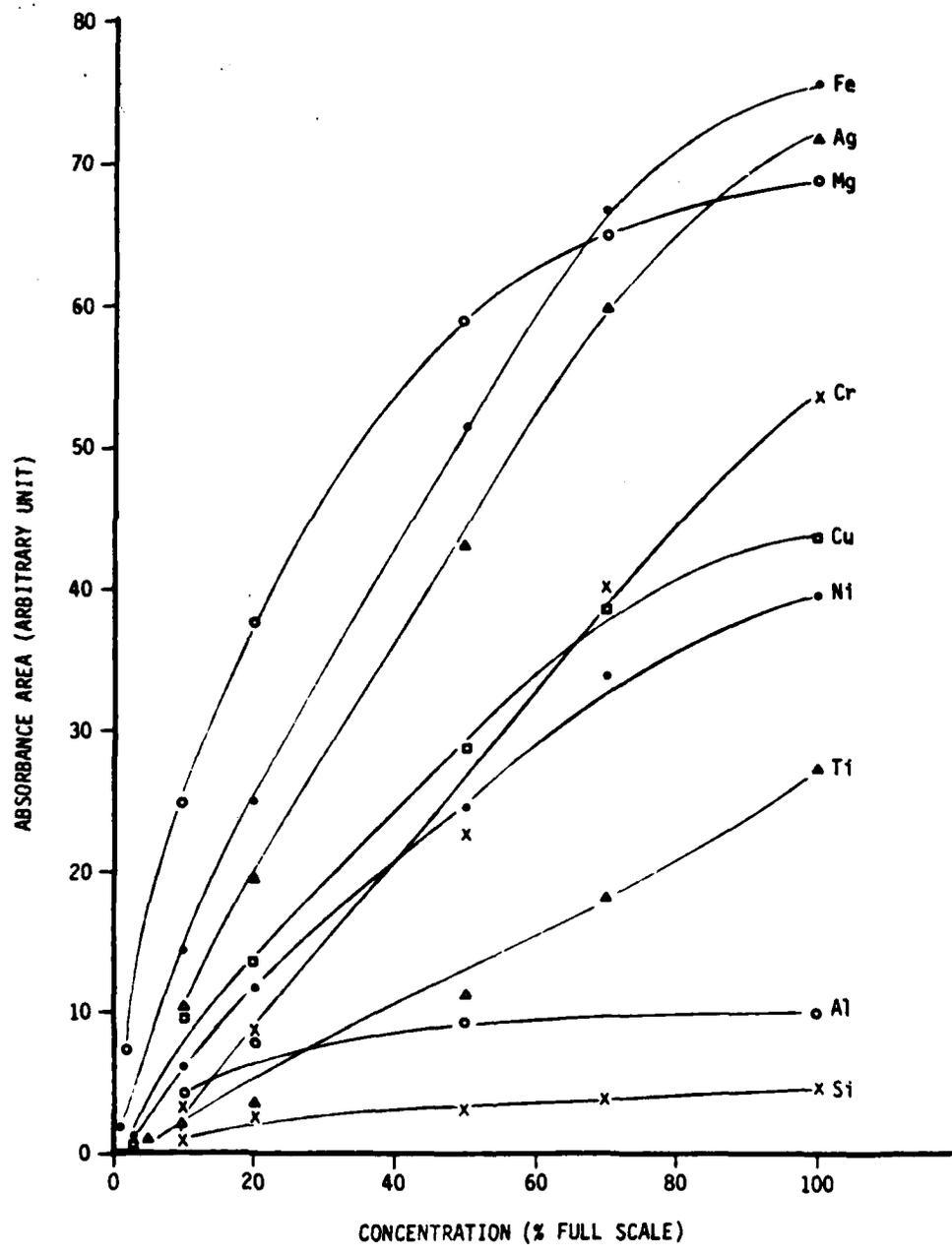


Figure 3-3. Analytical Curves for Metals in MIL-L-6082 Oil

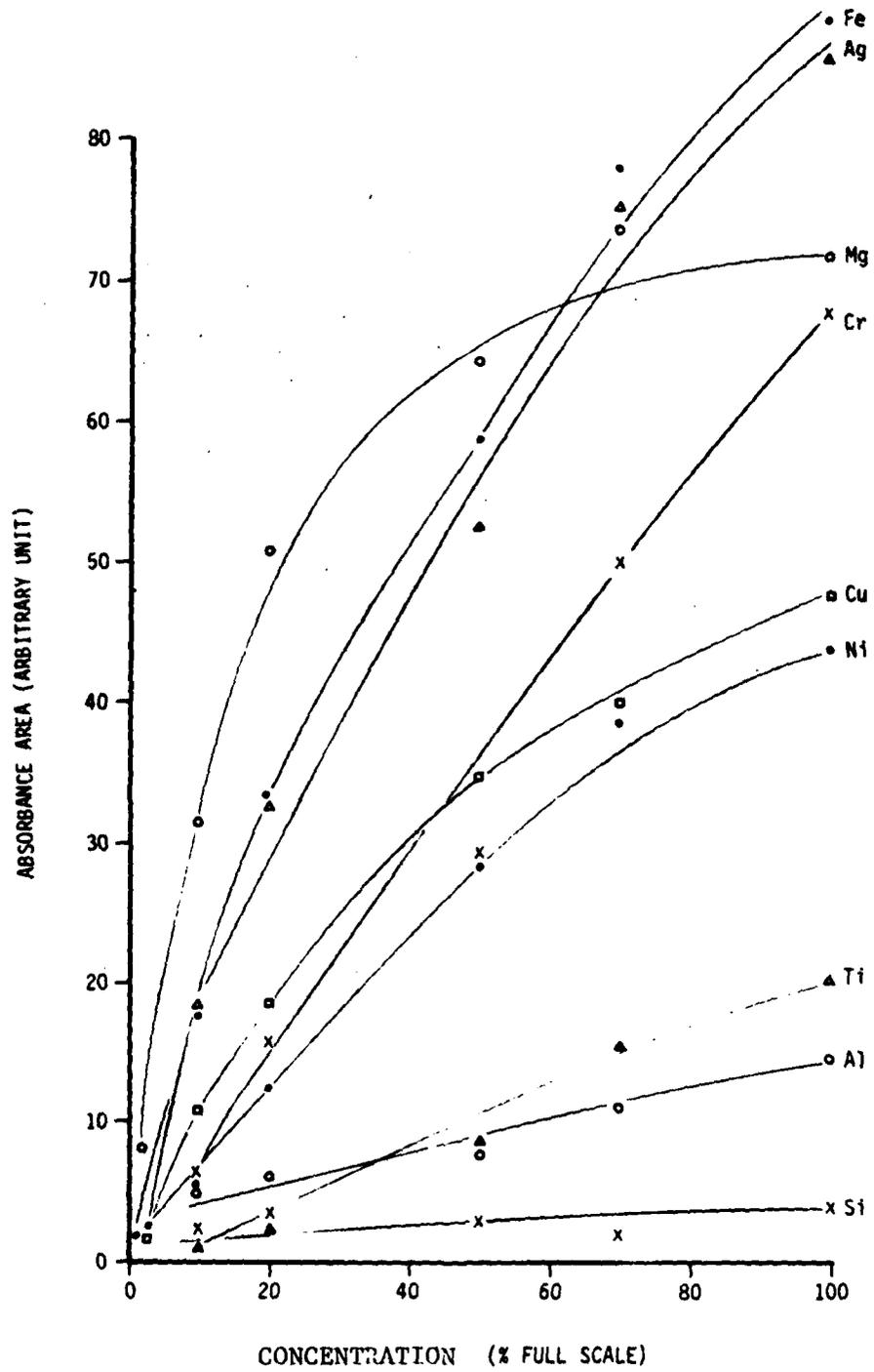


Figure 3-4. Analytical Curves for Metals in MIL-L-7808 Oil

SECTION IV  
RESULTS AND DISCUSSION

4.1 DATA HANDLING

The PWMA is under complete microcomputer control. Two HCLs containing nine metals are pulsed alternately to provide the absorption lines for the analysis. One feature incorporated into the PWMA is the background correction capability. In AA spectroscopy, the "background" is primarily due to the matrix molecular absorption and scattering. Absorption/scattering usually affects wide band signals instead of the narrow line absorptions that occur in atomic transition. This background contribution can be removed using a correction scheme. In the PWMA, HCL No. 1 emits spectral lines for Ag, Al, Cu, Cr, Fe, and Mg and HCL No. 2 emits spectral lines for Ni, Si, and Ti. The two lamps are pulsing alternately. Because the multi-element HCLs emit a complex spectrum, there are some emission lines in HCL No. 2, adjacent to the absorptions lines of HCL No. 1, which are nonatomic lines. These nonatomic lines serve as background correction lines for the elements in HCL No. 1, and vice versa. As an example, HCL No. 1 emits radiation at 385.99 nm, which is the Fe absorption line. HCL No. 2 emits radiation at 385.81 nm, which is a nonatomic line and will not contribute to the Fe absorption. However, both 385.99 nm and 385.81 nm lines absorb backgrounds that can be measured. Thus, the background signal can be removed by properly processing these two signals.

The PWMA HCL pulsing cycle is shown in Figure 4-1. Six different intensity signals are measured and the absorbance is calculated according to:

$$A = \log \frac{I_{OS} - I_{DC}}{I_{FS} - I_{FE}} - \log \frac{I_{OB} - I_{DC}}{I_{FB} - I_{FE}}$$

- $I_{OS}$  = initial signal line intensity transmitted without absorption
- $I_{OB}$  = initial background line intensity transmitted without absorption
- $I_{FS}$  = signal line intensity after absorption
- $I_{FB}$  = background line intensity after absorption
- $I_{DC}$  = dark current of the detector
- $I_{FE}$  = furnace emission intensity

The first term represents the atomic absorption signal of interest and the second term represents the background absorption. During the testing period using the commercial instrument and subsequent testing with the brassboard, no background signals were found. This is due mainly to the high char temperature which results in the oil matrix being completely burned. For simplicity, the background correction was not used in the brassboard testing.

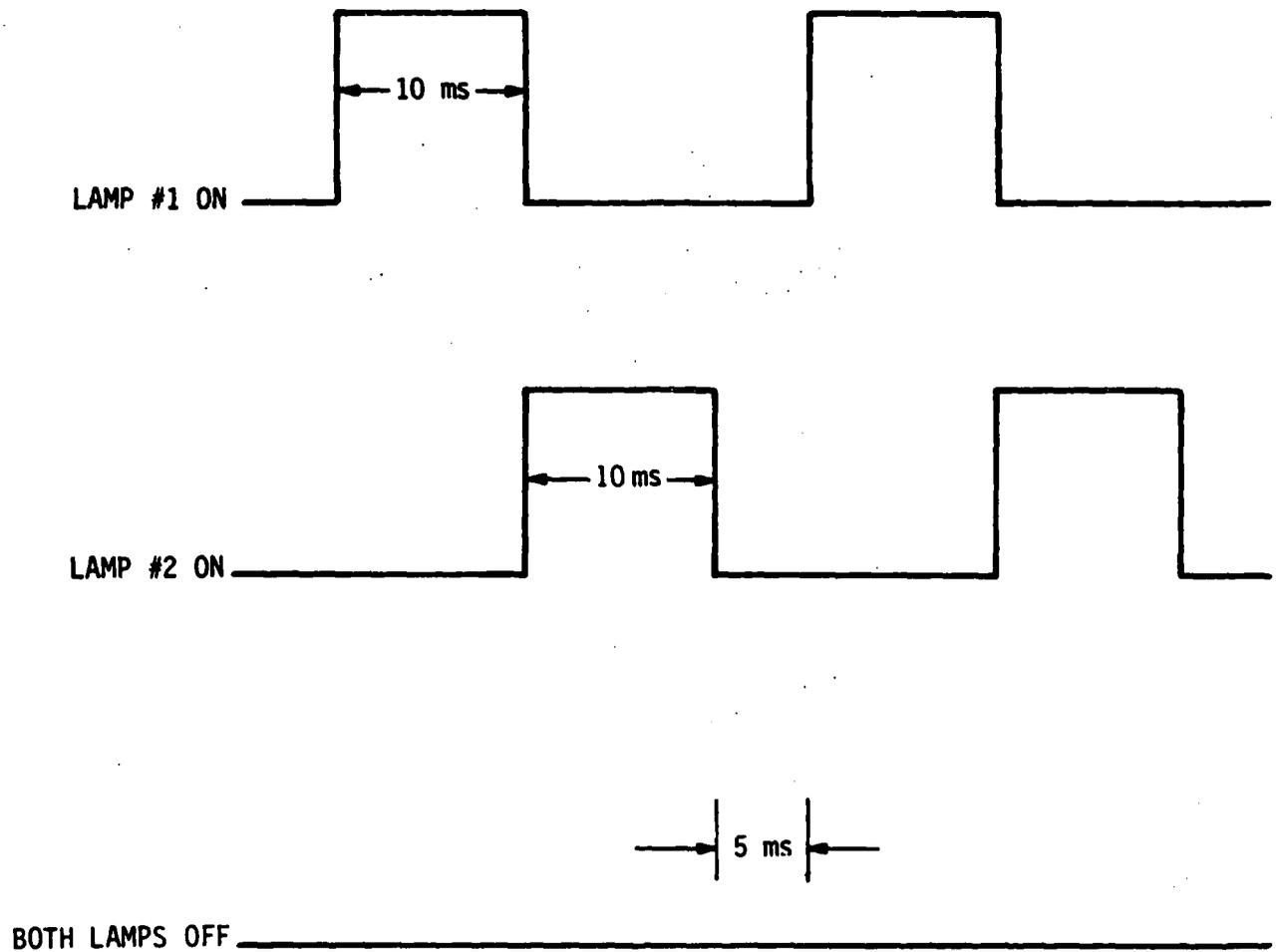


Figure 4-1. PWMA Lamp Pulsing Cycle

The absorbance calculated from the above formula represents a single data point on the absorption curve. For the PWMA application, peak area measurement was selected, primarily because the area measurement was less affected by the furnace temperature variation. The testing data obtained from the commercial instrument also showed that peak area measurements are more reproducible than peak height measurements. The area calculation is simply the summation of each data point over a predetermined sampling time. The number of data points sampled and the period of sampling for each metal are determined by the absorption curves.

#### 4.2 CALIBRATION

As pointed out in Section 3.5.2, most of the analytical curves tend to bend toward the concentration axis at higher concentrations. Different algorithms were developed to fit these nonlinear curves so that the concentration of an unknown sample can be calculated accurately. The basic calibration equation used in the PWMA is the same equation as used in P-E Model 5000 AA Spectrometer. The calibration equation is as follows:

$$C = \frac{K_3 A^2 + K_1 A}{K_2 A - 1}$$

C = Concentration

A = Absorbance area measured

$K_1, K_2, K_3$  = Calibration constants to be determined

In this equation there are three unknowns; thus, three calibration standards are required. The three standards generate three independent equations, enabling the three calibration constants to be solved. For an unknown sample, the sample concentration is calculated using the same calibration equation. This calibration equation can also be used for two-standards calibration where  $K_3$  is set to zero. For one-standard calibration, the calibration curve is a straight line represented by  $C = KA$ . In general, three-standards calibration will obtain a better curve fit. Using fewer standards would simplify the calibration procedure and minimize the human error. In any case, the most concentrated sample in the calibration standard should be higher than the highest concentration anticipated in the unknown sample.

One of the difficulties encountered in the brassboard testing was the  $K_2 A - 1$  factor in the denominator. The concentration approaches infinity as this factor approaches zero. In the commercial instrument, proper algorithms are incorporated to detect this anomaly and the operator has to repeat the calibration if the anomaly occurs. In the PWMA, nine sets of calibration constants are calculated and the probability for anomalies increases. It is impractical to incorporate all the error detection algorithms because doing so would complicate system operation. A possible alternative is to characterize the shapes of all the calibration curves and store the calibration constants in the computer. During operation, only one standard is needed to readjust the slope of the calibration curves. This approach would depend on the instrument stability.

The capability of adjusting the slope of the calibration curves is provided by the "reslope" function. The sensitivity of the instrument might change slightly from time to time as a function of operating conditions. The operator need only enter one mid-standard using the reslope mode. A reslope constant is then calculated, and the sensitivities for the subsequent samples are corrected.

#### 4.3 SUMMARY OF TEST DATA

The PWMA Phase I demonstration test with the Brassboard configuration was conducted on August 2 and 3, 1983. The test plan and the test report including all the data are attached in the Appendix. In general, the performance of Ag, Cr, Cu, Fe and Ni are satisfactory; Mg, Al, and Ti are marginal; and Si does not meet specifications. Detailed data analysis and areas of improvement are also discussed in the appendix.

#### 4.4 SOURCES OF FLUCTUATION

##### 4.4.1 SHOT NOISE

Shot noise, resulting from random fluctuations of electron emission from the cathode and dynodes of the PMTs, is the dominant noise in the PWMA. Shot noise is proportional to the square root of the number of photons entering the PMT, the quantum efficiency of the photocathode, and the signal bandwidth. Therefore, the noise level is the highest for the magnesium channel because the magnesium line at 202,58 nm is the weakest emission line. Shot noise can be minimized by reducing (filtering) the bandwidth of the system frequency response. However, the degree of filtering is limited by the requirement that the signal not be distorted. For the PWMA, the maximum tolerable time constant is about 2 ms and the corresponding peak-to-peak noise is about 15% of the signal level. Fortunately, the peak area integration method is employed. This integration method statistically averages the noise. The magnitude of the noise reduction is proportional to the square root of the number of data points.

##### 4.4.2 SAMPLE INTRODUCTION

The sample introduction step is usually the most significant single error in the AA analysis. Several commercial sample introduction devices were determined unsatisfactory. The present system is easy to operate and can introduce approximately 10  $\mu$ l of oil without dilution. However, the error introduced during sample injection is still larger than the other sources of error. With the brassboard sample tip, the relative standard deviation is approximately 2.6% for MIL-L-7808 oil and approximately 5.5% for MIL-L-6082 oil. As mentioned in Section 3.4, the performance may be improved with a molded design.

Another error related to the sample introduction is the statistics of particle size. As an example, silver has a specific gravity of 10.5, and for a spherical particle with a diameter of 20  $\mu$ m, the weight is 44 ng. For a sample size of 10  $\mu$ l, this quantity is equivalent to approximately 5 ppm. The full scale range of silver is 10 ppm and only two particles are in the oil. No practical method can be used to improve the statistics. However, it will be beneficial to carefully examine the actual particle size requirements for each metal individually.

#### 4.4.3 CALIBRATION

If the analytical profile of a certain element is linear, very little error is introduced by calibration. When the profile has a curvature, the error at higher concentrations is amplified. A comparison of standard deviations between absorbance and concentration for magnesium and iron, shown in Table 4-1, illustrate this characteristic. For magnesium absorbance, the relative standard deviation is a factor of 4 better than that for the concentration. This shows that a small error in absorbance results in a large error in concentration due to severe curvature. The difference of relative standard deviation between absorbance and concentration for iron is only a factor of 1.4 because analytical curve for iron is more linear than the analytical curve for magnesium. The analytical curve for magnesium should be improved and it is discussed in Appendix B.

Table 4-1. Comparison of Relative Standard Deviations Between Absorbance and Concentration (ppm) for Magnesium and Iron

Element/ Sample #	Mg		Fe	
	Absorbance	Concentration	Absorbance	Concentration
1	72.3	23.1	60.1	44.6
2	74.5	25.8	62.1	46.7
3	73.7	24.7	64.9	69.5
4	76.3	28.1	65.8	50.5
5	76.8	29.0	67.0	51.8
6	71.8	22.6	59.6	44.1
7	73.2	24.1	68.6	43.5
8	74.2	25.4	63.7	48.3
9	79.6	33.6	67.6	52.4
10	75.4	27.0	65.8	50.5
11	74.7	26.0	64.3	48.9
12	75.2	26.7	63.9	48.5
13	73.5	24.5	64.0	48.6
14	76.8	28.9	64.7	49.3
15	72.4	23.3	64.0	48.6
<b>Average</b>	74.69	26.18	64.4	49.05
<b>Standard Deviation</b>	2.08	2.87	2.49	2.59
<b>Relative Standard Deviation</b>	0.028	0.109	0.038	0.053

SECTION V  
CONCLUSION

Atomic absorption spectroscopy has been considered to be a single-element measurement technique for over three decades. Multi-element analyses are usually performed only in research laboratories. The PWMA brassboard testing successfully demonstrated the concept of a "true" multi-element furnace AA spectrometer. The capability of analyzing oil samples without dilution and the ease of operation would enable a person with minimum training to perform the lubricating oil analyses accurately.

The GFPS developed for the PWMA is the smallest high current power supply ever designed. This power supply, together with a uniquely constructed air-cooled furnace, comprise a compact graphite furnace system. A state-of-the-art nine channel polychromator has achieved a one Angstrom resolution with a focal length of only 20 cm. The packaging of these assemblies into two ruggedized containers, including a self-contained argon supply, will allow USAF personnel to perform routine oil analyses at any forward base.

The PWMA brassboard tests have demonstrated the use of graphite furnace AA spectrometry to perform nine simultaneous wear metal analyses from undiluted engine oil samples. The actual analysis readout time for each sample is less than 90 seconds, and up to 15 oil samples may be analyzed within one hour. All brassboard tests were performed using the air-cooling mode with the entire analysis cycle for all nine wear metals under full microcomputer control.

## SECTION VI

### RECOMMENDATIONS

The brassboard testing demonstrated that the multi-element graphite furnace AA can perform the task of analyzing wear metals in aircraft engine oil. Several problems and their resolution have been identified and are outlined in Appendix B. Some general topics are discussed here.

Precise calibration is an important factor for accurate measurement. Calibration requires careful measurement and often repeated analyses are necessary. In order to simplify PWMA operation, an alternate approach is to self-calibrate each instrument semi-automatically. The calibration constants, i.e., digitized calibration curves, are stored in the microcomputer. During operation, a mid-range standard is introduced to reslope the calibration curves, i.e., to introduce a sensitivity factor to the calibration constants. For improved accuracy, an average value of two or three measurements can be used. This scheme will reduce the effort of the operator by minimizing the number of calibration standards to be carried out. The criterion for using the method is that the sensitivity of the instrument does not change over a wide range so that the shapes of the calibration curves will remain approximately the same. The feasibility of using this method will be determined by testing preproduction units.

The accuracy and the repeatability of the sample introduction method directly affects the analysis. In the brassboard testing, the calibration standards were prepared in MIL-L-6082 lubricating oil and the test samples were prepared primarily in MIL-L-7808 lubricating oil. Because these two types of oil have distinctly different viscosities, the sample volumes dispensed under the same conditions were also different, thus introducing error. It would also be difficult to optimize the sample introduction conditions for both types of oils. In the future, it would be preferred to calibrate the instrument with MIL-L-7808 oil so that the sample volume and the sample matrix are the same.

Most of the spectrometric techniques cannot detect large particles. The PWMA Brassboard testing showed that large particles can be measured, provided proper sampling periods are selected. One of the limitations will be the statistics of the number of large particles in the sample volume. As pointed out in Section 4.4.2, a 20 micrometer silver particle is equivalent to 5 ppm for a 10  $\mu$ l oil sample. There is no easy way to resolve this problem; however, since different metals are used for various parts of the aircraft engine, a study is recommended to reassess the actual particle size requirement for each metal.

APPENDIX A  
BRASSBOARD TEST PLAN

APPLICATION		REVISIONS			
NEXT ASSY	USED ON	LTR	DESCRIPTION	DATE	APPROVED
		A	Sec. 3.2.3 Change 70% to 50% Delete RSD	8/29/83	<i>[Signature]</i>
			3.2.5 Delete Mil-L-7808 oil A/R Change "prototvpe" to "preproduction"		

UNLESS OTHERWISE SPECIFIED  
DIMENSIONS ARE IN INCHES

TOLERANCES  
ANG ±0°30'  
DEC .XX ± .XXX ±

MATERIAL:

CONTRACT NO.  
F33615-81-C-2080

DWG NO.

DRAWN

CHKD

DESIGN *[Signature]* 6/27/83

*[Signature]* 8/27/83

*[Signature]* 8/24/83

**PERKIN-ELMER**  
AEROSPACE DIVISION

PWMA PHASE I  
DEMONSTRATION PLAN

SIZE **A** CODE IDENT NO. **26581**

SCALE SHEET 1 OF 18

83-0931

## 1.0 SCOPE

This test plan applies to the use of the PWMA Brassboard configuration to demonstrate that the PWMA design complies with the performance requirements specified in Section 4.1.1 of the contract, dated December 20, 1982.

## 2.0 BRASSBOARD CONFIGURATION

### 2.1 BRASSBOARD

The primary purpose of the PWMA Brassboard will be to show compliance with the performance requirements; however, the design philosophy is such that most of the components used on the Brassboard can be packaged into the first preproduction unit with a minimum of effort.

### 2.2 CONFIGURATION

#### 2.2.1 Polychromator

The Polychromator will be the same as the final design.

#### 2.2.2 Polychromator Cover

The basic configuration and outline will be the same as for the final design, except the Brassboard cover is taller to facilitate integration with the optical bench components.

#### 2.2.3 Transfer Optics and Cover

The layout of the transfer optics will be the same as the final design, except laboratory components are used. Commercial optical mounts and covers are used for Brassboard only and appropriate ones will be designed for the preproduction units.

#### 2.2.4 Graphite Furnace

The furnace and the cooling pins will be the same as the final configuration; however, the furnace mounting bracket and the forced-air cooling ducts will be redesigned for the preproduction units.

#### 2.2.5 Argon Supply

The plumbing arrangement of the valves, regulators, and restrictors will be the same as the final design. However, needle valves and capillary lines will be used as restrictors instead of orifices for the brassboard. Their use enables flow adjustment during test.

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### 2.2.6 Sample Introduction System

The sample tip design is similar to the final design except prototype machined tips are used for the Brassboard testing, whereas molded tips will be used with the preproduction units.

## 2.3 ELECTRONICS AND CONTROL

### 2.3.1 Graphite Furnace Power Supply (GFPS)

The breadboard GFPS will be used for the demonstration.

### 2.3.2 Card Cage

The card cage assembly will be similar to the final design; therefore, the assembly and most of the wiring for the Brassboard can be used for the first preproduction unit.

### 2.3.3 Electrometer, PMT Supply, and HCL Supply

The circuit design will be the same for the final design except the component layout will be redone and modular power supplies will be used.

### 2.3.4 Controls

The controls will include power on/off, mode selection, furnace open/close, and start. Alarm functions will not be included.

## 2.4 SOFTWARE AND DISPLAY

### 2.4.1 Function

The microcomputer will control the HCL pulsing and the graphite furnace atomization cycle. It will also calculate wear metal sample concentrations using the calibration routine.

### 2.4.2 Display

The panel meter will not be wired in; therefore, all of the wear metal concentrations will be displayed on a video panel and also printed out.

## 3.0 VERIFICATION TEST

### 3.1 GENERAL

#### 3.1.1 Sample Preparation

The sample used in the verification test will be prepared from the CONOSTAN metallo-organic standards in MIL-L-6082, Grade 1100 reciprocating engine oil.

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For the particle size independence tests, wear metal powders suspended in MIL-L-7808 lubricant oil will be used.

Since each wear metal has a different full-scale level, multi-element standards will be prepared from single CONOSTAN standards and the concentration will be expressed in terms of percentage of the full scale for each wear metal. For example, a 50% full-scale standard will contain 50 PPM of iron, 25 PPM of magnesium and aluminum, 20 PPM of copper, 15 PPM of nickel, 10 PPM of silicon and titanium, 5 PPM of silver and chromium. Refer to Figures 1 and 2.

### 3.1.2 Calibration

The PWMA will be calibrated using three multi-element standards of all wear metals plus a blank, i.e., standards of 0, 20%, 50%, 100% of the full scale, each done twice and averaged, prepared in MIL-L-6082 oil. A calibration will be done before each performance test.

### 3.1.3 Operation

The air-cooling mode will be used for all Brassboard testing. Following warmup, the operator will inject a 10 $\mu$ l sample, push the START button and the analysis will begin. At the end of the four-minute analysis cycle, the READY light will come on and the PWMA will be ready for the next sample.

## 3.2 TEST Refer to Figures 3 and 4.

### 3.2.1 Multi-element Measurement, Dynamic Range and Analysis Time

This test will be used to verify three of the Phase I performance requirements, i.e., Sec. 4.1.1.1 Measurements, Sec. 4.1.1.3 Dynamic Range, and Sec. 4.1.6 Analysis Time.

A multi-element sample of all of the wear metals at their full-scale dynamic range concentrations (PPM) will be prepared, to include:

Ag 10	Cu 40	Ni 30
Al 50	Fe 100	Si 20
Cr 10	Mg 50	Ti 20

The wear metals sample will be prepared in MIL-L-7808 lubricant using Conostan organometallic calibration standards. Following calibration, five replicates will be analyzed, and their mean value for each wear metal concentration will be compared with those of the wear metals sample.

The acceptance criteria for this combination test is as follows:

- 1) Measurements - The simultaneous multi-element analysis of all nine wear metals is by definition and will be indicated by concentration readings of each.

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- 2) **Dynamic Range** - The dynamic range performance is TBD; however, a design goal of  $\pm 2.5\%$  of the full scale wear metal concentrations is anticipated.
- 3) **Analysis Time** - The period of time from sample injection to wear metals' concentrations will not exceed three minutes (180 sec). The capability to analyze 15 samples in one hour will be included with the Repeatability Test (Sec. 4.1.1.5).

### 3.2.2 Sensitivity (detection limit)

A multi-element sample will be prepared containing 1 PPM of each of all nine wear metals. The sample will be prepared in MIL-L-7808 lubricant oil using Conostan organometallic calibration standards. Following calibration, five replicate MIL-L-7808 blanks will be analyzed, followed by five 1PPM multi-element samples. The averages of the two oil samples, i.e., blank and 1PPM, will be compared to verify 1PPM sensitivity.

The acceptance criteria for this test is as follows:

- 1) Each of the nine wear metals will be measured with a detection limit of 1 PPM; however, fractions of a PPM will be read out to one place.
- 2) The sensitivity test will be done under full simultaneous multi-element analysis conditions.

### 3.2.3 Accuracy and Repeatability

This test will be used to verify two of the performance requirements, i.e., Sec. 4.1.1.4 Accuracy, and Sec. 4.1.1.5 Repeatability.

Multi-element samples of two different concentrations of all of the wear metals will be prepared. One sample will contain 10% of the dynamic range of all wear metals, the other sample will contain 50%. The samples will be prepared in MIL-L-7808 lubricant using Conostan organometallic calibration standards. Fifteen (15) replicates of each sample will be analyzed. For the Accuracy test, the mean concentration of each wear metal will be computed and compared with its actual concentration for the respective (10%, 50%) samples. For the Repeatability test, the standard deviation will be calculated from the previous mean concentration data for each wear metal for the respective (10%, 50%) samples.

The acceptance criteria for these two tests are as follows:

- 1) The repeatability performance is  $\pm 5\%$  of the 15 replicates for the 10% dynamic range wear metals and  $\pm 2.5\%$  of the 15 replicates for the 50% dynamic range wear metals sample, or  $\pm 1$ PPM, whichever is greater.

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- 2) The accuracy performance, as a proposed design goal, will be the same as for repeatability.

### 3.2.4. Particle Size Independence

This test will verify Sec. 4.1.1.7 of the performance requirements for large metal particles. For this performance test, two iron particle samples will be prepared in MIL-L-7808 oil. One sample will contain  $\sim 5\mu$  iron particles and the other will contain  $\sim 16\mu$  particles. The samples will be made up to 100 PPM. Additional samples may be provided for evaluation.

The acceptance test criteria is as follows:

- 1) Wear metal analysis will be independent of particles over the range of 0-20 $\mu$ , based upon the particle distribution.

### 3.2.5. Sample Composition

Multi-element samples containing all of the wear metals at 50% of their dynamic ranges will be prepared in MIL-L-23699 oils. Following calibration, five replicates of each sample will be analyzed and their mean value for each wear metal concentration will be compared with those of the actual wear metals sample for each kind of oil.

The acceptance criteria for this test is as follows:

- 1) The sample composition requirement is TBD; however, a design goal is presented for the 50% dynamic range. The design goal accuracy for MIL-L-23699 will be  $\pm 2.5\%$  or 1PPM, whichever is greater.
- 2) The accuracy performance of Sec. 3.2.3. will supercede the above performance requirement.

## 3.3 SAMPLE METHOD CRITERIA

### 3.3.1. Sample Injection

The prototype Pressurized Sample Injection System (PSIS) will be used for all sample injection into the graphite furnace.

Argon gas will be used as the sample injection propellant.

The sample volume will be 10 $\mu$ l. The prototype sample tip, Dwg. No. 353959-001, will be used in conjunction with a standard pipette tip as a tip holder.

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3.3.2. Graphite Furnace Graphite Tube

The prototype partially-ribbed graphite tube will be used and will be conditioned prior to any performance testing.

As a design goal, it is anticipated that the tubes can be used for a maximum of 200 tests before being replaced.

3.3.3. Additional Test Samples

Test samples from aircraft engines may be furnished for analysis.

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STANDARD	OIL	Ag	Al	Cu	CR	Fe	Mg	Ni	Si	Ti	PURPOSE
1	6082	10	50	40	10	100	50	30	20	20	100% CALIBRATION STANDARD
2	"	5	25	20	5	50	25	15	10	10	50% CALIBRATION STANDARD
3	"	2	10	8	2	20	10	6	4	4	20% CALIBRATION STANDARD
4	"	0	0	0	0	0	0	0	0	0	OIL BLANK
5	7808	1	1	1	1	1	1	1	1	1	SENSITIVITY
6	7808	1	5	4	1	10	5	3	2	2	10% ACCURACY, REPEATABILITY
7	7808	5	25	20	5	50	25	15	10	10	50% ACCURACY, REPEATABILITY
8	7808	0	0	0	0	0	0	0	0	0	OIL BLANK
9	7808	5	25	20	5	50	25	15	10	10	SAMPLE COMPOSITION
10	23699	0	0	0	0	0	0	0	0	0	OIL BLANK
11	23699	5	25	20	5	50	25	15	10	10	SAMPLE COMPOSITION
12	7808					100					PARTICLE SIZE INDEPENDENCE
13	7808	10	50	40	10	100	50	30	20	20	100% DYNAMIC RANGE
14	7808	8	45	36	9	90	45	27	18	18	90% DYNAMIC RANGE

FIGURE 1 BRASSBOARD TEST STANDARDS  
(VALUES IN PPM)

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PERFORMANCE TEST*	TEST STANDARDS													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
SMA	X													
SENSITIVITY					X									
DYNAMIC RANGE												X	X	
ACCURACY						X	X							
REPEATABILITY						X	X							
ANALYSIS TIME	X	X	X	X	X	X	X	X	X	X	X	X	X	
PARTICLE SIZE INDEPENDENCE												X		
SAMPLE COMPOSITION								X	X	X	X			
CALIBRATION STANDARDS	X	X	X	X										

\*EACH PERFORMANCE TEST WILL BE PRECEDED BY A COMPLETE CALIBRATION (BLANK PLUS THREE STANDARDS).

FIGURE 2 BRASSBOARD PERFORMANCE TESTS MATRIX

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**PWMA BRASSBOARD**

**DATA SHEET**

DATE 3 August 1983

REFERENCE PARAGRAPH 3.2.1 Dynamic Range

OPERATOR Bill Niu

TYPE OF SAMPLE 90% Dynamic Range

OIL TYPE 7808

ELEMENT	Ag	Al	Cr	Cu	Fe	Mg	Ni	Si	Ti
SAMPLE NO. 1	10.7	40.5	16.5	42.3	99.8	53.5	31.4	1.3	19.9
NO. 2	11.4	31.5	18.7	43.4	100.5	51.6	31.7	1.1	28.9
NO. 3	11.0	32.6	18.1	41.6	100.2	51.3	31.4	1.6	32.7
NO. 4	11.1	27.9	17.3	37.8	95.1	52.0	31.1	2.5	33.7
NO. 5	11.1	33.4	18.1	42.5	100.0	52.7	30.9	2.3	36.6
AVERAGE	11.06	33.18	17.74	41.52	99.12	52.22	31.30	1.76	30.36
SAMPLE CONCENTRATION	10.1	45	9.1	36.1	90	45	27	18.1	18

SIZE <b>A</b>	CODE IDENT NO. <b>26581</b>	<b>83-0931</b>
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**DATE** 3 August 1983

**REFERENCE PARAGRAPH** 3.2.1 Dynamic Range

**OPERATOR** Bill Niu

**TYPE OF SAMPLE** 100% Dynamic Range

**OIL TYPE** 7808

<b>ELEMENT</b>	<b>Ag</b>	<b>Al</b>	<b>Cr</b>	<b>Cu</b>	<b>Fe</b>	<b>Mg</b>	<b>Ni</b>	<b>Si</b>	<b>Ti</b>
<b>CONCENTRATION (PPH)</b>									
<b>SAMPLE NO. 1</b>	11.4	32.2	19.6	41.3	105.8	52.6	32.7	2.8	41.4
<b>NO. 2</b>	11.6	34.0	19.8	43.4	105.3	47.6	33.1	3.2	46.4
<b>NO. 3</b>	12.0	27.3	20.6	40.2	106.7	53.5	32.6	3.9	46.3
<b>NO. 4</b>	11.5	26.3	18.8	41.4	105.0	42.9	31.9	2.6	49.8
<b>NO. 5</b>	11.7	26.4	19.6	42.2	106.0	50.2	32.1	3.3	47.9
<b>AVERAGE</b>	11.64	29.24	19.68	41.7	106.08	49.36	32.48	3.16	46.36
<b>SAMPLE CONCENTRATION</b>	11.2	50.1	10.1	40.2	100.1	50.0	30.1	20	20.1

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REFERENCE PARAGRAPH 3.2.2 Sensitivity

OPERATOR Bill Niu

TYPE OF SAMPLE Blank

OIL TYPE 7808

ELEMENT	Ag	Al	Cr	Cu	Fe	Mg	Ni	Si	Ti
CONCENTRATION (PPM)									
SAMPLE NO. 1	0.0	0.3	1.3	0.4	1.1	0.1	0.9	0.0	-0.5
NO. 2	0.0	-0.1	0.1	1.1	0.1	0.0	0.0	-0.5	-0.6
NO. 3	-0.0	0.0	0.0	1.5	-0.0	0.0	0.0	-0.6	-1.2
NO. 4	0.0	-0.3	0.0	0.0	0.1	0.0	0.1	-0.3	-1.2
NO. 5	0.0	1.1	0.2	0.1	0.1	0.0	0.1	-0.7	-1.6
AVERAGE	0.0	0.2	0.32	0.62	0.28	0.02	0.22	-0.42	-1.02
SAMPLE CONCENTRATION	0	0	0	0	0	0	0	0	0

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REFERENCE PARAGRAPH 3.2.2 Sensitivity

OPERATOR Bill Niu

TYPE OF SAMPLE 1 PPM Multielement

OIL TYPE 7808

ELEMENT	Ag	Al	Cr	Cu	Fe	Mg	Ni	Si	Ti
CONCENTRATION (PPM)									
SAMPLE NO. 1	1.5	3.9	1.7	2.0	1.4	1.7	1.0	-1.1	-0.1
NO. 2	1.3	3.6	1.6	1.8	1.3	1.1	0.9	-0.4	-0.2
NO. 3	1.4	3.4	1.5	2.1	1.3	1.1	0.9	-1.0	-0.1
NO. 4	1.4	5.4	2.3	1.8	1.5	1.2	1.0	-0.9	-0.0
NO. 5	1.4	2.6	1.9	2.0	1.2	1.3	0.8	-0.8	0.0
AVERAGE	1.4	3.78	1.8	1.94	1.34	1.28	0.92	-0.88	-0.08
SAMPLE CONCENTRATION	1.1	1.2	1.1	1.2	1.1	1.2	1.1	1.1	1.1

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PMMA BRASSBOARD

DATA SHEET

DATE 2 August 1983

REFERENCE PARAGRAPH 3.2.3 - Accuracy, Repeatability

OPERATOR Bill Niu

TYPE OF SAMPLE 10% Dynamic Range

OIL TYPE 7808

ELEMENT	Ag	Al	Cr	Cu	Fe	Mg	Ni	Si	Ti
SAMPLE NO. 1	2.1	8.5	3.7	5.0	15.0	11.8	3.8	0.7	3.8
NO. 2	1.9	*18.9	1.4	4.0	13.0	9.3	3.3	0.7	3.4
NO. 3	2.2	7.3	2.0	5.7	15.7	11.7	3.9	1.0	4.0
NO. 4	2.1	7.6	1.9	4.3	14.9	12.0	3.5	2.2	3.7
NO. 5	2.2	8.0	1.9	4.7	15.6	11.1	3.4	3.1	3.5
NO. 6	2.3	11.4	2.0	5.3	15.9	11.5	3.7	1.0	3.9
NO. 7	2.5	9.6	2.2	5.3	17.1	13.5	3.9	1.2	3.5
NO. 8	2.3	7.9	2.3	5.5	16.2	11.1	4.0	0.4	3.8
NO. 9	2.2	7.7	2.0	5.2	15.3	10.8	3.9	3.0	4.7
NO. 10	2.1	9.7	1.5	4.6	14.4	10.6	3.3	0.8	2.5
NO. 11	2.0	10.2	1.5	3.5	13.7	9.8	3.2	0.9	2.2
NO. 12	2.1	9.2	1.7	5.2	14.2	10.3	3.6	0.1	3.2
NO. 13	2.2	7.3	2.1	4.6	15.4	12.0	3.9	1.7	3.6
NO. 14	2.0	11.2	2.3	5.6	14.2	10.6	3.4	3.5	4.9
NO. 15	1.9	9.2	1.8	3.3	13.9	10.9	3.2	3.8	4.0
AVERAGE	2.14	8.91	2.02	4.78	14.96	11.13	3.6	1.61	3.7
SAMPLE SPECIFICATION (PPM)	±1	±1	±1	±1	±1	±1	±1	±1	±1
STANDARD DEVIATION	0.16	2.91	0.54	0.74	1.08	1.02	0.29	1.2	0.76

\*\* STD DEV WITHOUT \* POINT

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PMMA BRASSBOARD

DATA SHEET

DATE 2 August 1983

REFERENCE PARAGRAPH 3.2.3 - Accuracy, Repeatability

OPERATOR Bill Niu

TYPE OF SAMPLE 50% Dynamic Range

OIL TYPE 7808

ELEMENT	Ag	Al	Cr	Cu	Fe	Mg	Ni	Si	Ti
SAMPLE NO. 1	5.1	24.7	8.6	21.2	44.6	23.1	15.5	1.9	16.5
NO. 2	5.3	24.6	9.0	20.6	46.7	25.8	16.5	2.3	19.6
NO. 3	5.7	22.5	8.7	19.2	49.5	24.7	16.3	2.1	19.6
NO. 4	5.9	20.1	8.0	21.0	50.5	28.1	17.3	2.5	19.4
NO. 5	5.8	25.2	8.9	21.0	51.8	29.0	16.9	2.1	17.1
NO. 6	4.9	18.0	8.1	18.1	44.1	22.6	15.0	1.3	18.4
NO. 7	5.6	17.8	*15.0	18.3	53.5	24.1	17.2	3.2	17.3
NO. 8	5.7	21.1	6.5	17.7	48.3	25.4	15.8	2.2	15.0
NO. 9	6.0	26.7	8.4	19.9	52.4	*33.6	17.0	2.8	16.1
NO. 10	5.8	18.5	7.7	20.2	50.5	27.0	17.0	1.8	17.5
NO. 11	5.6	17.8	7.6	19.0	48.9	26.0	16.4	2.2	18.1
NO. 12	5.8	20.4	6.6	17.6	48.5	26.7	16.2	2.8	17.0
NO. 13	5.8	17.5	7.1	18.3	48.6	24.5	16.6	1.8	17.8
NO. 14	5.8	18.5	7.6	17.8	49.3	28.9	16.6	1.8	18.6
NO. 15	5.7	17.6	7.2	20.7	48.6	23.3	16.0	2.1	18.3
AVERAGE	5.63	20.7	7.86	19.37	49.1	25.66	16.42	2.19	17.72
SAMPLE SPECIFICATION (PPM)	±1	±1	±1	±1	±1.3	±1	±1	±1	±1
STANDARD DEVIATION	0.3	3.2	2.04	1.35	2.59	2.88	0.65	0.48	1.32
			**0.8		**	2.09			

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REFERENCE PARAGRAPH 3.2.4 Particle Size Independence

OPERATOR Bill Niu

TYPE OF SAMPLE 20-30μ

OIL TYPE 7808

ELEMENT	Ag	Al	Cr	Cu	Fe	Mg	Ni	Si	Ti
CONCENTRATION (PPM)	4.7	-	0.1	0.7	6.1	47.1	-	-	-
SAMPLE NO. 1									
NO. 2									
NO. 3									
NO. 4									
NO. 5									
AVERAGE	10	.50	10	30	100	50	30	20	20
SAMPLE CONCENTRATION	Not Analyzed								

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REFERENCE PARAGRAPH 3.2.4 Particle Size Independence

OPERATOR Bill Niu

TYPE OF SAMPLE 10-20 $\mu$

OIL TYPE 7808

ELEMENT	Ag	Al	Cr	Cu	Fe	Mg	Ni	Si	Ti
CONCENTRATION (PPM)									
SAMPLE NO. 1	5.1	133	5.2	15.4	7.3	31.6	0.0	4.2	-
NO. 2									
NO. 3									
NO. 4									
NO. 5									
AVERAGE									
SAMPLE CONCENTRATION	10	50	10	30	100	50	30	20	20
	Not Analyzed								

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DATE 3 August 83

REFERENCE PARAGRAPH 3.2.4 Particle Size Independence

OPERATOR Bill Niu

TYPE OF SAMPLE 2.5 $\mu$  Fe

OIL TYPE 7808

ELEMENT	Ag	Al	Cr	Cu	Fe	Mg	Ni	Si	Ti
CONCENTRATION (PPM)									
SAMPLE NO. 1					13.3				
NO. 2					11.8				
NO. 3					15.4				
NO. 4					15.1				
NO. 5					10.1				
AVERAGE					13.14				
SAMPLE CONCENTRATION					100				
EXTENDED WINDOW SAMPLING									
Refer to Section 3.2.4.									
									117.1

SIZE <b>A</b>	CODE IDENT NO. <b>26581</b>	83-0931
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REFERENCE PARAGRAPH 3.2.4 Particle Size Independence

OPERATOR Bill Niu

TYPE OF SAMPLE ~16 $\mu$  Fe

OIL TYPE 7808

ELEMENT	Ag	Al	Cr	Cu	Fe	Mg	Ni	Si	Ti
CONCENTRATION (PPM)									
SAMPLE NO. 1					0.9				
NO. 2					0.4				
NO. 3					0.4				
NO. 4					-				
NO. 5					-				
AVERAGE					0.57				
SAMPLE CONCENTRATION					100				
EXTENDED WINDOW SAMPLING					83.9				
Refer to Section 3.2.4									

SIZE <b>A</b>	CODE IDENT NO. <b>26581</b>	83-0931
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**PWMA BRASSBOARD**

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REFERENCE PARAGRAPH 3.2.5 Sample Composition

OPERATOR Bill Niu

TYPE OF SAMPLE 50% Dynamic Range

OIL TYPE 23699

ELEMENT	Ag	Al	Cr	Cu	Fe	Mg	Ni	Si	Ti
SAMPLE NO. 1	8.0	15.9	10.6	24.0	64.7	50.1	21.2	1.4	14.1
NO. 2	7.9	16.3	10.6	23.2	63.4	43.9	20.1	0.8	14.4
NO. 3	8.2	18.4	10.2	24.3	65.9	38.0	20.8	1.8	10.5
NO. 4	7.9	19.9	9.9	26.4	63.4	48.0	20.5	-0.2	13.1
NO. 5	8.5	20.1	11.0	27.3	68.3	39.2	22.3	0.0	14.3
AVERAGE	8.1	18.1	10.46	25.04	65.14	43.8	20.98	1.27	13.28
SAMPLE CONCENTRATION	5.6	25	5.1	20.1	50	25	15	10	10

SIZE <b>A</b>	CODE IDENT NO. <b>26581</b>	83-0931
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APPENDIX B  
BRASSBOARD TEST REPORT

## PWMA PHASE I DEMONSTRATION TEST REPORT

### 1. SUMMARY

The PWMA Phase I Demonstration Test with the PWMA Brassboard was conducted on August 2 and 3, 1983 according to the revised PWMA Phase I Demonstration Plan, TP 83-0931. The Demonstration Plan, along with the test data, is appended to this report. Tests included analysis time, dynamic range, sensitivity, repeatability, particle size independence, and sample composition. Particle size independence was tested using particulate oil samples furnished by WPAFB. Jet engine oil samples furnished by Demonstration attendees were analyzed and showed results comparable to the parallel JOAP data; however, this data will not be included in the Design File Memo (DFM).

The PWMA Brassboard tests have demonstrated the use of graphite furnace AA spectrometry to simultaneously perform nine wear metal analyses from undiluted engine oil samples. The actual analysis readout time for each sample is less than 90 seconds, and up to 15 oil samples can be analyzed within one hour. All brassboard tests were performed using the air-cooling mode and with the entire analysis cycle for all nine wear metals under full microcomputer control.

### 2. BRASSBOARD TEST DATA

For the demonstration, calibration standards were prepared in MIL-L-6082, grade 1100 reciprocating engine oil and used for brassboard calibration. Test samples were prepared gravimetrically in MIL-L-7808 lubricating oil using Conostan organometallic standards and wear metal particles as required. The sample composition test samples were prepared in MIL-L-23699 lubricating oil.

All test data were recorded on data sheets provided with the test plan and are attached to this DFM. The data are discussed in the order presented in the test plan and the applicable test plan paragraphs are referenced in parentheses.

The brassboard configuration is described in the demonstration test plan. Most assemblies employed in the Brassboard are of final designs.

The present GFPS can heat the graphite tube to approximately 2650°C, thus affecting measurement performance for Ti, Si, and Al wear metals. A new, more powerful GFPS design, along with more efficient electrical connections, will provide furnace temperatures to 2900°C as required in the design specification.

2.1 MULTI-ELEMENT MEASUREMENT, DYNAMIC RANGE AND ANALYSIS TIME (Ref Para 3.2.1)

The brassboard atomization cycle was set up as follows:

Preatomization - 2 seconds

Step 1 - ramp to 100°C in 5 sec and hold for 5 sec

Step 2 - ramp to 700°C in 10 sec and hold for 10 sec

Step 3 - ramp to 1300°C in 12 sec

Step 4 - ramp to 2100°C in 1 sec and hold for 5 sec

Step 5 - increase to 2650°C in 0 sec and hold for 5.3 sec

Step 6 - turn off GFPS and then shut off the argon flow after 3 sec

Note that the upper temperature in Step 5 is limited by the capability of the present GFPS. A new power supply will be designed and assembled that will be capable of achieving higher temperatures as required.

The atomization cycle requires 58 seconds and the concentration readout data is printed approximately 30 seconds later; thus, the analysis time requirement is 88 seconds. A cooling time of 170 seconds is provided for air-cooling of the graphite furnace; thus, the entire time requirement is four minutes. Air-cooling mode was used for all of the Brassboard tests. During the repeatability accuracy test, 15 test samples were analyzed within one hour, thus meeting the 15 analyses per hour performance requirement. The water-cooling mode was available during the testing but was not used.

For the dynamic range test, five replicates of 90% and 100% of full scale for all wear metals were prepared in MIL-L-7808 lubricant and analyzed. Their mean values were then compared to verify that the Brassboard can differentiate between these two dynamic ranges.

- a. Ag, Cr, Fe, and Ni at 90% of full scale concentration are clearly distinguished from that of 100%; however, the differences are not exactly 10%. This performance is related to calibration curvature at high concentrations and will be discussed later.
- b. A buildup of Ti concentration was observed when consecutively measuring both of the dynamic ranges. This is caused by the graphite tube memory effect and can be eliminated by having a final cleaning step at a higher graphite furnace tube temperature.
- c. Magnesium signals are saturated at these high concentrations. The saturation phenomenon is probably due to the following:

Nonabsorbing Mg emission lines enter the Mg slit of the polychromator, limiting the true Mg absorbance. Reduction of nonabsorbing emission

can be accomplished by narrowing the Mg slit. An additional cause is that when the Mg concentration is high, Mg atoms do not completely atomize at Step 5 of the atomization cycle and the residual atoms atomize at Step 6. Extending the atomization time could resolve this problem.

- d. Cu signals also are close to the saturation level at these high concentrations. The causes and the recommendations for improved performance are the same as those mentioned for Mg.
- e. Al and Si performance will be discussed in Section 3.2.6.

## 2.2 SENSITIVITY (Detection Limit) (Ref Para 3.2.2)

Five replicate MIL-L-7808 lubricating oil blanks were analyzed and their mean value calculated. Five replicates of a multi-element sample containing 1 ppm of each of all nine wear metals were then analyzed and their mean values calculated.

- a. With the exception of Si, all wear metals indicated a discernible level, i.e., < 1 ppm, above the respective blank values.
- b. In the case of Ti, the blank mean value is -1.02 ppm and the sample mean value is -0.08 ppm; thus, the discernible level is +0.94 ppm. The negative zero reading for Ti is due to memory effect and autozero during calibration.

## 2.3 REPEATABILITY - ACCURACY (Ref Para 3.2.3)

From the demonstration, 10% and 50% of full scale multi-element test samples were prepared in MIL-L-7808 lubricating oil. Fifteen replicates of each test sample were analyzed and their standard deviation values calculated.

For the 10% of full scale repeatability test, the standard deviations for each of the wear metals are essentially within  $\pm 5\%$  of the average of the 15 replicates for each wear metal or  $\pm 1$  ppm, whichever is greater. Al and Si, however, are excepted.

- a. Al and Si have standard deviations of  $\pm 1.38$  and  $\pm 1.2$  ppm respectively. Their performance will be further discussed in Section 3.2.6.

For the 50% of full scale repeatability test, the following test results were recorded and discussed:

- a. Ag, Cr, and Ni have standard deviations within  $\pm 1$  ppm or  $\pm 2.5\%$ .
- b. Fe has a standard deviation of  $\pm 2.5$  ppm which is equivalent to  $\pm 5\%$  of the average. Optimizing the sample introduction system should improve Fe performance since it has the highest concentration level, i.e., 100 ppm full scale.

- c. The standard deviations of Mg and Cu are 2.09 and 1.35 ppm, respectively. Because they are very sensitive elements, secondary lines were selected for their measurement. These secondary lines are from the nonground state transitions and are generally weaker in intensity. These weaker lines result in noisier outputs which contribute to part of the fluctuation. The Signal to Noise Ratio (SNR) can be improved by increasing the efficiency of the optics. For example, to use a ruled grating blazed at the Mg wavelength could have an efficiency of 75%, which is twice as efficient than the holographic grating presently employed. Also, the fluctuation of the Mg signals is amplified by the calibration curve, i.e., when the data points are beyond the linear portion of the calibration curve, a small difference in absorbance would result in a large difference in concentration. The modifications proposed in Section 2.1 to extend the atomization time for Mg would also improve repeatability.
- d. The standard deviation for Ti is slightly larger than 1 ppm. Again, as mentioned in Section 2.1, an improved GFPS would improve the Ti performance.
- e. Cr has one bad data point. It is possibly caused by spurious light since the Cr slit is relatively wide. Narrowing the slit should reduce the spurious light problem. In addition, an order sorting filter could be placed in front of the Cr PMT to block any second order spectra. Al and Si performance will be discussed in Section 3.2.6.
- f. Changing the specification from  $\pm 2.5\%$  to  $\pm 5\%$  would eliminate the need for some of the above changes and still provide good trend analysis performance.

#### 3.2.4 PARTICLE SIZE INDEPENDENCE (Ref Para 3.2.4)

WPAFB furnished single-element wear metal particle samples dispersed in 7808 lubricant. The particle samples were furnished in two size ranges, i.e., 10-20  $\mu\text{m}$  and 20-30  $\mu\text{m}$ . Prior to analysis, all of the test samples were placed in an industrial ultrasonic bath for 20 minutes to assure dispersion. Each sample was then hand-shaken prior to actual sample introduction. Due to time constraints, only one analysis was made for each test sample; thus, the data is not statistically conclusive. Fortunately, the data does indicate some mechanisms of the atomization of large wear metal particles.

- a. Graphite furnace AA is normally considered a particle size independent method because of long sample residence times and available high temperatures. The PWMA atomization cycle analyzes all nine wear metals with only three different consecutive temperatures; therefore, some of the wear metals do not receive the sufficient energy (temperature) as they normally would in single element analysis where the atomization temperature is optimized for each wear metal. A generally accepted mechanism for graphite furnace AA is that organometallic

molecules decompose into bare metal, either by thermal decomposition or reduction on the heated graphite tube surface; then, the metal vaporizes into an atomic cloud. Because of the small metal quantity involved and the metal being in good contact with the graphite tube surface, the vapor pressure of the metal is the predominant parameter. For particles, it seems apparent that the samples have to be melted first prior to complete atomization. The melting point, then, is an additional parameter involved. The Brassboard test data indicates that metals having low melting points, e.g., both Al and Mg have melting points of 650°C, were almost completely recovered. Ag has a melting point of 900°C and has a recovery of 50%. The absorbance signals of Fe particle analyses shows that a small portion of Fe atomizes at Step 4 and a large portion atomizes at Step 5. This suggests that large particles were melted at the 2100°C step and atomized at 2650°C step. Experimentally extending the sampling time for Fe indicated a recovery greater than 80%. Further studies are needed to confirm the "extended window" approach.

- b. Another parameter involved is the molecular weight of the wear metal. Heavy metals tend to settle in oil with time and it is difficult to maintain uniform dispersion in the oil sample. This difficulty was verified using a low-power ultrasonic bath to disperse the Fe particle sample. After 20 minutes, part of the Fe particulate material was still visible at the bottom of the container. Adequate particle dispersion directly before sample introduction, then, is critical for wear metal particle analysis.
- c. The extension of graphite furnace sampling time should improve the recovery of large particles for most of the wear metals. Emission and absorption spectra for each of the wear metals should be examined carefully to determine the sampling time required without affecting the normal analysis.

It is interesting to discuss data reported by the University of Dayton group (Ref 1). They used a Baird A/E 35U-3 emission spectrometer to measure wear metal particles. The findings are that Al and Mg have the best recovery; Fe, Cr, and Cu have poor recovery; Ag and Ni have the worst. This trend is, in general, consistent with our data except for Ag. The sample transport of heavy particles is a problem in the Dayton group's emission instrument (Ag is the heaviest wear metal). They attribute the causes of particle size dependency to poor sample transport and insufficient energy from the spark source emission spectrometer.

### 3.2.5 SAMPLE COMPOSITION (Ref Para 3.2.5)

Five replicates of multi-element samples with 50% of the full scale concentrations prepared in MIL-L-23699 oil were analyzed. The overall results are high. This is probably due to an oil matrix effect. The same finding was reported by the University of Dayton group (Ref 1). They used a Baird A/E35U-3 emission spectrometer and found that wear metal measurements in the MIL-L-23699 oil are more sensitive than with other oils. From a standpoint of trend analysis, the performance is acceptable.

### 3.2.6 ALUMINUM AND SILICON PERFORMANCE

- a. The main cause for the data fluctuation of Al is that its absorption spectrum contains more than one peak, presumably including some chemical forms of Al such as aluminum oxides. These peaks appear as fast spikes and the accurate sampling of them is difficult. By examining the absorbance spectrum of the aluminum particle sample, a well-defined peak is observed. This suggests that the sampling time can be set up to enclose the Al peak but exclude the spikes. To use this sampling method, a more sensitive absorption line should be selected to improve sensitivity.
- b. Silicon is the most difficult element to analyze so far. Recent tests indicated that changing the char temperature improves the Si analysis. Lowering the char temperature and extending the measuring time should improve Si analysis. This approach should be investigated. Another possibility is that silicon carbides are formed which decompose at 2700°C. With a larger graphite furnace power supply operating the graphite furnace at < 2800°C, Si analysis should be improved.

### 3.2.7 SAMPLE INTRODUCTION

The sample introduction system used in the Brassboard is probably the easiest method for introducing an oil sample directly into the graphite tube. With this system, the sample volume dispensed for MIL-L-6082 oil is about 80% for that of the MIL-L-7808 oil. Four approaches are presented to solve this problem.

- a. Use two different size sample tips to compensate for the test sample viscosity differences. The tips can be colorcoded for each lubricant.
- b. Establish a correction factor in the data reduction routine of the microcomputer. The difficulty of this approach is that the factor would be different for each wear metal and would depend on the shape of the calibration curve.
- c. Make the Conostan standards in MIL-L-6082 oil a factor of 1.25X more concentrated than the standard sample in MIL-L-7808 oil. Doing so would empirically compensate the sample volume differences.
- d. Calibrate with Conostan standards prepared in MIL-T-7808 oil, i.e., calibrate with the same lubricant as the test samples.

### 3.2.8 CALIBRATION

For the demonstration test, a two point calibration is used for Mg, Cu, Ag, Ni, and Fe. One point calibration is used for Al, Si, Ti, and Cr. Each calibration data point is the average of two samples. A calibration algorithm using a rational equation developed by the Perkin-Elmer Instrument Division is used. This type of equation was designed for single element measurements where all the analysis parameters can be optimized. The equation has a  $K_n A^{-1}$  factor ( $K_n$  = calibration constant; A = absorbance) in the denominator; thus, an infinite number could result when  $(K_n A^{-1}) = 0$ . Restriction safeguards are applied in

the Perkin-Elmer commercial instruments that require the operator to redo the calibration when the calibration is not satisfactory. In addition, the wear metal sample concentrations must be smaller than the highest concentrations in the calibration standards. This presents a problem when analyzing 100% of the full scale concentrations in MIL-L-7808 oil because of the sample volume problem mentioned in the previous paragraph. The approach for improving the calibration routine would be the following:

- a. Use a cubic equation (or least squares fit) with a three point calibration. The calibration should emphasize on the lower concentration range with a slight compromise in accuracy at the high concentration region.
- b. Prefit the calibration curve and store in the microcomputer. Use one sample (or an average of two to three samples) to reslope the instrument in the field as required. This approach would require an increase in operation time data from the preproduction PWMA instruments so that the performance of the calibration curves could be characterized.

#### 4. CONCLUSION AND RECOMMENDATIONS

The Phase I Demonstration Test has sufficiently verified the use of graphite furnace atomic absorption spectrometry (GFAAS) for simultaneous multi-element analyses performance by the PWMA. However, the performance tests results have identified several improvements that need to be incorporated into the PWMA design so that the first preproduction unit will meet performance specifications. These improvements are as follows:

- a. Optimize the full scale dynamic range performance for Mg and Cu.
- b. Build a GFPS of sufficient power to furnish the atomization temperatures required for refractory wear metal measurement and a cleaning step.
- c. Optimize the sample introduction assembly to improve the repeatability performance required for trend analysis.
- d. Reduce the spurious radiation in the Cr channel to improve spectral resolution.
- e. Verify - optimize the "extended window" approach for wear metal particle analysis.
- f. Modify the calibration procedure and algorithm to improve curve-fitting accuracy.

- g. Improve the sensitivity for both Al and Si.
- h. Use calibration standards prepared in the type of oil under test, i.e., MIL-L-7808.

Reference

- 1. W.E. Rhine, C.S. Saba, R.E. Kanffman, "Wear Metal Particle Detection Capabilities of Rotating Disk Emission Spectrometers", JOAP International Symposium Proceedings, May 1983, Pg. 379.

APPENDIX C

LIST OF ABBREVIATIONS

Ag	Silver
Al	Aluminum
Cr	Chromium
Cu	Copper
Fe	Iron
Mg	Magnesium
Ni	Nickel
Si	Silicon
Ti	Titanium
Amp	Ampere
AA	Atomic Absorption
A/D	Analog to Digital
ASCR	Asymmetrical Silicon Controlled Rectifier
°C	Centigrade
CFM	Cubic Feet Per Minute
DFM	Design File Memo
DoD	Department of Defense
EPROM	Electrical Programmable Read Only Memory
FAA	Flame Atomic Absorption
g	Gravity
CFPS	Graphite Furnace Power Supply
HCL	Hollow Cathode Lamp
He-Ne	Helium-Neon
HGA	Heated Graphite Furnace
Hz	Cycles Per Second
I/O	Input/Output
JOAP	Joint Oil Analysis Program
kHz	Kilohertz

APPENDIX C

LIST OF ABBREVIATIONS (Continued)

MPU	Microprocessor Unit
ml/min	Milliliters Per Minute
$\mu$ s	Microsecond
PMT	Photomultiplier Tube
ppm	Parts per Million
PWMA	Portable Wear Metal Analyzer
psi	Pounds Per Square Inch
psig	Pounds Per Square Inch Gage
%	Percent
RAM	Random Access Memory
ROM	Read Only Memory
SCR	Silicon Controlled Rectifier
sec	Second
SOAP	Spectrometric Oil Analysis Program
USAF	United States Air Force
VAC	Volt Alternating Current

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