

THESIS



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ZEEMAN BACKGROUND CORRECTION WITH AN ELECTROTHERMAL GRAPHITE BRAID ATOMIZER

presented by

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has been accepted towards fulfillment of the requirements for

Ph.D. degree in Chemistry

J. R. Croul

Major professor

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ZEEMAN BACKGROUND CORRECTION WITH AN ELECTROTHERMAL GRAPHITE BRAID ATOMIZER

By

James T. Gano

A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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ABSTRACT

ZEEMAN BACKGROUND CORRECTION WITH AN ELECTROTHERMAL GRAPHITE BRAID ATOMIZER

By

James T. Gano

The characterization of an electrothermal atomic absorption spectrometer employing an analyte-shifted Zeeman background correction technique is described. The spectrometer utilizes a microcomputer for data acquisition and to control the heating levels of the graphite braid electrothermal atomizer. In this Zeeman background correction technique, a constant magnetic field is applied to the atomizer in a direction perpendicular to the incident hollow cathode light. The absorption-time profile of the hollow cathode light polarized parallel and perpendicular to the magnetic field is recorded and the difference in these absorptions is proportional to the atomic density.

Transmittance vs. magnetic field strength studies were performed on several elements to determine the optimum conditions for analysis. The background correction capabilities of the spectrometer were also tested by analyzing cadmium in the presence of a NaCl matrix. To Dad and Mom:

My way of saying I love

you both very much

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I. INTRODUCTION

It has long been the desire of the analytical chemist to develop spectrometric methods for elemental analysis that are accurate, precise, sensitive, selective, low cost, and free from interferences. Early workers in this area investigated atomic emission spectrometry as a possible solution to this problem. Initially flames (1,2) and electrical discharges (3,4) were used as spectrochemical sources, and more recently electrodeless plasma sources (5-9) have become very popular. In some respects these techniques approach the characteristics desired by the chemist; however, each has inherent limitations that preclude it from being the "ideal" method.

In the late 50's and early 60's flame atomic absorption (AA) spectrometry came into its own as an analytical technique. At that time it was hailed as the ultimate method for analyzing metals in solution, and for many applications it did indeed meet all of the desired characteristics. For certain analyses, however, it quickly became apparent that the requirement of freedom from interferences was not being obeyed (10). Metals analyzed in the presence of a complex matrix seemed to give high results. Further testing showed that, in these cases, the matrix itself

seemed to absorb light at the same frequency as the analyte. Whether the matrix was actually absorbing the light or simply scattering it has been a major topic of interest since its discovery. From the perspective of the instrumentation, however, it is irrelevant which phenomenon is responsible; the net effect appears to be an absorption.

Although matrix absorption was known to occur in flame AA, it was not until electrothermal atomizers came into widespread use that it became a real problem. The atomization process in these systems produces considerably more matrix absorption than in the case of flames. To correct for this non-specific absorption (or background absorption as it is more commonly known) several different background correction systems were developed. The present work deals with the characterization of a new background correction system used in conjunction with an electrothermal graphite braid atomizer. In order to understand the capabilities of the system, it is instructive to review briefly the various types of interferences that are commonly encountered in AA.

A. Interferences in Atomic Absorption Spectrometry

Interferences in AA spectrometry have traditionally been classified into three groups: physical, chemical, and spectral (11,12). Physical interferences are the result of changes in the physical properties such as solution

viscosity, surface tension, density, and vapor pressure of the sample relative to that of the standards. In flames, these changes can affect the aspiration rate of the sample, the flame temperature, the rate of evaporation of the sample, and the shape or form of the flame (13). Fluctuations in any of these parameters generally lead to severe errors. With electrothermal systems, however, these problems will not exist provided that the sample delivery is quantitative for both samples and standards and that the sample is desolvated completely. The only physical interference that has been known to occur is the occlusion of the analyte within the matrix (14).

Chemical interferences include any chemical process that reduces the population of free atoms in the gas phase. Examples in flame AA include the phosphate depression of calcium, the formation of refractory oxides of metals such as Al and Mo, and ionization interferences of the alkali metals. These interferences can be suppressed somewhat by increasing the flame temperature and by using a fuel-rich reducing environment (15). In electrothermal atomization systems, however, the problem cannot be solved as easily. Atomization temperatures can be increased, but usually only to an upper limit of 3000°K (16). The real problem arises in the temperature of the gas phase above the surface of the atomizer. Even in totally confined furnaces, the gas phase rarely reaches the atomization temperature.

Also, at the outer edges of the furnace, the gas phase encounters room temperature gases and the atomized sample tends to condense (17).

Spectral interference refers to the absorption of the source light by species other than the analyte atoms. 0ne type of spectral interference is the absorption of light by concomitant atoms that have direct spectral overlap with the analyte. In AA spectrometry, however, this is very rare because the hollow cathode source emits an extremely narrow emission line source (typically halfwidths of these lines are 0.001 to 0.005 nm) (18). Therefore, spectral interference from atomic species is limited to those atoms that have overlap of their absorption profile with that of the hollow cathode line. The non-specific type of spectral interference (background absorption) does not exhibit the narrow absorption profile that atoms do. Instead, background absorption appears as a broad absorption band caused by molecular absorption and/or particle scattering from the incompletely atomized sample matrix.

Figure 1 illustrates the absorption profile that results when an AA measurement is made in the presence of background absorption. The background is generally considered to have a flat spectral response across the bandpass of the monochromator, whereas the atomic absorption peaks at a specific frequency and has a very narrow absorption profile. The atomic absorption profile also has a slight



Figure 1. The atomic absorption profile in the presence of background absorption.

frequency shift due to the Lorentzian effect. The hollow cathode emission will thus be absorbed by both the analyte atoms and the background.

B. Background Correction Techniques

The background correction systems developed in the late 60's were designed specifically to compensate for the broadband background absorption. One of the first to be developed was the two-wavelength method (19). This method involved measuring the absorbance of the sample at the atomic resonance wavelength and at a nearby nonabsorbing wavelength. The difference between the two absorbances would then be proportional to the atomic concentration of the sample. This method relies on the assumption that the background absorption is identical at the two wavelengths. Unfortunately, this is not always the case (20). Another problem for many elements is that the light source may not contain a convenient nearby nonabsorbing line, or, if it does, it may be a weak emitter.

Another early background correction system that overcame some of the limitations of the two-wavelength method was the continuum source reference (21,22). The theory of its operation is as follows. In a single beam AA spectrometer the monochromator is used only to isolate the different spectral lines emitted by the hollow cathode lamp. Even though other species may absorb wavelengths

that are within the bandpass of the monochromator, only those absorbing at the hollow cathode wavelength contribute to the measured AA signal. As shown earlier, the absorption of the hollow cathode light consists of the atomic and the background absorption. If a continuum light source (for example a deuterium arc lamp) is used in place of the hollow cathode, the monochromator will pass all of the continuum radiation within the bandpass. Absorption of this light will be almost entirely due to the broadband background absorption with the remaining negligibly small amount due to the atomic absorption. Therefore, the continuum source functions as a reference beam and the hollow cathode source as the sample beam. The difference between the absorption of these two beams is proportional to the atomic concentration.

Although continuum source correction systems have gained much popularity and have become a commercial success, they have disadvantages (20). As would be expected with a two source system, the problem of fluctuations and drift in the two lamps requires continual adjustments to keep the light intensities matched. Another major difficulty is optical alignment. Because atomic concentrations and interferences vary widely with respect to location in the atomic vapor, it is necessary that the sample beam and the reference beam illuminate the same area. The wavelength range of the continuum background correction

system is another disadvantage (23). Most commercial systems use a deuterium arc source as the continuum source and, consequently, the wavelength range is restricted mainly to the ultraviolet. Finally, this system is only accurate when the average of the background absorption over the bandpass of the monochromator is equal to the background at the atomic absorption wavelength (24).

From the discussion just presented, it is obvious that a superior background correction system could be obtained if the desirable characteristics of each of the earlier techniques is utilized. For example, a single light source would eliminate the fluctuations of a two-source system and provide a single optical path. Also, monitoring the background absorption within the bandpass of the monochromator, or better yet at the same wavelength as the atomic absorption, would be more accurate than utilizing a nearby line outside the bandpass or a continuum source. The next chapter elaborates on how the Zeeman effect can be used to exploit these features to yield a new background correction system.

II. HISTORICAL

During the last 10 years extensive literature has appeared concerning the application of the Zeeman effect to background correction in electrothermal AA spectrometry (25,28-61). A variety of different approaches have been taken in the instrumental design; however, all can be classified as either being source-shifted or analyteshifted (25). In this chapter the principles of the Zeeman effect are presented and then a brief review of sourceshifted and analyte-shifted Zeeman background correction systems is given to provide the literature background upon which this research builds.

A. The Zeeman Effect

Atoms in free space can only exist in discrete electronic energy states. Transitions from one level to another can be accompanied by the emission or absorption of energy. For instance, cadmium, in its lowest energy state, occupies a ${}^{1}S_{0}$ energy level. By absorbing a photon of the proper energy it can be promoted to the ${}^{1}P_{1}$ energy level. This behavior is illustrated in Figure 2 for the transition labelled field-free. However, when a transverse magnetic field is applied to the atomic vapor, splitting of



Figure 2. The normal Zeeman effect splitting pattern.

degenerate levels can occur due to the interaction of the external magnetic field with the magnetic moment associated with the angular momentum of the atom (26,27). Each energy level is split into 2J + 1 components, each of which corresponds to an individual M_j quantum number of the atom. The 1P_1 level, therefore, has 3 components, $M_j = \pm 1$, 0, and -1, while the 1S_0 level has 1 component, $M_j = 0$. This is shown in Figure 2 for the transitions labeled magnetic field. As a distinguishing feature, the transitions with $\Delta M_j = \pm 1$ are termed σ lines and the transitions with $\Delta M_j = 0$ are termed π lines.

The change in energy of each component is governed by the following equation (26,61):

$$-\Delta Tm = M_{j} \cdot g \cdot B \cdot H$$
 (1)

where Δ Tm is the shift in energy from the zero field line, M_j is the magnetic quantum number, and B and g are the Bohr magneton and Landé factors, respectively, defined below:

$$B = \frac{he}{4\pi mc^2}$$
(2)

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$
(3)

The Bohr magneton is a constant derived from Planck's constant, the electronic charge, the mass of the electron, and the velocity of light. The Landé factor is a function of the spin (S), orbital (L), and total (J) angular momentum quantum numbers.

The relative intensities of the π and σ components are given by the following equations (61):

For $J \rightarrow J$ transitions

 $I_{\sigma} = (J \pm M_{j} \pm 1) (J \mp M_{j}) \text{ for } M_{j} \rightarrow M_{j} \pm 1$ $I_{\pi} = 4M_{j}^{2} \text{ for } M_{j} \rightarrow M_{j}$

For $J \rightarrow J + 1$ transitions

$$I_{\sigma} = (J \pm M_{i} + 1) (J \pm M_{i} + 2) \text{ for } M_{i} \rightarrow M_{i} \pm 1$$

$$I_{\pi} = 4(J+M_j+1) (J-M_j+1) \text{ for } M_j \rightarrow M_j$$

The ${}^{1}S_{0} - {}^{1}P_{1}$ cadmium transition shown in Figure 2 is a singlet to singlet transition with the Landé factor equal to 1. Such transitions are termed normal Zeeman transitions and yield a three-line splitting pattern consisting of one unsplit π line with a σ line on either side. The above equations predict that the intensity ratio for these lines will be 1:2:1.

In addition to being split to different energies and

having different intensities, the π and σ lines also exhibit different states of polarization. That is, the π transition emits or absorbs only light polarized parallel to the transverse magnetic field, while the σ transition emits or absorbs only light polarized perpendicular to the magnetic field.

When the light emitted by atoms in the magnetic field is viewed parallel to the field, the characteristics of the Zeeman pattern change drastically. In this situation, the π transition $\Delta M_j = 0$ is forbidden and only the σ lines are observed. The state of polarization of these lines are also altered. Instead of being linearly polarized, the σ lines are now circularly polarized; one clockwise and the other counterclockwise.

B. Source-shifted Zeeman Background Correction Systems

The first successful application of the Zeeman effect to background correction in electrothermal AA spectroscopy was reported by Hadeishi and McLaughlin in 1971 (28). In their original approach a transverse magnetic field was applied to a Hg electrodeless discharge lamp containing only the ¹⁹⁹Hg isotope. The Zeeman effect shifted the emission lines of some of the split hyperfine components slightly out of the absorption profile of the atomized Hg vapor. After being absorbed by the Hg and the background in the atomization cell, the light passed through a 253.7 nm filter. A beam splitter then directed the light to two detectors. In order to reach the first detector, the light passed through a Hg vapor resonance monochromator. This detector, therefore, would see only the absorption due to the background. The other detector directly observed the absorption of both the Hg and the background. Electronic subtraction of these two signals, consequently, produced the background-corrected absorption.

In many respects this first source-shifted Zeeman background correction system was quite similar to the neighboring line method discussed previously. It did have the advantage, however, of having the reference line very close to the analyte line. The disadvantages, though, were in the two-detector arrangement and in only being applicable to Hg analysis.

The next major improvement in the source-shifted Zeeman system was again reported by Hadeishi (29). In the new design a 7 kG longitudinal magnetic field was applied to a light source which contained only 198 Hg. As a result of the Lorentz shift and broadening of the Hg absorption profile, the circularly polarized σ^{-} line fell on top of the absorption peak, while the opposite circularly polar-ized σ^{+} line was shifted off to the side of the peak. By rotating a $\lambda/4$ wave plate in front of a stationary linear polarizer, it was possible to detect the two σ

lines alternately with a single detector. Electronically subtracting the σ^+ line absorbance from the σ^- line absorbance again produced the desired background-corrected absorbance.

This new system represented a major advance in the area of background correction technology. For the first time the difference in the polarization of the sample and reference beam (which were both within the bandpass of the monochromator) was used as a selection process in separating the two components. However, before the technique would be more generally accepted, it had to be useful for more than just the analysis of Hg.

Early in 1975, Hadeishi et al. published the results obtained with yet another background correction system that utilized the Zeeman effect (30,31). This system, though specific for Hg, would be the prototype of a new design capable of background correcting in the determination of several elements. In this system, a transverse 15 kG magnetic field was applied to an electrodeless discharge lamp containing only 204 Hg. At this field strength, the two σ lines were split sufficiently far from the σ line so that they would not be within the absorption profile of the Hg. They would, thus, act as a reference beam, absorbing only the background. The unsplit π line, however, would act as the sample beam, being absorbed by both the Hg and the background. A variable-phase retardation plate,

followed by a linear polarizer, alternately transmitted the σ lines and then π line through the atomization cell. Therefore, the detector would alternately observe the absorption of the Hg plus background and then background alone.

By this time other workers became involved with the development of source-shifted Zeeman background correction Stephens published extensively on the construcsystems. tion and characterization of magnetically-stable spectral sources (32-34) for elements other than Hg and on the experimental and theoretical results obtained with them (35-38). Koizumi and Yasuda, utilizing an experimental design very similar to Hadeishi's (39), demonstrated that a light source consisting of natural isotopic abundance Hg could also be used instead of only pure isotopes. They were also able to apply the same instrument to the determination of lead, cadmium, and zinc (40). In later work, they classified the types of Zeeman patterns exhibited by several other elements and were able to show that the source-shifted technique would work even for elements with extremely complex Zeeman patterns (41). More importantly though, in this same work they described another possible method of applying the Zeeman effect to correct for background absorption.

C. Analyte-shifted Zeeman Background Correction Systems

The first publication reporting the use of the analyteshifted Zeeman background correction system was by Koizumi, Yasuda, and Katayama (42). In their system, a magnetic field was applied to the atomization cell in a direction perpendicular to the light path. When the magnetic field was large enough, the absorption profile of the atomic vapor was split by the Zeeman effect. If the analyte exhibited a normal Zeeman pattern, the π line absorption profile would remain at the field-free absorption frequency, but would only absorb light polarized parallel to the applied magnetic field. The σ lines, however, would be split away from the hollow cathode frequency, and consequently, would not absorb hollow cathode light regardless of its state of polarization. This behavior is shown in Figure 3 for an atom with a normal Zeeman pattern. The hollow cathode light polarized parallel $(p_{||})$ to the magnetic field, therefore, becomes the sample beam, while the hollow cathode light polarized perpendicular $(p_{|})$ to the magnetic field serves as the reference beam.

The improvement in the background correction characteristics which this technique has demonstrated over the other currently available techniques has drawn much interest (43-50). Several commercial instrument companies have shown interest in the technique (51,52) and one has



Figure 3. The principle of the analyte-shifted Zeeman background correction technique.

gone as far as to market an instrument (53). Application articles have appeared regularly in the literature (54-60) since the first commercial instrument became available and recently, a comprehensive review article has been published on the method (61).

Much more fundamental research still remains to be performed in order to optimize the experimental parameters more intelligently. In the early stages of development of the Zeeman background-correction systems, researchers examined the detailed structure of the atomic absorption profiles and correlated them with the experimental data. Within the past 5 years, however, many other elements have been determined using the analyte-shifted method without having any knowledge of the actual absorption profiles.

In this work, the analyte-shifted Zeeman backgroundcorrection system will be utilized in conjunction with a graphite braid atomizer. The experimental conditions for optimum analysis of several metals will be studied and correlated with the expected atomic absorption profile and Zeeman pattern of the metal.

III. COMPUTERIZED INSTRUMENTATION

A. Introduction

A block diagram of the analyte-shifted Zeeman background corrected atomic absorption spectrometer is shown in Figure 4. At the heart of the instrument is an electrothermal graphite braid atomizer (GBA) which is positioned between the pole caps of a variable field electromagnet. Light emitted from a hollow cathode lamp is collimated perpendicular to the magnetic field and passes through the atomic vapor above the atomizer. The component of light polarized either parallel or perpendicular to the magnetic field is transmitted through the polarizer, dispersed by the monochromator, and detected by the photomultiplier tube. The resulting photocurrent is converted to a voltage by a high quality current-to-voltage amplifier and then digitized in the computer interface. The output of the current amplifier is also monitored by a voltmeter or an oscilloscope.

A PCM-12 microcomputer (62), equipped with a Data Systems dual floppy disc drive, a Decwriter printer, and a Tektronix 4006-1 graphics terminal, supervises instrumental operation. Through the custom built interface, the microcomputer controls instrumental timing, atomizer heating


The block diagram of the analyte-shifted Zeeman background correction instrument. Figure 4.

levels, and data acquisition. The microcomputer also performs the data analysis and, upon request, can store the atomic absorption data on a floppy disc.

The remainder of this chapter focuses attention on selected components of the instrument. The atomization cell is discussed first, followed by the electromagnet system, the instrument optics, the optical temperature controller, and finally, the computer interface electronics.

B. Atomization Cell

The atomization cell used in this work is similar to that designed by Baxter and Pals (63,64) but has been significantly modified to incorporate new improvements. The Baxter and Pals atomization cell was designed for automated x-y movement to map the atomic profile above the graphite braid atomizer. Their work showed that the maximum atomic concentration existed at the surface of the atomizer and that the concentration decreased as the vertical distance from the atomizer increased. The magnitude of the concentration decrease was highly dependent on the particular metal atomized. The lateral profile exhibited similar behavior. The atomic concentration decreased with increased horizontal distance from the atomizer. Again, the magnitude of the decrease was dependent on the metal. With this in mind, it was deemed necessary to keep a

vertical adjustment of approximately 1/2 inch in the new atomization cell. The vertical positioning was accomplished by turning a thumbwheel in the base of the cell. If necessary, this positioning provided a convenient method of reducing the sensitivity. The amount of horizontal adjustment was limited by the fact that the magnet pole gap was only 1-3/4 inches wide. A Hall effect probe to monitor the magnetic field strength also had to be placed on the magnet pole face which further reduced the available space. Therefore, to fit the cell into the magnet pole gap, the width of the Baxter and Pals design was reduced, and no horizontal adjustment was built into the atomization cell. The braid holders were permanently fixed in the center of the atomization cell, so that the braid would lie parallel to the optical path. Thus, when the cell was at maximum vertical height, the optical beam was centered over the braid and directly above it.

The new atomization cell is equipped with two optical temperature sensors located above the optical path and directed down at a 45 degree angle toward the atomizer (67-69). Each sensor is mounted in an aluminum housing along with a focusing lens and an optical filter. The sensors and their associated electronics are described in more detail in a later section.

A final point to be made about the atomization cell concerns the actual construction materials. The cell

must be able to withstand the exceedingly high ashing and atomization temperatures and the strong magnetic fields which may permeate it. To avoid disrupting the magnetic field and to prevent the possibility of the cell being attracted to the magnetic poles, the cell is made entirely of non-magnetic materials. The base and side supports are constructed of aluminum, the movable inner cell of plexiglass, and the electrodes and the braid holders of brass. The brass electrodes are also designed to function as heat sinks to conduct the heat away from the plexiglass immediately adjacent to the atomizer. However, even with this precaution, care should be taken to avoid melting the plexiglass parts by prolonged ashing or atomization at elevated temperatures.

A structural diagram of the atomization cell is shown in Figure 5, and Figure 6 is a photograph of the cell in its operating position. It should be noted that in the photograph one of the optical temperature sensors has been removed so that the graphite braid atomizer can be viewed. The atomizer is located at the center of the magnetic field with the magnetic pole caps on each side. Also of special interest is the Hall effect probe taped on the right pole cap of the electromagnet.



Figure 5. The atomization cell.



Figure 6. Photograph of the GBA spectrometer.

C. Magnet System

The constant magnetic field applied to the atomization cell was provided by a Varian V-3603 electromagnet (65). Attached to the pole pieces of the magnet are tapered pole caps which result in a 1-3/4 inch air gap between the pole faces. The low-impedance, twelve-inch electromagnet utilizes a V-2500 current regulated power supply. The water cooled, solid state power supply can deliver currents from as low as 2 A up to a maximum of 168 A. With this power supply magnetic field strengths can be continuously varied from 0 kG up to 13 kG. Above 13 kG the magnet and power supply overheat and trigger an automatic thermal shutdown.

The magnetic field strength is controlled by a Fieldial Mark II field regulator. A Hall effect crystal positioned in the magnetic field functions as a magnetic field sensing probe. When a magnetic field is present the crystal produces an output voltage proportional to the magnetic field strength. This voltage is compared to a reference voltage and a resulting error signal is obtained. The error signal is coupled to the magnet power supply, which promptly changes the current delivered to the magnet (and consequently the magnetic field) by the proper amount to reduce the error signal to zero.

D. Optics

In an analyte-shifted Zeeman background corrected instrument there is a variety of possible optical configurations; the optimum configuration is highly dependent on the experimental set-up. The instrument built in this work had certain constraints imposed on the optical layout due to the electromagnet employed. The extremely large size of the magnet required the construction of a special non-magnetic optical rail. Also, because the magnetic field is not totally confined to the region between the pole caps, special consideration was necessary in the placement of the hollow cathode lamp and the photomultiplier tube, because both are sensitive to external magnetic fields. For stable operation they were positioned as far as possible from the magnetic pole gap.

The relatively large separation of the hollow cathode lamp and the photomultiplier tube along with other experimental conditions degraded the light throughput severely. It was found necessary to place an aperture over the entrance slit of the monochromator to limit the amount of atomizer blackbody emission observed by the photomultiplier tube. However, this also limited the amount of hollow cathode light observed. Fortunately, the braid was mounted parallel to the optical axis which kept the amount of blackbody emission observed to a minimum and allowed for a large 3 mm aperture. When two quartz lenses were added to

collect and collimate the hollow cathode output, the light level increased substantially. This increase, however, was offset by the introduction of the polarizer. Although the polarizer was UV transmitting, the light level was reduced by approximately half. The particular hollow cathode lamp used also had a great influence. Though all lamps were relatively new, some had much greater output than others under similar experimental conditions. To attain maximum sensitivity, two different photomultiplier tubes were used.

Above 300 nm a RCA 1P28A photomultiplier tube was used, while below 300 nm a Hamamatsu R166 solar blind photomultiplier was found to have superior sensitivity.

After optimizing the optical system the light throughput was still very low. This necessitated using high amplifications of the photocurrent, operating the hollow cathode lamps at nearly their maximum allowable currents, and employing wide monochromator slit widths. The latter two conditions resulted in a stray light problem which will be further discussed in a later chapter.

An analyte-shifted Zeeman background corrected instrument distinguishes the background absorption from the analyte absorption by taking the difference between two absorption measurements. One measurement is of the analyte and background absorption simultaneously and the other is of the background absorption alone. The former measurement

is the absorption signal of the hollow cathode light planepolarized parallel to the applied magnetic field, and the latter measurement is the absorption of hollow cathode light plane-polarized perpendicular to the applied magnetic field. To make these absorption measurements a polarizer is placed in the optical path to transmit only plane polarized light. Both parallel and perpendicular measurements are obtained by rotating the polarizer about its optical axis.

The polarizer used is an Oriel 2540-1 ultraviolet transmitting Glan-Foucault calcite prism polarizer mounted in a metal tube with a 10 mm aperture. The wavelength range is 220 nm to 2500 nm and the extinction coefficient is 1 x 10-5.

Figure 7 shows a diagram of the rotation platform constructed to spin the polarizer. The polarizer sits in a three-corner, bearing-suspended cradle and is rotated by belt drive from a 2500 rpm d.c. motor. The entire platform is mounted on two translation stages for independent x-y movement. The platform also has a tilt and yaw capability so that the polarizer can be precisely aligned. The rotation of the polarizer is optically monitored. Light from a tungsten lamp passes through a fiber optic bundle and strikes the highly reflective surface of the spinning polarizer housing. Non-reflective marks were made on the housing at positions corresponding to when the polarizer was transmitting hollow cathode light



Figure 7. Photograph of the rotation platform.

polarized either parallel or perpendicular to the magnetic field. A phototransistor monitors the surface of the polarizer housing and is "on" when light is reflected. When the polarizer spins past a point where hollow cathode light is polarized, either parallel or perpendicular to the magnetic field, light is not reflected from the housing, and the transistor turns "off" momentarily. The resulting voltage pulse triggers the data acquisition electronics in the interface. Two of these optical sensors are mounted on the platform; one monitors when the polarizer is transmitting perpendicular polarized light, and the other monitors when the polarizer is transmitting parallel polarized light. The spinning can also be stopped and measurements of only one polarization can be made.

E. Electronics

1. Microcomputer

The electronics controlling the instrument are configured around a PCM-12 computer system. The PCM-12 is a twelve-bit word length microcomputer utilizing a CMOS Intersil 6100 microprocessor as the central processing unit. The microcomputer is equipped with 16 K words of static random access memory, a serial I/O interface, a floppy disc controller board, and a CPU board. The PCM-12 recognizes the Digital Equipment Corporation PDP 8/E binary

instruction set and thus, with all but a few exceptions, will run all DEC software. The PCM-12 does not have an extended arithmetic element and its instruction cycle time is about twice as long as the PDP 8/E's cycle time; therefore, its program execution time is considerably slower.

A backplane mounted vertically behind the card cage carries the PCM-12 bus lines. The backplane has 80 conducting lines of which 64 are used by the PCM bus. These lines are connected in parallel to 15 edge connectors. The PCM uses nine of these connectors; one each for the CPU, memory extender, and the floppy disc controller boards, two for the serial I/O boards and four for the memory boards. A board which is absent is a bus terminator board.

Figure 8 is a block diagram showing the relationship between the computer and the computer interface. Briefly, selected PCM 12 bus lines are connected to the backplane of another card cage which contains the computer interface. The interface tasks are divided among three circuit boards; the Timer-Clock board, the GBA Temperature Controller board, and the Analog-to-Digital Conversion (ADC) board. As their names imply each of these boards performs a specific function in the control of the instrument. The rest of this chapter is devoted to a detailed discussion of the bus expansion and each of these boards.





2. Bus Expansion

It was only necessary to connect the PCM lines required for interfacing to the bus expansion backplane. The relevant lines consist of the data-address lines, the CPU control lines, the data-transfer timing lines, and the interrupt lines. The data-address lines are a multiplexed set of lines to read data to or write data from memory or an external device and to address memory or an external device. The present interface employs a programmed I/O as opposed to a memory mapped I/O or a direct memory access I/O. To accomplish programmed I/O, the CPU control lines and the data-transfer timing lines are utilized.

In order to have a working knowledge of the interface, it is necessary to understand the sequence which occurs during an input/output transfer (IOT) instruction. Figure 9 is a diagram showing the T-states, LXMAR, DEVSEL, XTC and the data-address lines of the PCM during an IOT instruction (66). An IOT instruction begins at A when the instruction address is driven onto the DX lines. On the falling edge of B, the address is latched into the memory, and at C, the CPU reads the IOT instruction from the memory. As far as the interface is concerned the next series of events is the most important. At D, the CPU drives the IOT instruction onto the DX lines, and on the falling edge of E, the instruction is latched into the interface. To determine what action is to be taken (CPU read, CPU write, or skip





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the next instruction), the CPU reads the control lines at H. These lines must be exerted by the interface prior to H. At G, the interface drives the data to be read by the CPU onto the DX lines, and the DX lines can then be read when the DEVSEL line is low and the XTC line is high. The CPU drives the data to be written into the interface onto the DX lines at I. The CPU can then write to the interface when the DEVSEL line is low and the XTC line is low.

The actual bus expansion electronics are located on two printed circuit boards. One board plugs into an edge connector on the 80 line PCM bus and the other plugs into the 116 line bus expansion backplane. The two boards communicate through a shielded 40 line ribbon cable. Figure 10 is a schematic diagram of the bus expansion boards. The 74365 hex tri-state buffers, located on the board in the PCM, are used to buffer the PCM bus lines. All of the IOT instruction decoding circuitry is located on the board in the bus expansion card cage.

The twelve-bit IOT instructions are designated by four octal numbers; one number for each three bits. In an IOT instruction, bits 0-2 are always set to 110 or opcode 6. The next two octal digits (bits 3-8) are the tens and ones digits of the device select code respectively, and the last octal digit (bits 9-11) is the assignment code. As Figure 10 shows, the last three digits (bits 3-11) are decoded to an active low one-of-eight output by the three





7442 chips. In fact, on every falling edge of the LXMAR line, the interface decodes whatever is on the DX lines at that time. Fortunately, the $\overline{\text{DEVSEL}}$ and the XTC lines distinguish an IOT instruction from extraneous signals which are decoded. As was mentioned earlier, the $\overline{\text{DEVSEL}}$ and the XTC lines are active low during a CPU read, and thus, to obtain a unique output state (for a CPU read); the $\overline{\text{DEVSEL}}$, XTC, the tens and ones digits of the device select code, and the assignment code must all be ORed together. For a CPU write, the XTC line must be inverted before it is ORed with the other lines.

The major feature of the bus expansion is the large number of lines involved. This occurs because the twelve PCM DX lines are demultiplexed into twelve "data in" lines and twelve "data out" lines and decoded into sixteen device codes and eight assignment codes. Except for the LXMAR line, which latches the IOT instruction into the bus expansion, the rest of the lines (the data-transfer timing lines, the CPU control lines, and the interrupt lines) are connected directly from the buffer chips to the bus expansion backplane.

3. Timer-Clock Board

Next to temperature control, timing is the most critical aspect in electrothermal atomization. Accurate data acquisition timing and precise timing of the atomizer

heating levels are necessary if reproducible results are to be attained. At the time of this work, PCM Inc. did not have a real time clock board available for their computers so an alternate timing system was needed. Initially. it was believed that software timing loops would be the optimum method for timing. However, at times this turned out to be undesirable because software loops monopolized the CPU and thus, diminished computing power. Other software timing methods which incorporate timing and program execution together tend to be inaccurate unless great care is taken in the programming. For these reasons a good data acquisition clock and interval timer board was constructed. As much flexibility as possible was designed into the Timer-Clock board so that, through software modifications, timing intervals could be changed and the method by which the computer monitors the timer could be altered. In this way, for very short time intervals, the CPU could constantly monitor the timer's progress (by a skip test), or, for long time intervals, the CPU could perform other tasks and only service the timer when the timing interval was done (by pulling an interrupt).

Figure 11 is a schematic diagram of the data acquisition clock portion of the Timer-Clock board. The basic timing frequencies of the board are derived from a 1 MHz crystal oscillator and a programmable frequency divider chain. The data acquisition clock employs a Mostek 5009



The schematic diagram of the data acquisition clock. Figure 11. divider chip which functions as a decade divider of the crystal oscillator frequency. This provides stable frequencies from 1 MHz to 0.01 Hz, as well as time periods of 1 minute, 10 minutes and 1 hour. The desired frequency is obtained by loading the appropriate data into the four inputs of the 5009 chip. These inputs are connected to the computer DX lines through quad latch A. Therefore, the computer can latch the timing data to the 5009 chip by executing an IOT instruction.

As was mentioned earlier, a unique output state is obtained during a CPU write IOT instruction when the XTC, DEVSEL, the tens and the ones digit of the device select code, and the assignment code are ORed together. Since five input OR gates do not exist, the five lines are ORed in two steps. First the XTC, the DEVSEL, and the tens digit of the device select code are ORed together with the resulting output then being inverted. This circuitry will decode the first two digits of the four digit IOT instruction. The inverted output is then ORed with the ones digit of the device select code and the assignment code which results in a high output when all five inputs are low. An example of this is the 6304 software command which latches the timing data, preset in the computer accumulator, out to the 5009 decade divider latches. The XTC line, the DEVSEL line, and the tens digit of the device select code (DEV 3X) are ORed together, inverted, and then ORed with

the ones digit of the device select code (DEV XO) and the assignment code (ASI 4). This produces a positive pulse which clocks the accumulator contents into the latches.

In order to provide additional analog-to-digital conversion frequencies, the output of the 5009 decade divider undergoes further frequency division by TTL logic circuitry. The output of the decade divider is split into three different paths. One path leads to a 7490 decade counter which is configured for divide-by-five operation. Another path leads to a 7474 toggle flip-flop which divides by two. The final path (divide-by-one) leads directly to the 74153 4-line to 1-line multiplexer where the paths are all brought back together. The desired frequency is selected by the two address bits of the multiplexer. The computer writes the two address bits to quad latch B, and thus to the multiplexer, at the same time it writes to the 5009 decade In this configuration, the electronics are divider latch. capable of providing output frequencies from as low as 0.00027 Hz to as high as 0.2 MHz. Of these, the ones which are useful data acquisition frequencies are listed in Table I along with their accumulator control bit settings.

Events of relatively long duration, compared to the computer instruction cycle time, are best timed with the interval timer. These events, which include the desolvation time, the ashing time and the delay times, may last from five seconds up to as long as one minute. In order

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Frequency	Divisor	ACC Bits 2,3	Base Frequency	ACC Bits 8,9,10,11
1	1	00	100	0110
2	5	10	101	0101
5	2	01	lol	0101
10	1	00	lOl	0101
20	5	10	10 ²	0100
50	2	01	10 ²	0100
100	1	00	10 ²	0100
200	5	10	103	0011
500	2	01	103	0011
1000	l	00	103	0011
2000	5	10	10 ⁴	0010
5000	2	01	104	0010

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Table I. The Data Acquisition Accumulator Bit Setting.

to cover such a wide variety of times, the versatility of a programmable timer was necessary. However, unlike the discrete time periods produced by the data acquisition clock, the interval timer was designed to be continuously variable.

The interval timer (Figure 12) is basically a decade counter which can be preset to the number of clock cycles from the 5009 decade divider that will equal the desired time interval. Consequently, the time interval equals the number preset into the counter multiplied by the time period of the decade divider. When signaled by the computer, the counter counts clock pulses from the decade divider until an underflow occurs. The underflow condition indicates that the time interval is over and the timer then informs the computer that it is done by either jumping out of a skip test or by pulling an interrupt.

The data acquisition clock pulse must pass through one last gate before proceeding on to the analog-to-digital conversion board. This gate functions as an on-off switch for the clock. The multiplexer's output is one input of gate C; the other being a control input from the Q output of flip-flop D. If the computer issues a 6312 command (A/D clock enable), the Q output is clocked high allowing the gate's output to follow the data acquisition clock. If the computer issues a 6311 command (A/D clock disable), the Q output is cleared low regardless of the state of



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the data acquisition clock. The data acquisition clock is also disabled upon instrument power-up by a hardware triggered initialization pulse.

For time intervals which are non-integer order of magnitude multiples, two timing intervals must be performed in succession. For example, if the desired time interval were fifteen seconds, the counter would time for one count with a decade divider frequency of 0.1 Hz. This first time interval would take ten seconds to complete. The computer would then quickly reload the counter to five, change the modulus of the decade divider to obtain 1 Hz, and time for another five counts. This second time interval would complete the last five seconds of the fifteen second total. If more significant figures in the time interval were required, more timing steps could have been added until the desired precision was attained. Because the computer is extremely fast compared to the fifteen second time interval, the short time necessary to reload the counter and change the divider modulus is negligible. However, as the time intervals approach the computer instruction cycle time, the time required to reload the counter can become significant.

To function correctly, the interval timer must execute a specific set of IOT instructions in the proper sequence. A complete list of these IOT instructions, as well as the IOT instructions which operate the data acquisition clock,

are given in Table II. The first instruction in the sequence causes the clock input of the counter to be held high. This must be done to assure proper operation of the counter because, before a level change can be made at the enable input of the counter, the clock must be high. The circuitry to accomplish this is similar to the A/D clock enable/disable circuitry. The Q output of flipflop B is one input to gate A, and the other input is the clock source from the 5009 decade divider. When the preset input of the flip-flop is pulsed low, the Q output goes high, holding the output of gate A high. Execution of the second IOT instruction disables the counter by pulsing the preset input of flip-flop C low which sets the counter enable high. The next IOT loads the timing data present in the computer accumulator into the counter, while simultaneously loading the 5009 decade divider and the multiplexer channel.

Once the counter has been loaded and disabled, the clock input can be reactivated. An IOT instruction clocks the Q output of flip-flop B low which allows the clock signal to pass through gate A to the counter. The timing interval can now be started by executing an IOT instruction to pulse monostable D. The monostable fires a 10 µs pulse which synchronizes all the components of the timing circuit. The rising edge of the negative pulse from the Q output clocks the Q output of flip-flop C low

Table II. The Timer-Clock Board Commands.

 6300	Preset clock output high
6306	Enable clock
6316	Disable timer
6304	Load clock frequency, timer count, and multiplexer channel
6305	Start timer
6311	Disable ADC clock
6312	Enable ADC clock
6313	Skip test timer
6314	Disable timer interrupt facility
6315	Enable timer interrupt facility

and thus enables the counter. The Q output of the monostable resets the 5009 decade divider on the falling edge of the positive pulse. This restarts the output frequency of the divider within one microsecond after the falling edge of the pulse. This slight time delay in the start of the 5009 divider output ensures that the counter is enabled before the first clock pulse arrives.

4. GBA Temperature Controller Board

Controlling the final temperature and the rate of heating of the atomizer during the three-stage heating program is of the utmost importance. In the first heating stage (the desolvation stage) the atomizer must be heated slowly and evenly in order to avoid spattering the sample off of the atomizer. This was found to be especially true for viscous samples which contain large amounts of organic matter. Critical temperature control is necessary in the second heating stage, the ashing stage. During this stage, the temperature must be raised high enough to pyrolyze the sample matrix, but yet kept below the appearance temperature of the analyte. The final heating stage is the analyte atomization stage. In this stage, the final temperature attained, as well as the rate of heating, drastically affect the transient peak shape, the peak amplitude, and to a lesser extent, the peak area. Thus, for a given set of samples and/or standards, it is imperative that these

heating levels be absolutely reproducible.

Because the GBA is a resistively heated device, the temperature of the atomizer is largely dependent on the electrical power it dissipates. Commercial electrothermal atomizers, which are much more massive than the GBA, have a fixed resistance (at room temperature) and can achieve control of the electrical power through the atomizer by employing either a constant current or a constant voltage control over the power supply. However, because of its small mass, the GBA's resistance and mass change considerably during routine operation due to sublimation of the graphite. For this reason, Baxter and Pals (63,64) developed a new method which actually controls the amount of electrical power delivered to the atomizer instead of the atomizer current or voltage. This was accomplished by using an AD532J four-quadrant analog multiplier IC which was configured so that its output was proportional to the product of the current through the atomizer and the voltage across it. Montaser (67) demonstrated that this type of temperature programming was superior to either current or voltage programming, and, for low temperature control (below approximately 450°C), the present instrument employs this same power control circuitry.

To improve the temperature control of the atomizer in the higher temperature ranges, the optical temperature controller of the Baxter and Pals instrument was

redesigned. The optical sensor used in their work was a single phototransistor (Texas Instrument TIL 64). The performance of this sensor was inadequate at low temperature because of poor sensitivity and at high temperature because of the limited dynamic range inherent to phototransistors. To increase the upper temperature range, a neutral density filter had to be inserted between the phototransistor and the atomizer to reduce the amount of light incident upon the phototransistor. This was inconvenient and limited the sensor either to high or low temperature control.

The new temperature controller consists of two optical sensors; one optimized for low temperature control and the other for high temperature control. The low temperature sensor must have high sensitivity to be able to detect low infrared light levels and should be relatively fast to prevent temperature overshoot. To accomplish this and to be cost effective, a MRD 360 photodarlington transistor was used. The photodarlington transistor turned out to be so sensitive that ambient room light caused it to saturate. Since only infrared light emitted by the atomizer needed to be monitored, a visible cutoff filter to exclude room light was added. A series of Wratten long-wavelength filters with visible cutoffs starting at 580 nm and extending to 740 nm were tested. The optimum filter was found to be the Wratten No. 87 which transmits

light from 740 nm to 2000 nm. The photodarlington transistor package contains a lens to focus incident light onto the active area of the transistor, therefore, it was only necessary to construct a housing to hold the filter and the transistor. The control system using this sensor is capable of a temperature range of 450°C to 700°C.

For higher temperatures it is desirable to have an optical sensor (67-69) that can monitor a wide range of temperatures. Like the low temperature sensor, the sensor should be sufficiently fast to prevent temperature overshoot. A Hewlett Packard 5082-4220 PIN photodiode was found to be well suited for this application. The diode was mounted in a housing identical to the one used for the photodarlington transistor. The diode did not need an optical filter, however, it did require an external lens to focus the atomizer blackbody emission onto the active area. The photodiode controlled the temperature from approximately 700°C up to the instrument's maximum temperature of 2500°C.

The circuitry that implements the atomizer temperature control is shown schematically in Figures 13 and 14. This circuitry regulates the amount of current the GBA power supply delivers to the atomizer and, in this way, controls the temperature of the atomizer. The construction and operation of the GBA power supply is described in detail by Montaser (67) and Pals (64). However, to gain a



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Figure 14. The schematic diagram of the temperature monitoring circuitry.

better understanding of the temperature control circuitry, a brief description of the current-regulating portion of the circuitry will be presented.

The actual current-controlling element of the circuitry is the 2N3440 transistor shown in Figure 13. The emitter of this transistor is connected in a darlington configuration to the base of the first power transistor in a pass transistor bank. The emitter of this power transistor is in turn connected to the bases of thirteen other power transistors. Thus, by controlling the base current of the 2N3440 transistor, the current output of the GBA power supply is controlled.

The entire temperature control circuitry functions as an electronic feedback loop between the atomizer and the GBA power supply. Figure 14 is a diagram of the circuitry that provides the atomizer temperature feedback signal. The actual temperature sensors in the figure are, from top to bottom, the photodiode, the photodarlington transistor, and the analog multiplier IC. Both of the optical temperature sensors, which produce a current output proportional to the atomizer temperature, employ identical operational amplifier current-to-voltage converters. To increase the temperature monitoring range of the current-to-voltage converters, one of four possible resistors can be placed in the amplifier feedback loop.

An AH5012 quad analog current switch with either a
1K Ω , 10K Ω , 100K Ω , or 1M Ω resistor in series with each of the switches is placed across the feedback loop. The particular resistor is selected by applying an active low to the JFET switch gate while holding the other gates high. The gate of each switch is connected to each Q output of a 7475 quad latch with the D inputs being connected to the DX lines of the bus expansion backplane. Once the computer accumulator is loaded with the data representing the desired feedback resistor, an IOT instruction clocks this data into the latch. The latch output will close the appropriate switch connecting the correct resistor across the feedback loop. The amplification of the photodarlington transistor and the photodiode current-to-voltage converters can be changed independently by issuing different IOT instructions. A complete list of the IOT instructions which operate the temperature controller board is given in Table III.

The other temperature sensor is the analog multiplier IC shown at the bottom of Figure 11. This sensor produces a voltage proportional to the power dissipated by the atomizer. The input circuitry has been extensively described by Pals (64), and the temperature control characterization was done by Baxter (63) and Montaser (67,68). The only change made to the Pals design was the addition of a unity-gain inverting amplifier to the output of the IC.

Table III. The GBA Temperature Controller Board Commands.

6642	Temperature sensor channel select
6643	Photodiode amplification select
6644	Phototransistor amplification select
6645	Clear DAC (kill burn)
6646	Load the burn data into the latches
6647	Start the burn

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During the programmed heating stages of the atomizer, only one temperature sensor is activated at a time. The desolvation stage invariably employs the analog multiplier IC sensing circuitry because of the low temperatures involved. Whether the ashing stage employs the analog multiplier or the photodarlington transistor sensing circuitry depends upon the ashing temperature. The atomization stage always uses the photodiode sensing circuitry.

In order to be able to use all three temperature sensors under computer control, a switching circuit was designed. The outputs of the two optical temperature sensing circuits are connected to an AD7513 analog switch, and the inverted analog multiplier IC output is connected to an identical switch. The particular temperature sensing circuit to be used is activated by setting the corresponding switch address low while holding the other switch addresses high. Like the current-to-voltage amplification switches, these switches have their addresses connected to a 7475 guad latch that is connected to the DX lines. Loading the computer accumulator with the correct data and issuing the proper IOT instruction closes the appropriate switch and activates the specified temperature sensing circuitry. The outputs of the three switches are all tied together and connected to a unity-gain inverting amplifier.

In heating the atomizer, two voltage signals are compared; a negative reference voltage proportional to the

final atomizer temperature and a positive feedback voltage proportional to the instantaneous atomizer temperature. The reference voltage is derived from the digital-to-analog converter and the feedback signal from the temperature sensing circuitry. Initially, the reference voltage is zero and the atomizer is at room temperature. The temperature sensing circuitry is biased such that at room temperature the feedback signal is a few millvolts positive. The positive feedback signal and the zero reference are summed together by the op amp adder circuit in Figure 13. This produces a negative output voltage and drives the comparator output negative. When the comparator is negative there is no current into the base of the 2N3440 transistor, which consequently keeps the pass transistors off. To start a heating cycle the digital data representing the reference voltage are loaded into the first pair of hex 74174 latches by an IOT instruction. Next, the appropriate temperature sensing circuit and amplification factor are selected. The "start burn" pulse from the Analog-to-Digital Conversion board or an IOT instruction will then clock the data from the first pair of latches into the second pair of latches. The DAC is a complementary device and in order to retain normal logic these data are inverted before entering the DAC. Upon receiving the data, the DAC immediately swings positively to the specified voltage. The DAC output is then inverted and attenuated by an inverting amplifier

before entering the adder. The adder output swings positive, which drives the comparator positive and turns the transistor and the GBA power supply on. The power supply will remain on until the temperature of the atomizer increases sufficiently to bring the feedback signal positive enough so that the adder sums to zero again. The atomizer will then hold that temperature until the IOT instruction is issued to clear the latches and set the DAC output to zero volts.

5. Analog-to-Digital Conversion Board

One of the major advantages of computer-automated instrumentation is its ability to acquire data at very high rates in real time. To this end, a circuit board was designed that employs a twelve-bit analog-to-digital converter along with the necessary computer interface circuitry to operate it. In addition, the board contains the logic circuitry to synchronize the start of the atomization heating cycle with the data acquisition timing.

Figure 15 is a schematic diagram of the analog-todigital converter (ADC) and the associated interface circuitry. The ADC employs a successive approximation conversion technique to produce a twelve-bit complementary binary output in eight microseconds. The ADC is wired for 0 to +10 V operation, which is well within the voltage range of the sample-and-hold amplifier (SHA). The events





occurring during the acquisition of a single data point start with SHA informing the computer that it has switched into the hold mode. The computer responds by issuing an IOT instruction to pulse the start conversion input of the ADC. While the ADC is performing the conversion, the computer goes into a skip test wait loop. Upon completion of the conversion, the ADC "end-of-conversion" (E.O.C.) output goes low and clocks the Q output of flip-flop A low. This enables the CPU control lines of tristate B. These control lines, when read by the CPU, cause the computer to skip out of the wait loop. The computer then issues an IOT instruction to read the data. The ADC digital output lines carrying the data are connected to the bus expansion DAX lines which are tristated onto the computer DX lines. During the "read data" IOT instruction, the computer reads the control lines of tristate C, which causes the interface to jam transfer the data into the computer accumulator. Once the data are in the accumulator, the software stores them in memory and starts the data acquisition process over again.

The timing synchronization circuitry on the ADC board is shown in Figure 16. This circuit activates one of two possible data acquisition timing sources and coordinates it with the beginning of the atomization cycle. To insure that conflicting logic levels do not occur, the circuitry is initialized to a specific configuration when the





instrument is powered up.

The two timing sources are the ADC clock, originating on the Timer-Clock board, and the signal from the polarizer position monitoring electronics. Both sources are disabled at the outset of an experimental run by either an initialization pulse or by IOT instructions from the com-The ADC clock is held low by the circuitry desputer. cribed in the Timer-Clock board section, and the polarizer position monitoring signal is held low by clearing the output of flip-flop A low which forces the output of gate The particular timing source desired is enabled B low. and will pass through gate C and onto gate D. Gate D is disabled by clearing the output of flip-flop E low and is enabled by clocking the output high. Once enabled the first rising edge from the timing source to pass through gate D starts the atomization heating cycle by clocking the burn data into the DAC on the GBA temperature controller Simultaneously the SHA is switched into the hold board. mode by clocking the output of flip-flop F high. This also initiates the data acquisition process by clocking the Q output of flip-flop G low. The CPU, which has been in a skip test wait loop, reads the CPU control lines of tristate H and jumps into the data acquisition sequence. The computer commands which implement these actions are listed in Table IV.

Table IV. The Analog-to-Digital Conversion Board Commands.

6531	Disable start burn pulse
6534	Disable optointerrupter pulse
6532	SHA in the sample mode
6421	Clear SHA skip flag
6423	Clear ADC skip flag
6533	Enable optointerrupter pulse
6530	Enable start burn pulse
6420	Skip test SHA
6422	Take data pulse
6424	Skip test ADC end of conversion
6425	Jam transfer data

IV. SOFTWARE

A. Introduction

The microelectronic revolution of the 70's has resulted in the proliferation of microcomputers in both the scientific and consumer communities. The initial thrust in these areas has been centered around the 8-bit family of microprocessors. In the consumer market, cost has been a prime consideration in the overall system design, and, therefore, the software supplied with the microcomputer usually consists only of a keyboard monitor and a BASIC interpreter. The decrease in the price of mass storage peripherals has allowed some home computerists to acquire floppy disc-based systems that significantly increase the speed and sophistication of their computers. However, the small software package and the expense of additional software support are the limiting factors in furthering the capabilities of the typical home computer.

The scientific computer is differentiated from the home computer more by the software than by the hardware. Often, scientific computers incorporate the same microprocessor as the home computer, but have much more memory and are equipped with mass storage devices. Scientific

computerists, however, have much more extensive software support in terms of the availability of programming languages and operating systems.

B. <u>Selecting the Microcomputer</u>

At the time this work was initiated, our research group was utilizing a Digital Equipment Corporation (DEC) PDP 8/e minicomputer with the OS/8 version 3D operating system. Because OS/8 is not a multi-user system, individual computer time was at a premium. To upgrade the computer system to a multi-user system, Pals and Joseph (70) designed a multi-micro system with the PDP 8/e at the top of a distributed microcomputer hierarchy. The design of the multi-microsystem was developed so that the individual microcomputer would appear to the main computer as a peripheral terminal. In this way, programs and/or data could be shipped serially between the main computer and the microcomputer. The main computer would be delegated the more complex tasks of data analysis and compiling programs, and the microcomputer would carry out the simple instrumental control and data acquisition functions.

In choosing the microcomputer for this system a few very important criterion needed to be fulfilled. First, a relatively powerful and inexpensive microcomputer that would be easily interfaced to a variety of scientific

instrumentation was needed. Second, it was desired that the microcomputer's instruction set be simple enough and versatile enough so that implementation of the software necessary to operate the system could be mastered quickly.

The ideal microcomputer to meet these demands turned out to be a model 12 Pacific Cybermetric (PCM). This microcomputer is based on the 12-bit Intersil 6100 microprocessor (66) which has the same micro instruction set as the PDP 8/e. Thus, assembly language programs written for use with the 8/e could be run on the microcomputer without any drastic modifications. In fact, most programs compiled on the 8/e could be directly down loaded through the serial link to the microcomputer and subsequently executed.

In the course of designing the analyte-shifted Zeeman atomic absorption spectrometer, we found that the magnet system which would be employed was located in a site too remote from the main computer to utilize the serial link. To alleviate this problem, the microcomputer was converted to a stand alone computer. Dual floppy disc drives were added, and the OS/8 operating system was used directly on the PCM 12. This was the one main feature which gave the instrument so much power and flexibility in terms of programming capabilities. With all but a few exceptions, the microcomputer could execute all of the software available to the PDP 8/e.

C. Selecting the Programming Language

Once the operating system was chosen, the programming language was restricted to one of those supported by OS/8. This immediately limited the decision to one of three assembly languages (PAL 8, SABR, or RALF) or one of three higher level languages (BASIC, FORTRAN II, or FORTRAN IV). Because of their very basic nature, the exclusive use of assembly language was never seriously considered as an efficient means of programming in this application. The complexity of the data analysis, the significant amount of I/O and data file manipulation, and the extensive text strings that would be used required the power of the higher level programming languages.

In selecting the particular high level language to be used, a number of factors were taken into consideration. FORTRAN IV at first was thought to be the superior language of the three. The DEC supplied FORTRAN IV is fully ANSI compatible and has many advantages over BASIC or FORTRAN II (71-73). In addition, the extensive FORTRAN IV software which controlled the PDP 8/e interfaced GBA was available. It was thought that with minor modifications this software could be adapted to the microcomputer interfaced instrument. This process, however, turned out to be impractical due to the radical changes that were made in the computer interface. The present instrument requires extensive assembly language I/O commands which necessitated

rewriting most of the FORTRAN IV and all of the RALF assembly code. Attempts to completely rewrite the entire program in FORTRAN IV also proved to be extremely difficult due to the complexities involved in combining the FORTRAN IV source code and the RALF assembly code.

It seemed that the advantages offered by FORTRAN IV were far outweighed by the programming difficulties it presented.

Upon closer examination, some of the advantages of FORTRAN IV disappeared when it was used with the microcomputer. For instance, the FORTRAN IV compiler, when run on the PDP 8/e, utilizes the extended arithmetic element (EAE) to increase calculation speed. Since the microcomputer does not contain an EAE, this powerful advantage is lost. Also, the virtual memory overlay feature of FOR-TRAN IV is a great advantage when the power and speed of the minicomputer is coupled to the high baud rate of the hard disc. When this is carried over to the relatively slow microcomputer and floppy disc system, overlaying becomes a very time consuming process.

Of the two remaining programming languages, FORTRAN II appeared to be the most acceptable. Even though it is not quite as powerful as BASIC, the ease of programming with the FORTRAN II assembly code (SABR) more than offset this difference. BASIC was not considered because problems similar to those encountered with FORTRAN IV could be foreseen with BASIC; that is, the difficulties involved in combining the assembly code with the BASIC source code.

After a short period of programming with the DEC supplied FORTRAN II, our group acquired a new version of FORTRAN II called FORTRAN (extended) or FORTX (74). Because of its superior capabilities compared to FORTRAN II, the entire programming for the analyte-shifted Zeeman atomic absorption spectrometer was written in FORTX.

D. FORTRAN (extended)

FORTX is a hybrid of the DEC OS/8 FORTRAN II compiler (FORT) and, to a lesser extent, the FORTRAN IV instruction set. FORTX remains downwardly-compatible with all standard OS/8 FORTRAN II programs, but has incorporated many of the more useful instructions normally found only in FORTRAN IV. FORTX has thus combined the best features of both languages; the simplicity of inserting assembly language code (from FORTRAN II) and a more powerful set of instructions (from FORTRAN IV).

One of the most useful features of FORTX is the extensive set of logical expressions that are available. The logical operations .AND., .OR., and .NOT. have been assimilated into FORTX and can all be used in logical IF statements, logical assignment statements, and logical operation statements just as in FORTRAN IV. The logical constants and variables used in these expressions must be

specified to the compiler at the outset of the program by a LOGICAL type statement.

```
LOGICAL X, Y, Z
IF (X) GO TO 10
X = .TRUE.
X = (.NOT. Y) .AND. (.NOT. Z)
```

Also adopted from FORTRAN IV are the relational operations .EQ., .NE., .GT., .LT., .GE., and .LE.. These operators compare either two integer or two real operands and return a logical result. These operators can be used as the hypothesis of an IF statement or in a simple logical operation statement.

REAL X, Y LOGICAL Z IF (X .EQ. Y) Z = .TRUE. Z = X .EQ. Y

Some of the preceding examples have illustrated the use of the logical IF statement that exists in FORTX. In addition, FORTX also has the BLOCK IF statement that can be used to execute a block of statements if a given condition is true. REAL W, X LOGICAL Y, Z IF (Y) THEN W = X Z = .TRUE. ENDIF

An optional ELSE statement can be added to execute another block of statements if the condition is false.

REAL W, X LOGICAL Y, Z IF (Y) THEN W = X Z = .TRUE. ELSE W = -(X) Z = .FALSE. ENDIF

A new type of structured DO loop, incorporated into FORTX, eliminates the need to specify a statement number at the termination of the loop. The format is

DC ? I = 1, 10, 1 X = 1.0 + X ENDDO where the ? is required so that the compiler is aware that it is compiling a structured DO loop. To retain compatibility with FORTRAN II, FORTX will also execute the ANSI standard DO loop.

FORTX has many more subtle modifications that improve its performance characteristic over that of FORTRAN II. Especially important are the improvements made in the error traceback messages. In FORTRAN II, the execution of a fatal error causes the program to abort to keyboard monitor without giving any useful error message. In contrast to this, FORTX calls a helper program (DIAG) that pinpoints the exact routine and line number where the error occurred. This feature greatly facilitates the debugging of user written programs. The thorough documentation provided with FORTX describes all of the new error messages and the major differences between FORTRAN II and FORTX (74).

E. Program Description

The software that supervises instrumental operation consists of a series of user written subroutines. Each of these subroutines is designed to carry out a specific task or set of tasks and then pass control back to the program that called it. Figure 17 is a block diagram showing the overall program structure. The FORTX program MAIN resides at the top of this hierarchy and oversees the execution of the subroutines immediately below it.





MAIN is a very short program with three primary functions. First, it sets up the COMMON storage area for the various instrumental parameters and the absorption data. Second, it activates hardware in the interface to initialize the digital logic circuitry. Finally, it calls the three major subroutines INPUT, START, and PLOT. These subroutines will be topics of discussion for the remainder of this chapter.

1. INPUT

Electrothermal atomization requires that a multitude of experimental parameters be carefully controlled. Unlike the static atomization conditions found in a flame, electrothermal atomization consists of a series of heating cycles culminating in the atomization of the sample. Because electrothermal atomization is a dynamic process, a transient atomic absorption signal is obtained. To optimize this transient peak, it is necessary to be able to vary all of the experimental conditions independently. To accomplish this, the user must utilize the subroutine INPUT.

INPUT's primary task is to acquire numeric, logical, or Hollerith values for each of the experimental parameters listed in Tables V and VI. Table V lists the atomization and data acquisition parameters, and Table VI lists the file description parameters and I/O options. Values for

Parameters
Acquisition
nd Data
Atomization a
. The
Table V

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Parameter	Monitor Code	Input Format	Range
Desolvation time	DT	13	0 - 999 sec
Ash time	СТ	13	0 - 999 sec
Atomization time	ΑT	F3.1	0 - 9.9 sec
Desolvation power	DP	F5.0	c - 4095
Ash power	СР	F6.1	0 - 4095
Atomization Power	AP	F6.1	0 - 4095
Data acquisition frequency	FR	14	1,2,3 x 10 0-3
External data acquisition (TRUE) (FALSE)	ОТ ОF	LOGICAL	
Acquire dark current	DA	LOGICAL	
Correct braid emission (TRUE) (FALSE)	BT BF	LOGICAL	
Ash radiation programming (TRUE (FALSE)	RT RF	LOGICAL	

Parameter	Monitor Code	Input Format
Data file title	TI	AG
Type of sample	SA	AG
Amount of sample	АМ	AG
Concentration of sample	CO	A6
Plotting option A (TRUE)	PA	LOGICAL
Plotting option B (TRUE)	PB	LOGICAL
Plotting option C (TRUE)	PC	LOGICAL
To to elemental library	11	
Print all parameters on LP	HP	
Print all parameters on TY	HT	
Print logical parameters on TY	$ extsf{TL}$	
Print times parameters on TY	TT	
Print power parameters on TY	TP	
Print sample parameters on TY	TS	
Print absorbance data on TY	TD	

Table VI. The File Description Parameters.

these parameters can originate from any one of three sources. One source is INPUT itself which assigns a default value to each parameter. These values are loaded into COMMON storage when the "OP" (old parameters) command is given in response to a prompt issued by INPUT. The second and most important source is the monitor routine of INPUT. This portion of the subroutine recognizes the specific two-letter monitor codes shown in Tables V and VI. Executing one of these codes allows the user to alter the experimental parameter listed next to it in the tables. The tables also list the input format and the range of values that each parameter will accept. The logical parameters, however, do not require an implicit input, but rather are true-false switches set by the code itself. The last source of parameter values is the element's library file. The library file contains the optimum parameter values for the individual element. The library file for a particular element is called by typing a "//". This gives the user access to the portion of INPUT that calls the files. The program will then accept a two letter abbreviation for the desired element and call the appropriate library file. For example, when the "//" monitor code is entered, INPUT responds with the message "element =". Typing "CD" then causes INPUT to call a subroutine from the elemental library that contains the optimum parameter values for the analysis of cadmium.

For maximum flexibility not only should INPUT be able

to accept parameter values, but it must be able to output them as well. To accomplish this, INPUT recognizes the two letter I/O options shown in Table VI. By utilizing the I/O subroutines provided with FORTX, INPUT can write the cummulative set of parameter values either to the line printer or the CRT terminal. Additional two-letter monitor codes that instruct INPUT to write only selected parameters to the terminal can also be entered.

INPUT calls two final subroutines, BURN and XAVE. BURN is used to clean impurities from a freshly mounted graphite braid. Typing "BU" causes the GBA power supply to turn on to approximately 22 A. This heats the braid to well above 2000°C and, consequently, drives the impurities out. Once the braid is cleaned, a carriage return causes the power supply to turn off, and this terminates BURN. XAVE is a routine that takes 100 ADC conversions acquired at a frequency of 100 Hz and returns the average to the calling program. INPUT uses XAVE in conjunction with the "DA" monitor command to record the dark current of the instrument.

Upon completing all of its assigned tasks, INPUT returns to MAIN.

2. START

To implement the sample atomization and data acquisition process, MAIN calls the subroutine START. START sequences through the operations outlined in Figure 18, retrieving from COMMON the required experimental parameters. Subroutine START can be conveniently divided into two parts; the section dealing with the parameter conversions, and the section that controls the atomizer heating levels.

The first section of START is concerned with manipulating the experimental control parameters stored in COMMON into a form usable by the interface. Parameters such as the data acquisition frequency, heating powers, and heating times all exist in the computer memory as either integer or real numbers. As described in Chapter III, however, the interface electronics can only accept binary information of a specific format.

The first experimental parameter converted is the data acquisition frequency (FREQ). This parameter can only take on the discrete integer values shown in Table I of Chapter III. Before being used by the interface, these values must be converted to the binary data listed adjacent to them in the table. To accomplish this, START calls the subroutine DRATE. DRATE acquires the integer FREQ from COMMON, determines the proper binary data corresponding to it, and then passes that value back to START as the variable IDRATE.

The next set of experimental parameters to be manipulated are the heating powers. The heating powers (DP, CP, and AT) are entered into the computer as real numbers



Figure 18. The flow chart for START.

in the range of 0.0 to 4095. This would seem compatible with the DAC which feeds the analog temperature control circuitry because it accepts 12-bit binary numbers in the range of 0 to 4095. The problem arises in converting a floating point real number to a 12-bit binary number. FORTX, like FORTRAN II, limits the range of integer numbers between -2048 and +2047. The integer numbers are essentially an 11-bit binary numbers with the 12th bit used as a sign bit. Therefore, a short segment of programming was written to convert the real number into a binary number by tricking the integer number system of the compiler.

START is also responsible for taking 100% transmittance reading. It does this just before the sample is deposited on the braid by calling the subroutine XAVE. XAVE functions in the same way as when it recorded the dark current reading, but in this case the shutter is left open.

The final parameter conversion task that START must perform is to set up all of the timing data. As described in Chapter III, the interval timer accepts timing data by decades. For example, a 25 second time interval must be broken down into 2 time intervals of the 10^1 second decade and 5 time intervals of the 10^0 second decade. Through a series of logical IF statements, START breaks down the desolvation and ashing times to their decade components.

Because the Timer-Clock board is busy producing the data acquisition pulses, the atomization time cannot be

handled in the same manner as the desolvation and ashing times. Instead the atomization time is controlled by a software counter. With the data acquisition frequency and the atomization time known, the computer simply calculates the number of data points (ICOUNT) to acquire. After this number of points have been taken, the computer kills the burn ending the atomization time.

Once all of the parameter conversions have been completed, START enters the heating control section. This section begins with the computer loading the desolvation heating data into the temperature control buffer latches. The desolvation timing data are then entered into the timing circuitry, the desolvation heating data are clocked from the buffer latches to the digital-to-analog converter, and the desolvation heating cycle is started. While this cycle is proceeding, the computer reloads the temperature control buffer latches with the ashing heating data. Immediately upon completing the desolvation cycle the ashing timing data are entered into the timing circuitry and the ashing cycle is begun. Once again the temperature control buffer latches are reloaded; this time with the atomization heating data. When the ashing cycle is finished, the data acquisition frequency (IDRATE) is entered into the timing circuitry. The first data acquisition pulse then initiates the atomization process by clocking the atomization heating data to the digital-to-analog converter. After ICOUNT

number of data points have been acquired, the computer terminates the atomization heating cycle.

START must check the status of the logical parameter BACK before returning to MAIN. If BACK is false, START simply returns to MAIN. If BACK is true, START cycles through the ashing and the atomization heating cycles again. The data are recorded as before except that no sample is atomized in this run. These data are utilized in the data calculation subroutine PLOT to subtract the contribution of the atomizer blackbody emission from the absorbance data.

3. PLOT

Plot is the final subroutine called by MAIN. Its responsibilities include calculating the absorbance data, plotting the absorbance-time data on the graphics terminal, and, if requested, outputting the data to a floppy disc. The way in which these tasks are carried out will be the topic of discussion for the remainder of this chapter.

The exact algorithm used to calculate the absorbance data is dependent upon the status of the logical parameters BACK and OPTO. If BACK and OPTO are both false, the absorbance of the individual data points is calculated using the normal formula

 $A = Log \frac{I_o}{I}$

In this case I_0 is the difference between the 100% light intensity reading (X100) and the 0% dark current reading (XDARK), both of which are the average of 100 readings acquired by the subroutine XAVE. I corresponds to an individual data point (RDATA) recorded during the sample atomization minus the average dark current reading. Therefore, PLOT calculates I = ICOUNT absorbance values by the formula

$$A(I) = Log \frac{(X100 - XDARK)}{(RDATA(I) - XDARK)}$$

The algorithm just shown is used when the blackbody emission from the atomizer is negligibly small. This occurs when the atomization temperature is low and the analysis wavelength is in the ultraviolet region. However, when one or both of these conditions is not met, and a blank run reveals that there is blackbody emission present, the logical parameter BACK must be set true, and another algorithm is used to correct for this emission.

As discussed in the previous section, when BACK is true, START performs a second atomization heating cycle, recording the blank data (SDATA) in exactly the same manner as it did the sample data. The algorithm PLOT uses to calculate the absorbance data under these circumstances is identical to that employed by Pals and Baxter (63,64). That is

$$A(I) = Log \frac{(X100 - XDARK)}{(RDATA(I) - SDATA(I)) + (X100 - XDARK)}$$

The second task that PLOT performs is the actual ploting of the absorbance-vs-time data. This portion of the program calls special subroutines from the Teklib library to execute graphics on the Tektronix terminal. First, the subroutine draws and labels the absorbance and time axes. Next PLOT must scale the real absorbance and time data to integer values to utilize the maximum dimensions of the screen. The Teklib subroutines then plot the individual absorbance data points as dots on the screen. PLOT then checks for specific plotting options. Currently PLOT employs only one possible option; plotting option C (PLTC). If PLTC and BACK are true, the blank blackbody data are plotted along with the existing sample absorbance data on the same screen. The blank data are connected by lines to distinguish them from the sample absorbance data.

The final function of plot is to output the raw absorbance - vs -time data if requested. The option PLTB must have been set true during the INPUT subroutine in order to access this portion of PLOT. If so, PLOT will query the user as to whether or not to keep the data. If yes, PLOT will then ask for a filename to give the data. It then opens an output file on the DSK device and writes the data to it. When completed, the file is closed and PLOT returns to MAIN to begin another data run.

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V. FUNDAMENTAL INVESTIGATION OF THE ZEEMAN BACKGROUND CORRECTION SYSTEM

The graphite braid has proved to be an excellent electrothermal atomizer for atomic absorption spectrometry (63,64,67,75-77). Calibration curves for standard metal solutions in distilled water were shown to be linear over 1.5 to 3 orders of magnitude (67). Detection limits were found to be comparable to those of carbon rod and carbon furnace atomizers (77). However, in preliminary studies it was discovered that matrix interferences by small amounts of inorganic salts could cause a depression of the atomic absorption signal (63,67). In the present work, this same behavior was observed for large amounts of inorganic salts and incompletely ashed organic material. In addition to depressing the atomic absorption signal, these matrix elements can absorb or scatter the hollow cathode light. Apparent absorption of this type frequently resulted in a second absorption peak. In the worst case, the interference peak can occur at the same time as the atomic absorption peak and completely obscure it. This nonspecific background absorption, if not corrected, causes erroneous results when a working curve is prepared from standards in distilled water. For this reason, it was deemed

necessary to construct and characterize a background correction system for the GBA.

A. Background Correction with the Normal Zeeman Effect

The present instrument utilizes an analyte-shifted Zeeman background correction system. As described previously, this technique involves the application of a magnetic field to the atomization cell in a direction perpendicular to the light path. When the magnetic field is sufficiently large, the atomic absorption profile of the atom is split into its characteristic Zeeman pattern. This splitting, and the difference in the state of polarization of each line of the Zeeman multiplet, is the basis of the background correction scheme.

Each element (in fact each electronic transition of a given element) exhibits a distinctive Zeeman pattern. To determine the conditions for optimum background correction, it was necessary to perform several studies for each element. The following two sections discuss some of these studies for the normal Zeeman transitions of zinc and cadmium.

1. <u>Zinc $({}^{1}S_{0} - {}^{1}P_{1})$ </u>

The most intense atomic absorption of zinc occurs at the 213.8 nanometer line. The Grotrian diagram of this transition is shown in Figure 19. In a magnetic field-free



Figure 19. The Grotrian diagram for a ${}^{1}S_{0} - {}^{1}P_{1}$ transition.
environment, one atomic transition occurs between the singlet ${}^{1}S_{0}$ energy level and the singlet ${}^{1}P_{1}$ energy level. However, in a constant magnetic field the Zeeman effect causes this transition to be split into three discrete transitions. This occurs because the magnetic moment associated with the total angular momentum vector J takes on 2J+1 discrete orientations with respect to the magnetic field. The projections of these orientations in the direction of the magnetic field correspond to the magnetic quantum numbers M_{j} . The ¹P₁ energy level with J = 1 acquires three projections, $M_{i} = +1$, 0, and -1. The ${}^{1}S_{0}$ energy level with J = 0 has only one projection, $M_i = 0$. As the figure shows, the transitions with $\Delta M_{i} = \pm 1$ are split to different energies, while the $\Delta M_{i} = 0$ transition remains at the same energy as the field-free transition. The former transitions are termed σ transitions and the later transition is termed a π transition.

The shift in the atomic energy of each component of the Zeeman multiplet is governed by Equation 1 (page 11). One of the fundamental parameters unique to each different type of Zeeman pattern is the Landé factor, g, in this equation. As equation 3 (page 11) shows, g is a function of the J, L, and S quantum numbers. In singlet transitions, such as the zinc 213.8 nm transition, the spin angular momentum vector of both energy levels is zero (S = 0). The total angular momentum vector is, therefore, equal to

the orbital angular momentum vector (J = L). Substituting these values into Equation 3 results in g = l. Transitions of this type are known as normal Zeeman transitions and always yield a 3 line splitting pattern as shown in Figure 20.

An important point about the Zeeman multiplet is the absorption characteristics of the individual lines. The σ lines absorb light polarized only perpendicular to the magnetic field and the π line absorbs light polarized only parallel to the magnetic field. Also, by substituting into the appropriate equations (page 12), it can be shown that the sum of the absorption due to the σ lines is equal to the total absorption of the π line.

To gain a better understanding of the relationship between the magnetic field strength and the splitting of the σ lines from the π line, a transmittance versus magnetic field strength study was performed. The results of this study are presented in Figure 21. The data are the peak transmittance values obtained by atomizing a constant amount of zinc at varying magnetic field strengths. Each of the points on the plot is the average of five runs with a relative standard deviation of 3% to 7%. The data for the σ lines were recorded with the linear polarizer positioned to transmit hollow cathode light polarized perpendicular to the magnetic field. The data for the π line were recorded with the polarizer positioned to transmit hollow



Figure 20. The Zeeman splitting pattern for a ${}^{1}S_{0} - {}^{1}P_{1}$ transition.



Figure 21. The transmittance <u>vs</u>. magnetic field strength plot for the Zn ${}^{1}S_{0} - {}^{1}P_{1}$ transition.

cathode light polarized parallel to the magnetic field.

The results follow the pattern we would intuitively expect. The unsplit π line remains at a constant transmittance at all applied magnetic field strengths. At low magnetic field strengths the σ lines also have a constant transmittance. At these low field strengths the σ lines have not been split far enough away from the hollow cathode emission profile to exhibit any difference in transmittance. However, when the field exceeds 4 kG, the σ lines definitely begin to deviate from a constant transmittance. As the field strength is increased further, the σ lines are shifted away from the hollow cathode emission profile and only the wings of the absorption profile remain at the frequency of the light source. Eventually, the σ lines would be split completely away from the hollow cathode profile and the transmittance would reach 100%. Figure 21 shows that the transmittance approaches 100%, but complete separation was not attained because of the limited magnetic field strength of the magnet.

2. <u>Cadmium $({}^{1}S_{0} - {}^{1}P_{1})$ </u>

The most intense atomic absorption of cadmium occurs at 228.8 nm and is a ${}^{1}S_{0} - {}^{1}P_{1}$ electronic transition. Like the zinc 213.8 nm transition, this transition has the normal Zeeman splitting pattern shown in Figures 19 and 20. Because zinc and cadmium are very similar in terms

of their atomic absorption characteristics and have identical Zeeman splitting patterns, it would be expected that the transmittance versus magnetic field strength studies of both metals would be very similar. The results of the transmittance versus field strength study for the cadmium 228.8 nm line are shown in Figure 22. Upon examination of Figure 21 and Figure 22 it is apparent that the results are indeed very similar.

From these studies, it is obvious that the maximum sensitivity will occur when the σ lines are completely split away from the hollow cathode emission. This will insure that the perpendicular polarized light (the reference beam) is measuring only background absorption while the parallel polarized light (the sample beam) is measuring both the background and the analyte atomic absorption. When the reference signal is subtracted from the sample signal only the analyte atomic absorption will remain. If a field strength is used where the σ lines exhibit appreciable atomic absorption, sensitivity will be lost. In this case, the reference beam will consist of the background absorption and some analyte atomic absorption. When the reference signal is subtracted from the sample signal, not only will the background be eliminated, but the net analyte atomic absorption will be decreased.

To illustrate this type of behavior, a series of calibration curves were recorded at various magnetic field



Figure 22. The transmittance <u>vs</u>. magnetic field strength plot for the Cd ${}^{1}S_{0} - {}^{1}P_{1}$ transition.

strengths for the cadmium 228.8 nm line. The data are presented in Figure 23. The zero kilogauss curve was recorded without background correction with the single beam instrument. This curve is a reference to show the maximum sensitivity possible for the instrument. The sensitivity (slope) of the background-corrected calibration curves increases as the magnetic field strength increases. This is due to the larger separation of the σ and π lines at the higher field strengths. The background-corrected curves would eventually become coincidental with the zero kilogauss line if high enough fields could be reached to totally separate the σ lines from the hollow cathode emis-The obvious bending of the calibration plots is due sion. to a stray light problem caused by the high hollow cathode lamp currents and the large monochromator slit widths used in this work.

B. Background Correction with the Anomalous Zeeman Effect

In addition to the normal Zeeman splitting pattern, many electronic transitions have splitting patterns which behave irregularly. These anomalous Zeeman patterns occur when one of the energy levels of the electronic transition has a non-zero spin angular momentum ($S \neq 0$). The anomalous patterns can have the components of the multiplet split more or less than that of the normal Zeeman effect and, in some cases, can have more than three lines in the



Figure 23. The calibration curves at varying magnetic field strength for the Cd ${}^{1}S_{0} - {}^{1}P_{1}$ transition.

multiplet. In this section the effect of different anomalous Zeeman patterns on the ability to background correct is examined.

1. Zinc
$$({}^{1}S_{0} - {}^{3}P_{1})$$

Zinc exhibits a relatively weak atomic absorption at 307.6 nm. Like the normal Zeeman pattern, this ${}^{1}S_{0} - {}^{3}P_{1}$ electronic transition is split into three distinct transitions as shown in Figure 24. However, the transition is anomalous in that the amount of splitting is not the same as in the normal Zeeman effect. The difference occurs because the excited state is a triplet electronic state. The ${}^{3}P_{1}$ level has the same magnetic quantum numbers (M_j = +1, 0, and -1) as the ${}^{1}P_{1}$ level of the ${}^{1}S_{0} - {}^{1}P_{1}$ normal Zeeman transition, but the Landé factor is different. The ${}^{3}P_{1}$ energy level has S = 1, L = 1, and J = 1 which, from Equation (3), yields g = 3/2. Equation (1) predicts that a g factor of 3/2 would cause the g lines to be split 1.5 times as far as the σ lines of the normal Zeeman lines. This type of splitting is shown in Figure 25. The dots indicate the amount of splitting the lines of the normal Zeeman effect would have under identical conditions.

The transmittance versus magnetic field strength plot (Figure 26) for the anomalous Zeeman pattern of zinc illustrates the effect of the larger amount of splitting. The σ lines begin to split away from the π line



Figure 24. The Grotrian diagram for a ${}^{1}S_{0} - {}^{3}P_{1}$ transition.



Figure 25. The Zeeman splitting pattern for a ${}^{1}S_{0} - {}^{3}P_{1}$ transition.



Figure 26. The transmittance <u>vs</u>. magnetic field strength plot for the Zn ${}^{1}S_{0} - {}^{3}P_{1}$ transition.

significantly even at the lowest applied field strengths. At approximately 5 kG the splitting is complete and the transmittance of the σ lines remains constant. The unsplit π line remains at a constant transmittance regardless of the applied field strength.

2. <u>Cadmium $({}^{1}S_{0} - {}^{3}P_{1})$ </u>

A second example of the ${}^{1}S_{0} - {}^{3}P_{1}$ anomalous Zeeman pattern is the cadmium 326.1 nm transition. The transmittance versus magnetic field strength plot, shown in Figure 27, is qualitatively identical to the plot of the zinc 307.6 nm transition shown in Figure 26. This is a reasonable outcome considering the similarities of the same type of plots for the normal Zeeman transitions of both metals. The main point to be noted about the plot is that at 5 or 6 kG the splitting of the σ lines from the π line reaches a maximum and the application of higher field strengths has very little effect.

The calibration curves for the cadmium 326.1 nm transition at different magnetic field strengths are shown in Figure 28. As in Figure 23, the data for the 0 kG curve were recorded without background correction with the single beam instrument. For the background corrected calibration curves the sensitivity increases with increased magnetic field strength. The 3 kG curve is definitely the least sensitive. The curves at 5, 7, and 10 kG, though



Figure 27. The transmittance <u>vs</u>. magnetic field strength plot for the cadmium ${}^{1}S_{0} - {}^{3}P_{1}$ transition.



Figure 28. The calibration curves at varying magnetic field strength for the Cd ${}^{1}S_{0} - {}^{3}P_{1}$ transition.

increasing in sensitivity, are very close to having the same sensitivity. This confirms what was said about the separation of the σ lines from the π line in Figure 27.

3. Lead $({}^{3}P_{0} - {}^{3}P_{1})$

Lead is one of the elements which presents an additional complexity in the Zeeman background correction technique. The lead 283.3 nm line is the ${}^{3}P_{0} - {}^{3}P_{1}$ atomic transition shown in Figure 29. This transition has the anomalous Zeeman splitting pattern shown in Figure 30. The Lande factor is 3/2 and, thus, the amount of splitting is identical to that of the ${}^{1}S_{0} - {}^{3}P_{1}$ transition of zinc and cadmium. On this basis alone, it would be expected that the transmittance versus magnetic field strength plot would be similar to the zinc and cadmium ${}^{1}S_{0} - {}^{3}P_{1}$ plots. Upon examining this plot for lead (Figure 31), it is evident that this is not the case.

The difference in the plots is a consequence of the relatively broad atomic absorption profile of lead compared to that of zinc and cadmium (78-80). This broadening is caused by the hyperfine structure of the different lead isotopes (78). The individual hyperfine components arise from two possible types of nuclear interaction with the electronic energy levels (81). One type of interaction (the isotope effect) is due solely to the difference in nuclear mass of the different isotopes. This type of



Figure 29. The Grotrian diagram for a ${}^{3}P_{0} - {}^{3}P_{1}$ transition.



Figure 30. The Zeeman splitting pattern for a ${}^{3}P_{0} - {}^{3}P_{1}$ transition.



Figure 31. The transmittance <u>vs</u>. magnetic field strength plot for the Pb ${}^{3}P_{0} - {}^{3}P_{1}$ transition.

interaction causes a slight frequency shift in the absorption of each isotope. The second type of interaction is due to the angular momentum associated with the nuclear spin quantum number I. In the same way that the L and S quantum numbers combine to give the total angular momentum quantum number J of the extranuclear electrons, now I must be similarly combined with J to give the total angular momentum F of the entire atom. This can result in a splitting of the electronic energy level by the coupling of the different orientations of the nuclear angular momentum with the angular momentum of the electrons.

Figure 32 shows the hyperfine components of lead in the neighborhood of the 283.3 nm absorption line (78). Naturally occurring lead consists of four isotopes of atomic mass 204, 206, 207, and 208 with abundances of 1.5%, 23.6\%, 22.6\%, and 52.3\%, respectively. The even mass isotopes have a nuclear spin of zero (I = 0) and absorb at different frequencies because of the isotope effect. The amount of absorption is directly proportional to the isotopic abundances. The 207 isotope, however, has a nuclear spin of I = 1/2 which interacts with the electronic energy level causing the absorption line to be split to two different frequencies. The lower energy transition (split by 10.35 GHz) is slightly more favorable as reflected by its higher intensity.

In the environment above the heated graphite braid,



Figure 32. The Pb hyperfine spectrum at 283.3 nm.

lead does not exhibit the line spectrum shown in Figure 32. Collisional processes and the Doppler effect cause the line structure to be smeared into a broad absorption profile with a bump on the low frequency side due to the absorption of the 207 lead hyperfine component. As Figure 31 shows, with increased magnetic field strength, the broad absorption profile of the σ components of lead is very slowly split away from the hollow cathode emission profile. The π line, however, remains at a constant transmittance as a function of the magnetic field strength.

The broadness of the atomic absorption profile causes a drastic change in the calibration curves for lead relative to that of the ${}^{1}S_{0} - {}^{3}P_{1}$ cadmium curves. The calibration curves at varying magnetic field strengths for lead are shown in Figure 33. As in the calibration curves presented previously, the data for the 0 kG curve was recorded without background correction. Like the data for cadmium in Figure 28, the sensitivity of the background corrected curves decreases with decreasing magnetic field strength. However, in the case of lead, the decrease for each field strength is much more pronounced. Considering the data from the magnetic field strength versus transmittance study, this is a logical outcome.



Figure 33. The calibration curves at varying magnetic field strength for the Pb ${}^{3}P_{0} - {}^{3}P_{1}$ transition.

4. Silver
$$({}^{2}S_{1/2} - {}^{2}P_{3/2})$$

Up to this point we have been dealing with electronic transitions which have the relatively simple three line Zeeman splitting pattern. However, as the Grotrian diagram in Figure 34 shows, some transitions have much more complex splitting patterns. In this ${}^{2}S_{1/2} - {}^{2}P_{3/2}$ transition, the magnetic field not only splits the excited state energy level, but also splits the ground state energy level. Because the amount of splitting of both energy levels is different, each quantum mechanically allowed transition occurs at a different frequency. This results in a Zeeman pattern with four σ lines and two π lines as shown in Figure 35.

Zeeman patterns such as this, in which there is more than one π line, present an interesting problem. In the previous three-line patterns, the transmittance of the π lines was not affected by the magnetic field. Therefore, to attain the maximum sensitivity, it was only necessary to split the σ lines completely away from the hollow cathode emission profile. In this way, the π line (the sample beam) would consist of the full atomic absorption and the background absorption while the σ lines (the reference beam) would consist only of the background absorption. After subtracting the reference signal from the sample signal, the net absorption.



Figure 34. The Grotrian diagram for a ${}^{2}S_{1/2} - {}^{2}P_{3/2}$ transition.



Figure 35. The Zeeman splitting pattern for a ${}^{2}S_{1/2} - {}^{2}P_{3/2}$ transition.

In contrast to this, the ${}^{2}S_{1/2} - {}^{2}P_{3/2}$ pattern has the two π lines being split at the same time that the σ lines are being split. The transmittance versus magnetic field strength study for the silver 328.0 nm line (Figure 36) illustrates this behavior. The σ lines immediately split away from the π lines and climb toward 100% transmittance. Initially, the π lines maintain a constant transmittance but at approximately 5 kG the transmittance starts to increase. This occurs because at low field strengths the π lines are not shifted far enough away from the hollow cathode emission profile to cause any significant change in the transmittance. However, at the higher field strengths the π lines slowly move away from the emission profile and, consequently, absorb less light.

Because the sensitivity is dependent upon the separation of the σ lines from the π lines, it is apparent from Figure 36 that as the field strength is increased the sensitivity will start out low, go through a maximum, and then decrease again. The calibration curves at varying magnetic field strength in Figure 37 prove this point. The maximum sensitivity occurs at 5 kG and decreases in the order of 7, 3, and then 10 kG. This same behavior is more clearly shown in Figure 38 which is a plot of the sensitivity (slope) of each calibration curve versus the magnetic field at which it was recorded. Again, the maximum sensitivity is seen to occur in the neighborhood of 5 kG.



Figure 36. The transmittance <u>vs</u>. magnetic field strength plot for the Ag ${}^{2}S_{1/2} - {}^{2}P_{3/2}$ transition.



Figure 37. The calibration curves at varying magnetic field strength for the Ag ${}^{2}S_{1/2} - {}^{2}P_{3/2}$ transition.



Figure 38. The sensitivity <u>vs</u>. magnetic field strength plot for the Ag ${}^{2}S_{1/2} - {}^{2}P_{3/2}$ calibration curves.

Since both the σ lines and the π lines are split by the magnetic field, there is no field strength where the σ lines are completely separated from the hollow cathode emission while the π lines remain at their 0 kG transmittance. For this reason, the background-corrected calibration curves can never attain the same sensitivity as the calibration curve for the single beam instrument without background correction.

5. <u>Copper $({}^{2}S_{1/2} - {}^{2}P_{3/2})$ </u>

The ultimate test of the background correction capabilities of the instrument occurs when the electronic transition of the analyte has both a complex anomalous Zeeman splitting pattern and also exhibits a considerable amount of hyperfine structure. This situation occurs in the analysis of copper at 324.7 nm. This particular copper line is a ${}^{2}S_{1/2} - {}^{2}P_{3/2}$ electronic transition and, thus, has the same Zeeman splitting pattern (Figures 34 and 35) as the silver 328.0 nm transition. However, due to its hyperfine structure, copper has an atomic absorption profile which is much broader than that of the silver transition (82,83).

Naturally occurring copper consists of two main isotopes with atomic masses of 63 and 65. The natural abundances of these isotopes are 69.1% and 30.9%, respectively. As was the case with lead, the two isotopes of copper absorb light of slightly different frequencies due to the isotope effect. The hyperfine structure is further complicated by the coupling of the nuclear spin of each isotope with the electronic spin. Both isotopes possess a nuclear spin of 3/2 which splits the electronic energy levels creating the complex hyperfine spectrum shown in Figure 39 (82). Of course collisional and Doppler broadening of the hyperfine components produce an absorption profile with two closely spaced peaks.

The large width of the absorption profile causes a profound change in the shape of the copper transmittance versus magnetic field strength plot (Figure 40) relative to the same plot for silver (Figure 37). The π lines of the copper transition show a slow, steady increase in transmittance with increased magnetic field strength. This is due to the fact that at the field strengths used the π lines are essentially broadened into one peak. At the higher field strengths the two π lines start to split apart, but the separation is not significant enough to cause an abrupt change in the transmittance as in the case of the silver transition. At low magnetic field strengths the copper σ lines behave like the σ lines of the silver transition. However, because of the broad atomic absorption profile, the σ lines are never split totally away from the hollow cathode emission. For this reason, the transmittance of the σ lines do not reach 100% even at the



Figure 39. The Cu hyperfine spectrum at 324.7 nm.



Figure 40. The transmittance <u>vs</u>. magnetic field strength plot for the Cu ${}^{2}S_{1/2} - {}^{2}P_{3/2}$ transition.
highest field strengths possible.

The calibration curves for copper recorded at varying magnetic field strengths are shown in Figure 41. The sensitivity of the calibration curves decreases in the order of 10, 5, 3, and then 7 kG. As would be expected, this order roughly corresponds to the separation of the σ lines from the π lines in Figure 40. It is also apparent that at the magnetic field strengths used in this work, the background corrected calibration curves cannot approach the single beam instrument's sensitivity.

C. <u>Application of the Analyte-shifted Zeeman Background</u> Correction System

1. Analysis of Cadmium in a NaCl Matrix

To test the effectiveness of the analyte-shifted Zeeman background correction system a chemical analysis was selected which was known to have a severe matrix interference (84). The analysis involves the determination of cadmium in the presence of a large amount of NaCl. This analysis is particularly difficult to accomplish for a number of reasons. First, the NaCl matrix cannot be eliminated in the ashing heating cycle because it is relatively involatile. Any attempt to ash the NaCl matrix at higher temperatures results in the premature atomization of the Cd. Second, selective volatilization of just



Figure 41. The calibration curves at varying magnetic field strengths for the Cu ${}^{2}S_{1/2} - {}^{2}P_{3/2}$ transition.

the Cd at temperatures below which the NaCl will not vaporize failed to atomize the Cd. Apparently, the great excess of NaCl retards the Cd atomization process. Increasing the atomization temperature to a point where Cd atomic absorption was detected also brought with it the scattering (or molecular absorption) signal caused by the NaCl. The only successful method for accomplishing this analysis has been to perform a prior extraction of the Cd from the matrix (85) or to utilize an instrument equipped with a very efficient background correction system.

Figures 42 - 44 are the absorbance-time data plots recorded for the background correction of 10 ppm Cd in a 3% NaCl (approximately 0.5 Molar) solution. The analysis was performed at 326.1 nanometers with a magnetic field strength of 10 kG. Referring to Figure 27, it can be seen that at this field strength the σ lines are split almost completely away from the hollow cathode emission. Therefore, the hollow cathode light polarized perpendicular to the magnetic field (the reference beam) will be absorbed by only the background. The hollow cathode light polarized parallel to the magnetic field (the sample beam), however, will be absorbed by both the π line and the background. Figure 42 shows the sample beam absorption-time plot for the atomization of 5 µL of solution. Subsequent experiments on the appearance time of Cd confirmed that the



Figure 42. The sample beam absorbance \underline{vs} . time plot for the analysis of Cd in a NaCl matrix.



Figure 43. The reference beam absorbance \underline{vs} . time plot for the analysis of Cd in a NaCl matrix.



Figure 44. The background-corrected absorbance \underline{vs} time plot for the analysis of Cd in a NaCl matrix.

first peak in the doublet is due to Cd atomic absorption while the later appearing larger shoulder peak is the background due to light scattering and/or molecular absorption by the NaCl.

Figure 43 is the absorbance-time plot for an identical sample. However, these data were recorded with the polarizer rotated 90 degrees and, therefore, represent the reference beam absorption. In this plot the atomic absorption has almost been totally eliminated while the background absorption has been unaffected. Figure 44 was obtained by subtracting the reference signal (Figure 43) from the sample signal (Figure 42). This is the backgroundcorrected absorption versus time plot showing just the absorption due to the Cd with the large background absorption from the NaCl eliminated.

An even more severe test of the background correction system is to use the more sensitive 228.8 nanometer absorption line for the analysis of cadmium in the presence of NaCl. Figure 45 shows the calibration curves obtained with and without background correction for the analysis of less than 100 ppb Cd in a 3% NaCl solution. It can be seen that the calibration curve obtained without background correction is offset to higher absorbances due to the scattering and absorption of the hollow cathode light by the NaCl matrix. In the background-corrected calibration curve this scattering has been subtracted and only



Figure 45. Calibration curves for the analysis of Cd in a NaCl matrix with (■) and without (●) background correction.

the absorbance of the Cd remains. The 3% NaCl blank solution has even been corrected to a negligibly small absorbance.

2. Double Valued Calibration Curves

One of the limitations of the analyte-shifted Zeeman background system is the possibility of obtaining a double valued calibration curve. For the 3-line Zeeman splitting patterns in which the field strength is high enough to split the σ lines completely out of the hollow cathode emission profile, while the π line remains unsplit, this will not be a problem. In this situation the π line will be absorbed by the sample beam and will, therefore, appear identical to the absorption signal obtained with the single beam instrument. The σ lines, however, will not be absorbed by the reference beam and will, thus, have an absorbance of 0 regardless of the concentration. This will make the background corrected calibration curve linear in the working concentration range and cause it to flatten out at very high concentrations just as in the standard single beam instrument.

The difficulty with double valued calibration curves arises when the reference beam is absorbed by the σ lines. This can happen for metals such as silver which have complex anomalous Zeeman splitting patterns. As was shown earlier, the highest sensitivity for silver was obtained by employing low magnetic field strengths which leads to the maximum separation of the σ lines from the π line. Under these circumstances the σ lines were not totally split away from the reference beam and therefore had an appreciable absorbance.

The absorption of the σ lines by the reference beam is by no means restricted only to complex anomalous Zeeman splitting patterns. If the applied magnetic field strength is too low for a metal which has a normal Zeeman splitting pattern, the σ lines will not be split out of the hollow cathode emission profile. Figure 46 shows an example of this. The figure shows the individual calibration curves of the reference beam (composed of the absorbance of the σ lines) and the sample beam (composed of the absorbance of the π line) for Cd at 228.8 nm at an applied field strength of 10 kG. As seen in Figure 22, the σ lines still exhibit considerable absorbance by the reference beam at this field strength. The π line has a fairly linear calibration curve at the lower concentrations. However, in the higher concentration range the absorbance flattens out due to the stray light present in the system. The σ lines, because they have a small overlap with the reference beam, do not have the stray light problem to the same extent as the π line and therefore, do not have as severe of curvature.

The difference between the sample beam and the



Figure 46. Calibration curves for the sample (π) and reference (σ^{\pm}) beams for Cd.

reference beam calibration curves gives the backgroundcorrected calibration curve shown in Figure 47. The curve is linear at low concentrations but at the higher concentrations is double valued in absorbance. This is a direct outcome of the results plotted in Figure 46.

The double valued nature of the data plotted in Figures 46 and 47 is the result of a severe stray light problem. However, this same trend would have eventually been seen at higher concentrations even if the stray light were extremely small. Under these circumstances, the sample beam's calibration curve would have flattened out at higher concentrations. The σ lines' absorbance would still be linear at this point and the net result would still be a double valued calibration curve.



Figure 47. The double valued calibration curve for Cd.

VI. PERSPECTIVES

This work has shown that the analyte-shifted Zeeman background correction technique could be successfully used in conjunction with the graphite braid atomizer. The presence of a very high magnetic field had no adverse effects on the nearby electronics. The GBA temperature monitoring photodiode and photodarlington transistor continued to function properly even though they were positioned in the center of the magnetic field. The hollow cathode lamp, on the other hand, was found to be very sensitive to the magnetic field. This problem was easily eliminated, however, by moving the lamp further down the optical rail away from the magnet.

The characterization studies performed with standard metal solutions in distilled water showed that the metals with 3 line Zeeman splitting patterns would attain maximum sensitivity once the σ lines were totally split away from the hollow cathode emission. However, for metals which exhibit complex anomalous Zeeman splitting patterns, the technique had inherent limitations. For example, silver has a complex anomalous Zeeman pattern in which the four σ lines and the two π lines are all split by the magnetic field. This pattern made it impossible for the

background-corrected calibration curves to attain the same sensitivity as the single beam instrument.

To overcome this problem, future workers should consider using a modulated magnetic field instead of the constant field. In such a system, a linear polarizer would be fixed to pass light polarized perpendicular to the oscillating magnetic field. When the field strength reaches 0 kG, the σ lines would not be split and, thus, the full atomic absorption would be seen. However, when the field strength increases, the σ lines will be shifted to different frequencies, and the hollow cathode will observe only the background. To be useful with the GBA, the magnet must have a high modulation frequency (>100 Hz) and be capable of high magnetic field strengths (>10 kG).

The major problem with the GBA instrument, however, is the atomizer itself. With the GBA, the atomic vapor is observed in the relatively cool environment above the atomizer. For standard metal solutions in distilled water, this is generally not a problem. However, for metals existing in a complex matrix, the concomitant species in the vapor phase tend to scavenge or condense the analyte atoms. Therefore, future work with the GBA should be directed toward samples that do not exhibit these effects.

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APPENDIX

SOFTWARE LISTING

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С **PROGRAM NAME:** MAIN.FT **PROGRAMMER:** J. T. GANO VERSION 1-A DATE 5-SEP-79 PROGRAM FUNCTION: MAIN PROGRAM TO RUN ZGBA **PROGRAM EXECUTION:** 1. THE MAIN PROGRAM FIRST EXECUTES A SHORT SABR ROUTINE TO INITIALIZE THE INTERFACE. THE COMPUTER AND THE INTERFACE ARE POWERED-UP, THE MAIN PROGRAM IS STARTED AND THEN ANY KEY IS STRUCK. THE COMPUTER SHOULD REPLY THAT THE INTERFACE HAS BEEN INITIALIZED. THE SUBROUTINE "INPUT" IS CALLED. THIS 2. THIS ROUTINE ALLOWS C C C C INPUT OF EXPERIMENTAL PARAMETERS AND I/O OPTIONS. THE SUBROUTINE "START" IS CALLED. THIS ROUTINE BEGINS 3. THE EXECUTION OF ZGBA HEATING PROGRAM AND DATA ACQUISITION. CCCCCCC THE SUBROUTINE "PLOT" IS CALLED. THIS ROUTINE DOES THE 4. DATA ANALYSIS AND PLOTTING. 5. THE MAIN PROGRAM JUMPS BACK TO "INPUT" FOR ANOTHER DATA BUN. COMMON IDATA, IBACK COMMON DEST, ASHT, ATMT, DESP, ASHP, ATMP COMMON SAMP, AMNT, CONC, MAG, FREQ, BACK, ICOUNT COMMON XDARK, X100, OPTO, ASHRAD, PLTA, PLTB COMMON PLTC, IABSA, IABSB, IABSC, PABSA, PABSB, PABSC INTEGER DEST, ASHT, FREQ, ARG, ELEM REAL IABSA, IABSB, IABSC, MAG LOGICAL OPTO, ASHRAD, DARK, PLTA, PLTB, PLTC, BACK DIMENSION IDATA (400), IBACK (400) WRITE (1,10) 10 FORMAT (//, 'ZEEMAN GRAPHITE BRAID ATOMIZER START-UP',//, 1 13X, 'VERSION 1-A') C C BEGIN THE INTERFACE INITIALIZATION COMMANDS. С S IOF S 6300 /BLOCK 5009 OUTPUT AT THE "OR" GATE CLA CLL S S TAD (0006 /LOAD TIMING DATA INTO THE ACC S 6304 /LATCH TIMING DATA OUT /ENABLE THE 5009 CLOCK AT THE "OR" GATE
/START THE 74190 TIMER S 6306 S 6305 **/CLEAR ACC AND CLEAR KEYBOARD FLAG** S 6032 CLA CLL SA, /TAD THE HEATING PROGRAM DATA INTO AC TAD (7353 S /LATCH TRANS. AMP CHANNEL S 6644 **/LATCH DIODE AMP CHANNEL** 6643

S	6642 /1	EMPERATURE PROGRAMMING CHANNEL SELECT	
S	6645 /0	LEAR DAC (KILL BURN)	
S	KSF /K	EYBOARD STRUCK?	
S	JMP A		
S	6032		
	WRITE (1,11) @	IF YES, TYPE INITIALIZATION MESSAGE	
11	FORMAT (///, 'ZGBA INITIALIZED',///)		
C			
C	CALL THE PARAMETER INPUT SUBROUTINE.		
C			
13	CALL INPUT		
C			
C	CALL THE SUBROUTINE TO START THE HEATING PROGRAM.		
C	AND DATA ACQUISITI	ON	
C			
	CALL START		
C			
C	CALL THE DATA ANAL	YSIS AND PLOTTING SUBROUTINE.	
C			
	CALL PLOT		
С			
Ċ	JUMP BACK TO "INPU	T" FOR ANOTHER DATA RUN.	
ē			
	GO TO 13		
	END		

С č С **PROGRAM NAME:** INPUT.FT **PROGRAMMER:** J. T. GANO VERSION 1-A DATE 6-SEP-79 PROGRAM FUNCTION: INPUT EXPERIMENTAL PARAMTERS AND I/O OPTIONS CALLING FORM: CALL INPUT **PROGRAM EXECUTION:** THE "INPUT" PROGRAM SETS UP INITIAL EXPERIMENTAL PARAMETERS 1. IN CONTON VIA A SERIES OF VARIABLE = DEFAULT PARAMETER STATEMENTS. IT THEN ENTERS THE MONITOR SECTION WHICH ACCEPTS TWO LETTER 2. COMMANDS WHICH ALLOW DISPLAY AND ALTERATION OF EXPERIMENTAL PARAMETERS. WHEN "INPUT" IS COMPLETED THE PROGRAM RETURNS TO MAIN. 3. č SUBROUTINE INPUT С С COMMON IDATA, IBACK CONTION DEST, ASHT, ATMT, DESP, ASHP, ATMP CONTION SAMP, AMNT, CONC, MAG, FREQ, BACK, ICOUNT COMMON XDARK, X100, OPTO, ASHRAD, PLTA, PLTB COMMON PLTC, IABSA, IABSB, IABSC, PABSA, PABSB, PABSC INTEGER DEST, ASHT, FREQ, ARG, ELEM REAL IABSA, IABSB, IABSC, MAG LOGICAL OPTO, ASHRAD, DARK, PLTA, PLTB, PLTC, BACK DIMENSION IDATA (400), IBACK (400) С C C C READ IN THE MONITOR COMMAND. IF THE COMMAND IS 'OP' (OLD PARAMETERS) USE THE PARAMETERS SET IN THE PROGRAM. READ (1,10) ARG FORMAT ('',A2) IF (ARG .EQ. 'OP') 1 10 $\begin{array}{r} \text{DEST} = 10\\ \text{ASHT} = 15 \end{array}$ ATMT = .5DESP = 75.0 ASHP = 125.0ATMP = 200.1FREQ = 200XDARK = 0.0 X100 = 0.0 SAMP = 'CADMIU' AMNT = 'UNKNOW' CONC = 'UNKNOW' MAG = 'UNKNOW'

OPTO = .FALSE. 11 = 'F' ASHRAD = .FALSE. 12 = 'F' DARK = .FALSE.13 = 'F' TITLE = 'NONEXX' PLTA = .TRUE.14 = 'T' PLTB = .FALSE. 15 = 'F'PLTC = .FALSE. 16 = 'F'BACK = .FALSE. I7 = 'F'IABSA = 0.0IABSB = 0.0IABSC = 0.0PABSA = 0.0PABSB = 0.0PABSC = 0.0ENDIF IF (ARG .EQ. '//') GO TO 99 IF (ARG .EQ. 'HP') GO TO 11 IF (ARG .NE. 'HT') GO TO 12 **G** GO TO THE LIBRARY FOR PARAMETERS • PRINT PARAMETERS AND DATA ON LP • PRINT PARAMETERS AND DATA ON TY GO TO 13 CALL OOPEN ('LPT', 0) 11 GO TO 14 13 CALL OOPEN ('TTY', 0) CALL OUPEN ('TIT', 0) WRITE (4,15) TITLE FORMAT ('TITLE: ', A6) WRITE (4,16) I1, I2, I3, I4, I5, I6, I7 FORMAT ('OPTO ',A2,' ASHRAD ',A2,' DARK ',A2, 1 'PLTA ',A2,' PLTB ',A2,' PLTC ',A2,' BACK ',A2) WRITE (4,17) DEST, ASHT, ATMT, FREQ FORMAT ('DEST ',I3,' ASHT ',I3,' ATMT ',F3.1, 14 15 16 17 1 ' FREQ ', I4) 1 ' FREQ ',14) WRITE (4,18) DESP, ASHP, ATMP FORMAT (' DESP ',F6.1,' ASHP ',F6.1,' ATMP ',F6.1) WRITE (4,19) SAMP, ANNT, CONC, MAG FORMAT (' SAMP ',A6,' AMNT ',A6,' CONC ',A6,' MAG ',A6) WRITE (4,20) IABSA, IABSB, IABSC, PABSA, PABSB, PABSC FORMAT (' IABSA ',F6.3,' IABSB ',F6.3,' IABSC ',F6.3, 1 ' PABSA ',F5.3,' PABSB ',F5.3,' PABSC ',F5.3) CAUL OCLOSE 18 19 20 CALL OCLOSE GO TO 1 PRINT LOGICAL PARAMETERS ON TY. 12 IF (ARG .EQ. 'TL') WRITE (1,16) 11, 12, 13, 14, 15, 16, 17 PRINT TIMING PARAMETERS ON TY. IF (ARG .EQ. 'TT') WRITE (1,17) DEST, ASHT, ATMT, FREQ

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С PRINT HEATING PARAMETERS ON TY. С IF (ARG .EQ. 'TP') WRITE (1.18) DESP. ASHP. ATMP PRINT SAMPLE PARAMETERS ON TY. IF (ARG .EQ. 'TS') WRITE (1,19) SAMP, AMNT, CONC, MAG PRINT DATA ON TY. IF (ARG .EQ. 'TD') WRITE (1,20) IABSA, IABSB, IABSC, 1 PABSA, PABSB, PABSC PRINT TITLE ON TY. С IF (ARG .EQ. 'TI') WRITE (1,15) TITLE IF (ARG .EQ. 'OF') ● OPTO FALSE OPTO = .FALSE. I1 = 'F' ENDIF IF (ARG .EQ. 'OT') e opto true ENDIF IF (ARG .EQ. 'RF') **G** RADIATION PROGRAMMING ON ASH FALSE ASHRAD = .FALSE. 12 = 'F'ENDIF IF (ARG .EQ. 'RT') **Q** RADIATION PROGRAMMIMNG ON ASH TRUE ASHRAD = .TRUE.12 = 'T' ENDIF IF (ARG .EQ. 'PA') **e PLOTTING OPTION 'A' TRUE** IF (ARG .EQ. ') PLTA = .TRUE. PLTB = .FALSE. PLTC = .FALSE. I4 = 'T' I5 = 'F' I6 = 'F' ENDIF IF (ARC .EQ. 'PB') **e PLOTTING OPTION 'B' TRUE**

 IF (ARG .EQ.)

 PLTA = .FALSE.

 PLTB = .TRUE.

 PLTC = .FALSE.

 I4 = 'F'

 I5 = 'T'

 I6 = 'F'

 ENDIF IF (ARG .EQ. 'PC') e PLOTTING OPTION 'C' TRUE PLTA = .FALSE. PLTB = .FALSE. PLTC = .TRUE. I4 = 'F' I5 = 'F'16 = 'T'

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ENDIF
          IF (ARG .EQ. 'BT')
                                        9 TAKE A BLANK READING
          BACK = .TRUE.
I7 = 'T'
          ENDIF
          IF (ARG .EQ. 'BF')
                                        © DO NOT TAKE A BLANK READING
          BACK = .FALSE.
          17 = 'F'
          ENDIF
          IF (ARG .EQ. 'DT') READ (1,21) DEST
                                                            e READ DESOLVATE TIME
          FORMAT (' DESOLVATE TIME = ', 13)
IF (ARG .EQ. 'CT') READ (1,22) ASHT
21
                                                            • READ ASH TIME
          FORMAT (' ASH TIME = ', I3)
IF (ARG .EQ. 'AT') READ (1,23) ATMT
22
                                                            @ READ ATOMIZATION TIME
          FORMAT (' ATOMIZATION TIME = ',F3.1)
23
          IF (ARG .EQ. 'FR') READ (1,24) FREQ
FORMAT (' DATA FREQUENCY = ', I4)
                                                            9 READ DATA FREQUENCY
24
          IF (ARG .EQ. 'DP') READ (1,25) DESP
                                                            e READ DESOLVATION HEATING LEVEL
          FORMAT (' DESOLVATE POWER = ', F5.0)
25
          IF (ARG .EQ. 'CP') READ (1,26) ASHP
FORMAT (' ASH POWER = ',F6.1)
                                                            9 READ ASH HEATING LEVEL
26
          IF (ARG .EQ. 'AP') READ (1,27) ATMP
FORMAT (' ATOMIZATION POWER = ', F6.1)
                                                            e READ ATOMIZATION HEATING LEVEL
27
          IF (ARG .EQ. 'SA') READ (1,28) SAMP
FORMAT ('SAMPLE = ',A6)
                                                            G READ SAMPLE TYPE
28
          IF (ARG .EQ. 'AM') READ (1,29) AMNT
                                                            e READ SAMPLE SIZE
          FORMAT (' AMOUNT = ', A6)
29
          IF (ARG .EQ. 'CO') READ (1,30) CONC
FORMAT (' CONCENTRATION = ',A6)
                                                            G READ SAMPLE CONCENTRATION
30
          IF (ARG .EQ. 'MA') READ (1,31) MAG
                                                            9 READ MAGNETIC FIELD STRENGTH
31
          FORMAT (' MAGNET STRENGTH = ', A6)
С
С
          CALL A ROUTINE TO DEGAS THE BRAID.
С
С
          TAKE A DARK CURRENT READING.
С
С
          IF (ARG .EQ. 'DA')
          WRITE (1,98)
FORMAT (' CLOSE SHUTTER TYPE CR')
98
S
          6032
SA,
          KSF
          JMP A
\mathbf{S}
\mathbf{S}
          6032
          CALL XAVE (XDARK)
          WRITE (1,97) XDARK
FORMAT (' DARK CURRENT = ',F6.1)
97
          DARK = .TRUE.
13 = 'T'
          ENDIF
          IF (ARG .EQ. 'EX') CALL EXIT
                                                  e EXIT TO KEYBOARD MONITOR
          IF (ARG .EQ. 'GO') RETURN
                                                  C RETURN TO MAIN
          GO TO 1
С
С
          BEGINNING OF ELEMENTAL PARAMETER LIBRARY.
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C			
99	READ (1.33) ELEM		
33	FORMAT (' ELEMENT = ', $A2$)		
	IF (ELEM .EQ. 'CD')		
	CALL CD		
	GO TO 1		
	ENDIF		
	IF (ELEM .EQ. 'CU')		
	CALL CU		
	GO TO 1		
	ENDIF		
	WRITE (1,34)		
34	FORMAT (' ELEMENT NOT IN ZGBA LIBRARY ')		
	READ (1.35) IR		
35	FORMAT (' RETURN TO ZGBA MONITOR? Y OR N '.A1)		
	IF (IR .EQ. 'Y') GO TO 1		
	GO TO 99		
	END		

C C PROGRAM NAME: XAVE.FT CCCCCC J. T. GANO PROGRAMMER: VERSION 1-A DATE 25-SEP-79 Ĉ TAKE 100 DATA POINTS AND RETURN THE AVERAGE **PROGRAM FUNCTION:** С CALL XAVE (XDATA) C CALLING FORM: С C **PROGRAM EXECUTION:** THE PROGRAM TAKES 100 DATA POINTS AT A FREQUENCY OF 100 HZ С 1. AND AVERAGES THEM. THE RESULT IS RETURNED TO THE С CALLING PROGRAM. С Ē С SUBROUTINE XAVE (XDATA) С **DIMENSION LDATA (100)** /BLOCK 5009 OUTPUT AT THE "OR" GATE \mathbf{S} 6300 /DISABLE THE START BURN PULSE 6531 S /CLOCK THE SHA INTO THE SAMPLE MODE /CLEAR SKIP ON HOLD FLAG S 6532 S 6421 **/CLEAR ADC DONE FLAG** S 6423 /ENABLE THE 5009 CLOCK AT THE "OR" GATE 6306 S S CLA S TAD (0224 /LATCH 100 HZ TIMING DATA /ENABLE START BURN PULSE 6304 S 6530 S DO ? I = 1, 100 @ TAKE 100 DATA POINTS MDATA = 0**/ENABLE ADC CLOCK** S 6312 /SKIP ON SHA HOLD 6420 SA, JMP A S /TAKE DATA PULSE S 6422 /SKIP ON CONVERSION DONE 6424 SB, 8 JMP B /JAM TRANSFER DATA TO THE AC 6425 S /CLOCK THE SHA INTO THE SAMPLE MODE 6532 S DCA mDATA S TA **© LOAD DATA INTO AN ARRAY** /CLEAR SKIP ON HOLD FLAG LDATA (I) = MDATA S 6421 /CLEAR ADC DONE FLAG 6423 S **ENDDO** С CONVERT THE DATA TO REAL AND TAKE THE AVERAGE. С С PSUM = 0.0TDATA = 0.0DO ? I = 1, 100 MDATA = LDATA (I) IF (MDATA .GE. 0) RDATA = FLOAT (MDATA)

ELSE
CLA CLL
TAD mDATA
AND (3777
DCA mDATA
RDATA = FLOAT (MDATA) + 2048.
ENDIF
TDATA = RDATA + TDATA
ENDDO
XDATA = TDATA/100.0
6300 /BLOCK 5009 OUTPUT AT THE "OR" GATE
6316 /DISABLE THE 74190 TIMER
6531 /DISABLE THE START BURN PULSE
6532 /CLOCK THE SHA INTO THE SAMPLE MODE
6421 /CLEAR SKIP ON HOLD FLAG
6423 /CLEAR ADC DONE FLAG
6311 /DISABLE ADC CLOCK
RETURN
END

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С Č C PROGRAM NAME: START.FT CCCCCC **PROGRAMMER:** J. T. GANO VERSION 1-A 19-SEP-79 START SUPERVISES THE ZGBA HEATING **PROGRAM FUNCTION:** PROGRAM AND DATA ACQUISITION C C CALLING FORM: CALL START C C C C C **PROGRAM EXECUTION:** CONVERT THE DESOLVATE, ASH AND ATOMIZATION HEATING PARAMETERS TO A FORM SUITABLE FOR LOADING INTO 1. C THE INTERFACE. Ċ 2. TAKE A 100% TRANSMITTANCE READING. DEPOSIT SAMPLE THEN TYPE CR. START DESOLVATION CYCLE AND TIMER. С 3. č 4. 5. START ASH CYCLE AND TIMER. CCCCC START ATOMIZATION CYCLE AND DATA ACQUISITION. IF (.NOT. OPTO .AND. BACK) DELAY 10 SECONDS THEN START A 5 SECOND ASH CYCLE FOLLOWED BY A BLACKBODY 6. 7. BLANK RUN. C 8. RETURN TO THE MAIN PROCRAM. С С SUBROUTINE START С С COMMON IDATA, IBACK CONTION IDATA, IBACK CONTION DEST, ASHT, ATMT, DESP, ASHP, ATMP COMMON SAMP, AMNT, CONC, MAG, FREQ, BACK, ICOUNT COMMON XDARK, X100, OPTO, ASHRAD, PLTA, PLTB COMMON PLTC, IABSA, IABSB, IABSC, PABSA, PABSB, PABSC INTEGER DEST, ASHT, FREQ, ARC, ELEM REAL IABSA, IABSB, IABSC, MAG LOGICAL OPTO, ASHRAD, DARK, PLTA, PLTB, PLTC, BACK DIMENSION UDATA (400) BACK (400) DIMENSION IDATA (400), IBACK (400) С С CALL SUBROUTINE DRATE TO CONVERT THE INTEGER DATA ACQUISITION C FREQUENCY (FREQ) TO THE INTERFACE COMPATIBLE FORM (IDRATE). С CALL DRATE (IDRATE) С С CONVERT THE REAL DESP TO AN INTEGER FOR LOADING INTO THE DAC. С IF (DESP .LT. 2048.) IDESP = IFIX (DESP) ELSE IDESP = IFIX (DESP - 2048.)S CLA CLL TAD IDESP S TAD (4000 S DCA IDESP S

ENDIF С CONVERT THE REAL ASHP TO AN INTEGER FOR LOADING INTO THE DAC С Ċ C AND STRIP OUT THE AMPLIFIER SETTING. IF (ASHP .LT. 2048.) IASHP = IFIX (ASHP) RASHP = FLOAT (IASHP) ELSE IASHP = IFIX (ASHP - 2048.) CLA CLL S TAD IASHP S TAD (4000 DCA IASHP S S S TAD IASHP AND (3777 S S DCA JASHP RASHP = FLOAT (JASHP) + 2048. ENDIF AMPC = (ASHP - RASHP) * 10.0 RAMPC = (2.0 ** AMPC) + 0.1 IAMPC = IFIX (RAMPC) С CONVERT THE REAL ATMP TO AN INTEGER FOR LOADING INTO THE DAC С AND STRIP OUT THE AMPLIFIER SETTING. С С IF (ATMP .LT. 2048.) IATMP = IFIX (ATMP) RATMP = FLOAT (IATMP) ELSE IATMP = IFIX (ATMP - 2048.) CLA CLL TAD IATMP S S TAD (4000 S S DCA iATMP TAD IATMP AND (3777 S S S DCA JATMP RATMP = FLOAT (JATMP) + 2048. ENDIF AMPA = (ATMP - RATMP) * 10.0 RAMPA = (2.0 ** AMPA) + 0.1 IAMPA = IFIX (RAMPA) С TAKE A 100% TRANSMITTANCE READING. С С CALL XAVE (X100) С ISSUE A PROMPT TO DEPOSIT THE SAMPLE THEN TYPE (CR). С С WRITE (1,99) 99 FORMAT (//, 'DEPOSIT SAMPLE TYPE CR', //) S 6032 SR, KSF JMP R S

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S 6032 CONTINUE IZ = 0JZ = 0LZ = 0MZ = 0IASHD = 0 IATMD = 0C CONVERT THE DESOLVATION TIMING DATA TO A FORM SUITABLE FOR С Ĉ LOADING INTO THE INTERFACE. IZ = DESTIZ = IZ - 1010 JZ = JZ + 1IF (IZ .GE. 10) GO TO 10 IF (IZ .LT. 0) JZ = 0IZ = IZ + 10ENDÌF С C C C CONVERT THE ASH TIMING DATA TO A FORM SUITABLE FOR LOADING INTO THE INTERFACE. LZ = ASHTLZ = LZ - 10MZ = MZ + 111 IF (LZ .GE. 10) GO TO 11 IF (LZ .LT. 0) MZ = 0LZ = LZ + 10ENDIF С Ċ C CALCULATE THE NUMBER OF DATA POINTS TO BE TAKEN AND CHECK FOR A COMMON OVERFLOW. С COUNT = (ATMT * FLOAT (FREQ)) IF (COUNT .GT. 400.) WRITE (1,15) FORMAT (' TO MUCH DATA. RETURNING TO INPUT') 15 CALL INPUT ENDIF ICOUNT = IFIX (COUNT) S CLA CLL /TAD THE DESP INTO THE AC S TAD IDESP **SSSSSSSCCC** 6646 /LOAD DAC BUFFER WITH THE DESP **CLA CLL** TAD (0015 /TAD POWER PROGRAMMING INTO AC /TEMPERATURE PROGRAMMING CHANNEL SELECT 6642 /BLOCK 5009 OUTPUT AT THE "OR" GATE /DISABLE THE 74190 TIMER /DISABLE ADC CLOCK 6300 6316 6311 START THE DESOLVATION CYCLE.

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DESOLVATION TIMING SEQUENCE FOR DEST GREATER THAN С 10 AND NOT AN INTEGER MULTIPLE OF 10. С C IF (JZ .GT. 0 .AND. IZ .GT. 0) S CLA CLL TAD JZ S S RTL S RTL S TAD (0007 /BLOCK 5009 OUTPUT AT THE "OR" GATE
/DISABLE THE 74190 TIMER S 6300 S 6316 /LATCH TIMING DATA OUT S 6304 /ENABLE THE 5009 CLOCK AT THE "OR" GATE S 6306 /LOAD THE DAC AND START THE BURN /START THE 74190 TIMER S 6647 S 6305 ŝ CLA CLL s S TAD 1Z RTL S RTL TAD (0006 \mathbf{S} /SKIP IF TIMER DONE SA, 6313 JMP A s /BLOCK 5009 OUTPUT AT THE "OR" GATE S 6300 /DISABLE THE 74190 TIMER S 6316 /LATCH TIMING DATA OUT S 6304 VENABLE THE 5009 CLOCK AT THE "OR" GATE VSTART THE 74190 TIMER S 6306 6305 С GO TO THE ASH TIMING CYCLE. С С GO TO 12 ENDIF С DESOLVATION TIMING SEQUENCE FOR DEST GREATER THAN С C C 10 AND AN INTEGER MULTIPLE OF 10. IF (JZ .GT. 0 .AND. IZ .EQ. 0) CLA CLL \mathbf{S} S TAD JZ S RIL S RIL $\bar{\mathbf{s}}$ TAD (0007 /BLOCK 5009 OUTPUT AT THE "OR" GATE
/DISABLE THE 74190 TIMER
/LATCH TIMING DATA OUT S 6300 ŝ 6316 S 6304 /ENABLE THE 5009 CLOCK AT THE "OR" GATE S 6306 /LOAD THE DAC AND START THE BURN S 6647 S 6305 /START THE 74190 TIMER С GO TO ASH TIMING CYCLE. С C GO TO 12 ENDIF С DESOLVATION TIMING SEQUENCE FOR DEST LESS THAN 10. С

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С IF (JZ .EQ. 0 .AND. IZ .GT. 0) CLA CLL TAD 1Z S S ~~~~~~ RTL RTL TAD (0006 6304 **/LATCH TIMING DATA OUT** 6306 /ENABLE THE 5009 CLOCK AT THE "OR" GATE /LOAD THE DAC AND START THE BURN 6647 6305 /START THE 74190 TIMER GO TO THE ASH TIMING CYCLE. С GO TO 12 ENDIF С Ċ C START THE ASH CYCLE. 12 CONTINUE CLA CLL TAD 1ASHP 888000000 /TAD THE ASHP INTO THE AC /LOAD DAC BUFFER WITH THE ASHP 6646 IF RADIATION PROGRAMMING IS TO BE USED DURING THE ASH CYCLE SWITCH THE TEMPERATURE PROGRAM CHANNEL TO THE PHOTOTRANSISTOR AND SELECT THE APPROPRIATE AMPLIFIER SETTING. IF (ASHRAD) S CLA CLL S TAD IAMPC 5555 CMA AND (0017 RTL RTL TAD (0007 DCA 1ASHD S \mathbf{S} ENDIF С IF RADIATION PROGRAMMING IS NOT TO BE USED KEEP THE POWER PROGRAMMING CHANNEL SELECTED. С С С IF (.NOT. ASHRAD) CLA CLL TAD (6735 S \mathbf{S} \mathbf{S} DCA IASHD ENDIF С С ASH TIMIMG SEQUENCE FOR ASHT GREATER THAN 10 AND NOT С AN INTEGER MULTIPLE OF 10. Ĉ IF (MZ .GT. 0 .AND. LZ .GT. 0) CLA CLL 8 TAD mZ \mathbf{S}

•
S	RTL	
S	RTL	
S	TAD (0007	
SB,	6313	SKIP IF TIMER DUNE
8	JMP B	ADI OOF BOOD OUTDIT AT THE BODE CATE
8	6300	VDLOUK DUDY UUIFUI AI IHE 'UR' GAIE
5	6310	ZIATCH TIMINC DATA AUT
5	4304 6304	VENABLE THE BOOG CLOCK AT THE "OR" CATE
8	6305	START THE 74199 TIMER
8	CLA CLL	BIARI IND FIFE IIIMA
S	TAD LASHD	TAD THE ASH CYCLE PARAMETERS INTO THE AC
š	6644	/LATCH TRANS. AMP CHANNEL
š	6642	/TEMPERATURE PROGRAMMING CHANNEL SELECT
ŝ	6647	/LOAD THE DAC AND START THE BURN
S	CLA CLL	
S	TAD 1Z	
S	RTL	
S	RTL	
S	TAD (0006	
SC,	6313	SKIP IF TIMER DONE
S	JMP C	
S	6300	BLOCK 5009 OUTPUT AT THE "OR" GATE
S	6316	/DISABLE THE 74190 TIMER
S	6304	VENADLE THE BOOD CLOCK AT THE SODS CATE
5	0300 6005	VENADLE INE DUUY CLUCK AI INE UN GAIE
5	0303	/SIARI INE (4190 IIAER
	CO TO THE ATOMIZ	ATION CYCLE
C	GO IO IIIE AIOMIA	LATION CIGLE:
9	GO TO 13	
	ENDIF	
С		
C	ASH TIMIMG SEQUE	ENCE FOR ASHT CREATER THAN 10 AND
C	AN INTEGER MULII	PLE OF 10.
С		
	IF (MZ .GT. 0 ./	AND. LZ .EQ. 0)
S	CLA CLL	
S	TAD mZ	
S	RTL	
S	RTL	
S	TAD (0007	OF THE TIME DOVE
SD,	6313	/SKIP IF TIMER DONE
3		ADI OCH BOOD OUTDITT AT THE BOR CATE
5	6916	ADIGADIE THE 74100 TIMER
5	0310 4904	ZIATCH TIMING DATA AUT
8	6306	VENABLE THE 5009 CLOCK AT THE "OR" GATE
5	6305	START THE 74190 TIMER
S	CLA CLL	
š	TAD IASHD	/TAD THE ASH PARAMETERS INTO THE AC
ŝ	6644	/LATCH TRANS. AMP CHANNEL
S	6642	/TEMPERATURE PROGRAMMING CHANNEL SELECT
S	6647	/LOAD THE DAC AND START THE BURN
С		

a

GO TO THE ATOMIZATION CYCLE. С С GO TO 13 ENDIF С C ASH TIMIMG SEQUENCE FOR ASHT LESS THAN 10. С IF (MZ .EQ. 0 .AND. LZ .GT. 0) CLA CLL S s TAD 1Z S RTL S RTL TAD (0006 S SE. /SKIP IF TIMER DONE 6313 S JMP E /BLOCK 5009 OUTPUT AT THE "OR" GATE S 6300 /DISABLE THE 74190 TIMER S 6316 S /LATCH TIMING DATA OUT 6304 /ENABLE THE 5009 CLOCK AT THE "OR" GATE
/START THE 74190 TIMER \mathbf{S} 6306 S 6305 \mathbf{S} **CLA CLL** S TAD IASHD /TAD THE ASH PARAMETERS INTO THE AC /LATCH TRANS. AMP CHANNEL S 6644 S 6642 /TEMPERATURE PROGRAMMING CHANNEL SELECT /LOAD THE DAC AND START THE BURN S 6647 С GO TO THE ATOMIZATION CYCLE. С С GO TO 13 ENDIF С С START THE ATOMIZATION CYCLE. С 13 CONTINUE CLA CLL S /TAD THE ATMP INTO THE AC s TAD IATMP $\bar{\mathbf{S}}$ 6646 /LOAD DAC BUFFER WITH THE ATMP \mathbf{S} **CLA CLL** S TAD IAMPA /TAD THE AMP SETTING INTO THE AC CMA S S AND (0017 /SELECT THE PHOTODIODE TEMPERATURE PROGRAM CHANNEL RTL RTL RTL RTL TAD (0013 DCA IATMD • S C **CLA CLL** C DATA ACQUISITION SEQUENCE FOR USE WHEN THE OPTO-INTERUPTOR TRIGGERS THE ADC CONVERSION. С С IF (OPTO) 6534 **/BLOCK THE OPTO SIGNAL AT THE "AND" GATE** S **/DISABLE ADC CLOCK** 6311 S

Q	6891	ZDISABIE THE START BURN PULSE
0	(500)	OLOCY THE SHALL DOLL TOLES
8	6532	CLOCK THE SHA INTO THE SAMPLE HODE
S	6423	CLEAR ADC DONE FLAG
S	6421	/CLEAR SKIP ON HOLD FLAG
8	6530	ZENABLE START BURN PULSE
6		
8		
8	TAD IAIMD	
SF,	6313	SKIP IF TIMER DONE
S	JMP F	
8	6642	TEMPERATURE PROGRAMMING CHANNEL SELECT
6	6643	ATCH DIODE AMP CHANNEL
0		ATOM DIVUD AM CMANNED
8	CLA LLL	
C		
C	TAKE ICOUNT NUM	BER OF DATA POINTS.
Ċ		
ŭ	DO 16 I = 1 IC	OT MALE AND A DECEMBER OF A
	10 10 1 - 1, 10	
	NDATA = 0	
S	6533	/ENABLE OPTO PULSES TO PASS
SG.	6420	/SKIP ON SHA HOLD
6	IMP C	
0	6400	TAVE DATA DII CE
3	0422	TAKE DATA FULSE
SH,	6424	SKIP ON CONVERSION DONE
S	JMP H	
S	6425	/JAM TRANSFER DATA TO THE AC
ē	6423	CLEAR ADC DONE FLAG
5	6401	CLEAR SKIP ON HOLD FLAC
5	0421	CLEAR SKIP ON DOLD FLAG
S	DCA nDATA	
	IDATA (I) = NDA	TA
16	CONTINUE	
S	6531	DISABLE THE START BURN PULSE
6	6601 664R	CLEAR DAC (KILL RURN)
8	0040	ADLOCK THE ODTO CLOWAL AT THE LAND! CATE
5	0034	BLUCK THE OFTO SIGNAL AT THE AND GATE
S	6532	CLOCK THE SHA INTO THE SAMPLE MODE
S	6300	/BLOCK 5009 OUTPUT AT THE "OR" GATE
S	6316	DISABLE THE 74190 TIMER
G	CLA CLL	
5		
5	TAD (0000	
8	6304	/LATCH TIMING DATA OUT
S	6306	/ENABLE THE 5009 CLOCK AT THE "OR" GATE
S	CLA CLL	
	ENDIF	
S	NOP	
0	NOI	
L L		
C	DATA ACQUISITIO	N SEQUENCE FOR USE WHEN THE DATA
C	ACQUISITION FRE	QUENCY IS CONTROLLED BY THE INTERNAL CLOCK.
C		
-	IF (NOT. OPTO)	
6	4894	ARIACK THE OPTO SIGNAL AT THE "AND" CATE
3		ADICADIE ADO CIOCV
5	0311	/ DIDADLE AUG GLUGK
S	6531	DISABLE THE START BURN PULSE
S	6532	CLOCK THE SHA INTO THE SAMPLE MODE
S	6423	CLEAR THE ADC DONE FLAG
5	6401	CLEAR SKIP ON HOLD FLAC
3	U741	ADVADLE OTADT DIDN DID SE
5	0030	/ENADLE START DURN FULSE
S	CLA CLL	

S	TAD IATMD	
SL,	6313	SKIP IF TIMER DONE
S	JMP L	
S	6642	/TEMPERATURE PROGRAMMING CHANNEL SELECT
8	6643	<pre>/LATCH DIODE AMP CHANNEL</pre>
S	CLA CLL	
8	TAD IDRATE	/TAD DATA ACQUISITION FREQUENCY INTO THE AC
8	6300	/BLOCK 5009 OUTPUT AT THE "OR" GATE
S	6316	/DISABLE THE 74190 TIMER
S	6304	/LATCH TIMING DATA OUT
S	6306	/ENABLE THE 5009 CLOCK AT THE "OR" GATE
8	6305	START THE 74190 TIMER
S	6312	ZENABLE ADC CLOCK
S	CLA CLL	
C		
C	TAKE ICOUNT NUM	BER OF DATA POINTS.
C	DO 14 J =1. ICO	UNT
	NDATA = 0	
SJ.	6420	/SKIP ON SHA HOLD
8	JMP J	
S	6422	/TAKE DATA PULSE
SK.	6424	SKIP ON CONVERSION DONE
8	JMP K	
S	6425	/JAM TRANSFER DATA TO THE AC
S	6532	CLOCK THE SHA INTO THE SAMPLE MODE
S	DCA nDATA	
_	IDATA (J) = NDA	TA
S	6421	CLEAR SKIP ON HOLD FLAG
S	6423	CLEAR THE ADC DONE FLAG
14	CONTINUE	
8	6531	/DISABLE THE START BURN PULSE
8	6645	/CLEAR DAC (KILL BURN)
8	CLA CLL	
S	TAD (7353	
8	6644	/LATCH TRANS. AMP CHANNEL
8	6642	TEMPERATURE PROGRAMMING CHANNEL SELECT
8	6643	✓LATCH DIODE AMP CHANNEL
8	6311	DISABLE ADC CLOCK
8	6532	CLOCK THE SHA INTO THE SAMPLE MODE
S	6300	∕BLOCK 5009 OUTPUT AT THE "OR" GATE
8	6316	/DISABLE THE 74190 TIMER
S	CLA CLL	
S	TAD (0006	
S	6304	∕LATCH TIMING DATA OUT
S	6306	∕ENABLE THE 5009 CLOCK AT THE "OR" GATE
S	CLA CLL	
	ENDIF	
S	NOP	
C		
C	IF OPTIONS "OF"	AND "BT" WERE SPECIFIED TAKE A BLANK
C	BLACKBODY RUN.	
C		
-	IF (.NOT. OPTO	.AND. BACKO
8	CLA CLL	
S	6300	/BLOCK 5009 OUTPUT AT THE "OR" GATE

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S	6316	/DISABLE THE 74190 TIMER
Ē	TAD (0226	
5	(004	A ATCH TINING DATA OFF
5	0304	LAIGH IIMING DAIA OUI
S	6306	ZENABLE THE 5009 CLOCK AT THE "UR" GATE
S	6305	/START THE 74190 TIMER
S	CLA CLL	
6	TAD IASUD	TAD THE ASHP INTO THE AC
8		A CAD THE DAC DIFFED WITH THE ACUD
S	0040	LUAD THE DAL BUFFER WITH THE ASH
S	CLA CLL	
S	TAD (0126	
SM.	6313	SKIP IF TIMER DONE
0	IMD M	
8		ADLACK BAAA AITTDITT AT THE BADE CATE
S	0300	BLUCK 5009 UUIFUI AI THE 'UN' GATE
S	6316	DISABLE THE 74190 TIMER
S	6304	∕LATCH TIMING DATA OUT
ŝ	6306	ZENABLE THE 5009 CLOCK AT THE "OR" GATE
6		
8		
S	TAD TASHD	
S	6644	/LATCH TRANS. AMP CHANNEL
S	6642	TEMPERATURE PROGRAMMING CHANNEL SELECT
ŝ	6305	START THE 74190 TIMER
6	6647	VIOAD THE DAC AND START THE BURN
8		DOAD THE DAG AND START THE DOR
S	ULA ULL	
S	TAD IATMP	TAD THE ATMP INTO THE AC
S	6646	/LOAD THE DAC BUFFER WITH THE ATMP
S	CLA CLL	
6	TAD LATMD	
3		OT FAR THE ADD DONE FLAC
S	6423	CLEAR THE ADU DONE FLAG
S	6421	CLEAR SKIP ON HOLD FLAG
S	6534	/BLOCK THE OPTO SIGNAL AT THE "AND" GATE
8	6531	DISABLE THE START BURN PULSE
ē	6822	CLOCK THE SHA INTO THE SAMPLE MODE
8	(5002	VENADI E OTADT DID DID CE
5	0530	CIVID IN MINOR DOWN
SN,	6313	SKIP IF TIMER DUNE
S	JMP N	
S	6642	TEMPERATURE PROGRAMMING CHANNEL SELECT
6	6643	ATATCH DIODE AMP CHANNEL
5		/ LATON DIODE AM CHAMMED
S	CLA CLL	
S	TAD IDRATE	TAD THE DATA ACQUISITION FREQUENCY INTO AC
S	6300	/BLOCK 5009 OUTPUT AT THE "OR" GATE
S	6316	DISABLE THE 74190 TIMER
0	6304	ATCH TIMING DATA OUT
0	(00)	VENADLE THE BOOD CLOCK AT THE SORS CATE
5	0300	PENABLE THE JUST CLOCK AT THE OR GATE
S	6312	ZENABLE ADC CLUCK
C		
Č	TAKE ICOUNT NUM	BER OF DATA POINTS.
č		
U U		AIDIT
	DO I f I = I, IC	
	NDATA = 0	
SO.	6420	/SKIP ON SHA HOLD
S	JMP O	
2	6422	TAKE DATA PILSE
3	V766 6 4 0 4	ANTE AN CONTEDETON DANE
sr,	0429	ADVIL AN CONACUSION DANG
8	JMP P	
S	6425	/JAM TRANSFER DATA TO THE AC

S	6532	CLOCK THE SHA INTO THE SAMPLE MODE
S	DCA nDATA	
	IBACK (I) = NDA	ΓΑ
S	6421	CLEAR SKIP ON HOLD FLAG
S	6423	CLEAR THE ADC DONE FLAG
17	CONTINUE	
8	6531	/DISABLE THE START BURN PULSE
8	6645	/CLEAR DAC (KILL BURN)
S	6311	/DISABLE ADC CLOCK
S	6532	CLOCK THE SHA INTO THE SAMPLE MODE
S	6300	/BLOCK 5009 OUTPUT AT THE "OR" GATE
S	6316	/DISABLE THE 74190 TIMER
S	CLA CLL	
S	TAD (0006	
S	6304	<pre>/LATCH TIMING DATA OUT</pre>
S	6306	/ENABLE THE 5009 CLOCK AT THE "OR" GATE
S	CLA CLL	
	ENDIF	
	CALL ERASE	
C		
C	RETURN TO THE MA	AIN PROGRAM.
L	RETURN END	

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PROGRAM NAME: DRATE.FT J. T. GANO **PROGRAMMER:** VERSION 1-A 24-SEP-79 **PROGRAM FUNCTION:** DRATE CONVERTS THE DATA ACQUISITION FREQUENCY SO THAT IT CAN BE PASSED TO THE INTERFACE **CALL DRATE (IDRATE)** CALLING FORM: **PROGRAM EXECUTION:** 1. LOAD THE DATA ACQUISITION FREQUENCY INTO THE AC. ROTATE THE AC LEFT AND INCREMENT NUM UNTIL THE 2. LINK IS SET. BRANCH TO THE APPROPRIATE PROGRAM SEGMENT TO SET IDRATE TO THE VALUE CORRESPONDING TO THE FREQUENCY. 3. THE DATA ACQUISITION FREQUENCIES ALLOWED ARE 1,2,5, 4. 10,20,50,100,200,500,1000 AND 2000 HZ. ANY OTHER FREQ. WILL BE INTERPRETED AS ONE OF THESE. RETURN TO THE CALLING PROGRAM. 5. SUBROUTINE DRATE (IDRATE) С С COMMON IDATA, IBACK CONMON DEST, ASHT, ATMT, DESP, ASHP, ATMP COMMON DEST, ASHT, ATMT, DESP, ASHP, ATMP COMMON SAMP, AMNT, CONC, MAG, FREQ, BACK, ICOUNT COMMON XDARK, X100, OPTO, ASHRAD, PLTA, PLTB COMMON PLTC, IABSA, IABSB, IABSC, PABSA, PABSB, PABSC INTEGER DEST, ASHT, FREQ, ARG, ELEM REAL IABSA, IABSB, IABSC, MAG LOGICAL OPTO, ASHRAD, DARK, PLTA, PLTB, PLTC, BACK DIMENSION IDATA (490) IBACK (490) DIMENSION IDATA (400), IBACK (400) С C S IOF **/CPU INTERUPT OFF** /BLOCK 5009 OUTPUT AT THE "OR" GATE /DISABLE THE 74190 TIMER S 6300 S 6316 S 6314 **/CLOCK BOARD INTERUPT DISABLE** S 6311 **/DISABLE ADC CLOCK** NUM = 0SC1, **/SABR COUNTER LOCATIONS** A SC2. Ø CLA CLL S 8 TAD C1 **ZERO AC ROTATION COUNTER** DCA C2 S 8 **CLA CLL** S TAD fREQ **/LOAD AC WITH FREQ DATA** 8 RAL SA, RAL /ROTATE TILL LINK IS SET ISZ C2 **/COUNT NUMBER OF AC ROTATIONS** 8

S	SNL	SKIP IF LINK SET
S	JMP A	∕TRY AGAIN
S	CLA CLL	
S	TAD C2	
S	DCA nUM	
-	GO TO (10, 11, 12, 13, 1	4.15.16.17.18.19.20) NUM
10	CONTINUE	
S	CLA	
8	TAD (1002	ZMART 2000 H7 DATA
5	DCA I IDRATE	FOUNT TO IDRATE
9	DETION	PECKE IC IDIGIE
11	CONTINUE	
5		WARE 1000 TO DATA
S	TAD (0003	MAKE IUUU HE DATA
S	DCA I IDRATE	/EQUAL TO IDRATE
	RETURN	
12	CONTINUE	
S	CLA	
S	TAD (0403	∕MAKE 500 HZ DATA
S	DCA I IDRATE	✓EQUAL TO IDRATE
	RETURN	
13	CONTINUE	
S	CLA	
ŝ	TAD (1003	∕MAKE 200 HZ DATA
ŝ	DCA I IDBATE	ZEQUAL TO IDRATE
0	BETTIRN	
14	CONTINUE	
6	CLA	
5		ZMAKE 100 H7 DATA
3	DCA I ADDATE	FOULT TO IDRATE
3	DCA I IDAALE DETUDN	/ EQUAL TO IDIGITE
15	CONTINUE	
S	CLA	WAVE BO WE DATA
S	TAD (0404	MAKE DU HZ DATA
S	DCA I IDRATE	ZEQUAL TO IDRATE
	RETURN	
16	CONTINUE	
S	CLA	
S	TAD (1004	∕MAKE 20 HZ DATA
S	DCA I IDRATE	∕EQUAL TO IDRATE
	RETURN	
17	CONTINUE	
S	CLA	
ŝ	TAD (0005	∕MAKE 10 HZ DATA
ŝ	DCA I IDRATE	ZEQUAL TO IDRATE
0	BETHEN	
18	CONTINUE	
S	CLA	
9	TAD (0405	MAKE 5 HZ DATA
0	DCA I IDDATE	FOULT TO IDRATE
3	DUAL I IDIALE DUTTION	
••		
19	CURTINUE	
2		INARTE O BY DATA
S	TAD (1005	ATAKE Z HZ DATA
S	DCA I IDRATE	ZEQUAL TU IDRATE

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	RETURN	
20	CONTINUE	
8	CLA	
S	TAD (0006	∕MAKE 1 HZ DATA
S	DCA I IDRATE RETURN END	∕EQUAL TO IDRATE

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С **PROGRAM NAME:** PLOT.FT **PROGRAMMER:** J. T. GANO 29-0CT-79 VERSION 1-A **PROGRAM FUNCTION:** PLOT CALCULATES THE INTEGRATED ABSORBANCE AND PLOTS THE ABSORBANCE VS TIME DATA CALLING FORM: CALL PLOT **PROGRAM EXECUTION:** INITIALIZE THE PEAK AND INTEGRATED ABSORBANCE TO 0.0. 1. CALCULATE THE 100 % (10) TRANSMITTANCE VALUE BY SUBTRACTING THE DARK CURRENT READING FROM THE FULL SCALE (SHUTTER 2. OPEN) READING. CONVERT THE INTEGER INTENSITY DATA (I) TO REAL FLOATING з. POINT. FIND THE INDIVIDUAL ABSORBANCE VALUES AND STORE THEM IN 4. AN ARRAY. CALCULATE THE INTEGRATED AND PEAK ABSORBANCE VALUES. IF A BLANK BRAID EMISSION READING WAS TAKEN, FOLLOW 5. 6. THE SAME PROCEDURE FOR BOTH THE ANALYTE DATA AND THE IN THE ABSORBANCE CALCULATION SUBTRACT THE BLANK DATA. BLANK FROM THE ANALYTE DATA. IF DATA WERE TAKEN USING THE "OPTO" OPTION, ALTERNATING DATA POINTS REPRESENT BACKGROUND AND BACKGROUND + ANALYTE 7. ABSORBANCE. CALCULATE THE TIME-ABSORBANCE PLOT FOR BOTH DATA SETS AND SUBTRACT THE BACKGROUND PLOT FROM THE BACK-GROUND + ANALYTE PLOT TO OBTAIN THE BACKGROUND CORRECTED DATA. PLOT THE DATA ACCORDING TO THE SPECIFIED OPTIONS. 8. 9. IF OPTION "PB" HAS BEEN SPECIFIED RECORD THE DATA ON THE DSK. SUBROUTINE PLOT COMMON IDATA, IBACK COMMON DEST, ASHT, ATMT, DESP, ASHP, ATMP COMMON SAMP, AMNT, CONC, MAG, FREQ, BACK, ICOUNT COMMON XDARK, X100, OPTO, ASHRAD, PLTA, PLTB COMMON PLTC, IABSA, IABSB, IABSC, PABSA, PABSB, PABSC INTEGER DEST, ASHT, FREQ, ARG, ELEM REAL IABSA, IABSB, IABSC, MAG LOGICAL OPTO, ASHRAD, DARK, PLTA, PLTB, PLTC, BACK DIMENSION IDATA (400), IBACK (400) DIMENSION AB1 (200), AB2 (200) INITIALIZE THE PEAK AND INTEGRATED ABSORBANCES TO 0.0. PABSA = 0.0IABSA = 0.0

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PABSB = 0.0IABSB = 0.0SIO = X100 - XDARK CALL ERASE С CALCULATIONS FOR OPTIONS "OF" AND "BF". С С IF (.NOT. OPTO .AND. .NOT. BACK) DO 21 I = 1, ICOUNT С C CONVERT THE INTEGER DATA TO REAL FLOATING POINT. С KDATA = IDATA (I) IF (KDATA .GE. 0) RDATA = FLOAT (KDATA) ELSE **CLA CLL** 8 TAD KDATA \mathbf{S} S AND (3777 S DCA kDATA RDATA = FLOAT (KDATA) + 2048. ENDIF С CALCULATE THE INDIVIDUAL ABSORBANCE VALUES, THE INTEGRATED С ABSORBANCE AND THE PEAK ABSORBANCE. С С AB1 (I) = ALOG (SIO / (RDATA - XDARKO) / 2.303 IF (PABSA .LT. AB1 (I)) PABSA = AB1 (I) IABSA = IABSA + AB1 (I) CONTINUE 21 С SCALE THE DATA FOR PLOTTING. C С IXS = (1000/ICOUNT)YS = 740./ PABSA ENDIF С CALCULATIONS FOR OPTIONS "OF" AND "BT". С Ċ IF (.NOT. OPTO .AND. BACK) BO 22 N = 1, ICOUNT С CONVERT THE INTEGER DATA TO REAL FLOATING POINT. С č KDATA = IDATA (N) JDATA = IBACK (N) IF (KDATA .GE. 0) RDATA = FLOAT (KDATA) ELSE CLA CLL S TAD kDATA \mathbf{S} AND (3777 DCA kDATA s S RDATA = FLOAT (KDATA) + 2048.

ENDIF IF (JDATA .GE. 0) SDATA = FLOAT (JDATA) ELSE S CLA CLL TAD JDATA AND (3777 S S S DCA JDATA SDATA = FLOAT (JDATA) + 2048. ENDIF С CALCULATE THE INDIVIDUAL (BLANK CORRECTED) ABSORBANCE VALUES, С THE INTEGRATED ABSORBANCE AND THE PEAK ABSORBANCE. Ĉ С AB1 (N) = ALOG (SIO / ((RDATA - SDATA) + SIO)) / 2.303 IF (PABSA .LT. AB1 (N)) PABSA = AB1 (N) IABSA = IABSA + AB1 (N) CONTINUE 22 IXS = (1000 / ICOUNT) YS = (740. / PABSA) ENDIF С Ĉ CALCULATIONS FOR OPTION "OT". С IF (OPTO) $\mathbf{M} = \mathbf{0}$ DO 26 N = 1, ICOUNT, 2 С CONVERT THE BACKGROUND INTEGER DATA TO REAL FLOATING POINT. Č KDATA = IDATA (N) IF (KDATA .GE. 0) RDATA = FLOAT (KDATA) ELSE CLA CLL S S TAD **kDATA** AND (3777 \mathbf{S} S DCA kDATA RDATA = FLOAT (KDATA) + 2948. ENDIF С CONVERT THE BACKGROUND + ANALYTE DATA TO REAL FLOATING POINT. С Ĉ JDATA = IDATA (N + 1)IF (JDATA .GE. 0) SDATA = FLOAT (JDATA) ELSE CLA CLL TAD JDATA AND (3777 S S S S DCA JDATA SDATA = FLOAT (JDATA) + 2048. ENDIF С

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CALCULATE THE BACKGROUND ABSORBANCE DATA AND THE BACKGROUND + ANALYTE ABSORBANCE DATA. SUBTRACT THE BACKGROUND DATA FROM
С
           ANALYTE ABSORBANCE DATA. SUBTRACT THE BACKGROUND DATA FROM
THE BACKGROUND + ANALYTE DATA TO OBTAIN THE BACKGROUND
CORRECTED DATA. CALCULATE THE INTEGRATED AND PEAK ABSORBANCE.
С
C
C
С
           M = M + 1
           AB2 (M) = ALOG (SIO / (RDATA - XDARK)) / 2.303
           ABS = ALOG (SIO / (SDATA - XDARK)) / 2.303
           AB1 (M) = ABS - AB2 (M)
IF (PABSB .LT. AB2 (M) PABSB = AB2 (M)
            IABSB = IABSB + AB2 (M)
            IF (PABSA .LT. AB1 (M)) PABSA = AB1 (M)
            IABSA = IABSA + AB1 (M)
           CONTINUE
26
            ICOUNT = ICOUNT / 2
           IXS = 1000 / ICOUNT
YS = 740. / PABSA
           ENDIF
С
С
           PLOT THE DATA ACCORDING TO THE SPECIFIED OPTIONS.
Ĉ
       FORMAT (///, 'A',///, 'B',///, 'S',///, 'O',///, 'R',///
1 ,'B',///, 'A',///, 'N',///, 'C',///, 'E')
WRITE (1,20)
           WRITE (1,10)
10
           FORMAT (///, 15X, 'T', 15X, 'I', 15X, 'M', 15X, 'E')
20
           CALL FDIS (0,20,780)
CALL FDIS (1,20,40)
           CALL FDIS (1, 1023, 40)
           DO 23 N = 1, ICOUNT
YI = (AB1 (N) * YS) + 40.
IY = IFIX (YI)
            IX = (IXS * N) + 20
           CALL FDIS (-1, IX, IY)
23
           CONTINUE
           IF (PLTC . AND. BACK)
           DO 24 I = 1, ICOUNT
           KDATA = IBACK (I)
           IF (KDATA .GE. 0)
           RDATA = FLOAT (KDATA)
           ELSE
           CLA CLL
TAD LDATA
S
S
S
           AND (3777
S
           DCA kDATA
           RDATA = FLOAT (KDATA) + 2048.
           ENDIF
           AB1 (I) = ALOG (SIO / (RDATA - XDARK)) / 2.303
           CONTINUE
24
           DO 28 N =1, ICOUNT
           YI = (AB1 (N) * YS) + 40.0
           IY = IFIX (YI)
           IX = (IXS * N) + 20
CALL FDIS (1, IX, IY)
28
           CONTINUE
```

	ENDIF
	IF (PLTC .AND. OPTO)
	DO 25 N = 1. ICOUNT
	YI = (AB2 (N) * YS) + 40.
	IY = IFIX (YI)
	IX = (IXS * N) + 20
	CALL FDIS (1, IX, IY)
25	CONTINUE
	ENDIF
	CALL HOME
C	
č	IF OPTION "PB" RECORD THE DATA ON THE DSK.
č	
u	IF (PLTB)
	BEAD (1.31) IA
31	FORMAT (' KEEP DATA? Y OR N '.A1)
•••	IF (IA, FQ, 'Y')
	BEAD (1.32) FNAME
32	FORMAT ('ENTER FILE NAME A6 '.A6)
	CALL OOPEN ('DSK', FNAME)
	DO 33 I = 1. ICOUNT
	WRITE (4.34) AB1 (1)
34	FORMAT ('RD', E15.5)
33	CONTINUE
	CALL OCLOSE
	ENDIF
	ENDIF
	RETURN
	END

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