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THE DEVELOPMENT AND CHARACTERIZATION OF AN

ELECTROTHERMAL VAPORIZATION SAMPLE INTRODUCTION

SYSTEM FOR THE INDUCTIVELY COUPLED PLASMA

by

Ⓒ DONALD R. HULL

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF DOCTOR OF PHILOSOPHY

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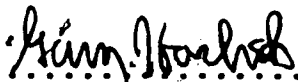
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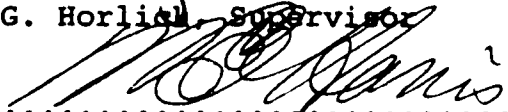
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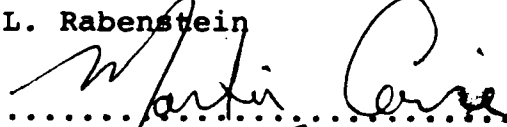
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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled THE DEVELOPMENT AND CHARACTERIZATION OF AN ELECTROTHERMAL VAPORIZATION SAMPLE INTRODUCTION SYSTEM FOR THE INDUCTIVELY COUPLED PLASMA submitted by DONALD R. HULL in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Analytical Chemistry.

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Dedication

The author wishes to dedicate this work to those who most made it possible, his parents.

My Father:

    He taught me that a man must continue on,

    even when he stumbles and falls.

My Mother:

    She showed me that the necessary courage

    is there if you only reach deep enough

    inside.

No son has ever received greater gifts or more love.

ABSTRACT

The analytical aspects of the use of a graphite cup electrothermal atomizer in combination with inductively coupled argon plasma-optical emission spectrometers has been investigated as a means of analyzing small volume samples in solution and for the direct analysis of solid samples.

Preliminary investigations using single element solutions and a single channel detector system have illustrated the temporal behavior and analytical capabilities of electrothermal atomization-inductively coupled argon plasma-optical emission spectroscopy. The temporal studies have shown that changes of emission background are present during atomization and that the analyte emission profile changes with increasing analyte amount. The analytical studies have shown that a linear dynamic range of three to four orders of magnitude is possible.

A study of the effect of a NaCl matrix on the emission of Pb has shown that changes take place in the vertical emission profile and in the background emission levels. Use of a matching reference blank and proper choice of slit height and position have been shown to allow correct analysis of lead at a NaCl concentration greater than that of sea water.

Spex G-Standards and National Bureau of Standards-Standard Reference Materials have been used to test the

direct analysis of solids. These studies show that matrix
effects are present but that direct solids analysis is
possible.

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Professor G. Horlick has exerted a major influence on the author's professional life during the course of this work. He helped develop the problem, offered invaluable suggestions and help in the experimental work, provided excellent experimental facilities and a stimulating environment in which the research could be conducted.

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CHAPTER I

Introduction

Optical emission spectroscopy (OES) utilizing an inductively coupled argon plasma (ICAP) source is the direct descendent of Bunsen and Kirchhoff's discovery that the spectra of flames colored by metallic salts were characteristic of the metals. In inductively coupled argon plasma-optical emission spectroscopy (ICAP-OES) the ICAP replaces the flame as an energy source capable of transforming a sample from a solid, liquid, or gas into atomic vapor and then exciting these atoms to a higher electronic energy state from which photon emission can take place. This photon emission process can be thought of as encoding information about the sample in terms of frequency, intensity, time, and space. Decoding and recovery of this information about the sample is generally accomplished by means of a spectrometer. A general diagram of this process is shown in Figure 1 (1).

Research in the use of an ICAP (then called an induction-coupled plasma torch) as an optical emission source was independently performed by Greenfield (2) and Fassel (3) in the early 1960's and the first commercial instrument was introduced in 1974 (4). In the six short years since, ICAP-OES sales have captured an important
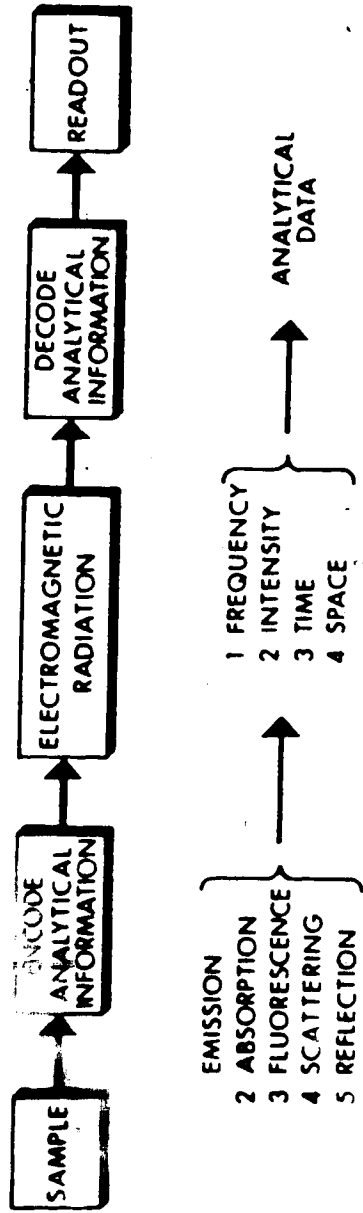
Figure 1. Spectrochemical measurement block diagram.

share of the OES instrument market because of several important characteristics of the ICAP source. The high temperature, chemical inertness and optical thinness of this source result in low detection limits, high sensitivities, linear responses of four to five orders of magnitude with respect to concentration, and low interference effects. ICAP-OES with the various commercial instruments can be used to simultaneously analyze qualitatively and quantitatively for 25 to 35 metal and metalloid elements in 30 or more samples per hour.

A major limit on ICAP-OES has been the almost exclusive use of pneumatic nebulization to introduce samples into the plasma. This sample introduction method requires that samples either be liquid or be converted to a solution and that several mL of sample be available. The use of samples in solution has several advantages such as the following, which are taken from an article by Boumans (5):

"a) Many samples are given as liquids, e.g. biological fluids, surface and effluent waters, oils, soil extracts, samples in wet chemical laboratories.
b) Dissolution of solids prior to analysis circumvents interferences due to the solid structure; consequently accurate results can be attained with relatively simple reference samples (standards).
c) Bulk analysis of inhomogeneous samples is feasible."

While most samples can be converted into a liquid form this is often a difficult and time-consuming process and

analytical errors often enter the analysis at this step.

These problems are again summarized well by Boumans (5):

"1)   the dissolution of a solid sample may be
      time-consuming and difficult;
 2)   there is a risk of contamination;
 3)   there is a risk of losses of volatile elements;
 4)   the dissolution of a solid entails a dilution,
      and this may lead to poor detection limits
      unless high efficiency of sample introduction
      and excitation compensate for this."

Boumans' summary of the performance of ICAP-OES and

other established methods is shown in Table I from Reference

5.   This comparison shows that ICAP-OES has the multi-

element capability lacking in flame atomic emission and

absorption (AES/AAS) or furnace atomic absorption (furnace

AAS) and better precision and/or accuracy than furnace

AAS, Arc AES, or liquid analysis with the spark-rotrode

combination.   X-Ray fluorescence spectrometry (XRFS) is

an excellent technique except that without preconcentration

its detection limits for liquid samples are approximately

three orders of magnitude greater than those of ICAP-OES.

The major weakness of ICAP-OES is then in the area of

solid sample analysis.   Another weakness of ICAP-OES, which

has received very little attention, is the requirement

that liquid samples have a volume of at least several

milliliters.   This is a requirement of the means used to in-

troduce the sample into the plasma, the pneumatic nebulizer.

Whether the nebulizer used is of a cross-flow or con-

centric construction type their liquid uptake rate is

Table I

Rough Overall Assessment of the Main Analytical Capabilities of Various

"Established" Spectroscopic Methods and ICP-AES

Capability for	Direct solid analysis	Direct liquid analysis	Multi-element analysis	Trace Analysis	Precise Analysis	Accurate Analysis
Flame AES/AAS	-	+	-	+	+	+
Furnace AAS	-')	+	-	+	+	(+)
Arc AES	+	-	+	+	-	-
Spark AES (metals)	+	-	+	(+)	+	+
Spark AES (rotrode)	-	+	+	(+)	+	+
XRFS	+	+	+	-")	+	+
ICP-AES	-')	+	+	+	+	+

Key: + good   - poor   (+) reasonable   (-) unsatisfactory

Notes: ') + with solid sampling technique
        ") + with preconcentration technique

generally between 2 and 5 mL per minute. Since flush out, signal stabilization, and analysis times generally total 1 to 2 minutes it is easy to see why a sample volume of several milliliters is required.

The ICAP was first developed by Reed (6) for use in growing refractory crystals. Figure 2 shows Reed's modified induction-coupled plasma torch. Reed's torch was the precurser of present analytical torches and consisted of three concentric quartz tubes with three independent gas flows. The plasma was formed and centered within the torch by the gas flowing through the outer and intermediate tubes. The powdered refractory material flowed through the central tube in a high velocity stream of gas. This stream was able to punch through the center of the plasma where it was efficiently heated. Reed's intent was to raise the temperature of the powdered refractory material only to the melting point so that it could resolidify and thus allow boules of these refractory materials to be grown. One area needing improvement noted by Reed was that when small particle sizes were used these small particles tended to vaporize and this caused a "considerable increase in radiation". This statement is the start of ICAP-OES.

Since this first application of the ICAP was with a solid material it might be supposed that strong development in this area would continue, however the majority of work has been with liquid sample techniques. The first report
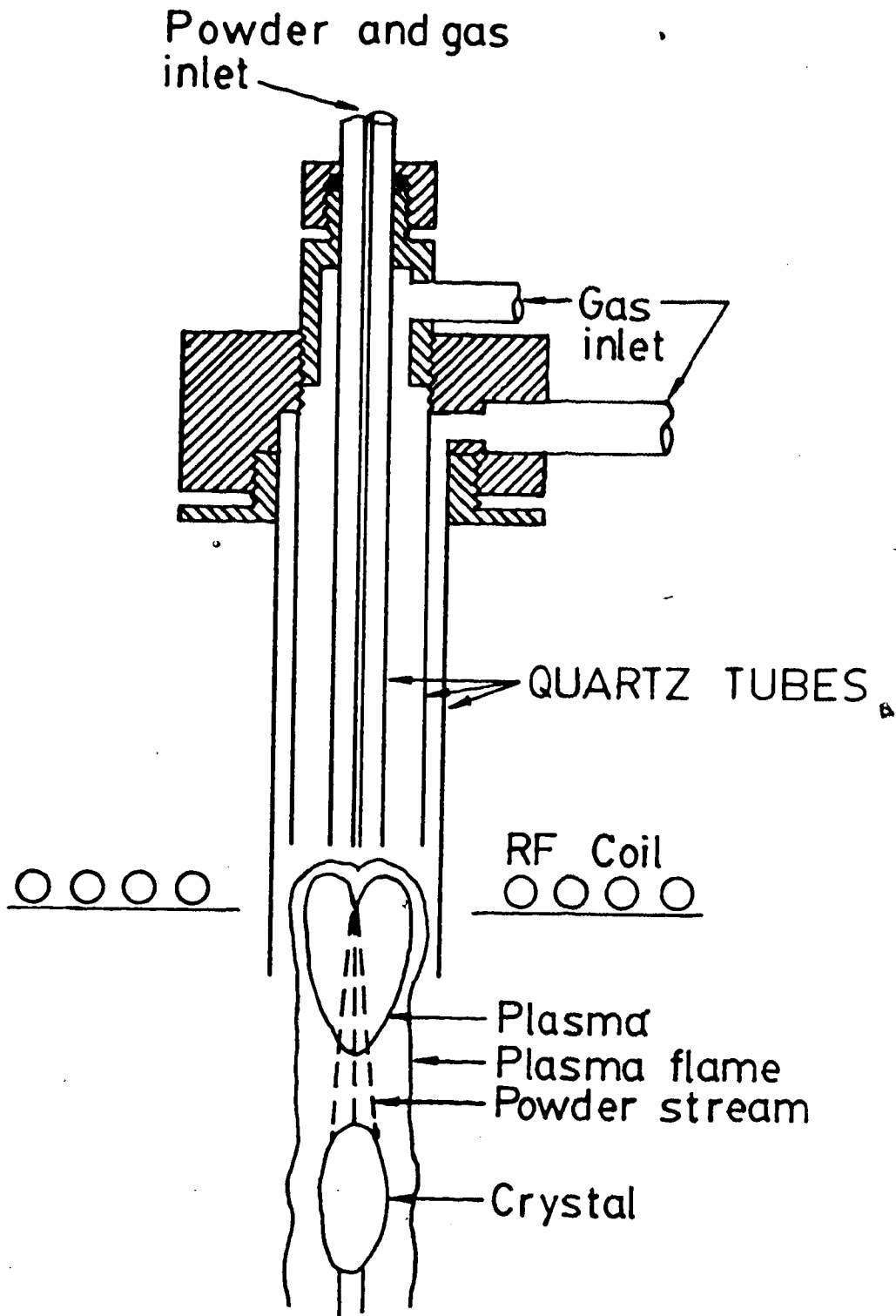
Figure 2. Induction-coupled plasma torch for crystal growth.

of solids analysis by ICAP-OES was in 1967 by Hoare and Mostyn (7). The system of Hoare and Mostyn was used for the analysis of powdered samples and is shown in Figure 3a. The sample was contained in a cup and a combination of mechanical agitation and swirling by a stream of argon gas caused the powder to become suspended in the argon stream for transport to the torch. Hoare and Mostyn reported no difficulty in transporting or smoothly exciting powders of widely different densities with this system, however they found that "the preparative history of the standards is of major importance and should be as near as possible identical to that of the samples". They also reported that it was necessary to use very small particle sizes (#300 mesh screen) and low injection rates since larger particles pass through the plasma virtually unchanged.

Aerosol injection of powders has also been reported by Dickinson (8) and by Dagnall, Smith, and West (9). The sample introduction systems used by Dagnall, et al. are shown in Figure 3b and 3c. The first of these is a swirl cup system similar to that used by Hoare and Mostyn (7). The second system utilized a fluidised bed design and according to the authors was found to work better than the swirl cup arrangement. Mechanical agitation of both systems was found to help smooth delivery of the powder to the plasma. The authors tested sample matrices and rejected several because of particle sticking, high emission

CAPILLARY TUBE
COOLING ARGON
PLASMA ARGON
INJECTION ARGON
RUBBER SEAL
AGITATOR
SILICA TORCH
SCREW CAP
SAMPLE POWDER

(c). Fluidized-bed chamber.
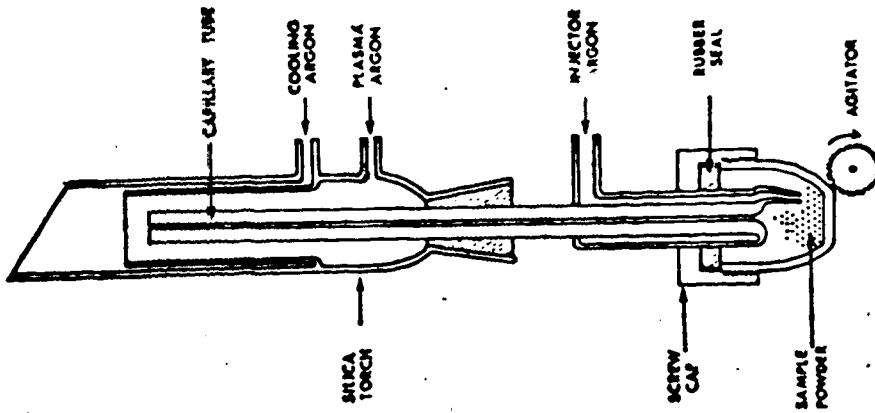
(b). Swirl cup chamber.

Figure 3 (a). Powder injection assembly.

background, or a high contamination level. With a MgO matrix they were able to analyze for added Be and B but found that the powder feed rate decayed exponentially, therefore readings had to be taken after a selected delay time. The calibration curves for Be or B are linear over only about two orders of magnitude compared to the normal three or four orders of magnitude range common to ICAP-OES.

In general the following seem to apply to direct aerosol injection of powders into a plasma:

a) Sample history and matrix are critical.

b) The sample particles must be non-sticking, less than about 10 μm in diameter, and have a small size range.

c) Sample sizes of several grams are required.

d) Emission may vary with time, thereby complicating the measurement.

Pneumatic nebulization of powdered samples suspended in liquid as a slurry has been reported by Chapman and Gordon (10) and Dahlquist (11) has reported vaporization of a slurry from a graphite yarn electrothermal vaporizer, however very little information is available about these procedures. Fassel and Dickinson (12) have reported that low-melting alloys can be analyzed by using ultrasonic nebulization of the molten material but this technique is obviously limited in applicability.

Conductive metals or briquetted materials have been analyzed by a combination of producing an aerosol by

sampling the material with a spark or an arc and then
exciting this aerosol to produce emission with an ICAP.
The use of a remote d.c. arc sampling device was first
reported by Dahlquist, Knoll, and Hoyt (13) in 1975. This
device, in the form of a small remote sampler known as a
Direct Solids Nebulizer (DSN), is now commercially available
from Applied Research Laboratories, Sunland, California.
The DSN has been applied to the analysis of a large
variety of metals ranging from aluminum to steels. The
DSN-ICAP combination has been reported as giving excellent
detection limits, linear calibration curves of two to three
orders of magnitude, minimum matrix effects, and excellent
precision. In contrast direct emission analysis by a.c.
spark or d.c. arc suffers from large matrix effects,
limited linear working ranges, poorer spark detection
limits, and poorer arc precision. The use of an a.c.
spark has been investigated by Human, Scott, Oakes, and
West (14), Norris and Watters, Jr. (15), Brech (16), and
Beaty, Crawford, and Wahlers (17). The SSEA, or Separate
Sampling and Excitation Analysis, discussed by Brech and
Beaty, et al. is based on the work of Norris and Watters and
makes use of a controlled waveform spark source for improved
sampling. While this system is not commercially available
it appears to have similar characteristics to the DSN
system. The major limit on these systems is that they

obviously require electrically conductive samples.

The combination of laser vaporization and separate
a.c. spark excitation for OES is a well known method for
microprobe analysis and for the analysis of nonconducting
materials. Laser vaporization with separate ICAP excitation
for OES has also been applied to the analysis of airborn
particulates collected on a filter by Abercrombie (18) and
for powders and metals by Salin, Carr, and Horlick (19),
Carr and Horlick (20), and Carr (21). Abercrombie con-
sidered the results to be only semiquantitative and used
the technique as a screening method. Carr and co-workers
results are more complete and show excellent detection
limits, fair precision, and reasonable analytical ranges
but severe matrix effects were noted. The expense of a high
power laser for vaporization must also be considered as a
drawback to this technique.

As mentioned earlier the use of a nebulizer for
analysis of liquid samples by ICAP-OES generally requires
a sample volume of several milliliters. In many cases,
such as with biological samples, this can be a severe
restriction. Often dilution of the sample cannot be used
since this might reduce the element of interest to below
an acceptable analytical concentration. In order to
analyze 50 to 100 µL size biological samples Baddiel and
Skerten (22) utilized a flow injection system connected to

an ICAP nebulizer. Greenfield and Smith (23) and Kniseley,
Fassel, and Butler (24) found that as little as 25 µL of
biological fluids could be analyzed by connecting a µL
pipette to the nebulizer liquid intake. A short pulse of
analyte aerosol was thus produced by each of these means and
carried to the ICAP torch in the normal manner. The
detection limits obtained with these pulsed emission
systems would be expected to be considerably higher than
those obtained with integration of a steady emission level
obtained by normal nebulization techniques. The poor
aerosol production by nebulizers (nominally 2-10%) also
means that the sample was inefficiently used.

In the field of atomic absorption spectroscopy electro-
thermal atomization has become an important technique
since it efficiently uses small liquid samples
and produces very low detection limits. Electrothermal
vaporization techniques have been applied to ICAP-OES for
liquids analysis by several researchers. Dahlquist, Knoll,
and Hoyt (13) have reported using a graphite yarn electro-
thermal vaporizer for simultaneous multielement analysis
of urine for Hg, As, and Pb with a 25 µL sample. Detection
limits comparable to or better than those obtained with a
nebulizer were reported for 28 elements and the linear
analytical range was given as greater than two orders of
magnitude. A tantalum strip electrothermal vaporizer was
reported by Nixon, Fassel, and Kniseley (25). Good precision

and very low detection limits were obtained with a sample size of about 100 µL. Recently Gunn, Millard, and Kirkbright (26), Kirkbright and Snook (27), and Millard, Shan, and Kirkbright (28) have reported in a series of papers their work with a graphite rod electrothermal vaporization device for ICAP-OES. This work has concentrated on the analysis of small liquid samples utilizing carrier distillation to lower the detection limits of several elements.

The reported uses of electrothermal vaporization have been limited to liquid samples, however one thermal vaporization technique has been reported for both liquid and solid samples. Salin and Horlick (29,30) have published preliminary results for a direct sample insertion device (DSID) in which the sample is placed in a d.c. arc cup electrode with a boiler cup and this combination directly inserted into the ICAP. Their early data indicates that detection limits and precision comparable to those of d.c. arc can be obtained for liquid samples and that the analysis of powdered samples is possible.

In consideration of some of the previous work above it was decided to investigate the possibility of developing a sample handling device which could be used for the analysis of both small volume liquid samples and solid samples. Requirements for this device were:

1. μL size liquid sample handling capabilities.

2. Solid sample handling capabilities.

3. Single or multielement analysis capabilities.

4. Reasonable analytical ease and speed.

5. Useful detection limits and sensitivity.

6. Useful accuracy and precision.

7. Low matrix effects.

In order to achieve the above goals it was decided to use an AAS graphite carbon cup electrothermal atomization device for sample vaporization and to transport the vaporized sample in a flowing argon stream to the ICAP for OES analysis. The major reasons for this decision were:

1. Carbon cup electrothermal atomizers are able to rapidly reach temperatures capable of vaporizing most elements.

2. The carbon cup electrothermal atomizer is relatively compact and thus could be enclosed in a small flow through cell to keep vapor volume at a minimum and thus detection limits low.

3. Liquid samples can be easily injected into the cup with a syringe allowing rapid and easy analysis of liquid samples.

4. The cup can be easily changed allowing solid materials to be added to the cups and sample weights determined externally.

5. Matrix effects are common in furnace AAS but separate

excitation with the ICAP was expected to reduce this.

6. A large body of literature was available on carbon cup or tube electrothermal vaporization.

CHAPTER II

Instrumentation: Description and Modifications

A generalized block diagram of a spectrochemical measurement system was given in Figure 1. In this chapter a more detailed description of the spectrochemical measurement system used for this experimental work will be presented. Two types of systems were used for decoding the analytical information, a monochromator-photomultiplier detector system and a photodiode array based direct reader system. Each of these systems are shown in detailed block diagrams in Figures 4 and 5 and are described in Section D of this chapter. The readout system is based on the use of a minicomputer for data storage and manipulation and is very similar for both detection systems and will also be described in Section D.

A. The Graphite Furnace

The graphite furnace used throughout this experimental work was developed from a commercially available Varian Model-63 Carbon Rod Atomizer (31). The Carbon Rod Atomizer as it is normally used for atomic absorption spectrometry is shown in Figure 6 from Reference 31. With the Model-63 unit either a tube furnace or a cup furnace may be used. The furnace is held between two graphite rod electrodes which are in turn held by water cooled chromium plated
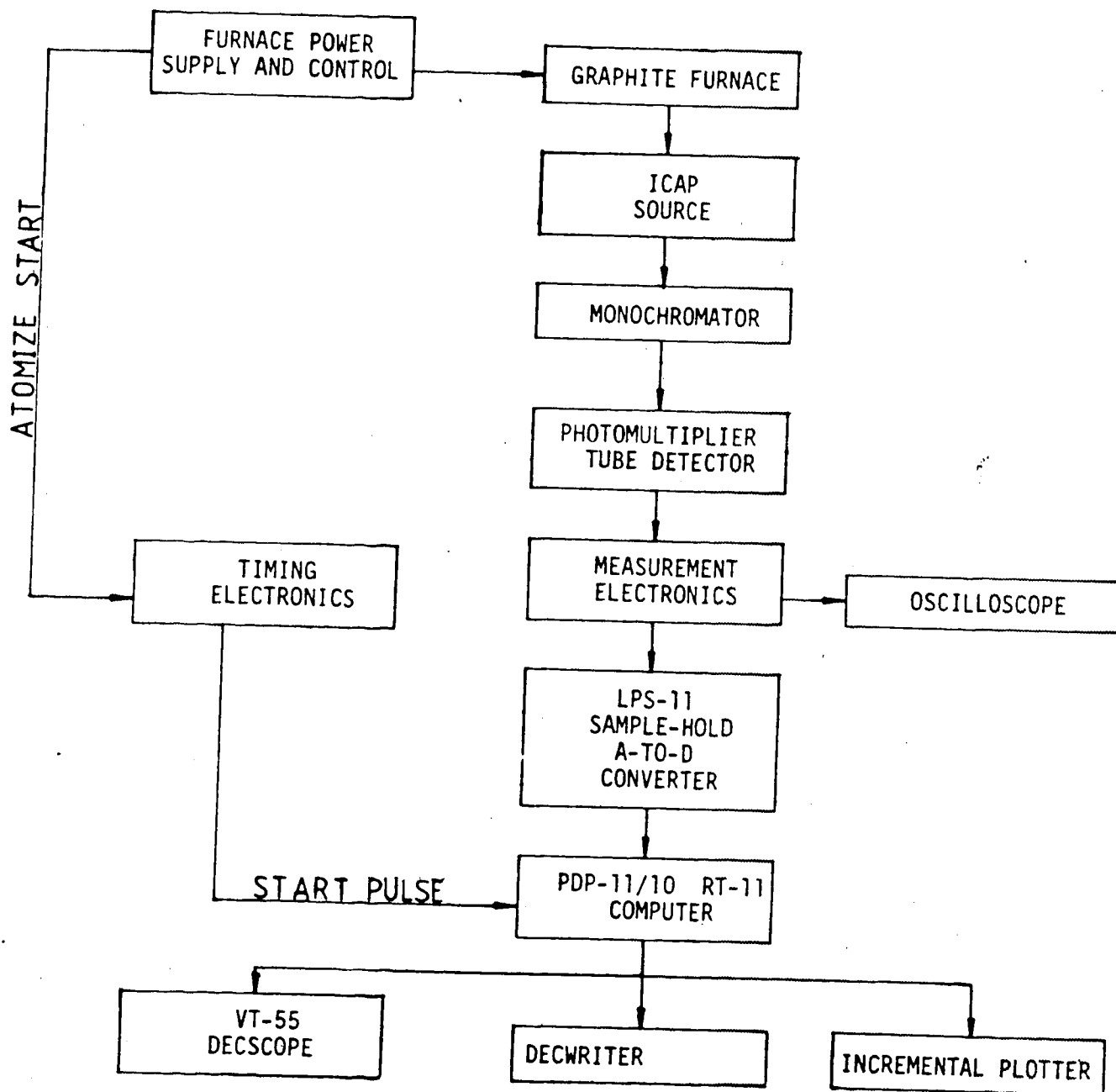
Figure 4. Block diagram of computer coupled photomultiplier spectrometer.

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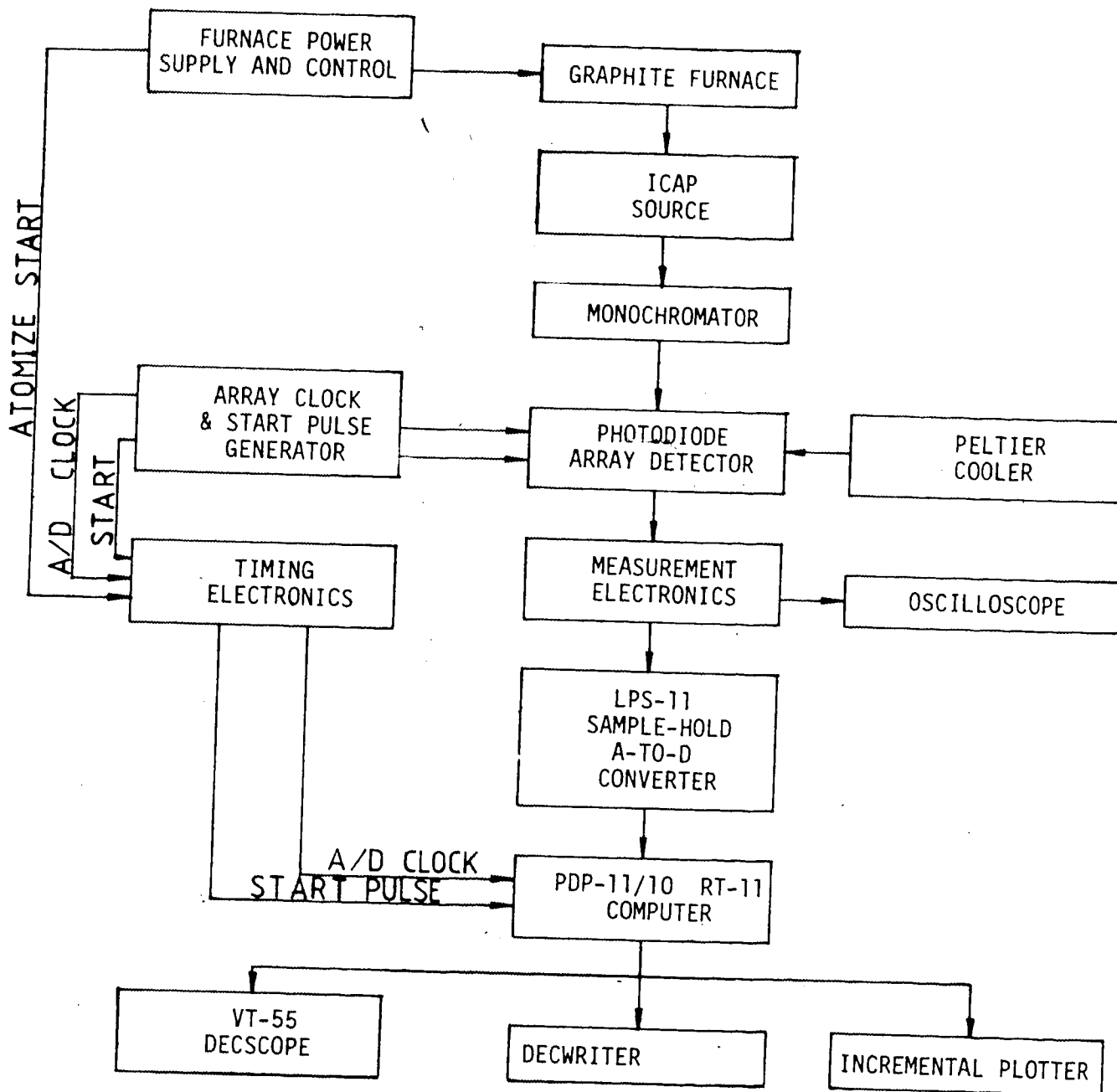
Figure 5. Block diagram of computer coupled photodiode array spectrometer.
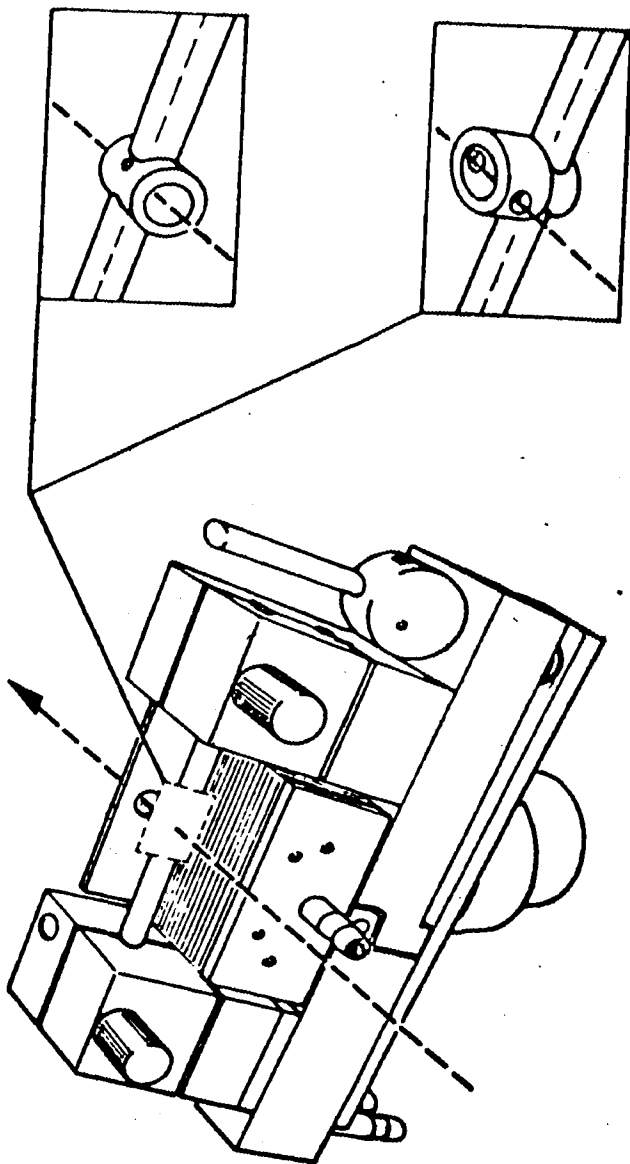
Figure 6. Varian Model 63 Carbon Rod Furnace.

steel clamps. Electrical contact with the electrodes-furnace assembly is also provided by these clamps. For this work the carbon cup shown in the lower right of Figure 6 was used although the carbon cup was modified.

The Model-63 Carbon Rod Furnace was enclosed in a quartz cell which was attached to the bottom of the ICAP torch by a 10 inch long Pyrex tube. The quartz vaporization cell, shown in Figure 7, is in two parts and is constructed from a quartz 35/20 ball-and-socket joint. The two piece construction allows easy access for sample or sample cup changing. The ball-and-socket joint construction also allows flexibility in joining the two halves of the cell after opening and for thermal expansion. Argon flowing through the cell sweeps the analyte vapor from the furnace, out the top of the vaporization cell, and into the plasma.

The vaporization cell is approximately 1 inch in diameter and 4 inches in height with a volume of about 50 mL. Emission intensity is dependent upon the concentration of the analyte in the argon gas introduced into the plasma therefore it is important to keep the vaporization cell volume small. The electrode rods pass through the walls of the lower half of the vaporization cell. O-rings form a seal between the vaporization cell and the steel clamps of the Model-63 Carbon Road Furnace assembly. These o-rings are made by punching a 3/16 inch diameter hole through a

ARGON TO PLASMA

4.1 cm

QUARTZ

CARBON ROD

5.3 cm

ARGON INLET
(REAR)

2.5 cm
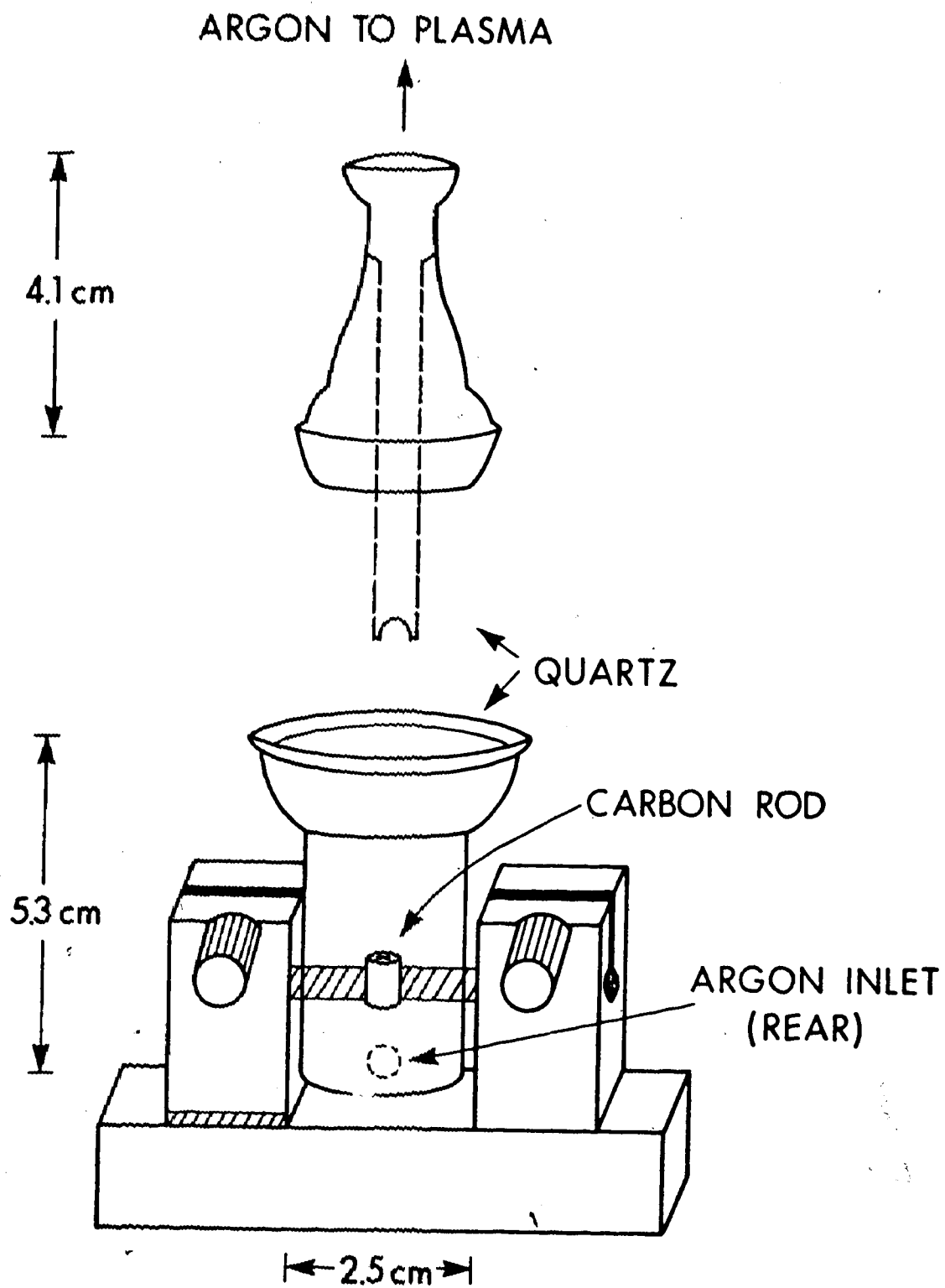
Figure 7.   Vaporization cell for graphite cup EA-ICAP-OES.

high temperature gas chromatograph septum.   O-rings made

from Varian No. 69-000179-01 septums have proven to be

useful for between 50 and 100 atomization cycles. The

argon gas inlet for the vaporization cell is located at the

lower rear of the bottom half of the cell.

The top of the upper half of the vaporization cell is

a 12/5 socket to allow connection to the ICAP torch by means

of the intermediate Pyrex tube mentioned earlier. Although

not shown in Figure II-2 an injection port was added to this

part of the vaporization cell to facilitate the intro-

duction of liquid samples.

The 10 inch intermediate tube which connects the

vaporization cell to the ICAP torch is constructed of 0.5 mm

internal diameter Pyrex tubing. The lower end of the tube

is a 12/5 ball to mate with the vaporization cell while the

upper end is a 12/5 socket which mates with the torch.

About 1 1/4 inches from the lower end is a 3-way stopcock

which allows the cell to be flushed to the atmosphere or

connected straight through to the plasma torch.

1. Modifications of the Graphite Cup

A detailed drawing of the graphite cup is shown in

Figure 8 to illustrate the first major modification. The

normal carbon cup is designed as a two part cup. Electrical

resistance heating takes place in the lower portion of the

← 0.220" →

← 0.115" →

0.180"

Upper
Half
Discarded

← Cut off here

0.180"

Lower
Half
Used

← 0.200" →
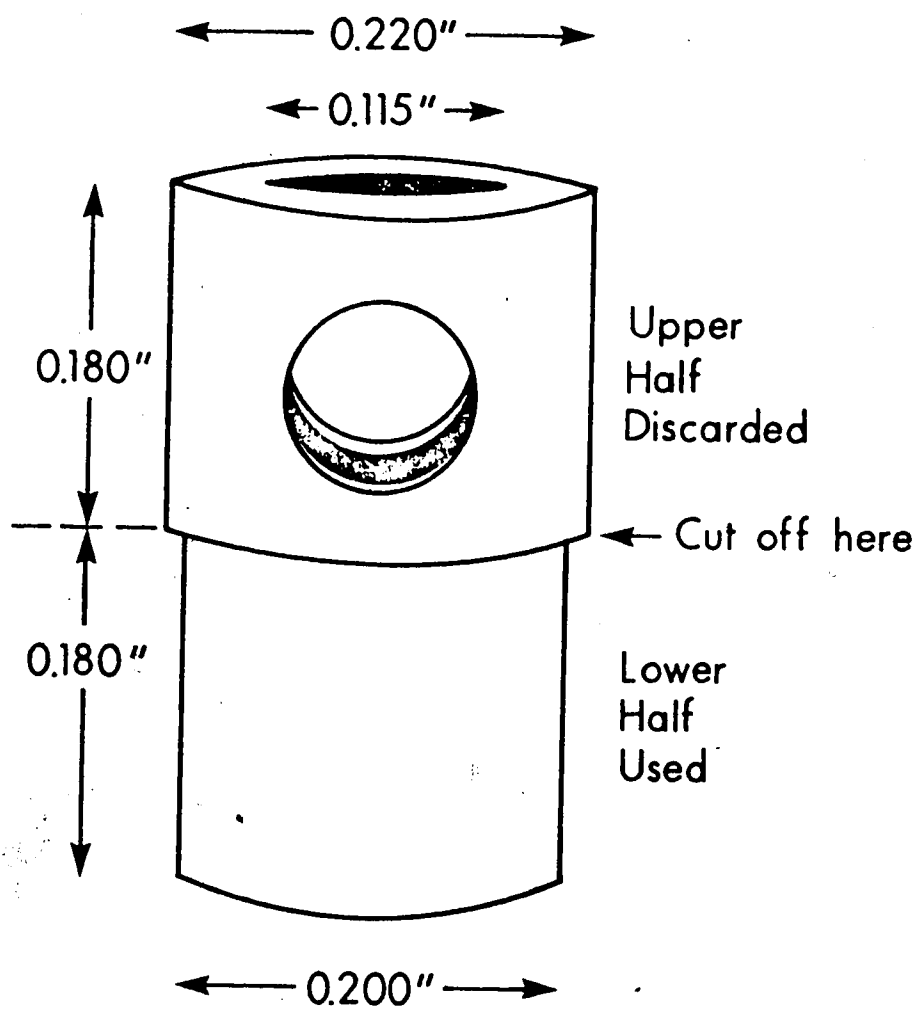
Figure 8. Modification of Varian graphite cup for use in
EA-ICAP-OES.

cup. This heating is controlled by varying the electrical voltage applied to the unit. With the Model 63 this heating control is in three seperate stages for sample drying, ashing, and atomizing.

The first two stages can range from 0 to 60 seconds long with the applied voltage changing instantly at the start of each stage and remaining constant in that stage. The atomization stage can be either a step heating or a ramp heating one. The step heating mode is like the drying and ashing ones except that it is limited to about 10 seconds or less. In the ramp heating mode the applied voltage increases linearaly as a function of time until a pre-selected maximum is reached and heating ceases. The slope for the voltage increase, and thus the heating rate, is variable over a wide range. Shown in Figure 9 (31) is a diagram of applied voltage vs time for the step mode of operation. Typically a temperature of 90-110°C is used for dryinc 500-900°C for ashing and during the atomization stage temperatures in excess of 2500°C may be used to allow atomization of virtually all elements.

The upper portion of the cup is the atomic absorption cell. The atomic vapor produced in the lower portion of the cell during atomization diffuses upward into the atomic absorption spectrometer optical beam, which passes through the apertures in the upper half of the cup, and then out
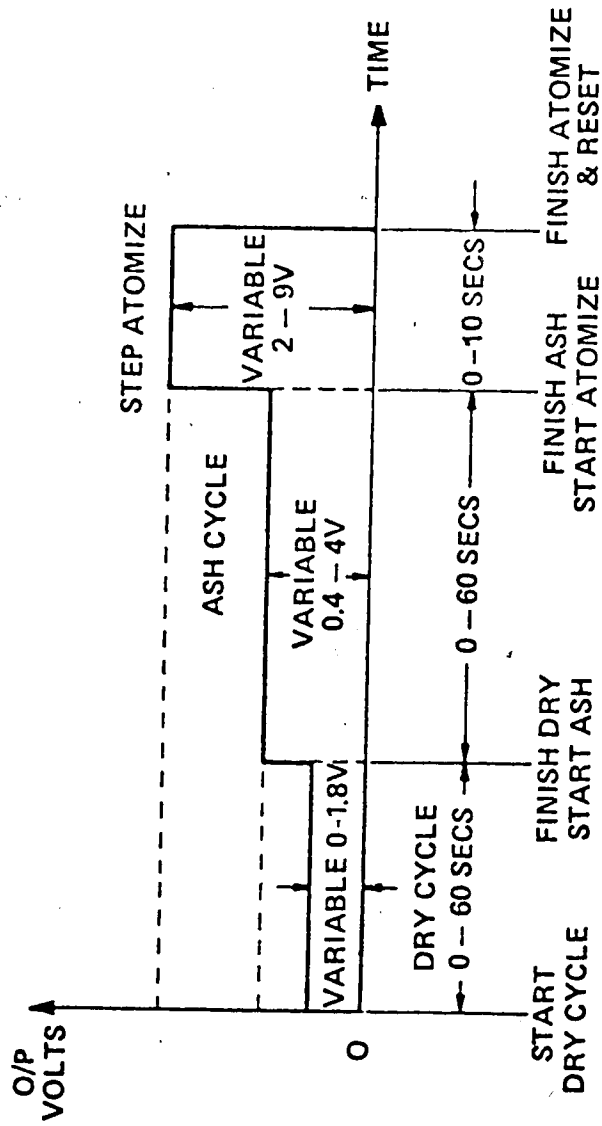
Figure 9. Applied voltage vs time for step mode of operation of the Varian Model 63 Carbon Rod Atomizer.

of the cup. For atomic absorption spectrometry it is de-
sirable to keep the vapor inside the absorption cell for a
fairly long time to simplify the absorption measurement and
to obtain the greatest absorption possible. A long vapor
retention time is achieved by making the cup quite deep with
respect to its width (2.4:1).

One of the difficulties that can be encountered with
this type of furnace is caused by the fact that while the
lower portion of the cup is heated electrically the upper
portion is only heated by conduction. The result is that
the temperature of the upper portion lags behind that of the
lower portion. When the bottom of the cup passes through
the vaporization temperature for the element of interest it
will vaporize and then condensation-revaporization can occur
in the upper portion of the cup. This process is accentuated
when ramp atomization is used since the slower heating allows
a longer time for the condensation-revaporization process
to occur. When this process does occur analyte vapor pro-
duction is not a smooth, continuous process but proceeds as
an irregular and prolonged process and the maximum analyte
vapor concentration is depressed.

The carbon cup atomizer was used in this experimental
work only as a sample vaporization device and a low re-
tention time for the sample vapor was desired. In order to
reduce the retention time most of the upper half of the

atomization cup was cut off and discarded. The small amount
of the upper portion left formed a small lip around the top
of the cup which aided in the vertical positioning of the
cup between the graphite electrodes. The remaining cup was
approximately 0.1 inch deep and had a volume of approximately
2×10^{-2} inches^3 or 30 L. This modification resulted in
four desirable changes.

1. The sample vapor retention time was reduced.

2. Condensation-revaporization in the upper part of the cup
   was eliminated.

3. The mass of the cup was reduced, therefore the heating
   rate was increased.

4. A higher temperature was obtained at any given power
   setting than with the larger normal cup.

The second modification was to change the nature of the
carbon cup itself. Normally graphite is a layered struc-
ture with an inner atomic distance of 1.415 Å within the
layer and a separation of 3.35 Å between the layers (32).
It is possible for many molecules or atoms to penetrate
this loose, layered structure at high temperatures.
Sturgeon and Chakrabarti (33) have determined that the
rate of loss of Mo and V atomic vapor from an uncoated
atomic absorbance graphite tube furnace was increased by
21% and 12%, respectively, over that obtained with pyro-
lytic-graphite-coated tubes. The pyrolitic-graphite coating

porosity, defined as the percentage of volume of the pores in relation to the total volume, is effecti zero, as compared to 17% for regular high-purity graphite (34). This reduction in porosity is brought about by the elimination of the layered structure of regular graphite. The use of pyrolytic-graphite-coated furnaces has become quite common since the reduction of loss through the furnace walls increases sensitivity. The pyrolytic-graphite-coating is also mechanically stronger and has a higher sublimation point than regular graphite therefore furnace life is extended. The Varian No. 56-1000159-00 carbon cup furnaces used in this experimental work were pyrolytic-graphite-coated.

Many elements are also known to react with carbon to form a variety of types of compounds. For atomic absorption spectroscopy the reduction of several metal oxides to the free metal by carbon is extremely beneficial, however some elements can react to form non-volatile refractory carbides. This loss of volatile analyte can be reduced by the use of pyrolytic-graphite-coated furnaces or by first converting the furnace carbon into a nonreactive form. This change is easily accomplished by treating the furnace with a suitable carbide-forming compound such as lanthanum, zirconium, silicon (35), or tantalum (36) prior to use. These stable carbide coatings can reduce carbide formation by other

elements in two ways. The first is by reducing the porosity in a manner similar to pyrolytic-graphite-coating and the second is by preventing contact between carbon of the furnace with the sample.

The treatment of the carbon cup furnaces used in this work with a TaF_5 solution in the   given in Reference 36 was used. The carbon cups were placed in a TaF_5 solution contained in a plastic dish in a vacuum desiccator. The desiccator was evacuated for about one minute and then allowed to refill with air. After a second evacuation the cups, filled with TaF_5 solution, were placed in an oven at 110°C for several hours. Immediately prior to use the furnace was assembled and three or four firings at high temperature completed the reaction between the Ta and the carbon of the furnaces. These firings also served to clean any contamination out of the furnaces. The experimental results indicated that there was some increase in the sensitivity of several elements but there was a loss in the mechanical strength of the furnace. This loss of strength was not important when liquid samples were analyzed and the cups were satisfactory for 50 to 100 atomization cycles. Deterioration was mainly caused by arcing between the electrode rods and the furnace cup. This arcing was present in untreated cups but was worse with the Ta treated cups, perhaps due to a change in electrical conductivity or to a

small change in dimensions causing gaps between the electrode rods and the cup. With solid samples the cups must be removed and replaced with each sample and the Ta treated cups were found to deteriorate much more rapidly than the untreated ones. Because of the design of the furnace used, this arcing problem could not be overcome and the use of Ta treated cups was discontinued with solid samples.

2. Modification of the Varian Model 63 Carbon Cup Atomizer Control/Power Supply

The controller/power supply of the Varian Model 63 Carbon Rod Atomizer normally controls all operation of the carbon rod furnace. This unit contains all necessary electronics for controlling the temperature and timing of the three sequential steps used - Dry, Ash, and Atomize (refer to Figure 9). In order to properly acquire data it was necessary to synchronize data acquisition and the atomization step. The "Trigger" pulse available from the controller/power supply was used for this purpose with the PMT data acquisition system. Additional external circuitry was necessary with the photodiode array spectrometer systems to accurately synchronize the start of the atomization step with the start of an integration cycle of the photo-diode array.

Timing in the Model 63 is by means of a series of three

ramp generator-comparator blocks. A simplified diagram of
a TIMER BLOCK is shown in Figure 10 (31).

When an INPUT TRIGGER pulse is received the HOLD
CIRCUIT opens the RESET SWITCH and closes the switch
connecting the +15 V supply to the RAMP GENERATOR input
circuit causing its output to ramp negative at a constant
rate. When the negative ramp exceeds the magnitude of
the TIME input voltage, set by a front pannel voltage
divider, the COMPARATOR output switches from -15 V to
This pulse is differentiated and the negative pulse is clipped
off to produce a positive OUTPUT PULSE. This pulse is fed
backward to the RESET of the HOLD CIRCUIT and forward as
the INPUT TRIGGER of the next TIMER BLOCK. At the com-
pletion of the Ash step the OUTPUT PULSE is also used as
the external TRIGGER pulse.

A complete diagram of the TIMER BOARD ASSEMBLY is
shown in Figure 11 (31) and a complete description of the
circuit operation can be found in Reference 3. In order
to connect the external circuitry necessary t synchronize
the photodiode array spectrometer systems it was necessary
to modify the connection between the ASH TIMER BLOCK and
the RAMP/STEP switch. The area modified is enclosed in
the heavy dashed line in Figure 11. The modification,
external circuit, and timing diagram are shown in Figure 12.

When switch S1 is in the INTERNAL position the Varian
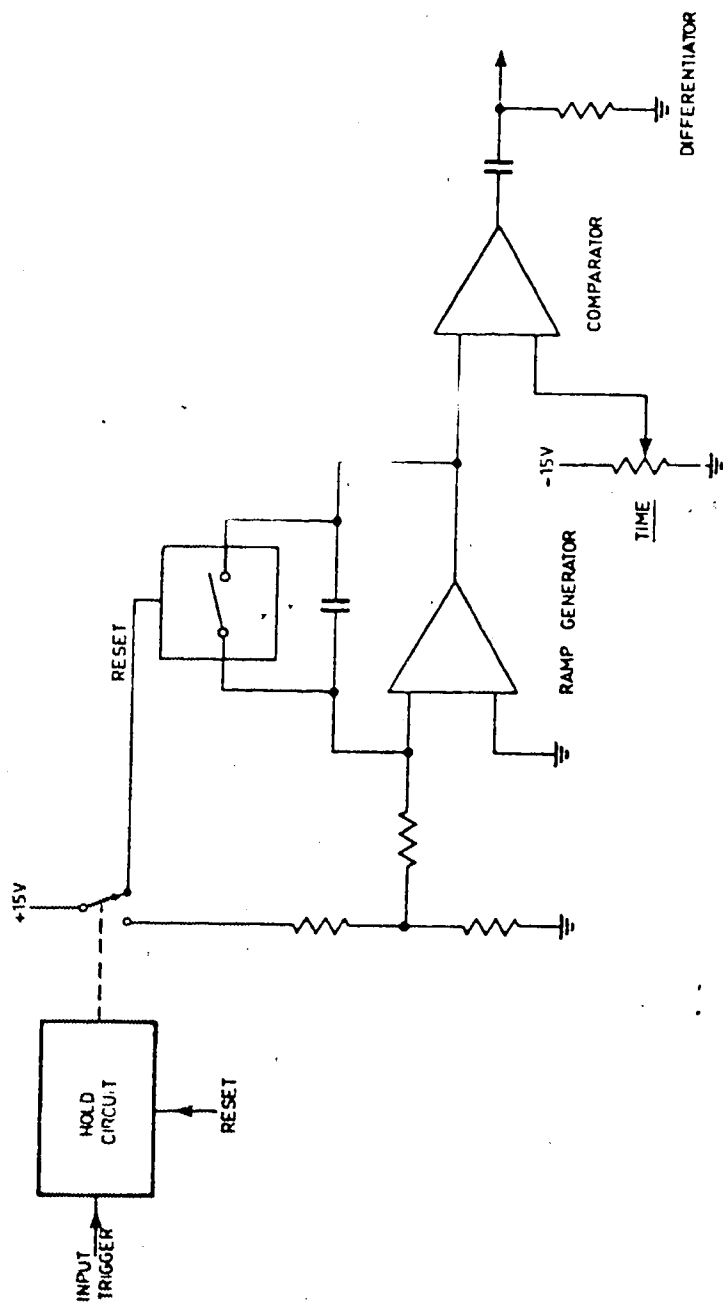
Figure 10. Timer Block – Varian Model 63 Carbon Rod Atomizer Controller/Power Supply.
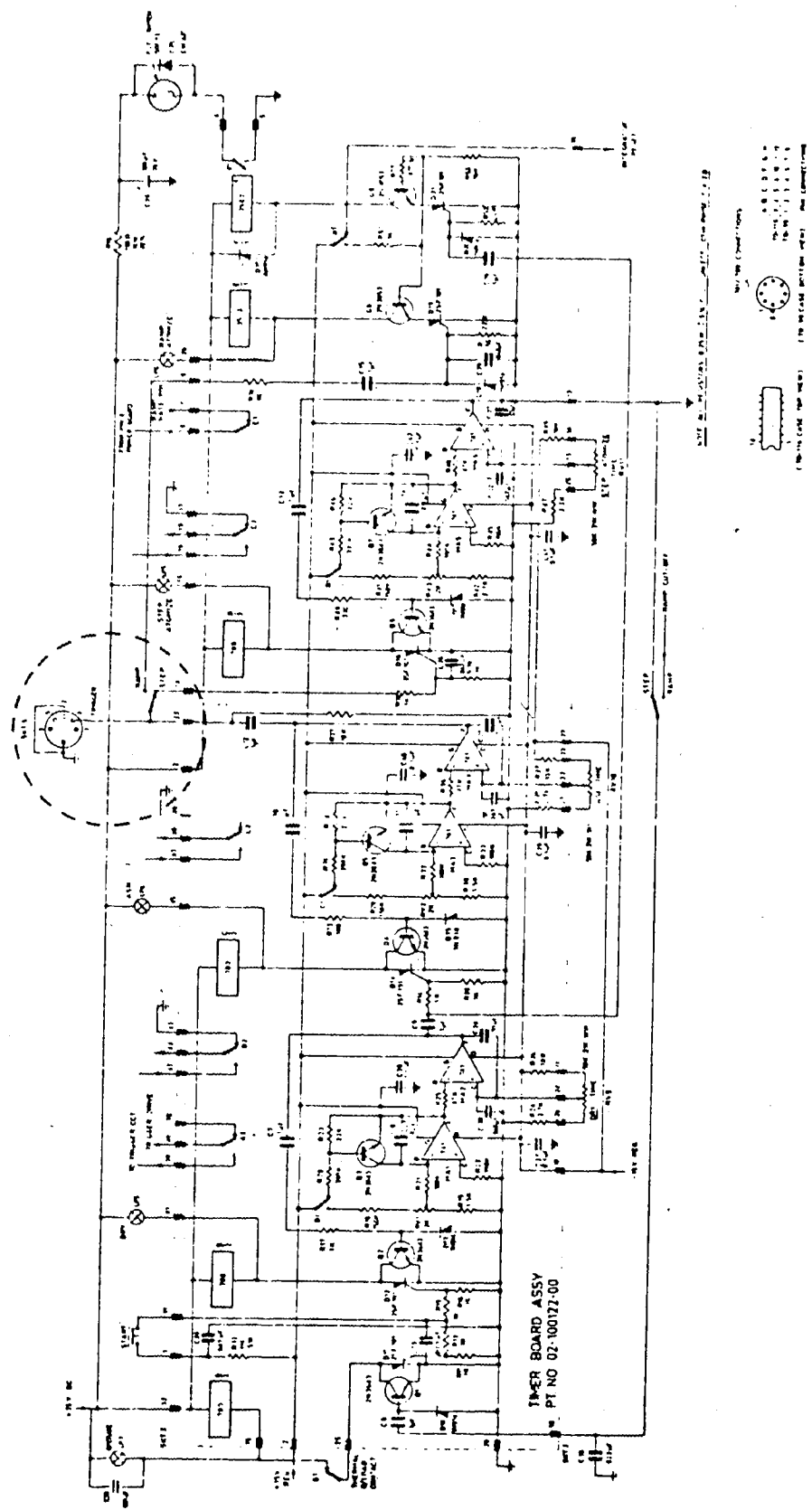
Figure 11. Timer Board Assembly - Varian Model 63 Carbon Rod Atomizer Controller/Power Supply. Circled area shows portion modified as shown in Figure 12.

(a)

(b)
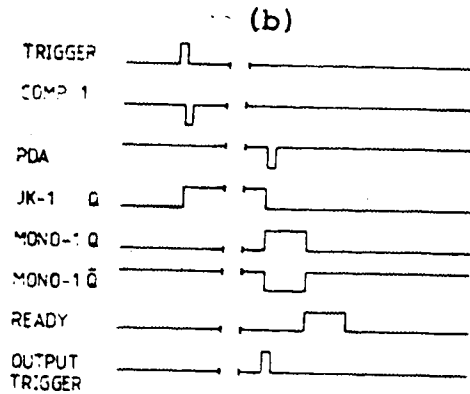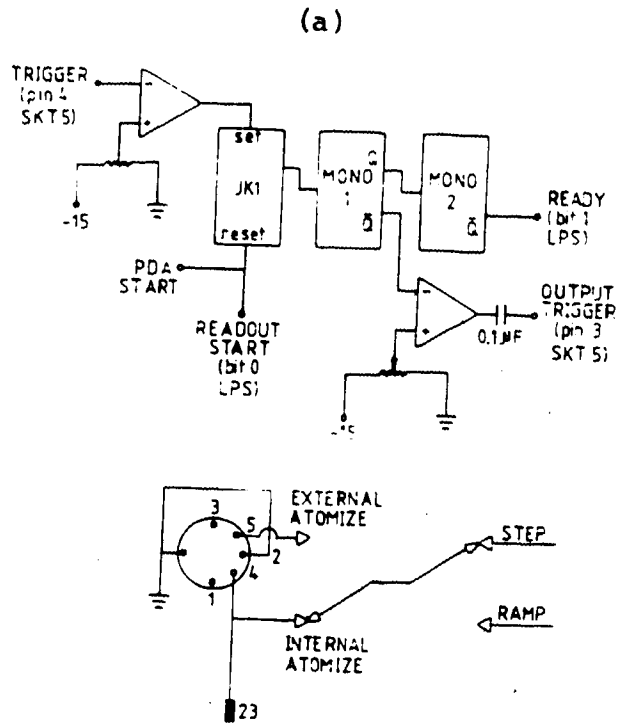
Figure 12. (a) External circuitry and Model 63 modification for synchronizing atomization and photodiode array spectrometer system data acquisition.

(b) Timing diagram.

63 power supply operates in the normal manner. When switch
S1 is in the EXTERNAL position an externally generated
INPUT TRIGGER is connected to the ATOMIZER TIMER BLOCK.
The model 63 TRIGGER pulse from SKT5 causes JK1 to be "set"
and then the next photodiode array READOUT START signal
"results" JK1. These operations produce a positive pulse
at the Q output of JK1, the negative edge of which triggers
MONO stable 1. When MONOstable 1 is triggered the $\bar{Q}$
output changes from -5 V to 0 V for 1 msecond, causing the
output of COMParator 2 to momentarily change from -15 V to
+15 V. This generates a pulse which is returned to the
RAMP/STEP switch via pin 5 of SKT5 and starts the atomization
step. At the end of the pulse from MONOstable 1 the $\bar{Q}$ output
of MONOstable 2 changes to 0 V for 1 msecond. This moment-
ary ground signal is transmitted to the LPS11 parallel
input and serves as the data acquisition READY flag.
Succeeding photodiode array READOUT START signals trigger
acquisition of photodiode array data.

B. Inductively Coupled Argon Plasma

The ICAP used for this work was a 5 KW ICAP manufactured
by Plasma-Therm Inc. (Kreston, N.J.). The ICAP torch used
is shown in Figure 13. The torch supplied by Plasma-Therm
has a constricted outlet for the central, or sample tube.
This central tube was replaced with a 1.5 mm internal diameter

PLASMA GAS
~17 LPM AR

AUXILIARY GAS
~1 LPM AR

AEROSOL GAS
~1 LPM AR
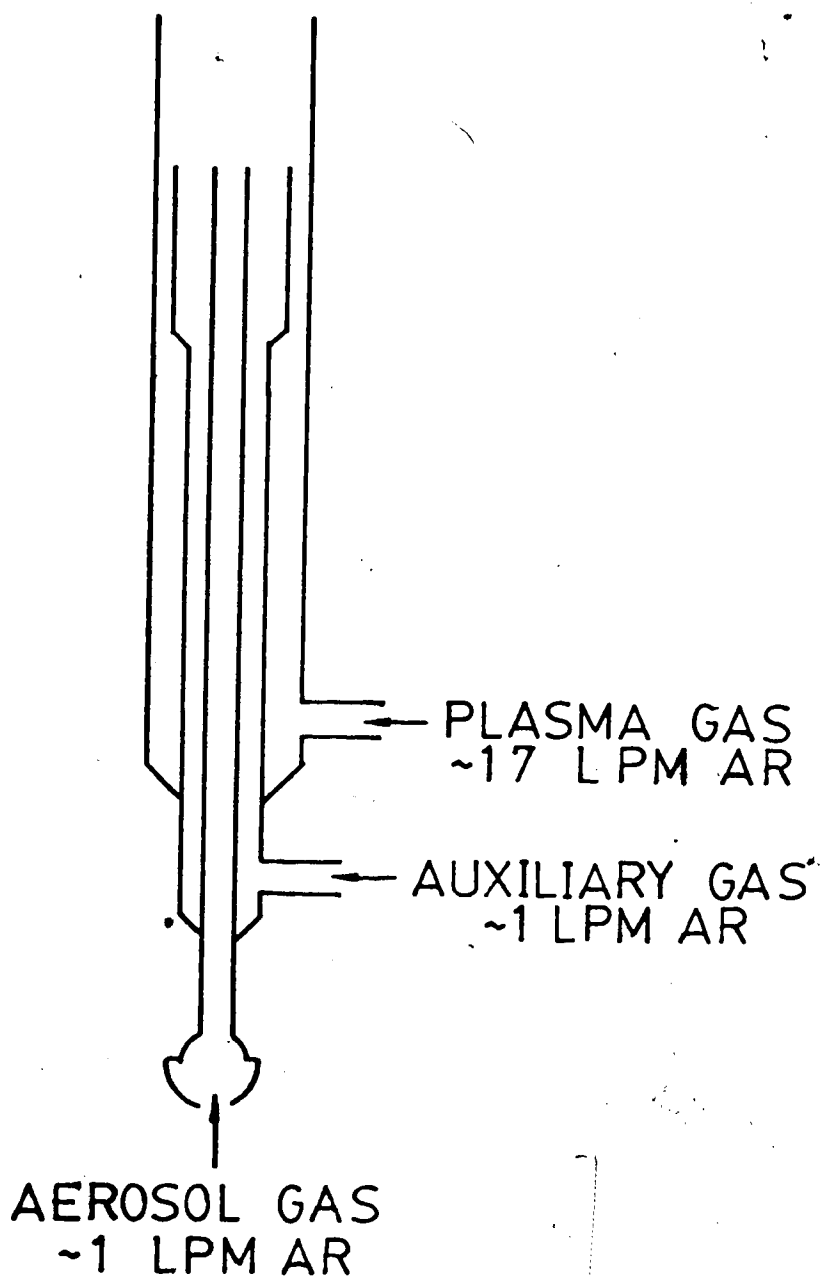
Figure 13. ICAP torch.

straight bore tube to provide a more laminar flow of sample gas through the torch and thereby reduce the chance of sample particles adhering to the walls of this tube. This type of torch proved to be easy to construct and operate and the operating characteristics were very constant from torch to torch. Table II lists the ICAP specifications and operating conditions.

C. Monochromator

The monochromator system used was the Heath Scanning Monochromator Model EU-700-70 with accompaning electronic Control Unit Model EU-700-51. This Heath monochromator is a single-pass Czerny-Turner design with folding mirrors to provide entrance and exit beams on a common optic axis. Selected specifications are given in Table III, from Reference 37.

The plasma was imaged on the entrance slit of the monochromator by a 100 mm focal length quartz lens. With the PMT data acquisition image magnification was -0.5. With the computer-coupled photodiode array spectrometer systems an image magnification of -0.5 was used for spectral studies and of -0.25 for spatial emission studies.

D. Detector-Readout Systems

The detector-readout systems used are of two basic

Table II

ICAP Specifications and Operating Conditions

Plasma:	ICP 5000 (Plasma-Therm)
R.F. Generator:	Type HFS 5000D (Plasma-Therm)
Frequency:	27.12 MHz
Power Available:	5.0 Kw
Power Used:	1.5 Kw
Plasma Argon Flow:	17.0 Lpm
Auxiliary Argon Flow:	∿1.2 Lpm
Sample Argon Flow:	0.8 - 1.0 Lpm
Observation Height:	Centered at 15-17 mm above load coil

Table III

Specifications for Monochromator Unit Model EU-700-70

Type of Mount:	Single-pass Czerny-Turner mounting with folding mirrors to provide entrance and exit beams on a common optic axis.
Aperature Ratio:	f/6.8 at 2000 angstroms.
Focal Length:	350 millimeters.
Resolving Power:	Better than 1 angstrom; Line-profile half-width less than 0.5 angstrom, with 3 mm slit height.
Stray Light:	0.1% or less within ± 1-1/2 bandwidths of a given line.
Reciprocal Dispersion:	Approximately 20 angstroms per mm at exit slit with 1180 lines per mm grating, depending on wavelength.
Grating:	Precision plane grating replica; 48 mm x 48 mm ruled area. Standard grating of 1180 lines per mm, blaze wavelength 2500 angstroms.
Slit Width:	Continuously variable between 5 and 2000 micrometers.
Slit Height:	12 mm maximum.

types--photomultiplier tube (P.M.T.) and photodiode array
(P.D.A.) based systems. The P.M.T. has a venerable history
as a single channel detector for O.E.S. The reasons for
the almost universal use of the P.M.T. detector are mainly
its low dark current, its high sensitivity, and a linear
response range of up to 6 orders of magnitude.

Multichannel detection in O.E.S. has traditionally
been done with a wavelength scanning single channel detec-
tor, a photographic plate multichannel detector, or a series
of single channel detectors as in a direct reader. Al-
ternatives to these systems which have been proposed for
multichannel detectors are television camera tubes (38,39)
and photodiode arrays (40,41,42,43). These electronic
multichannel detectors have the advantage of providing for
a real time readout of spectra. A response range of several
orders of magnitude can be easily obtained by using in-
tegration times varying from 100 msec. to 52.4 seconds for
each cycle of the array readout and by time averaging the
information from a number of readout cycles. The individual
cycles can also be used for time studies of O.E.S. signals
which vary with time (44).

Following either the P.M.T. or the P.D.A. detector
systems used in this work was a digital data acquisition-
readout system. The basic components of these systems were
amplifiers to condition the signals, an analog-to-digital

convertor, a computer for data storage and manipulation, a printer and an incrimental plotter. These systems will be discussed in greater detail in the following sections.

1. Monochromator-Photomultiplier Readout System

The P.M.T. was chosen as the detector for single element analysis in this experimental work because of the characteristics mentioned earlier. The long linear response range is particularly significant since it matches the similar linear response range of the ICAP.

The P.M.T. used was a 1P28 which was operated at 600.0 V. This P.M.T. was powered by and enclosed in a Heath Photomultiplier Module EU-701-30 which is a companion module to the Heath Monochromator Module EU-700-70. The spectral range covered with this P.M.T. is from about 185 nm to 650 nm. No work was attempted at wavelengths below 200 nm since light absorbance by O_2 begins to become significant in this range and because there were no emission lines pertinant to this work below this wavelength.

Conversion of the P.M.T. current signal into a voltage signal and amplification/filtering of this signal was per-formed by two systems in this work. In the early work a current-to-voltage convertor constructed from a Burr-Brown, Tucson, Arizona, 3308/12C operational amplifier which was used with a Tektronix Inc. (Beaverton, Origon), AM 502

Differential Amplifier to provide further amplification and filtering. In the latter part of the work a Keithly Instruments, Inc. (Cleveland, Ohio) Model 427 Current Amplifier was used. The Kiethly amplifier proved easier to use but no significant differences in performance were noted between the two systems.

The circuit diagram for the current-to-voltage convertor is shown in Figure 14. The i/v convertor has an RC time constant of 0.01 second which allows the rapid changes in emission intensity from electrothermally vaporized analytes to be accurately followed. The i/v convertor was constructed to allow operation in two amplifier ranges. The first has an output voltage of 10 V for an input current of -10^{-6} amps and the second has an output voltage of 10 V for an input current of -10^{-5} amps. Photomultiplier response is generally only linear up to about 10^{-6} amps therefore only the first amplifier range was used for analytical work and when the current exceeded 10^{-6} A a neutral density filter, OD1, was interposed between the ICAP and the Monochromator to reduce the P.M.T. current to less than 10^{-6} amps. Table IV lists the calibration data for this i/v convertor.

The Tektronix AM 502 Differential Amplifier used with the i/v convertor served mainly to provide final filtering if necessary, further amplification, and a d.c. offset to

Table IV

Calibration Data for Current-to-Voltage Convertor

$$i = V_{in}/R_{in} = V_{in}/1.000 \times 10^6 \ \Omega$$

V_{in}	i (μA)	V_o (10^{-6} Range)	V_o (10^{-5} Range)
1.0001	1.0001	10.16	1.002
0.5000	0.5000	5.07	0.501
0.7501	0.7501	7.62	0.751
0.2500	0.2500	2.54	0.250
0.1000	0.1000	1.015	0.100
0.0750	0.0750	0.762	0.0754
0.0500	0.0500	0.508	0.0502
0.0251	0.0251	0.255	0.0253
0.0100	0.0100	0.1029	0.0102
0.0075	0.0075	0.0768	0.0076
0.0050	0.0050	0.0521	0.0052
0.0024	0.0024	0.0252	0.0026
0.0011	0.0011	0.0118	0.0013
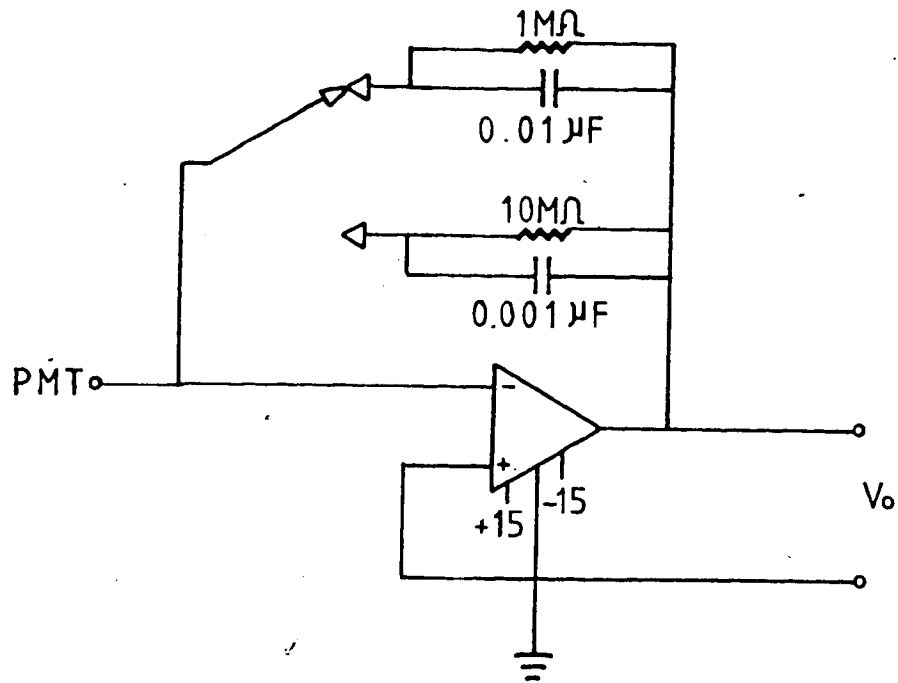
Figure 14. Current-to-voltage convertor for use with PMT detector in EA-ICAP-OES spectrometer system.

± 5 V before analog-to-digital conversion which was per-
formed at 100 Hz.

Digital data conversion was performed by a Digital
Equipment Corporation (DEC) Laboratory Peripheral System
Model LPS11 (45,46). This data acquisition unit contains
all the electronic components for connection to external
analog, digital, and timing signals and interfaces directly
to a DEC PDP-11/10 sixteen bit minicomputer. The LPS unit
contains a 12-bit analog-to-digital convertor giving a
resolution of 1:4096 and can perform conversion under
program control at up to 20,000 Hz (50 µsec/conversion). A
total of two or three digital inputs and one analog input
were used during data acquisition. The LPS11 internal
clock provided the A/D conversion clock.

The DEC PDP-11/10 minicomputer was operated under the
RT11-026 disk-based operating system with 16 K words of core
memory available. Programming was in Fortran and Macro 01C
assembly language. Mass storage was available by means of
a single 2.5 megabyte DEC RK-05J cartridge disk drive.
Alphanumeric and graphic display was available with a DEC
VT-55 video terminal. Hard copy output was available from
the internal printer of the VT-55, a Decwriter II, or a
Zeta Research Corporation, Lafayette, California, 100/1200
Series Incremental Plotter (45,47). A description of
software including a description and documented printouts
is contained in Appendices A and B.

2. Computer Coupled Photodiode Array Readout Systems

The computer coupled photodiode array readout systems
used in this work have been developed in this laboratory over
the last eight years. A number of articles have been written
about these systems by Horlick et al. but of particular
interest are References 48 and 49 which are general review
articles concerning the characteristics of these systems for
spectrochemical measurements.

The first system used was the computer coupled photodiode
array direct reading spectrometer shown in Figure 5. In
this system an array, consisting of 1024 photodiodes
0.001 inch wide by 0.017 inch tall, is placed horizontal-
ly in the exit focal plane of a Heath Monochromator Model
EU-700-70. The dispersion of this monochromator varies
slightly with wavelength but is approximately 20 $\overset{\circ}{A}$ per
mm and therefore the 1.024 inch photodiode array gives
a spectral window of slightly more than 50 nm (500 $\overset{\circ}{A}$).
The computer-based data acquisition system operates at up
to 20 KHz and the photodiode array is generally clocked at
this rate. Integration times of an array cooled to about
-20°C can vary from 0.1024 to 52.4287 seconds between
readout cycles of the photodiode array and individual
readout cycles can be stored under computer control or can
be time averaged and background subtracted.

The second photodiode array based system uses a photo-

diode array mounted vertically in the exit focal plane of
a Heath Mono█████████,Model EU-700-70. In this system an
array of 256 ██████es 0.001 inch wide by 0.001 inch tall
is used th██ ███████direct readout of the vertical spatial
emission i█te█████ of a s█urce (50,51). When clocked at
20 KHz integration cycle times between 0.0128 and 52.4280
seconds are possible when the photodiode array is cooled
to about -20°C. Time averaging of readout cycles and back-
ground subtraction are also available under computer control.

The remainder of the data acquisition system and readout
system are similar to that described in Section D1 with the
Tektronix AM 502 Differential Amplifier being used to
amplify and filter the photodiode array signals prior to
analog-to-digital conversion. With the photodiode array
systems A/D conversion clocking was provided by the photo-
diode array electronics. Software descriptions and doc-
umented printouts are contained in Appendices C, D, E, and
F.

CHAPTER III

Characterization of EA-ICAP-OES Emission Behavior

for Single Elements in Solution

The discussions in Chapters I and II introduced the concepts involved in EA-ICAP-OES, and descriptions of the systems used for data acquisition were provided. In this chapter the experiments using the PMT data acquisition system will be discussed.

Reference to Figure 1 will show that the emission information may be encoded in up to four ways--frequency, intensity, time, and space. With a single channel data acquisition system frequency decoding was performed entirely by the monochromator. Extensive spatial information is very difficult to decode for transient signals with a PMT-based data system as only one area at a time can be observed. It will be seen in Chapter IV that spatially resolved spectral measurements can be easily accomplished with a photodiode array mounted vertically in the exit focal plane of a monochromator. The PMT-based system is used best in decoding the emission signal to recover the time and intensity data.

A. Temporal Behavior of EA-ICAP-OES System

From the very beginning of this work it was apparant that the EA-ICAP-OES process would show a temporal behavior

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because of the use of an atomic absorption graphite furnace atomization system for sample vaporization. Sturgeon and Chakrabarti (33) give an excellent review and discussion of the temporal behavior of the carbon furnace atomizer process. The absorption pulse characteristic times is shown in Figure 15 (Reference 33, p. 40) for a graphite furnace. This same figure can also be used to describe the emission pulse characteristics of the EA-ICAP-OES process and to point out the similarities and differences between the two analytical methods.

At the beginning of the AAS atomization cycle a large current is passed through the furnace causing rapid heating. A curve representing furnace temperature vs time for such a case is shown in Figure 15. As the furnace temperature exceeds the analyte vaporization temperature the concentration of analyte atoms in the absorption cell starts to rise. At some point the absorbance signal will rise above the background level. This is the appearance time $(\tau_{appearance})$ which is measured from the start of the atomization cycle. There are a number of factors which may affect this appearance time such as:

1. Furnace heating rate.

2. Element being investigated.

3. Mass of analyte (and matrix if present)

4. Chemical form of element.
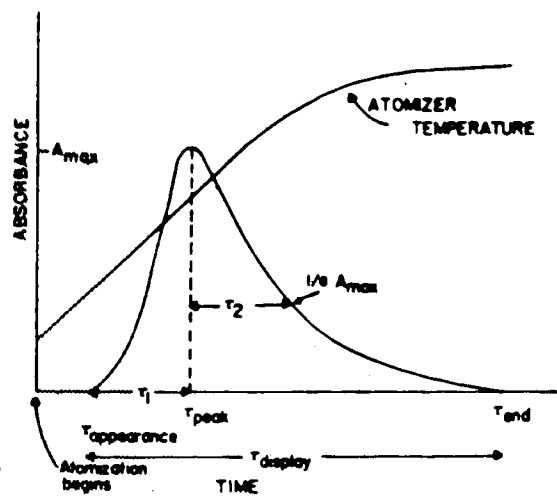
<u>Figure 15.</u> Pulse characterization times for a graphite furnace.

If there are no complicating competing processes, such as chemical reaction with the carbon of the furnace, and if heating continues long enough then atomization will continue until all of the analyte has been vaporized. Under normal conditions this is a rapid process and the result is that the concentration of analyte in the absorption cell rapidly increases to a maximum a the end of the analyte atomization. The time of maximum absorbances (τ_{peak}) is the sum of appearance time ($\tau_{appearance}$) and atomization time (τ_1).

Diffusion of the analyte out of the absorbance cell will cause the absorbance signal to fall after the τ_{peak} is reached. The residence time (τ_2) is the mean length of time spent by an atom within the absorbance cell and is the time necessary for the absorbance signal to fall to a value of $1/e \ A_{max}$. As the analyte continues to diffuse from the absorbance cell the absorbance will finally reach the background level again at τ_{end}.

The emission signal for the EA-ICAP-OES system used is very similar in appearance to the absorbance signal described above but the processes involved are different in detail. The vaporization cell replaces the absorbance cell and as the analyte is rapidly vaporized its concentration rapidly raises in the cell. As before, the maximum concentration is reached at the end of the vaporization and then

decreases. With the EA-ICAP-OES the reduction of vapor concentration within the vaporization cell is caused by the flushing of the vapor out the top of the cell to the plasma by the argon entering the bottom of the cell. $\tau_{appearance}$, τ_{peak}, τ_1, τ_2, and τ_{end} may then be determined, if desired, from the emission peaks in a manor analogous to their determination with graphite furnace AAS. With EA-ICAP-OES all times will be delayed about 0.5-0.6 seconds since the vapor must travel through the connecting tube and torch, a distance of about 16 inches, before emission can occur. Figure 16 is an example of the emission intensity obtained for 100 ng of lead using the EA-ICAP-OES system developed for this experimental work.

This experimental work was primarily an investigation into the use of a graphite furnace based system for analytical EA-ICAP-OES therefore vaporization conditions were adjusted to give as little variation in temporal behavior as possible in the emission signals of the various elements. The conditions which met this criteria were primarily the use of a standard and reproducible torch design, a fixed value of sample argon flow rate, and the highest possible furnace heating rate attainable with the equipment used. When these conditions were met the temporal behavior varied only a small amount from element to element, with the quantity present, and with the matrix. Typical values were:

PB142-100NG
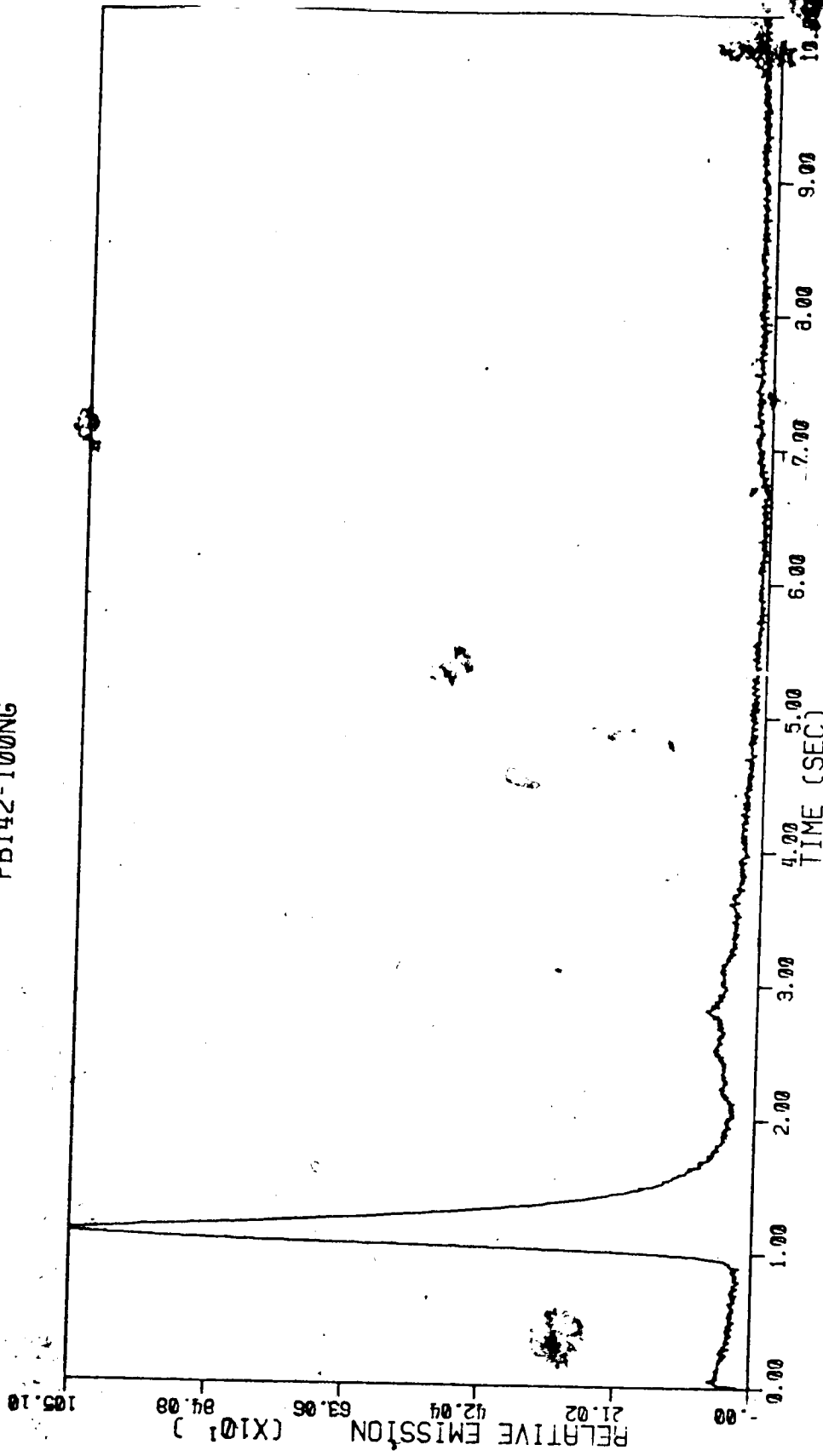
Figure 16. EA-ICAP-OES temporal profile for Pb(II) emission at 220.353 nm from 100 ng of Pb. Recorded with computer system.

$$\tau_{appearance} \quad - \quad 0.6\text{-}0.8 \text{ seconds}$$

$$\tau_{peak} \quad - \quad 0.9\text{-}1.2 \text{ seconds}$$

$$\tau_{end} \quad - \quad 2.0\text{-}3.5 \text{ seconds}$$

τ_2 values were not determined for the EA-ICAP-OES system.

The distribution of sample vapor was investigated by visually observing the spread of NH_4Cl vapor as it was vaporized from the furnace. The distribution was very unhomogeneous with the greatest concentration at the top of the cell and with almost no vapor being seen below the sample cup. This distribution was easily understood since there was approximately 0.8 Lpm of argon entering the bottom of the cell for the purpose of sweeping the analyte vapor out the top of the cell. Contributing to the unhomogeneous distribution was also the fact that the sample was vaporized from a cup which opens upwards, therefore the vapor was expelled in an upward direction. The fact that any vapor was seen below the vaporization cup was undoubtedly due to turbulent flow of argon in the cell.

When a pulse signal, such as found in graphite furnace AAS or in EA-ICAP-OES is to be analyzed, then care must be exercised in the design of the detection readout system. In many cases a chart recorder has been used to record the transient signal being obtained from the analytical system. Most early graphite furnace AAS systems used this readout system. The EA-ICAP-OES system of Nixon, Fassel and

Kniseley (25) and of Kirkbright et al. (26, 27, 28) also used chart recorders as readout systems. Chart recorders have a fairly long response time compared to the time behavior of either a graphite furnace AAS system or a.EA-ICAP-OES,therefore a great deal of distortion in the recorded signal could be expected. Sturgeon and Chakrabarti (33) discuss this problem thoroughly in connection with graphite furnace AAS and show clearly how increasing the time constant of the recording system reduces the peak height obtained while increasing τ_{end}. This distortion of the signal is accompanied by a loss of fine detail.

Figure 17 is a recording of the emission from 10 µL of 10 ppm Pb (100 ng) as recorded by a Heath Laboratory Strip Chart Recorder Model EU-20B. The response time of this recorder is 1 second full scale (0.1 sec/inch). If this recording is compared with Figure 16, which was recorded with the equipment described in Chapter II having a RC time constant of 0.01 second, the signal distortion is readily apparent. The strip chart recording has a peak height of 0.19×10^{-8} amps, including pen overshoot, as compared with a value of .2 × 10^{-8} amps from the detector-readout system developed for this experimental work.

Several features are clearly visible in Figure 18, a recording for 10 ng of Pb, that were less easily seen in Figure 16 which was recorded at a lower amplification level.

$0.19 \times 10^{-8} A$

10 SEC
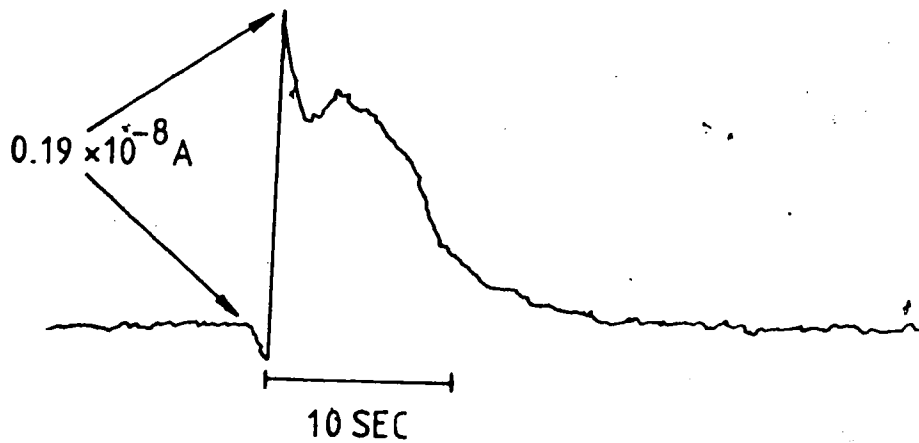
<u>Figure 17</u>. EA-ICAP-OES temporal profile for Pb(II) emission
at 220.353 nm from 100 ng of Pb. Recorded with
a Heath Strip Chart Recorder, Model # EU-20B.

PB149-10NG
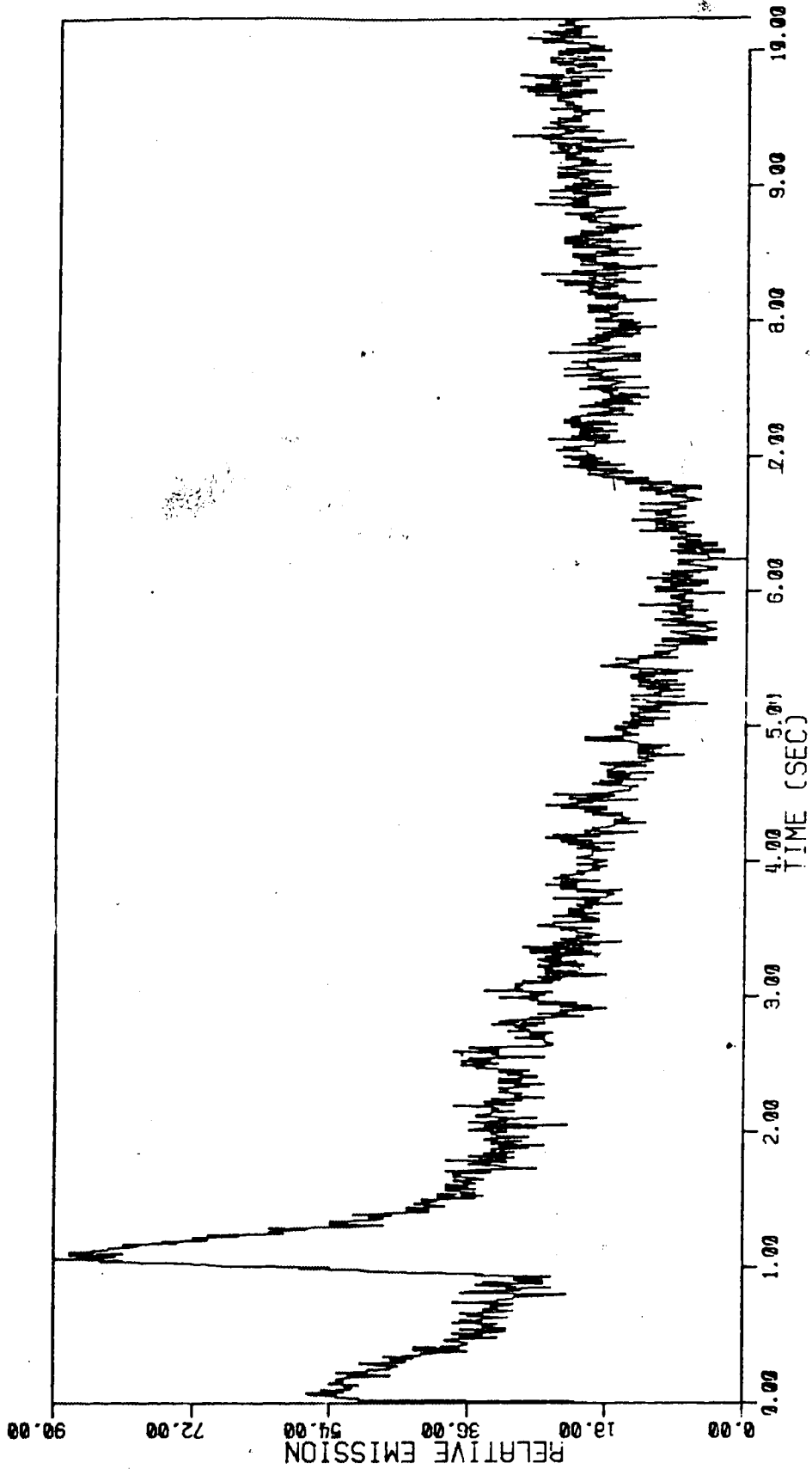
Figure 18.   EA-ICAP-OES temporal profile for Pb(II) emission at 220.353 nm from 10 ng of Pb. Recorded with computer system.

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In addition to the lead emission peak several rapid changes

in the background level are seen prior to the emission peak

and another change in background level is seen at between

6 and 7 seconds. These changes in background level are more

clearly shown in Figure 19 which is a recording of background

emission during atomization of a blank (1 µL of distilled

water). The rapid changes in background emission level

during the first second of the atomization cycle are ap-

parently caused by rapid changes in sample argon flow rate.

These changes are caused by the rapid heating of argon in

the vaporization cell causing a pressure increase and thus

an increase in the flow rate of the argon leaving the cell.

Similar plasma background emission level changes can be seen

in the temporal profiles published by Nixon and Fassel (25)

and by Kirkbright et al. (26,27,28). The rapid increase in

emission level between 6 and 7 seconds is caused by the

cooling of the argon in the vaporization cell at the com-

pletion of the atomization cycle.

The fast response of the system used in this experi-

mental work has proven very valuable in another area. In

Figure 20 the emission signal recorded is obviously not as

expected. In this case the electrode rods were found to be

making poor contact with the graphite cup furnace with the

result that heating and atomization did not proceed smoothly.

The sharp emission spikes at about 1.25 and 1.5 seconds in

Figure 19. EA-ICAP-OES temporal profile for Pb(II) emission at 220.353 nm from Pb blank. Recorded with computer system.

PBI43-BLANK
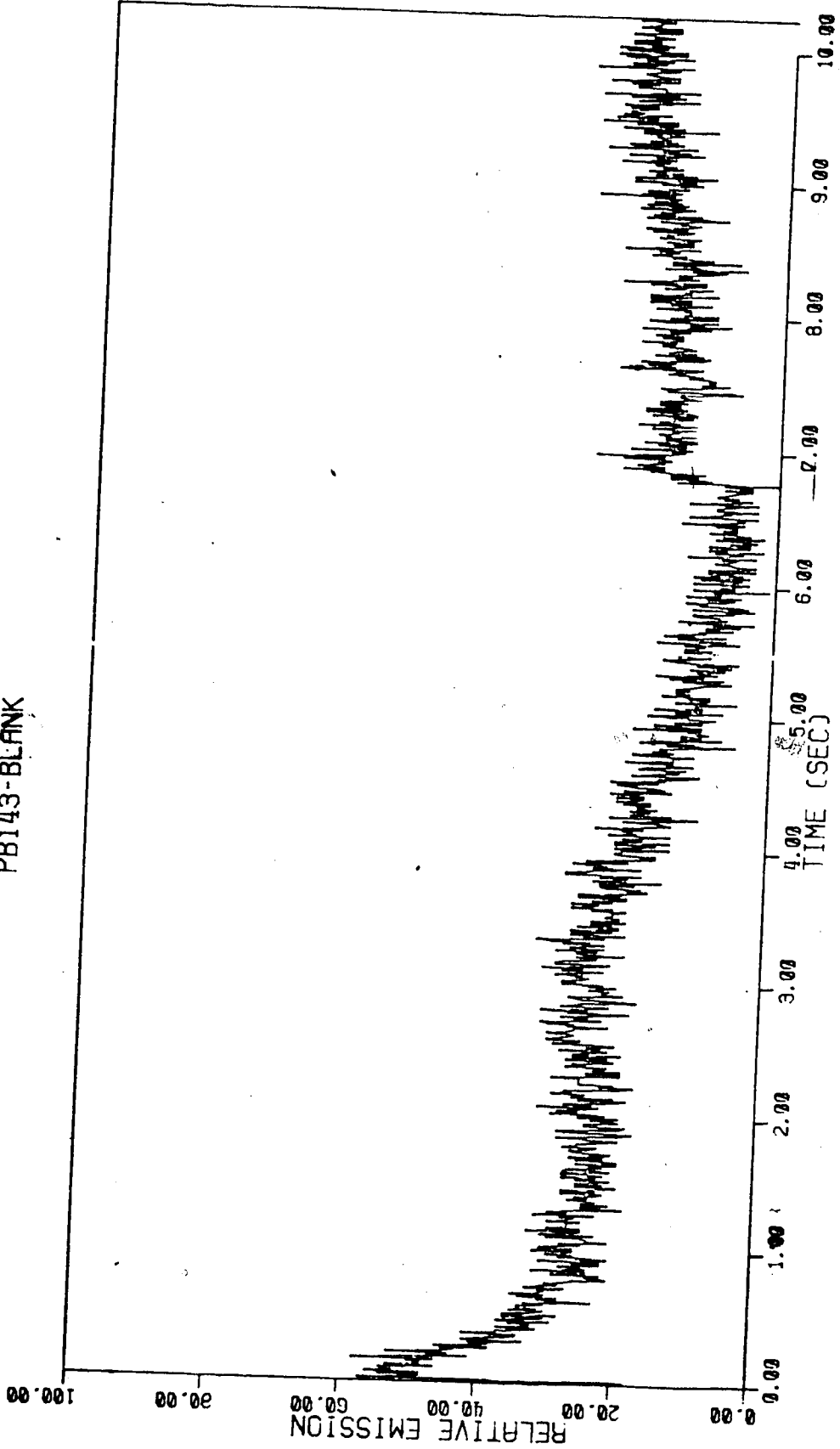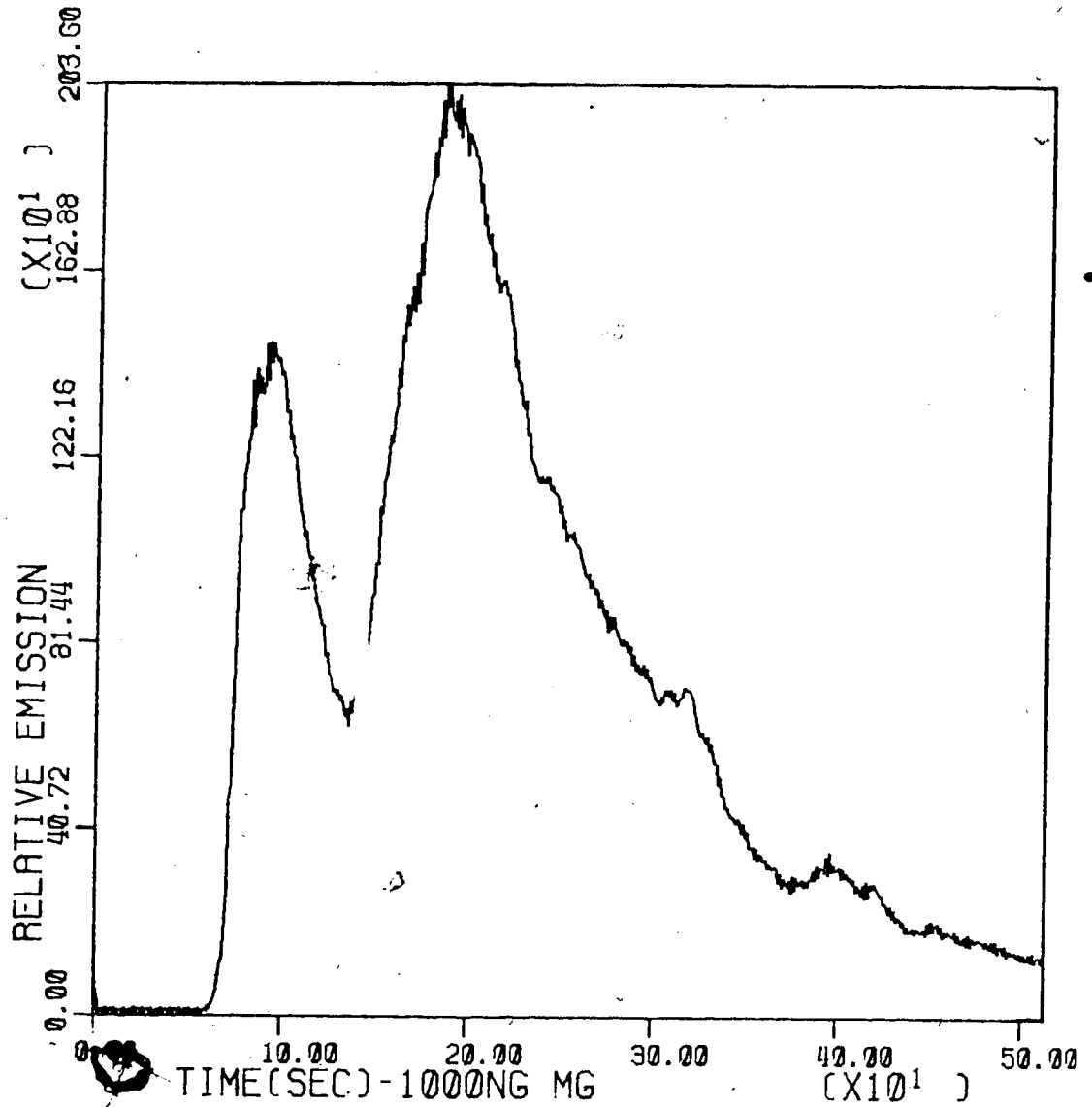
Figure 20. EA-ICAP-OES temporal profile for Mg(II) emission at 279.553 nm from 1000 ng Mg. Recorded with computer system.

Figure 21 are caused by particles containing Zn breaking loose from the vaporization cell. These spikes generally occur only after the system has been used for long periods of time without cleaning or after samples containing very high levels of analyte have been run and are eliminated by cleaning of the vaporization cell and connecting tube. The detail available in the emission recordings proved to be very valuable in system fault detection and maintenance.

B. Analytical Results for Single Elements in Solution

The emission pulses obtained with the electrothermal vaporization system developed for this work were shown in the previous section to have many similar features with those obtained by graphite furnace AAS. Because of these similarities it was at first assumed that, as with graphite furnace AAS, either the peak height value, E_p, or the background corrected integrated peak area, $\int E_t dt$, could be used to characterize the peak.

Early work disclosed several facts which led to the rejection of analytical measurements based on peak signal values. The first problem encountered was the fact that the emission signal is not exclusively due to analyte emission. The signal is the sum of the analyte emission and the changes caused in background plasma emission by the sample argon flow fluctuations during sample vaporization.
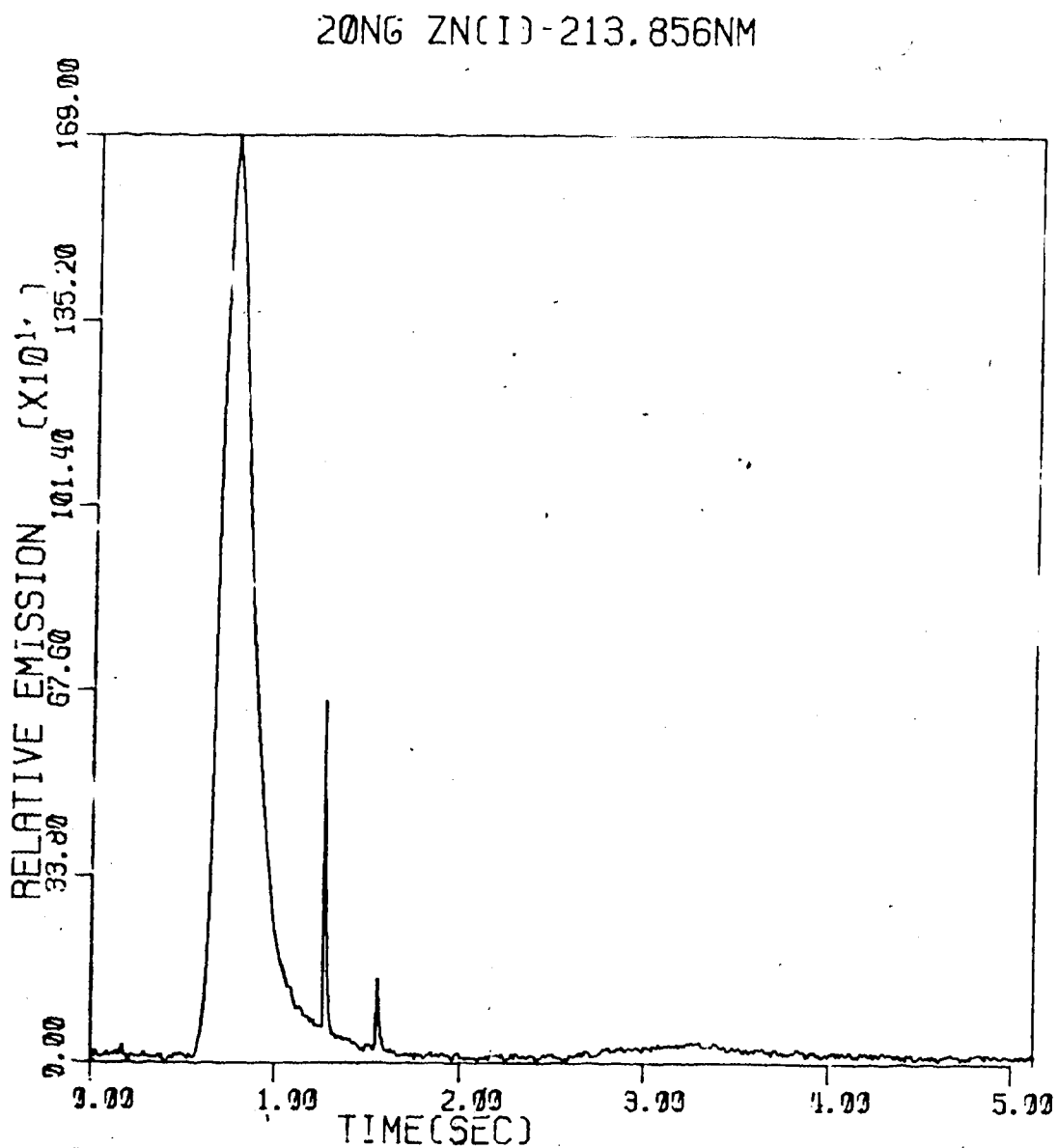
Figure 21. EA-ICAP-OES temporal profile for Zn(I) emission
at 213.856 nm from 20 mg Zn. Recorded with com-
puter system.

These plasma background emission changes were shown in Figure 19 and discussed in the previous section. Small changes in vaporization conditions were found to cause fairly large changes in the minimum found just before analyte emission starts to rise quickly and to a lesser extent in the background emission levels in general.

Background and analyte emission plots are shown in Figure 22 through Figure 29. Digital filtering of the data was performed prior to plotting to smooth the appearance of the plots. The background becomes too small with respect to analyte emission in Figure 26 through Figure 29 to be clear, but can be easily seen in Figure 22 through Figure 25. These backgrounds, which were collected immediately before the analyte data and under the same conditions, show the variations just mentioned. These changes are probably due to changes in the sample argon flow rate caused by fluctuations in the furnace heating rate. These background emission level changes from vaporization to vaporization made it impossible to assign a single point or area in an analyte emission plot as a background level for E_p measurement.

Integrated background values were found to be fairly consistent therefore an average value could be subtracted from the integrated emission area values to obtain analyte only integrated emission area for analytical uses.
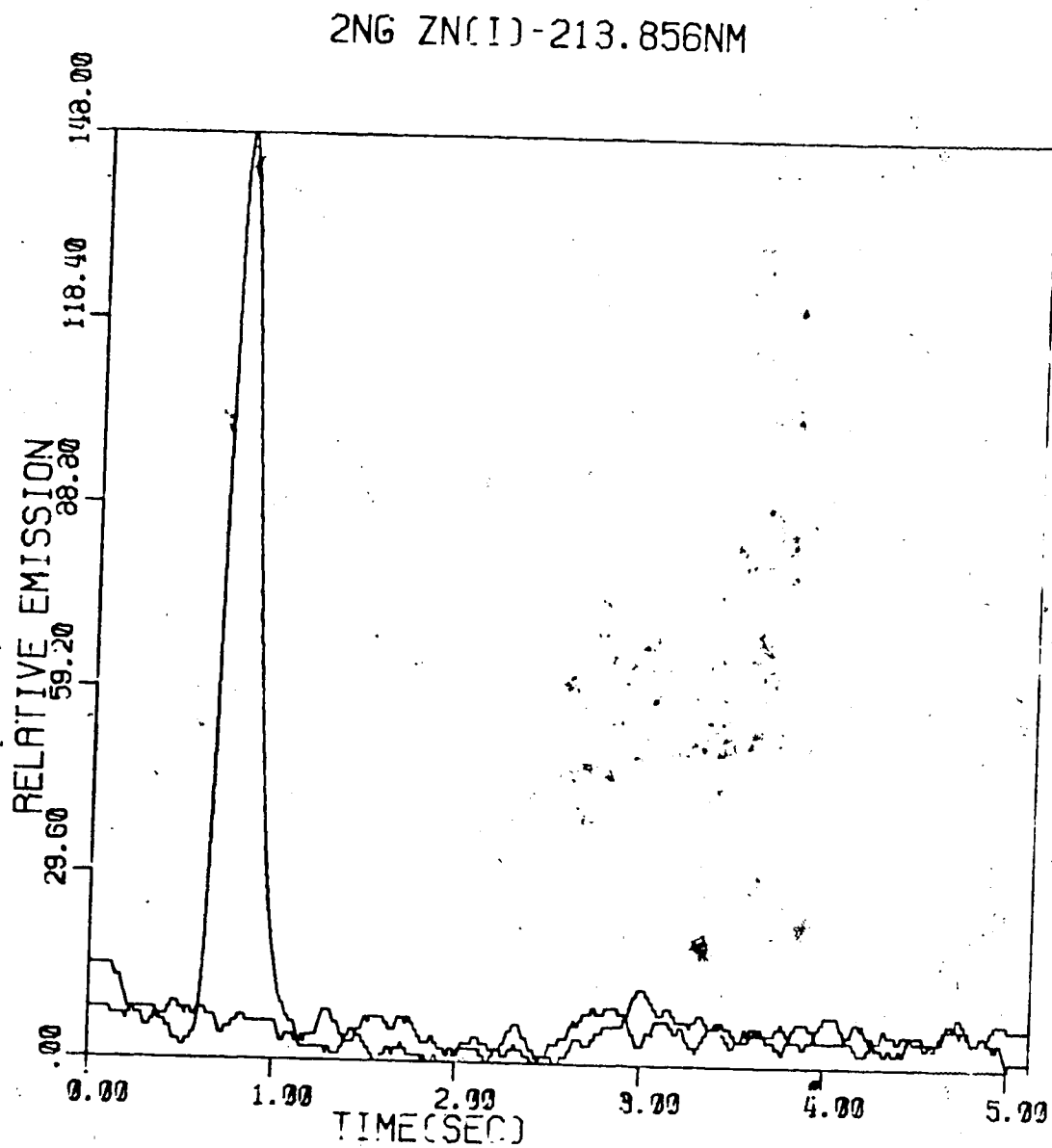
Figure 22. Temporal profile, 2 ng Zn(I) - 213.856 nm.
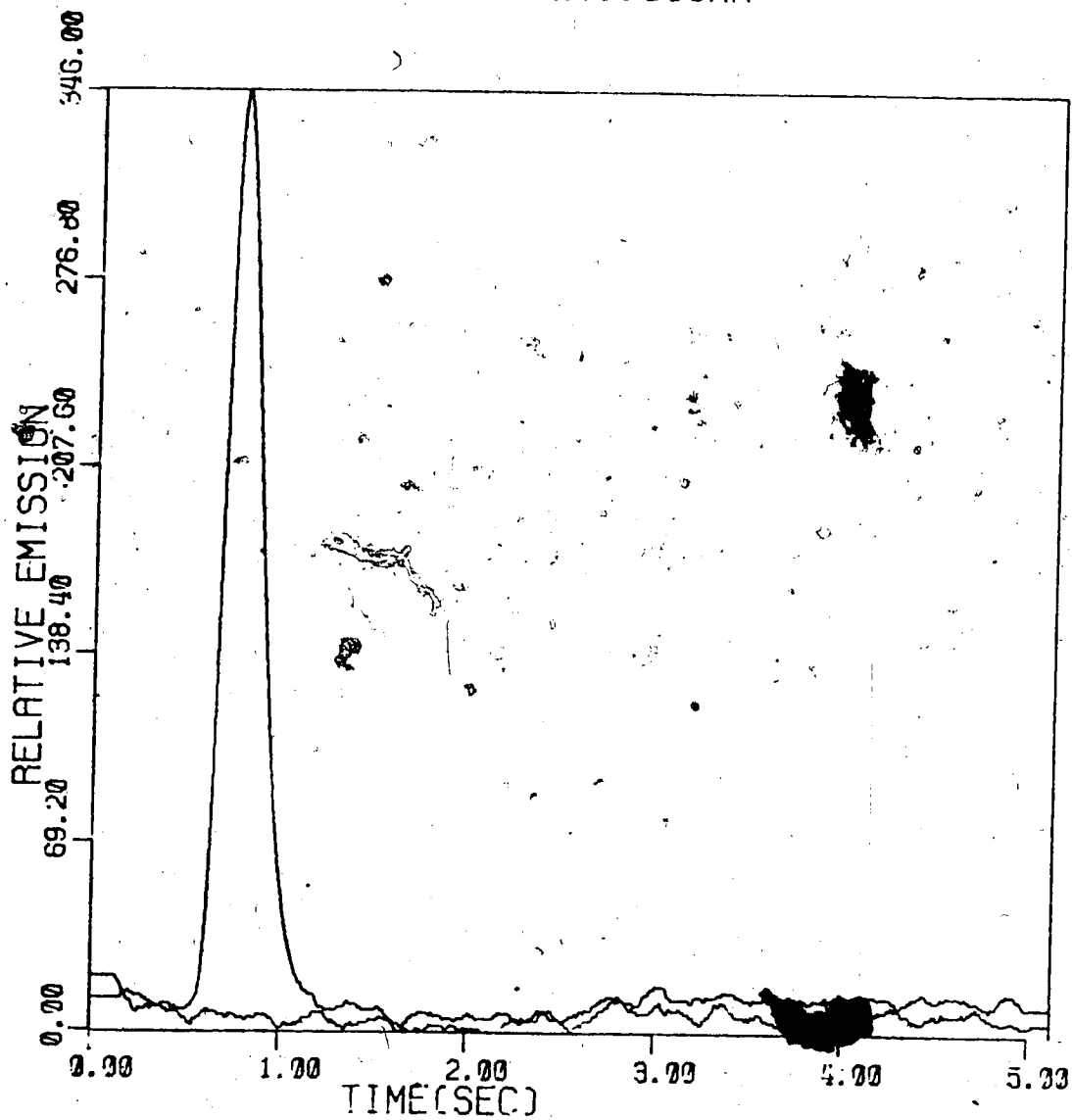
Figure 23. Temporal profile, 5 ng Zn(I) – 213.856 nm.

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20NG ZN(I)-213.856NM

RELATIVE EMISSION (X10⁴)

133.10
106.48
79.86
53.24
26.62
.00

0.00   1.00   2.00   3.00   4.00   5.00
TIME(SEC)
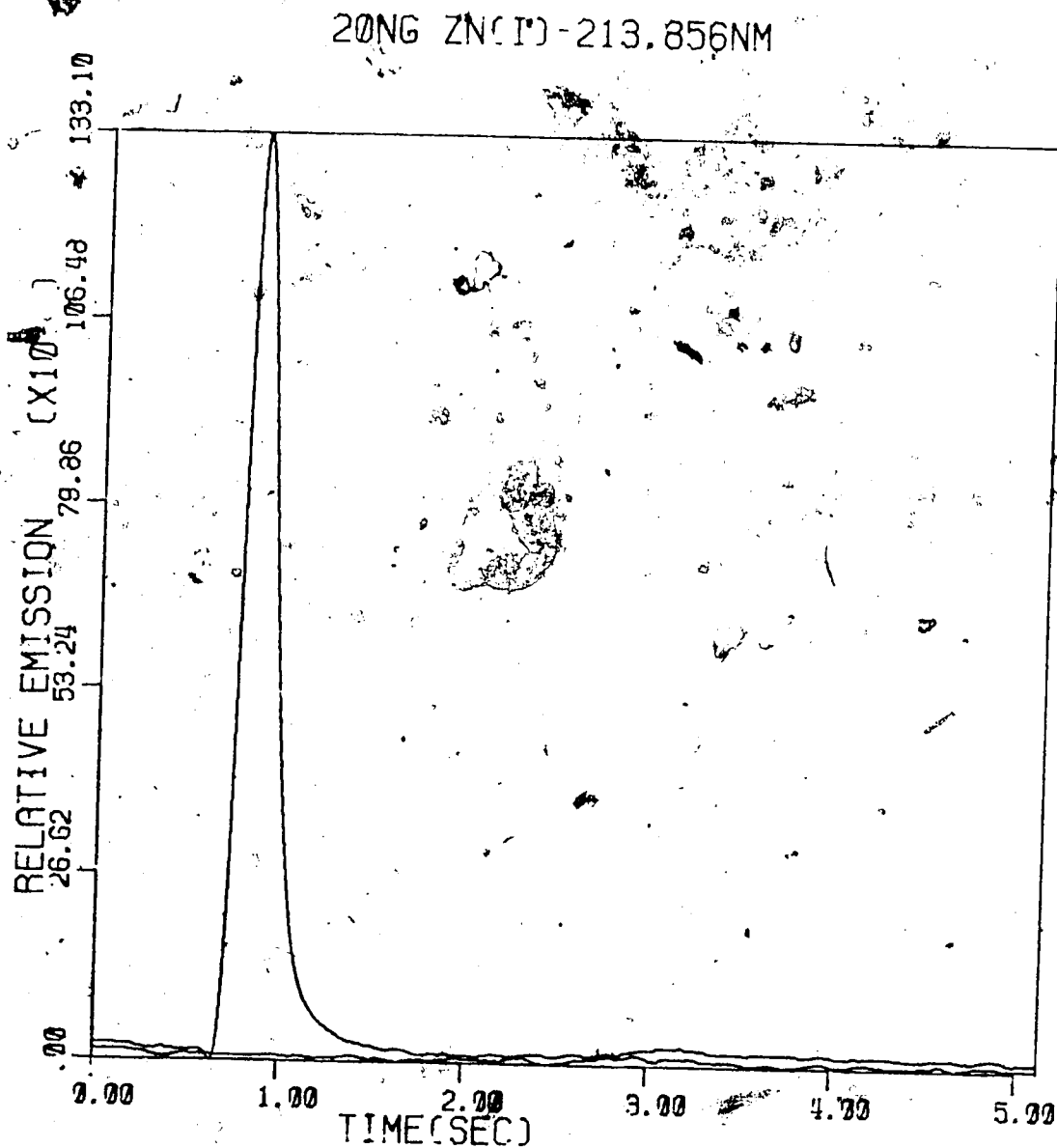
Figure 24. Tempora. profile, 20 ng Zn(I) - 213.856 nm.

50NG ZN(I)-213.856NM

RELATIVE EMISSION

360.00
288.00
216.00
144.00
72.00
0.00

0.00 1.00 2.00 3.00 4.00 5.00
TIME(SEC)
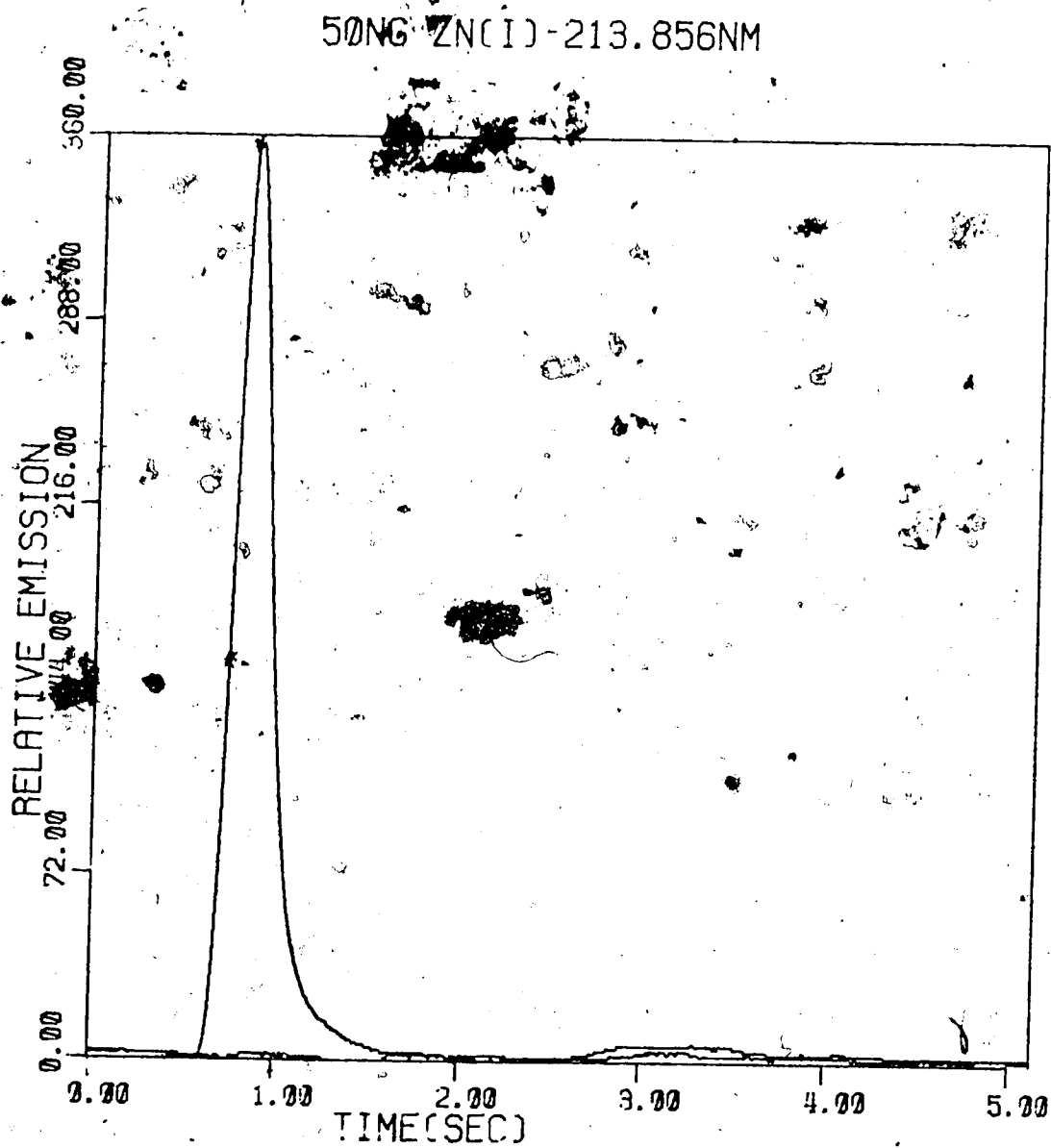
Figure 25. Temporal profile, 50 ng Zn(I) - 213.856 nm.
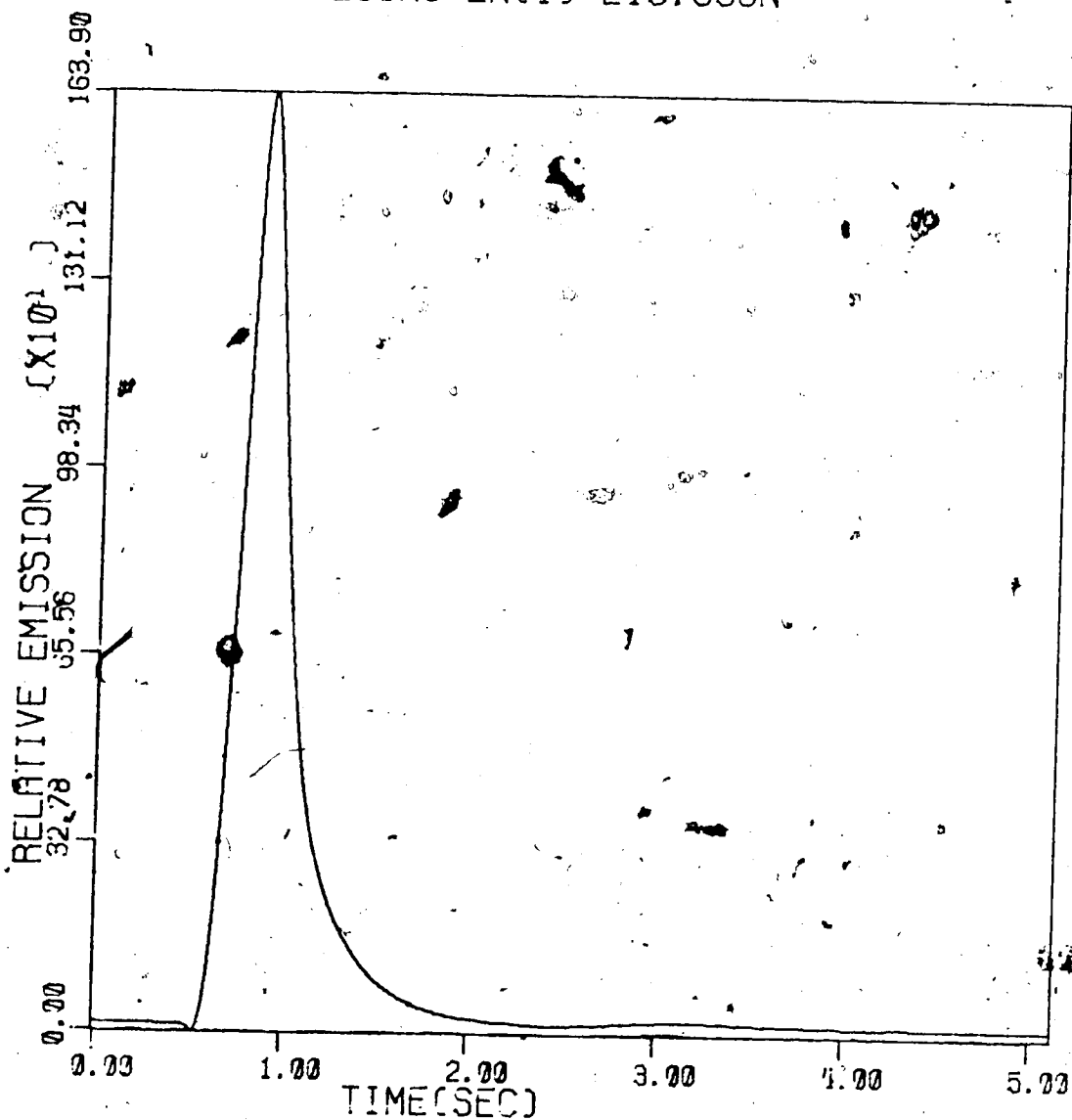
Figure 26. Temporal profile, 200 ng Zn(I) - 21? ?56 nm.

500NG ZN(I)-213.856N
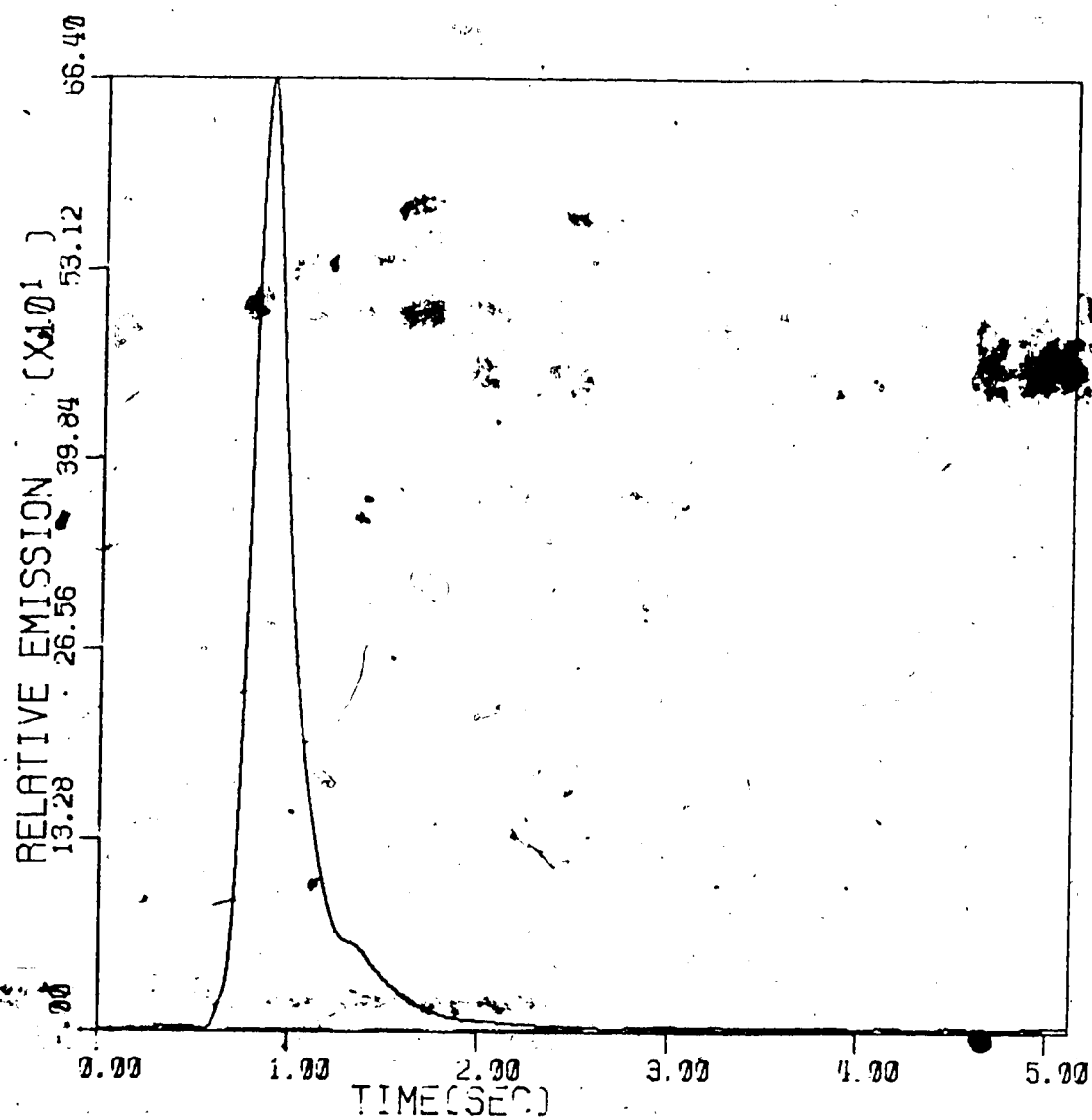
Figure 27.   Temporal profile, 500 ng Zn(I) - 213.856 nm.

2,000NG ZN(I)-213.85
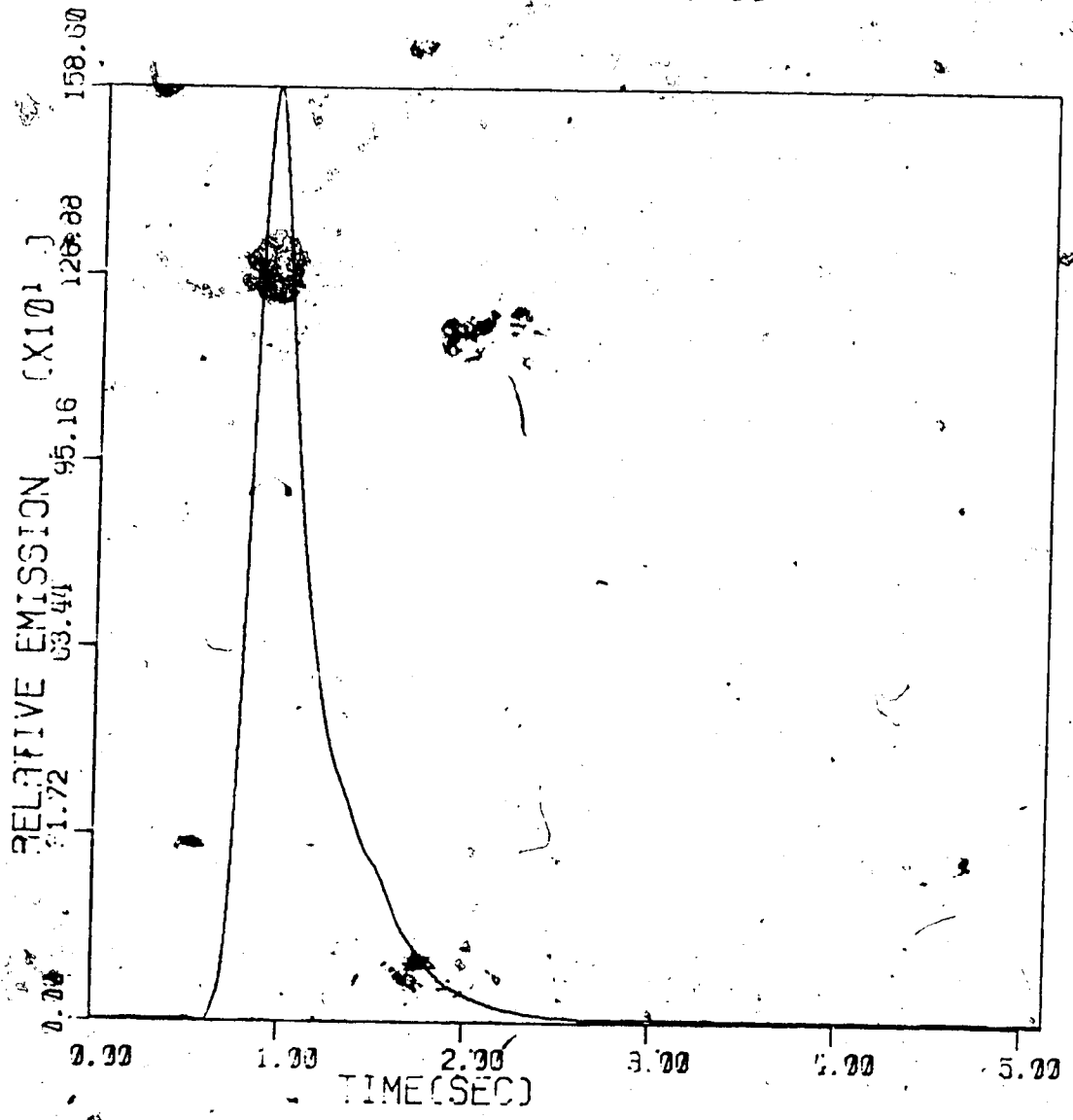
Figure 28. Temporal profile, 2000 ng Zn(I) ≙ 213.856 nm.
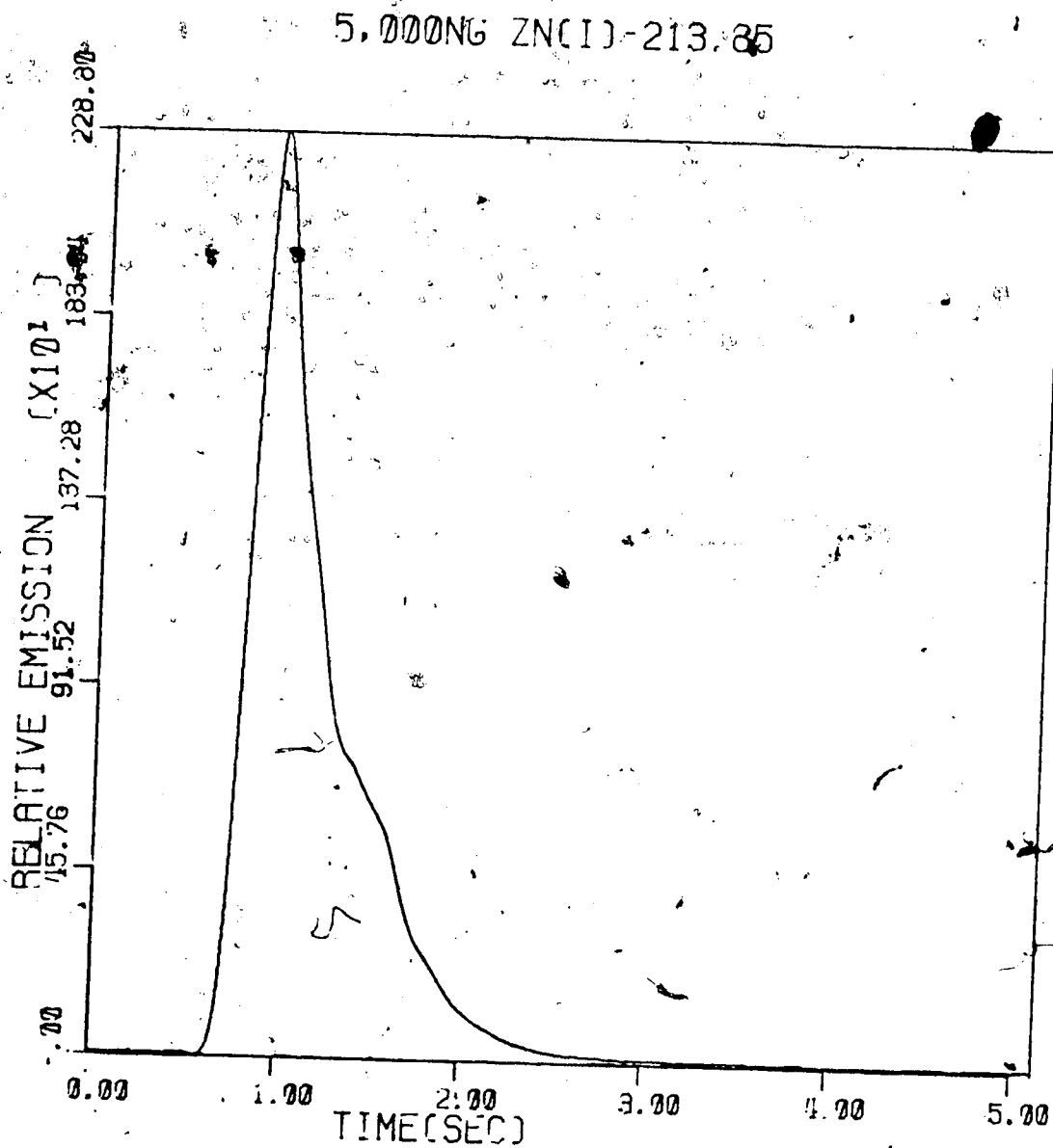
Figure 29. Temporal profile, 5000 ng Zn(I) at 213.856 nm.

The second problem encountered is one common to graphite
furnace AAS, that of changing temporal behavior with in-
creasing sample size or matrix. An example of one of the
changes possible is seen in the series of emission peak
recordings shown in Figures 22-29.

The same vaporization conditions were used throughout,
thus all of these peaks should superimpose, however as the
quantity of analyte increases τ_{peak} and τ_{end} increase and
the shape of the emission curve becomes irregular at the
highest quantities. Values of τ_{peak} and approximate τ_{end}
values are given in Table V. Even though these peak shapes
change with amount of analyte, the integrated emission area
should increase linearly with quantity.

A test of the use of peak height and integrated emission
area for characterization of the analyte emission peaks was
performed with magnesium. The Mg(I) emission line at 285.213
nm was used and the concentration range of 1 to 1000 ng
was covered. The amplifiers were set to give a full scale
signal for 10^{-7} amps up to 50 ng of Mg and then a full scale
signal for up to 10^{-6} amps up to 1000 ng. The results are
shown in Table VI and in Figure 30 through Figure 33. As is
shown by the data and figures, calibration plots can be
prepared with either peak height or background corrected
emission area values, but the relative standard deviation
(RSD) values are substantially less with the background
corrected integrated peak area values.

Table V

Emission Peak Characteristics for Zn(I) - 213.85 nm

Quantity (ng)	τ_{peak} (seconds)	$\sim\tau_{end}$ (seconds)
2	0.78	1.17
5	0.78	1.27
20	0.86	1.60
50	0.86	1.64
200	0.88	2.30
500	0.88	2.31
2000	0.94	2.65
5000	0.95	3.14

Table VI

Calibration Data for Mq(I) - 285.213 nm

Amount Mg (ng)	$\bar{E}_p$*	RSD %	$\int E_t dt$*	RSD %
1	57	7.0	7,311	4.6
2	101	12.6	12,010	7.5
5	346	17.5	27,698	6.0
10	496	22.5	46,294	3.7
20	928	11.9	86,729	5.8
50	2,154	15.1	231,149	4.0
100	4,953	9.7	418,640	4.5
200	7,647	7.1	778,950	2.5
500	13,883	10.7	1,848,150	5.4
1000	27,697	3.2	3,562,130	1.2
0 (10V=10^{-7} amps)	-	-	65,605	4.2
0 (10V=10^{-6} amps)	-	-	1,238,160	(0.7)

$\bar{E}_p$:

Slope = 0.89

R = 1.0

$\int E_t dt$:

Slope = 0.91

R = 1.0

*The average $\bar{E}_p$ or $\int E_t dt$ values are shown in their entirity for clarity, however it should be realized that based on the % RSD values these values are only accurate to 3 significant figures.
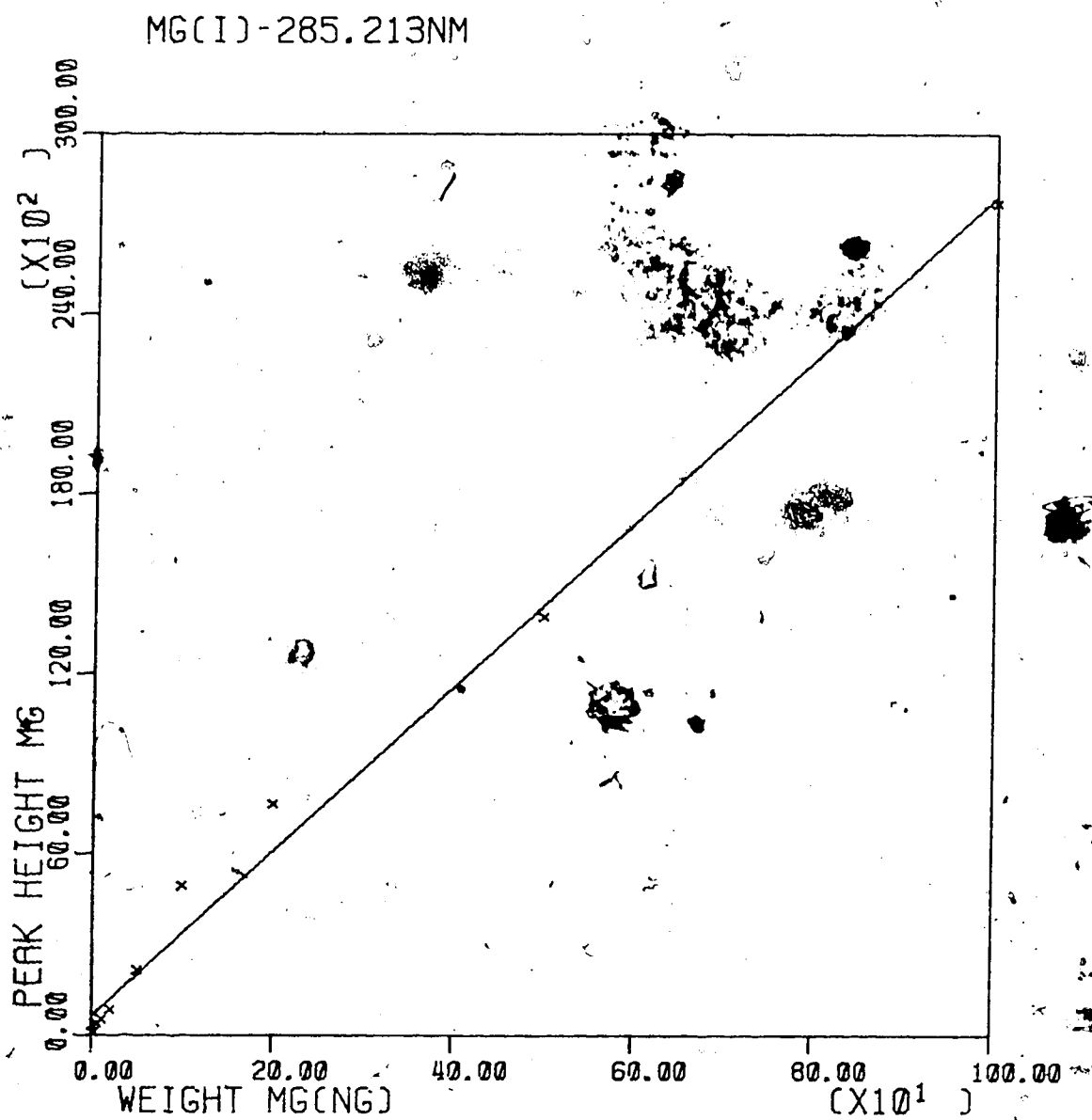
MG(I)-285.213NM

Figure 30. Linear calibration plot for Mg(I) - 285.213 nm, E_p data.

MG(I)-285.213NM
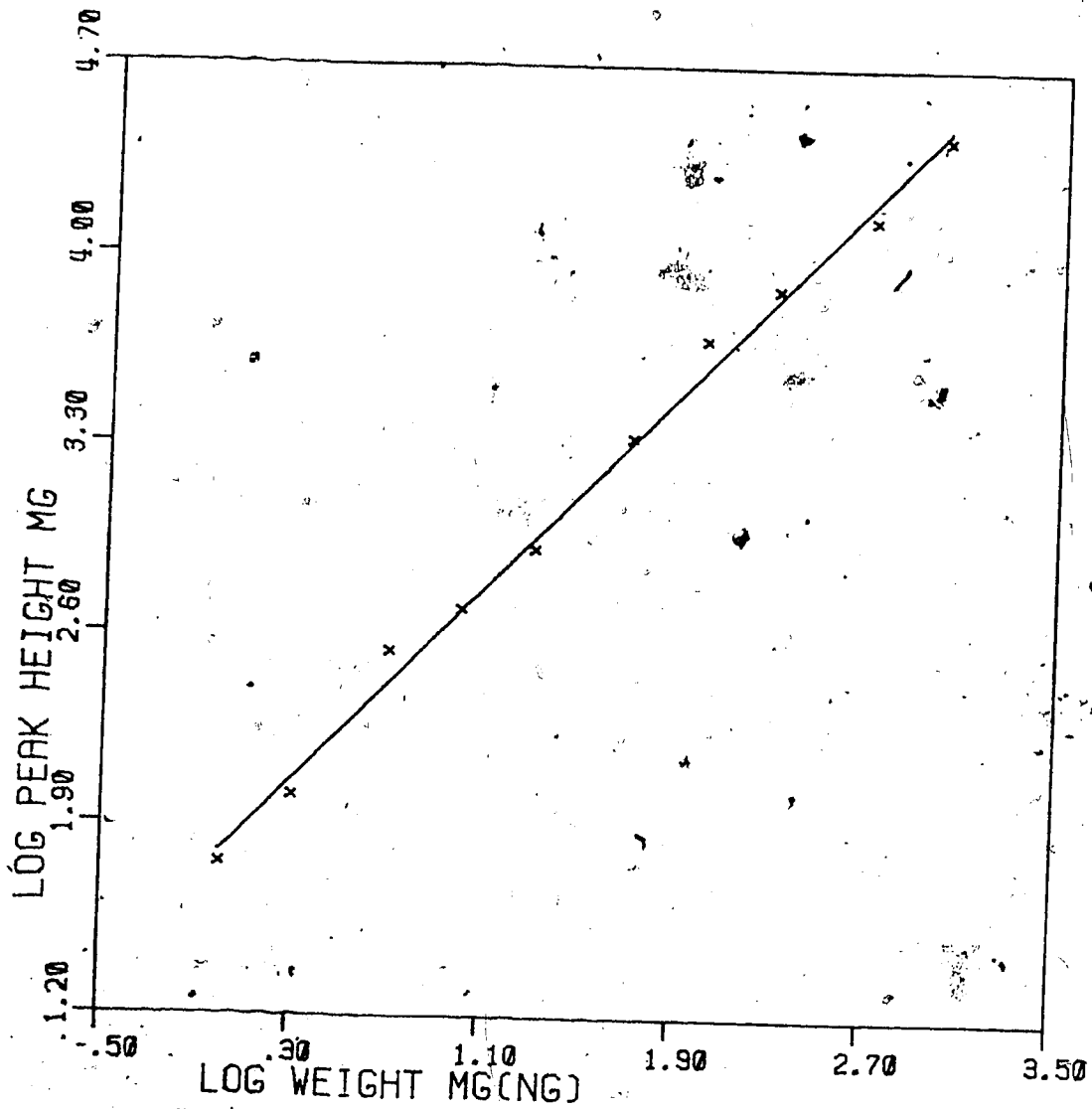
Figure 31. Log-log calibration plot for Mg(I) - 285.213 nm, E_p data.
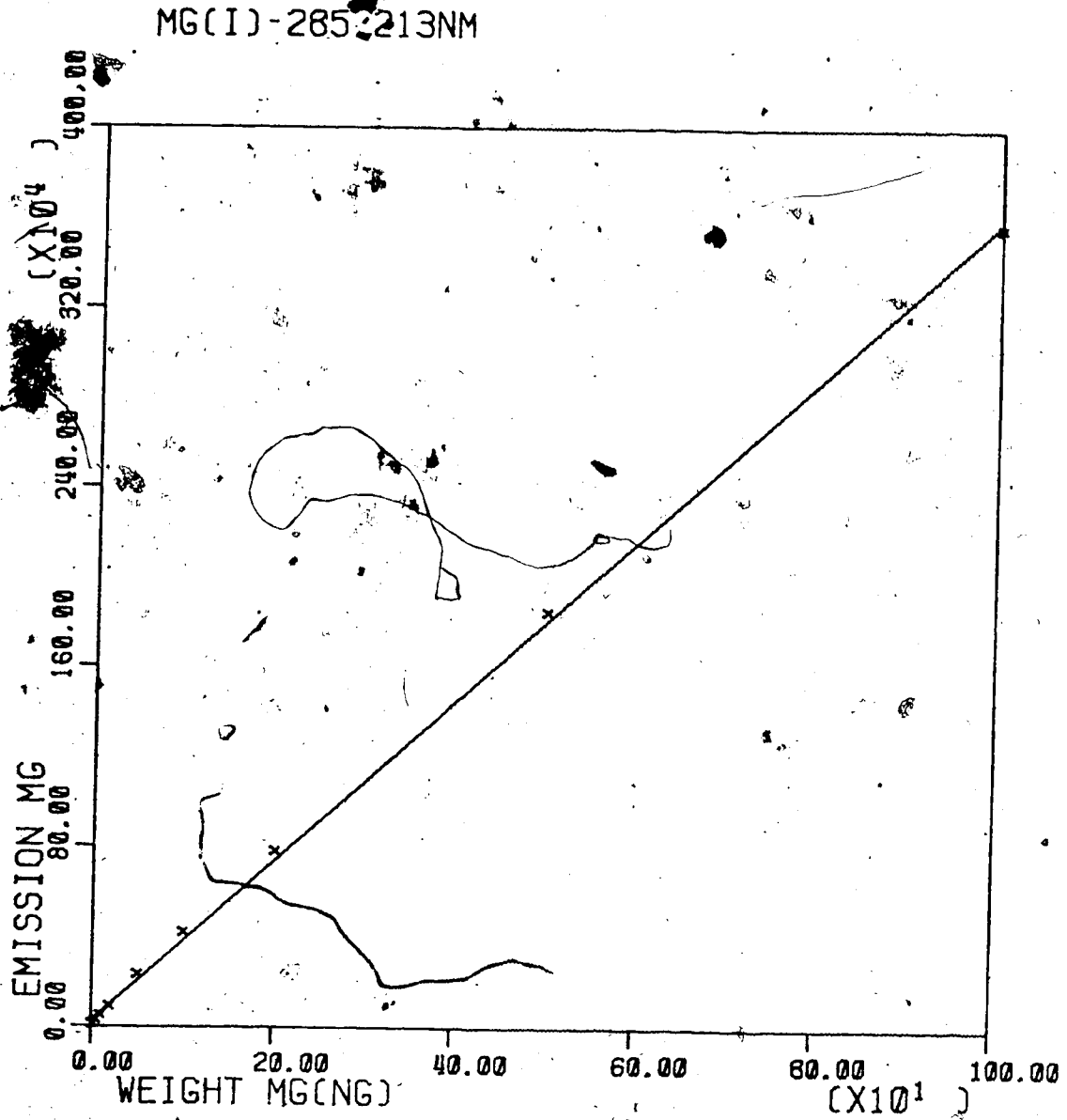
Figure 32. Linear calibration plot for Mg(I) - 285.213 nm, $\int E_t dt$ data.
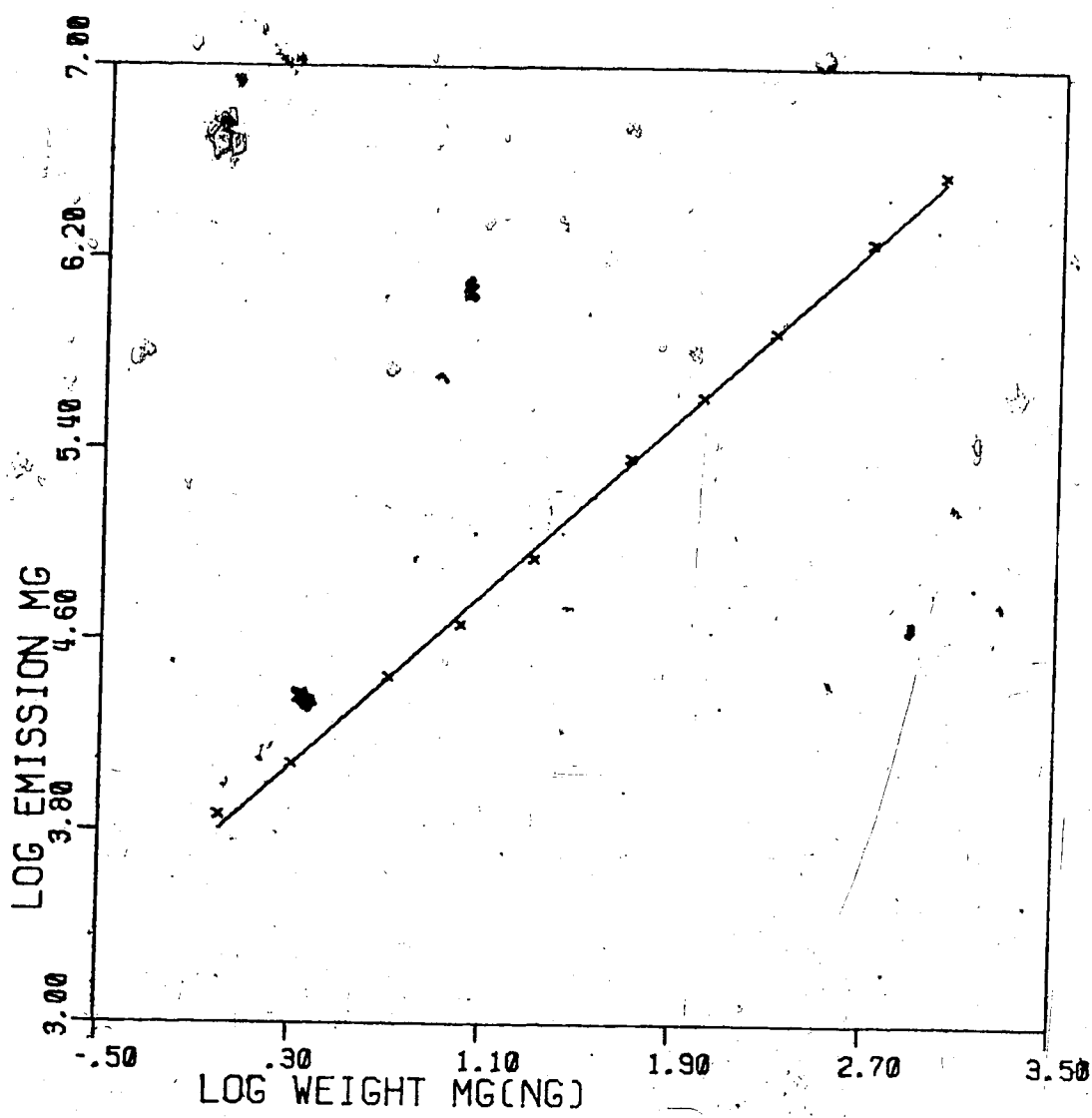
Figure 33. Log-log calibration plot for Mg(I) – 285.213 nm, $\int E_t dt$ data.

All subsequent analytical data were obtained by inte-
gration of the computer data system recorded emission peaks.
Table VII is a compilation of the analytical data for a
number of elements tested. Table VIII through Table XVI are
the calibration data for each element tested while Figure
34 through Figure 41 are the log-log calibration plots for
that data.

In order to compare the sensitivity of this EA system
with the normal nebulizer-based system calibration data
was collected for both the 405.783 nm Pb(I) and the 220.353
nm Pb(II) emission lines while using a commercial Meinhard
concentric glass nebulizer. The experimental arrangement
of plasma, monochromator, and PMT detector remained the same
as with the graphite furnace system but the Laboratory
Data Acquisition System developed in our laboratory by
M. Blades (52) was used for data acquisition. This Data
Acquisition System is a microprocessor-controlled integrat-
ing DVM based on the use of a voltage-to-frequency convertor
and counters. Full details of this Laboratory Data Ac-
quisition System are given in the above reference. The
results are summarized in Table VII and full data and
calibration plots are given in Table XVI and Table XVII
and Figures 42 and 43. When measured at about 100 times
the detection limits the RSD of both nebulizer and EA
systems are about equal. The detection limits are also about

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Table VII

EA-ICAP-OES Analytical Data

Analytical Line (nm)		Range (ng)	Detection Limit (ng)
Pb(I)	405.783	$10^1 - 10^4$	53
Pb(II)	220.353	$10^1 - 10^4$	9
Mg(I)	285.213	$10^0 - 10^3$	1.2
Mg(II)	279.553	$10^0 - 10^3$	0.1
Ag(I)	328.068	$10^0 - 10^3$	0.1
Cu(I)	324.754	$10^{-1} - 10^2$	0.06
Cd(I)	228.802	$10^0 - 10^4$	1.4
Cd(II)	214.438	$10^0 - 10^4$	1.0
Zn(I)	213.856	$10^0 - 10^4$	0.8

Meinhard Nebulizer

| Pb(I) | 405.783 | $10^0 - 10^3$ | 3.6 ppm |
| Pb(II) | 220.353 | $10^0 - 10^3$ | 1.0 ppm |

Table VIII

Calibration Data Pb(I) - 405.783 nm

Weight Pb ng	$\int E_t\, dt$	RSD %
50	7,807	80.3
100	30,056	21.8
200	61,974	16.2
500	115,621	19.7
1000	270,360	8.8
2000	541,627	19.5
5000	1,392,077	7.2
10,000	2,804,412	3.4

Slope = 1.1

R = 1.0

Table IX

Calibration Data Pb(II) - 220.353 nm

Weight Pb ng	$\int E_t dt$	RSD %
10	2,357	27.2
20	5,182	16.6
50	14,916	3.5
100	29,302	2.1
200	70,160	6.4
500	182,635	10.6
1000	358,830	2.6
2000	774,870	4.8
5000	1,696,250	5.1
10,000	4,029,133	4.6

Slope = 1.1

R = 1.0

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Table X

Calibration Data Mg(II) - 279.553 nm

Weight Mg ng	$\overline{\int}E_t\,dt$	RSD %
1	4,958	15.7
2	10,358	3.7
5	28,578	2.6
10	42,372	8.2
20	73,228	1.1
50	200,654	12.0
100	472,733	2.0
200	820,927	2.3
500	1,791,657	2.5
1000	2,813,737	3.9

Slope = 0.93

R = 1.0

Table XI

Calibration Data Ag(I)' - 328.068 nm

Weight Ag ng	$\int E_t\, dt$	RSD %
1	2,137	22.3
2	3,043	3.1
5	11,289	6.2
10	20,249	1.2
20	56,643	4.2
50	128,700	11.1
100	271,758	7.5
200	542,116	13.2
500	1,366,645	6.5
1000	3,016,789	–

Slope = 1.1

R = 1.0

Table XII

Calibration Data Cu(I) - 324.754 nm

Weight Cu ng	$\overline{\int E_t dt}$	RSD %
0.1	3,660	59.1
0.3	10,061	36.6
0.5	13,543	12.7
1	57,483	14.1
3	76,605	6.2
5	146,582	8.8
10	488,370	15.8
30	884,835	1.3
50	2,083,550	3.9
100	5,269,633	6.9

Slope = 1.6

R =   1.0

Table XIII

Calibration Data Cd(I) - 228.802 nm

Weight Cd ng	$\int E_t \, dt$	RSD %
1	483	24.2
3	3,390	33.4
10	13,316	18.3
30	69,050	5.7
100	415,967	5.0
300	3,564,925	3.4
1000	17,022,000	6.7
3000	39,943,000	6.3
10,000	115,312,250	5.7

Slope = 1.4

R = 1.0

Table XIV

Calibration Data Cd(II) - 214.399 nm

Weight Cd ng	$\overline{\int E_t\,dt}$	RSD %
1	839	622
3	11,952	39.4
10	60,260	14.3
100	2,216,100	8.2
1000	33,252,000	3.5
3000	75,508,333	4.7
10,000	213,180,000	7.0

Slope = 1.3

R =   1.0

Table XV

Calibration Data Zn(I) - 213.856 nm

Weight Zn ng	$\overline{\int E_t dt}$	RSD %
1	926	23.8
2	3,160	28.1
5	9,412	20.2
10	22,899	22.4
20	30,546	15.6
50	101,034	9.2
100	286.799	7.7
200	597,191	7.0
500	1,971,730	6.8
1000	4,361,705	5.2
2000	5,745,205	3.1
5000	11,718,955	2.3
10,000	16,440,230	1.8

Slope = 1.1

R = 1.0

Table XVI

Calibration Data Pb(I) - 405.783 nm - Meinhard Nebulizer

Conc. Pb ppm	$\int E_t \, dt$	RSD %
1	236	1061
10	12,220	22.8
100	75,732	4.9
1000	715,782	2.1

Slope = 1.1

R = 1.0

Table XVII

Calibration Data Pb(II) - 220.55 nm - Meinhard Nebulizer

Conc. Pb ppm	$\int E_t \, dt$	RSD %
1	3,538	49.8
10	35,800	16.0
100	318,892	4.3
1000	3,284,320	4.0

Slope = 1.0

R = 1.0

PB(I)-405.783NM
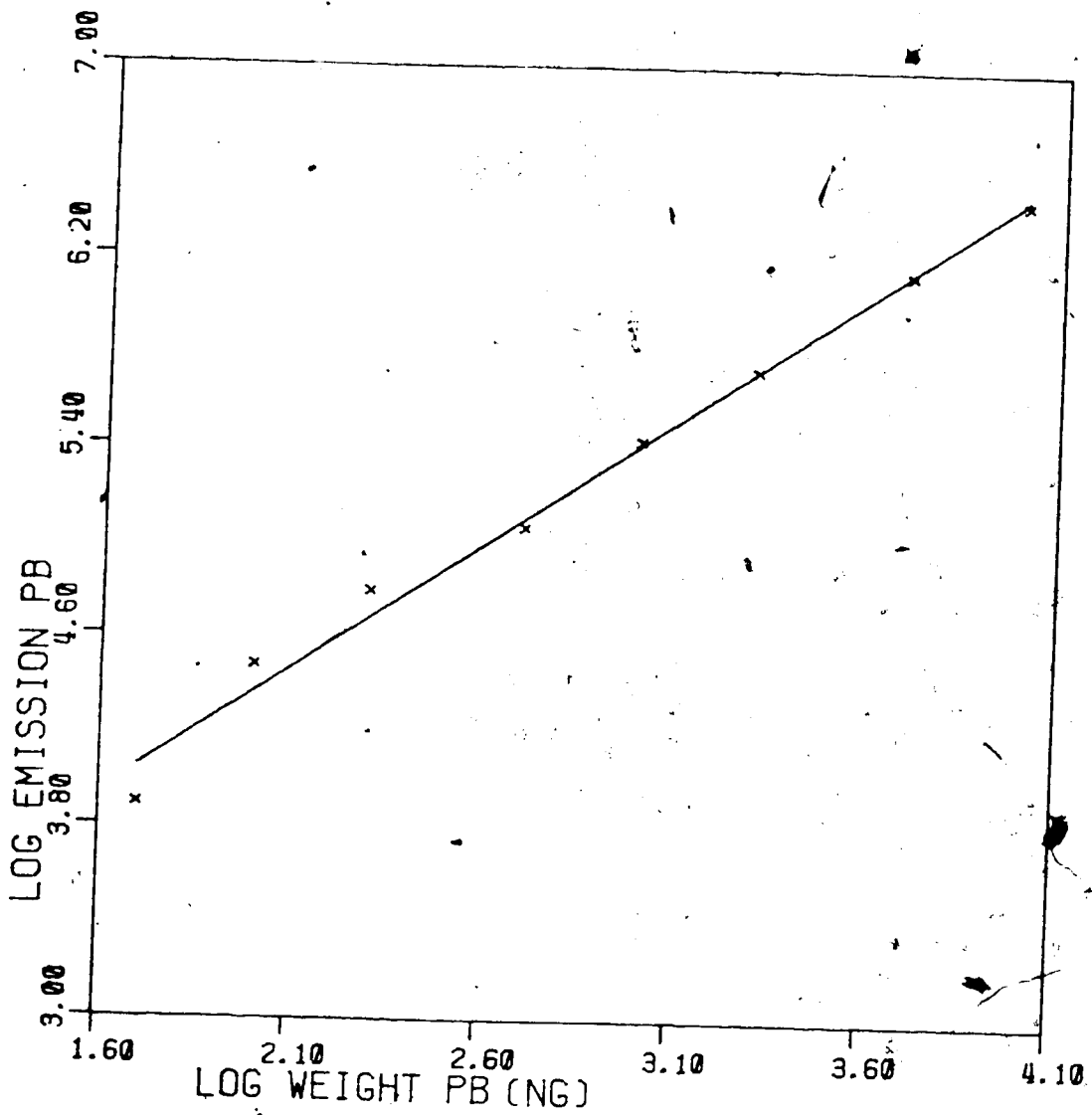
Figure 34. Log-log calibration plot for Pb(I) - 405.783 nm.
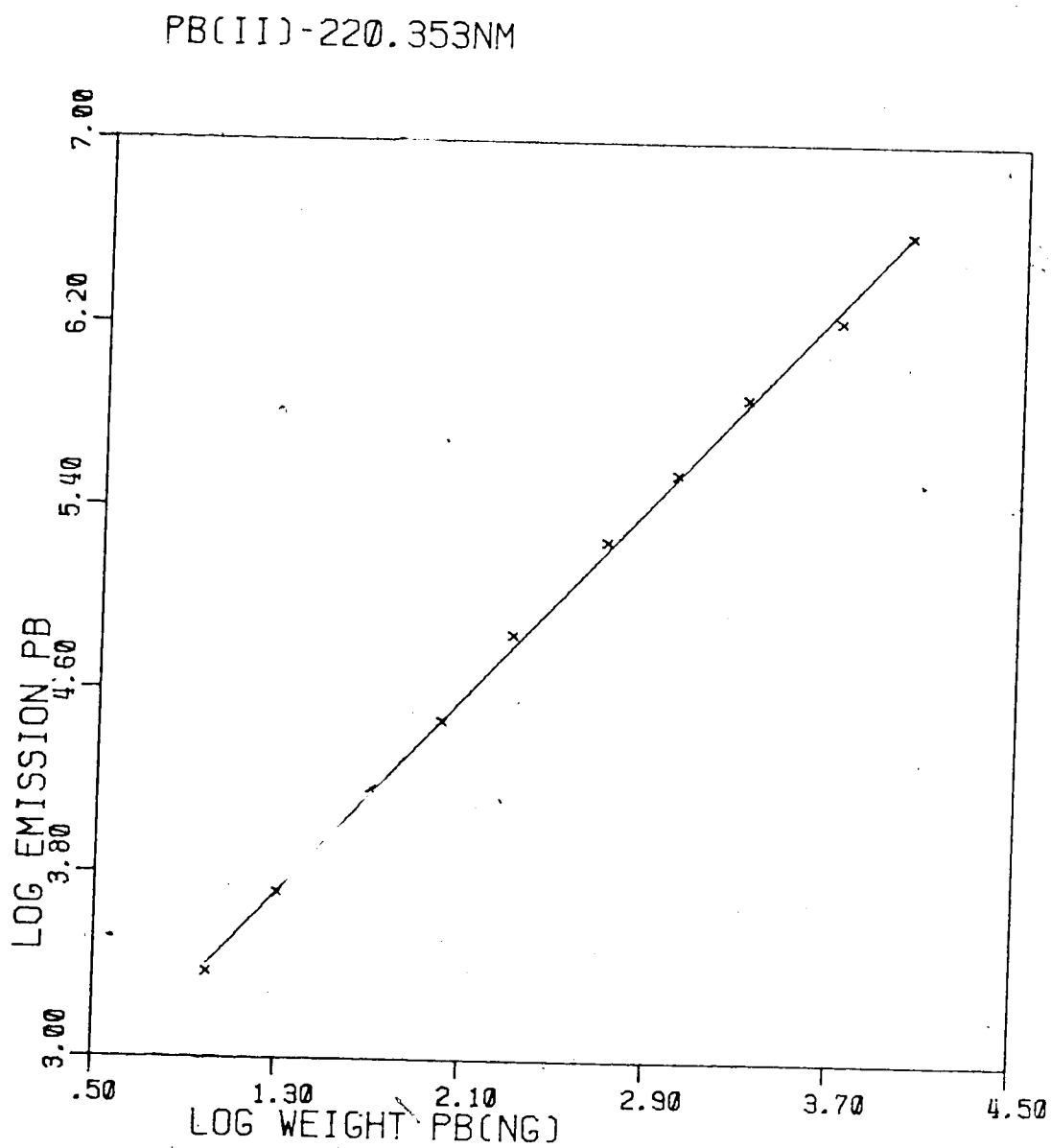
PB(II)-220.353NM

Figure 35. Log-log calibration plot for Pb(II) - 220.353 nm.
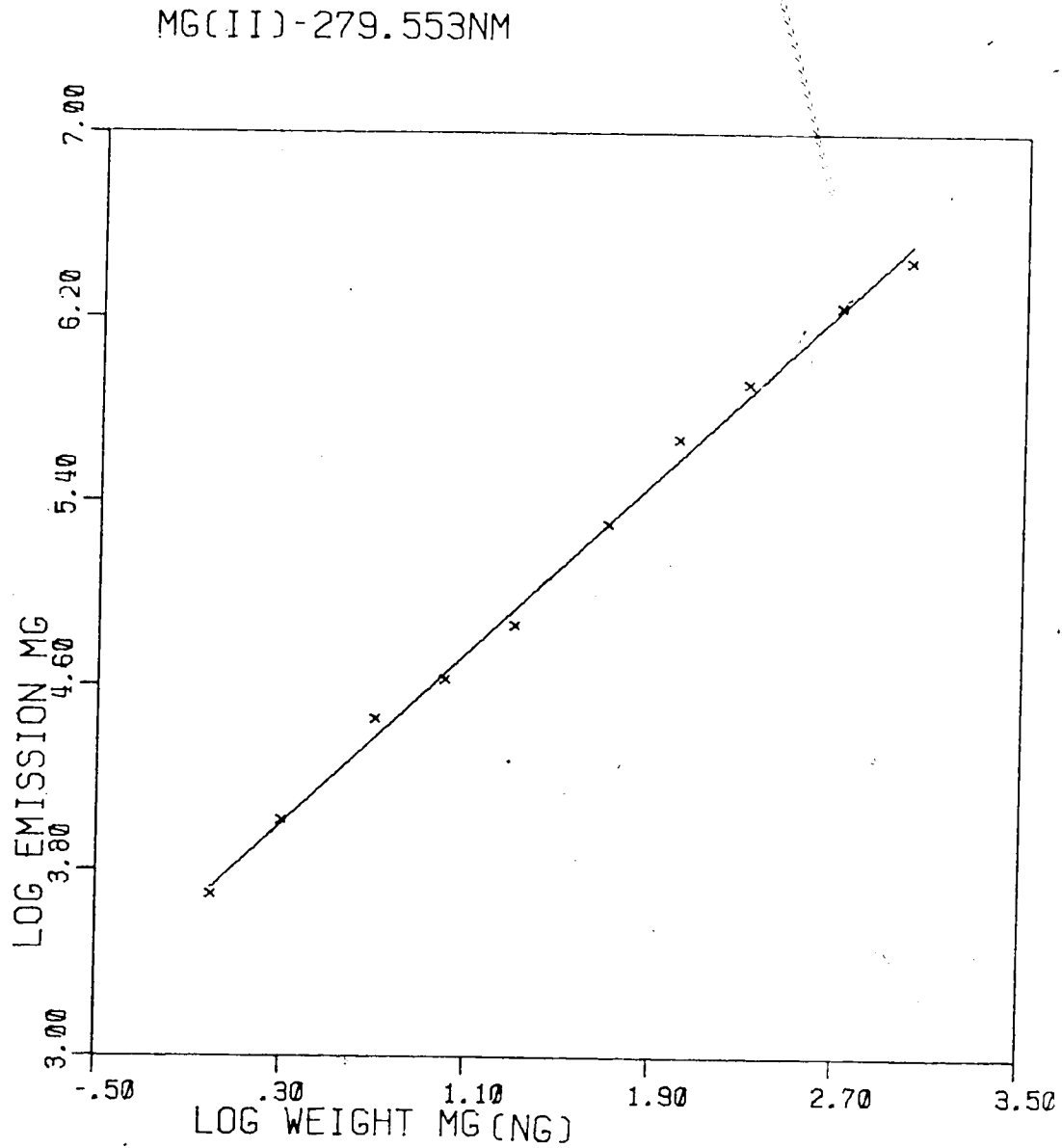
Figure 36. Log-log calibration plot for Mg(II) - 279.553 nm.

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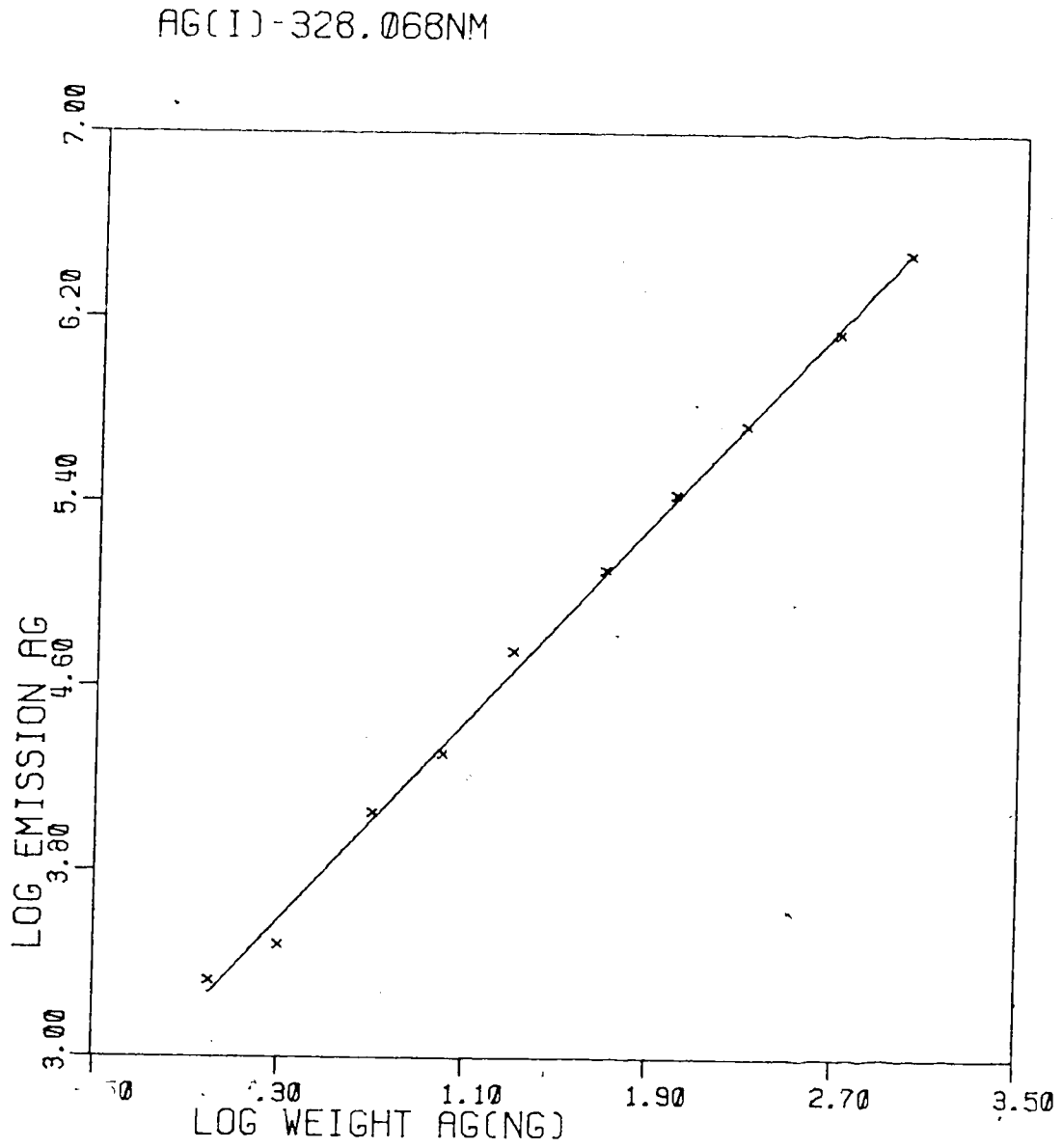
AG(I)-328.068NM

Figure 37. Log-log calibration plot for Ag(I) - 328.068 nm.
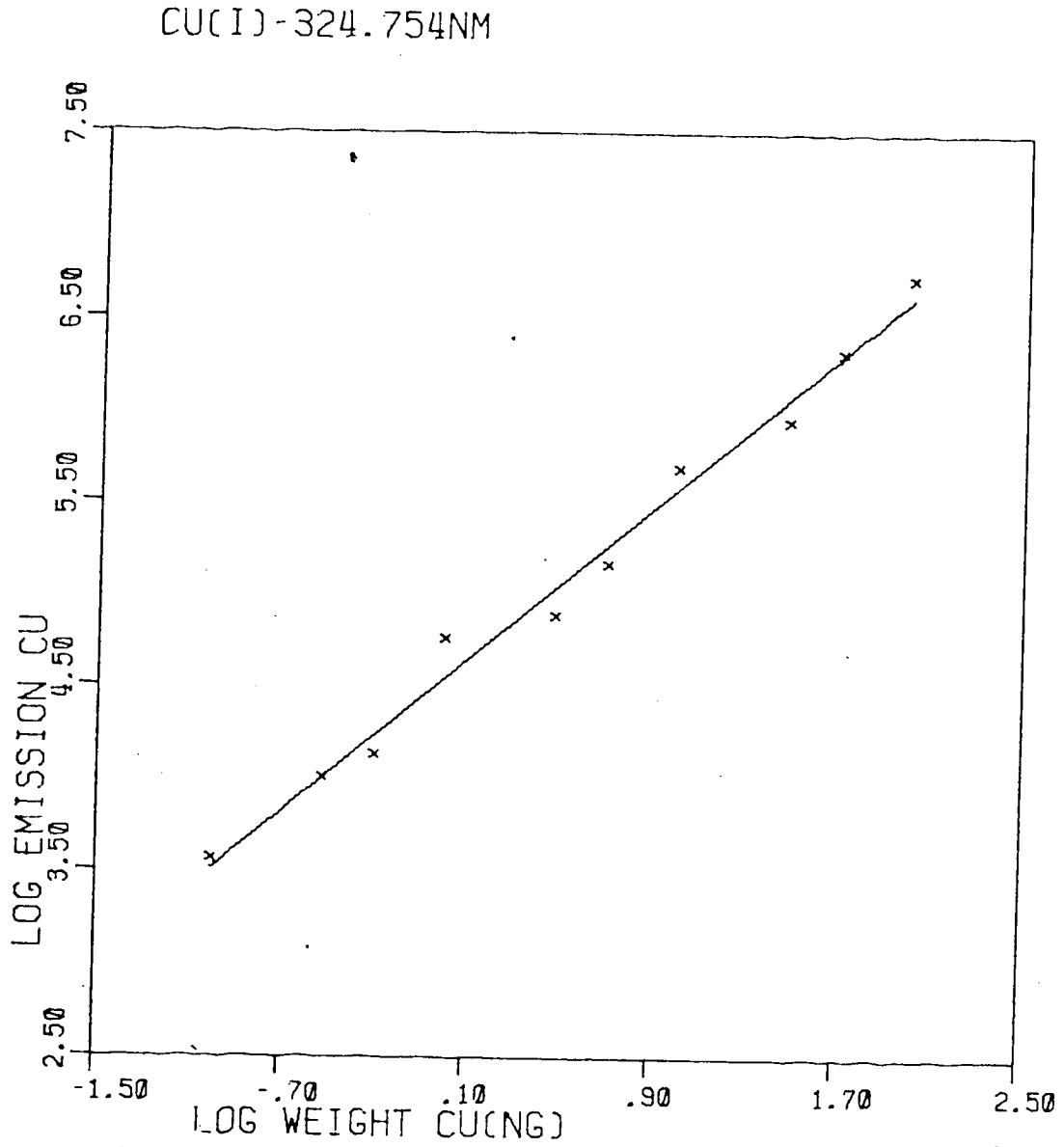
CU(I)-324.754NM

Figure 38. Log-log calibration plot for Cu(I) - 324.754 nm.
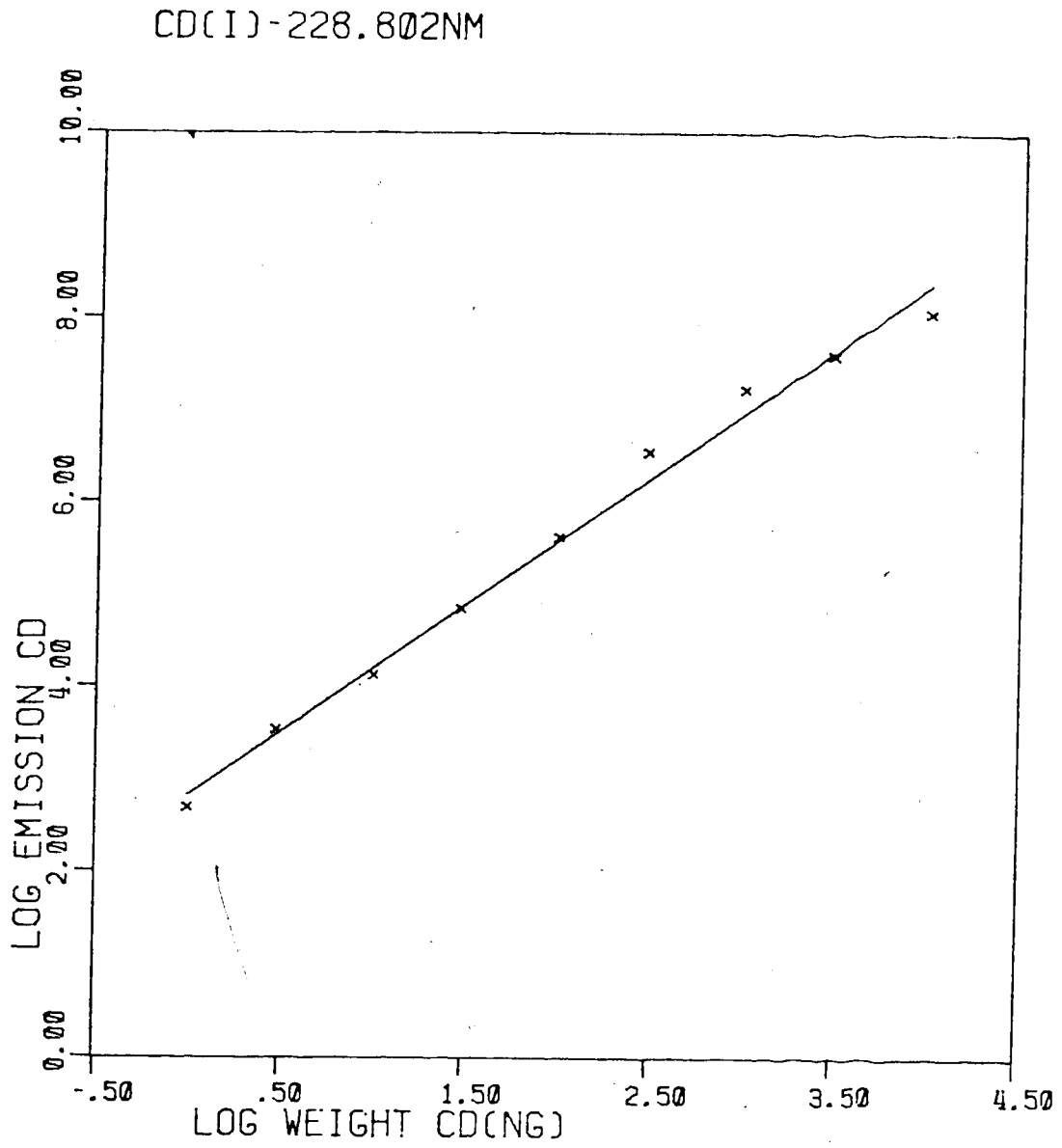
CD(I)-228.802NM

Figure 39. Log-log calibration plot for Cd(I) - 228.802 nm.
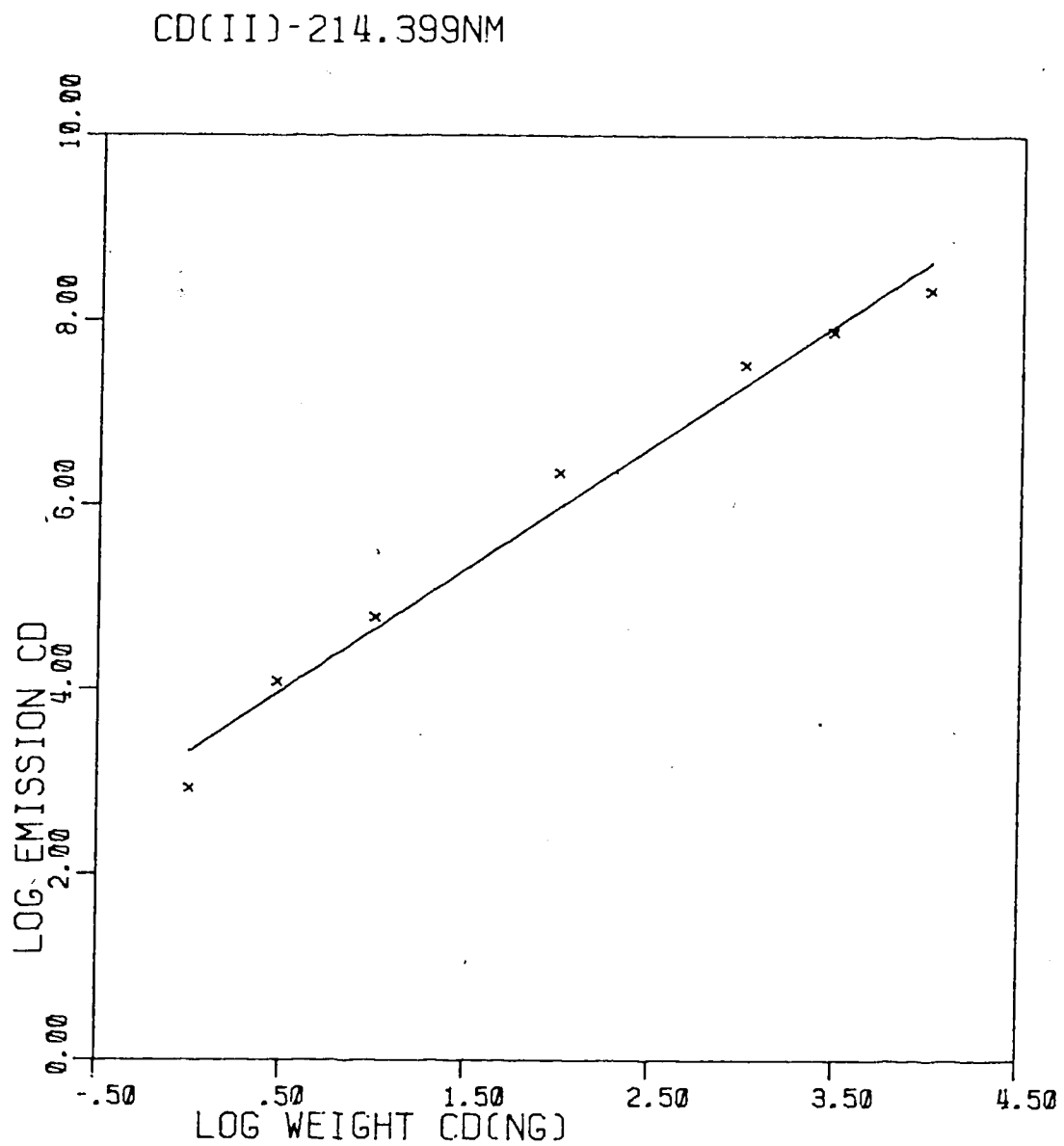
Figure 40. Log-log calibration plot for Cd(II) – 214.438 nm.
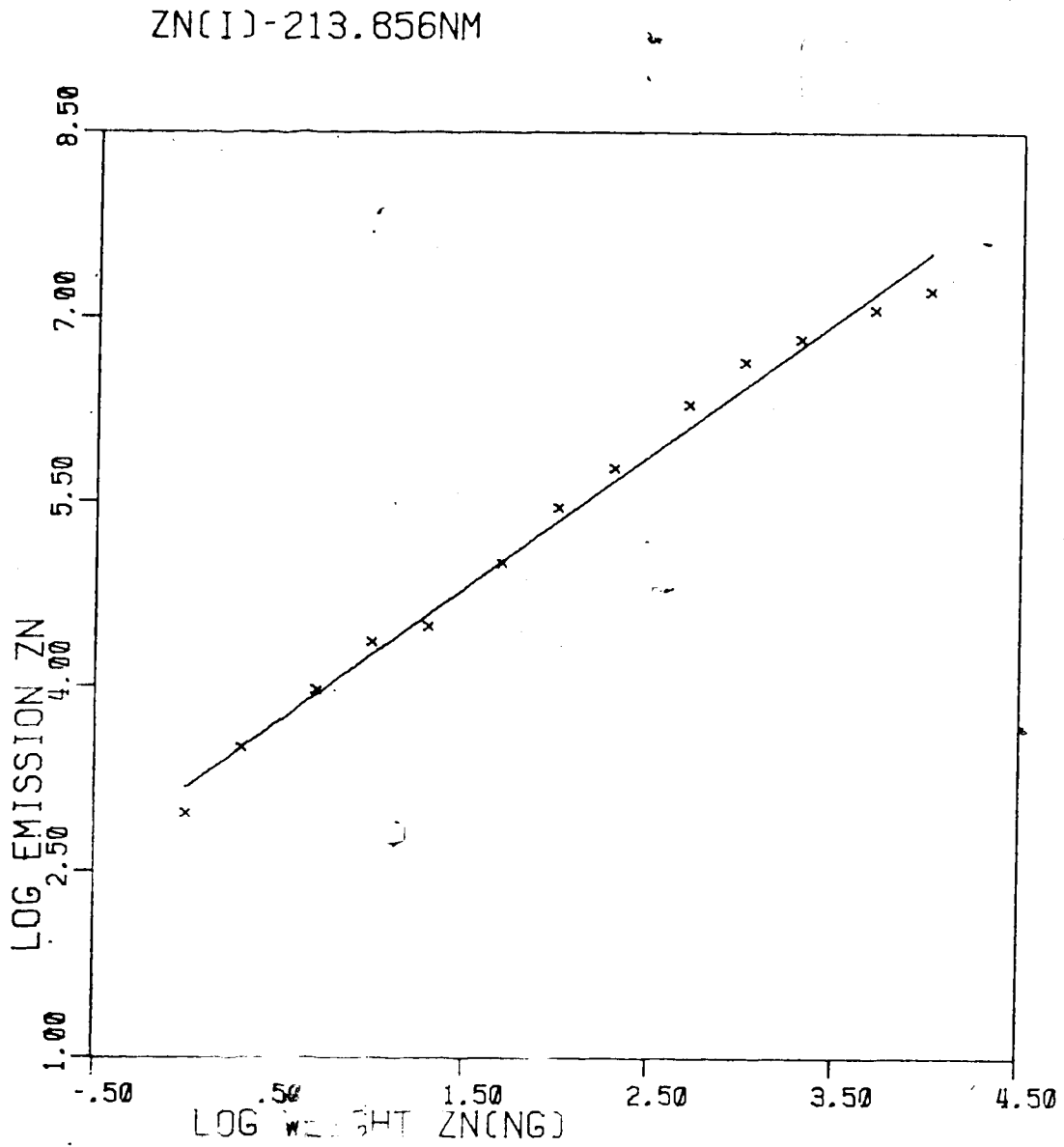
ZN(I)-213.856NM

Figure 41. Log-log calibration plot for Zn(I) - 213.856 nm.
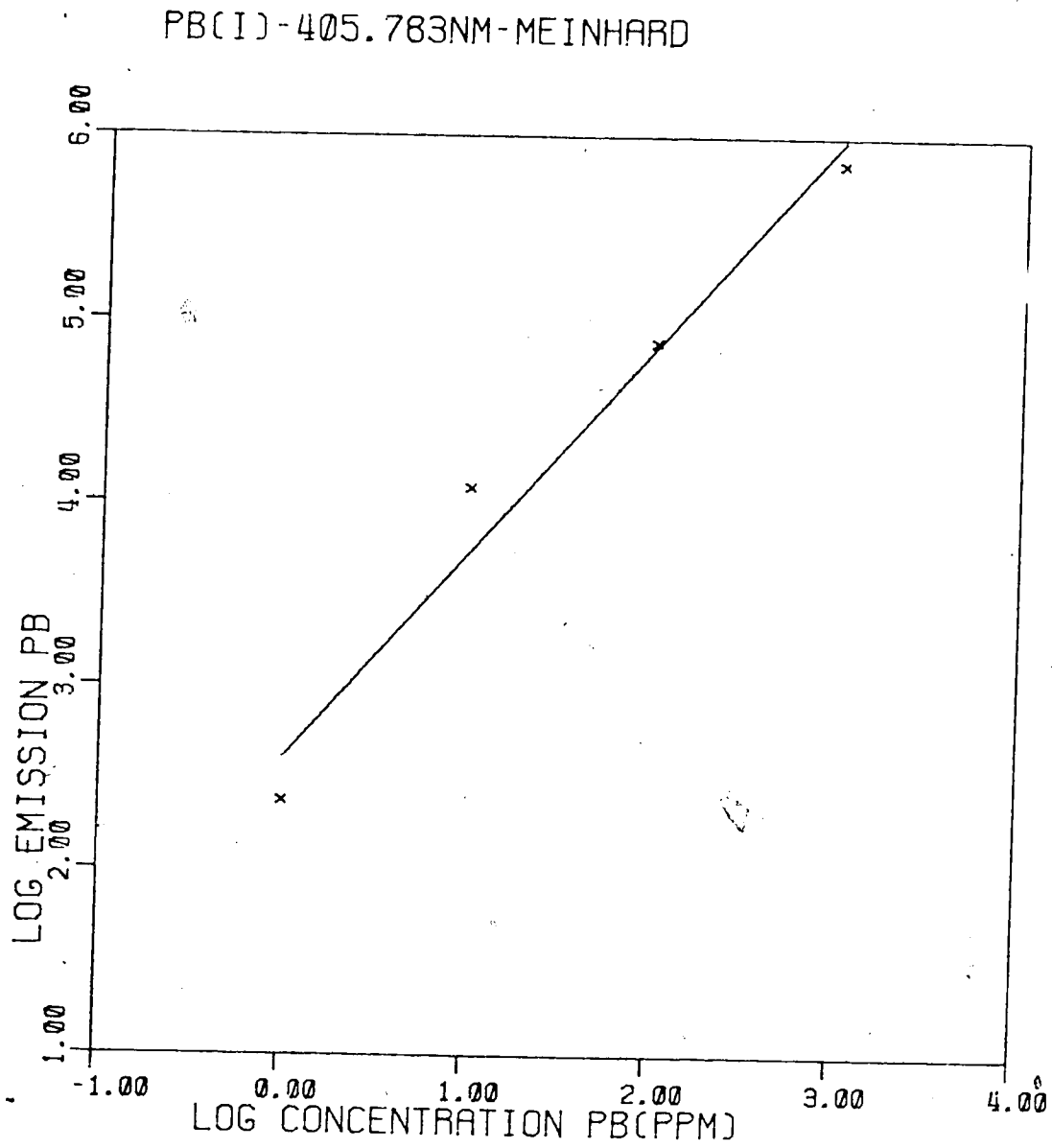
Figure 42. Log-log calibration plot for Pb(I) - 405.783 nm, Meinhard nebulizer.

Figure 43. Log-log calibration plot for Pb(II) - 220.353 nm, Meinhard nebulizer.

equal. The detection limit is defined as the concentration (or quantity) of analyte which gives a signal equal to twice the standard deviation in the background signal. A simple calculation will show that, for instance, the 1.0 ppm solution which can just be detected with the Pb(II) emission line and the nebulizer can just be detected when the graphite furnace EA system is used with a 10 μL sample since 10 μL × 1.0 ppm = 10 ng. Similar results are also obtained with the Pb(I) emission line. It is possible to extend the "concentration" detection limit for the graphite furnace EA system to a lower level by repeatedly adding 10 to 20 μL samples with drying between additions. This technique is commonly used in graphite furnace AA and has been found to work well.

CHAPTER IV

Effect of NaCl Matrix on Pb(II) EA-ICAP-OES Analysis

Perhaps one of the most widely analyzed materials by graphite furnace AAS is lead. Unfortunately this analysis suffers from severe matrix effects. The most common matrix which causes trouble is NaCl which is found in sea water, blood plasma, and urine. This matrix material causes loss of lead as molecular lead chloride, reducing the amount of lead produced as an atomic vapor. The NaCl also causes both molecular absorption and light scattering from recondensed NaCl particles which interfere in the light absorption measurement. These interference problems have been investigated by a large number of workers and several techniques have been developed to reduce these interferences. The use of background absorption correction helps but chemical modification techniques have also been shown to be very helpful. The most common chemical modification techniques are the use of added HNO_3 (53,54), NH_4NO_3 (55, 56), or $La(NO_3)_3$ (57,58). The use of a constant temperature Woodriff AAS furnace has also been suggested as a means of overcoming the interference effect of NaCl or other salts on Pb determination (59).

Matrix interference effects in ICAP-OES have generally been found to be quite small when compared to the inter-

ferences found in flame emission or in either flame or non-flame atomic abs rption spectrometery. A short review of the matrix interferences in ICAP-OES is given in Reference 5 and it is pointed out that when ICAP operating conditions are properly chosen these interferences can be reduced to negligible proportions.

The results presented in Chapter III have shown that with EA-ICAP-OES large amounts of analyte have caused changes in the vaporization behavior, but good analytical results could still be obtained by using a signal integration technique. The determination of Pb in a NaCl matrix was chosen as a test of the effect of matrix interference on EA-ICAP OES. This system was chosen because it was felt that EA-ICAP-OES might offer an alternative solution to determination of Pb by AAS.

This study of NaCl matrix interferences on Pb emission can be separated into three parts. The first is a study of Pb(II) emission and plasma background emission temporal changes, second is a study of background corrected Pb emission intensity changes, and the third is a study of changes in spatial emission intensity. The first two studies will be discussed in this section and the spatial study in the next.

A. Effect of NaCl Matrix on Pb(II) Emission Temporal Behavior and Emission Intensity

The study of changes in temporal behavior can be sum-
med up in four plots of emission intensity vs time. Figure
44 is a normal blank plasma background while Figure 45 is
the plasma background when 200,000 ng of sodium as NaCl
are vaporized as a blank. The NaCl blank shows a sig-
nificant rise in the plasma background emission level,
especially after the first two seconds while a distilled
water blank shows a decrease in plasma background emission
after the first two seconds. This change in plasma back-
ground emission is large enough to cause an increase in the
Pb emission intensity value at high NaCl levels unless a
blank of approximately equal NaCl concentration is used.

Figure 46 is a plot of emission intensity vs time for a
10 μL sample of 10 ppm solution (100 ng Pb) in distilled
water. The peak shape is normal in that it shows a quick
rise to a maximum and a smooth decay to a level background
level. Figure 47 is also an emission vs time plot for
100 ng of Pb, but with 200,000 ng of sodium as NaCl also
present. The peak height is obviously depressed, the decay
is no longer smooth, and emission is extended over a
slightly longer time. The temporal changes caused by the
large amount of matrix material appears to be similar to
those caused by a large amount of analyte. One possible
explanation of these temporal effects is that the larger
mass of material requires a longer time to vaporize, thus
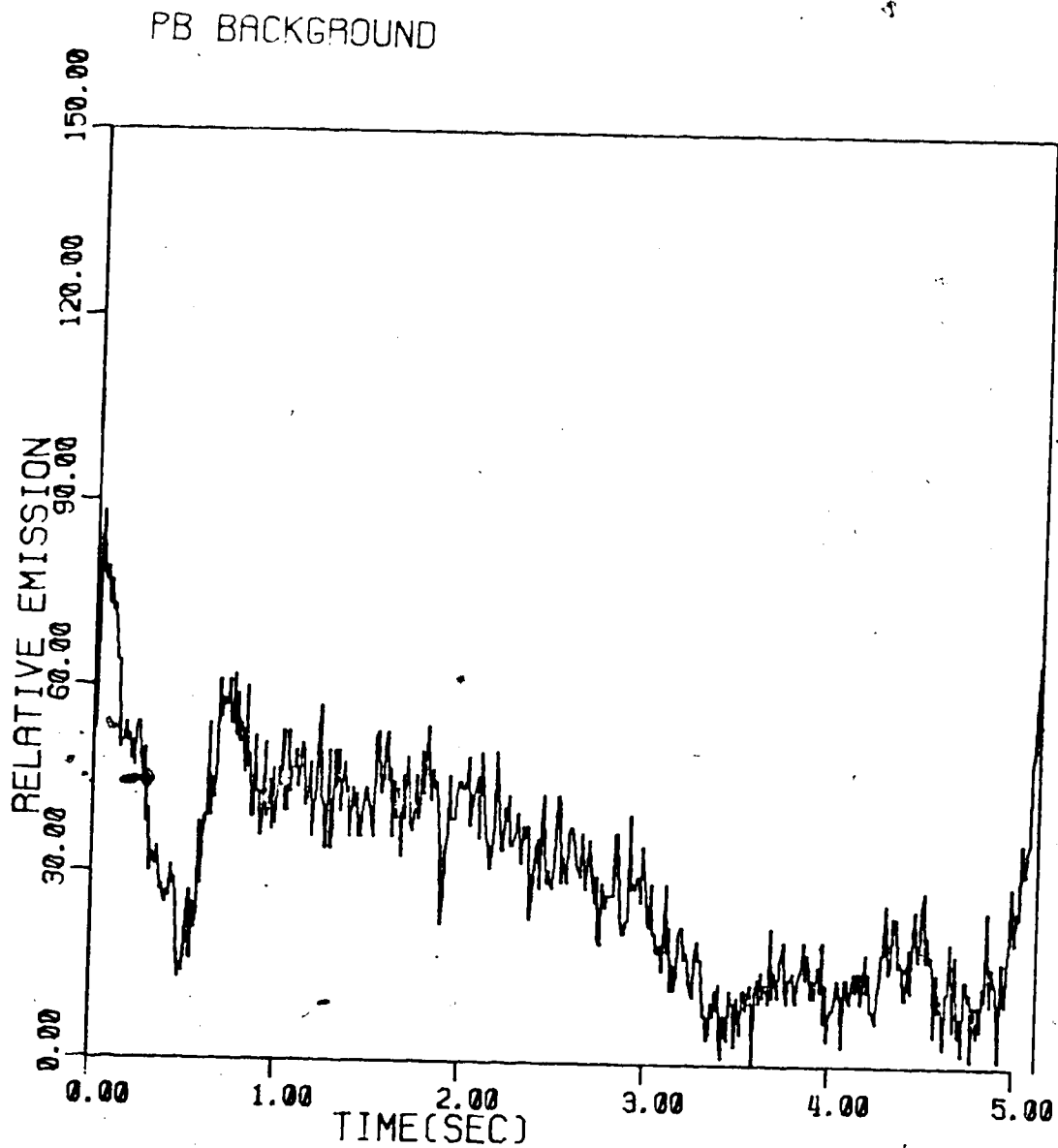
Figure 44. Temporal profile, blank Pb(II) - 220.353 nm.
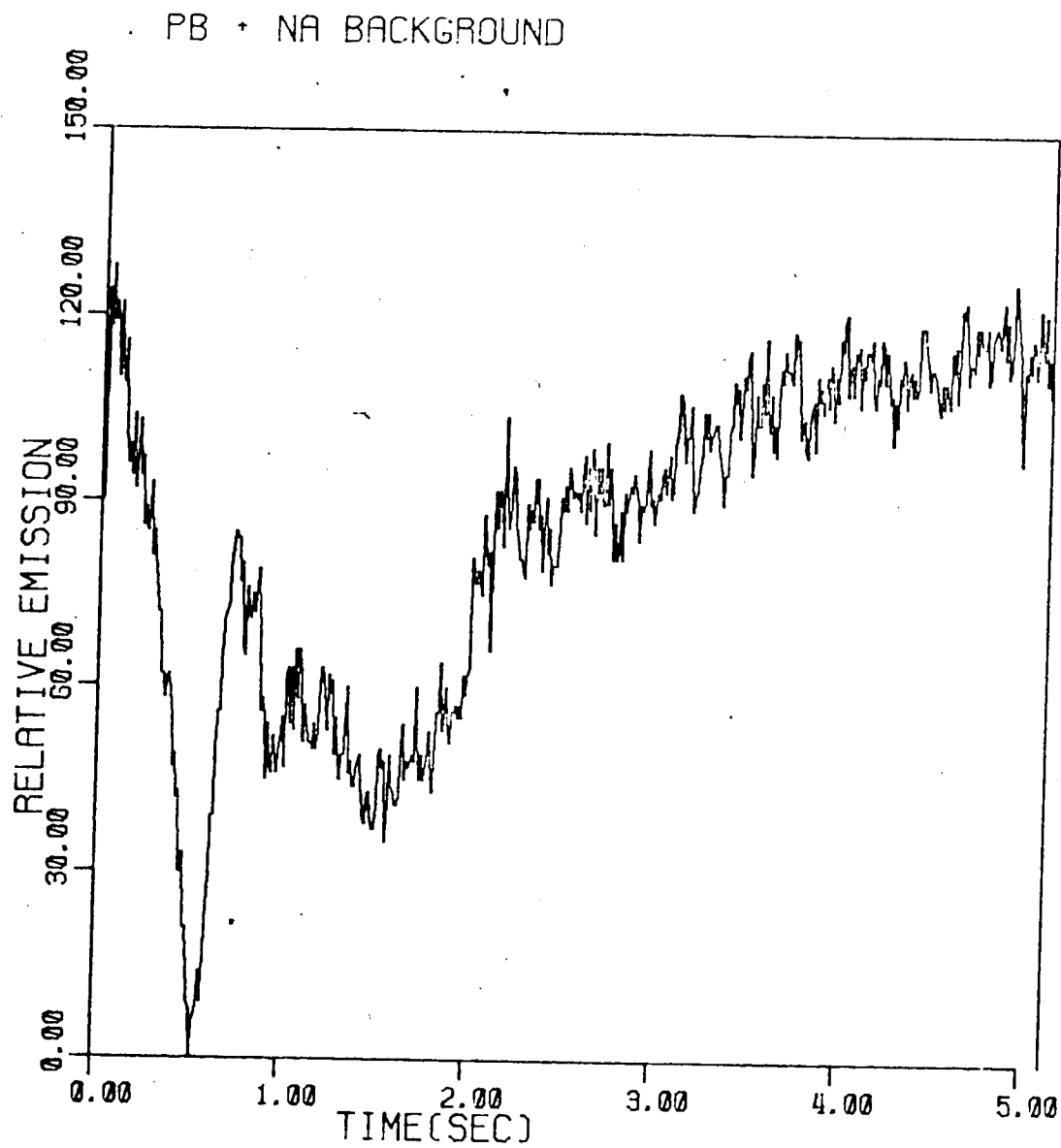
Figure 45. Tempral profile, blank containing 200,000 ng Na$^+$ as NaCl, Pb(II) – 220.353 nm.
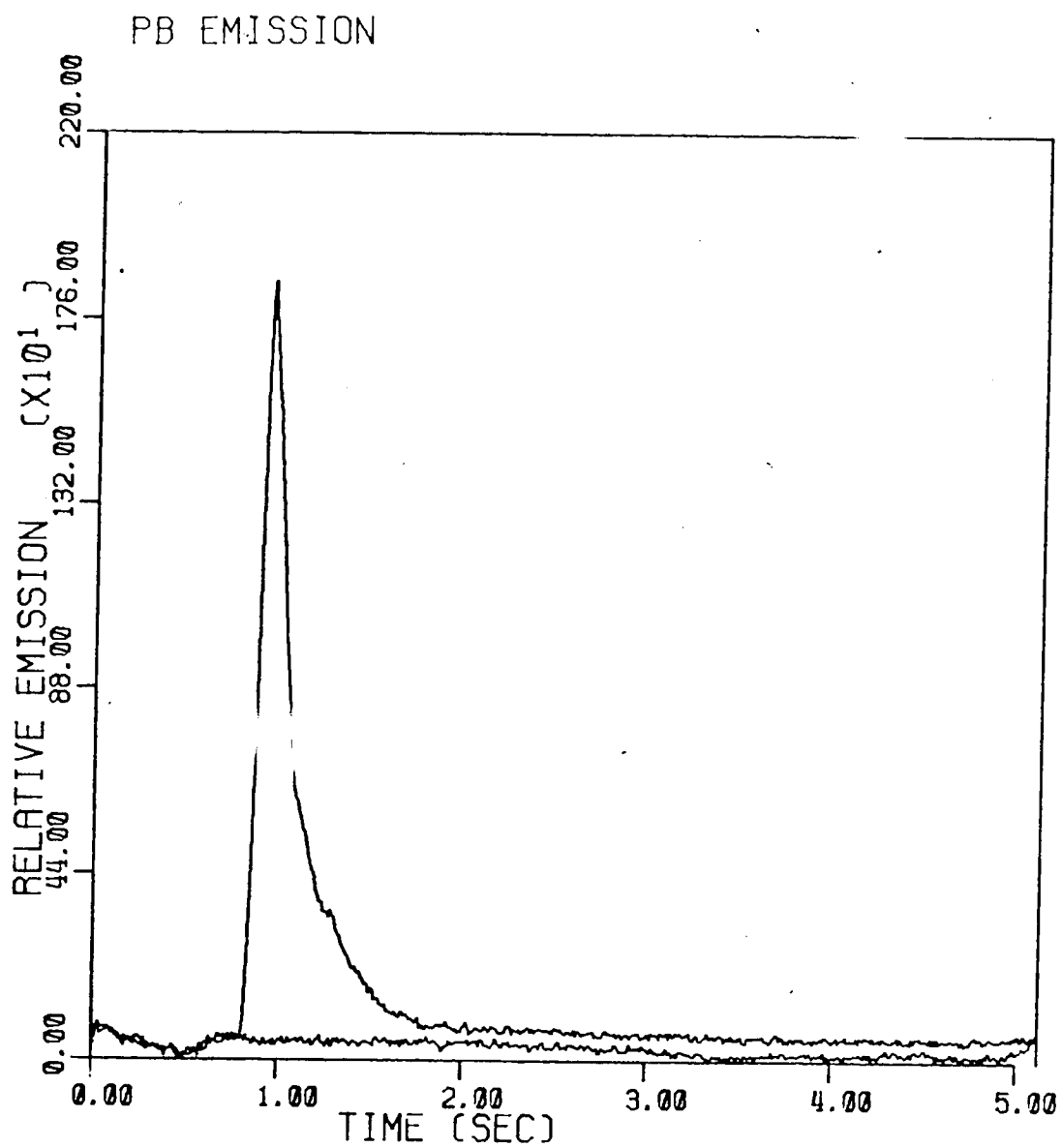
PB EMISSION

Figure 46. Temporal profile, 100 ng Pb(II) - 220.353 nm.
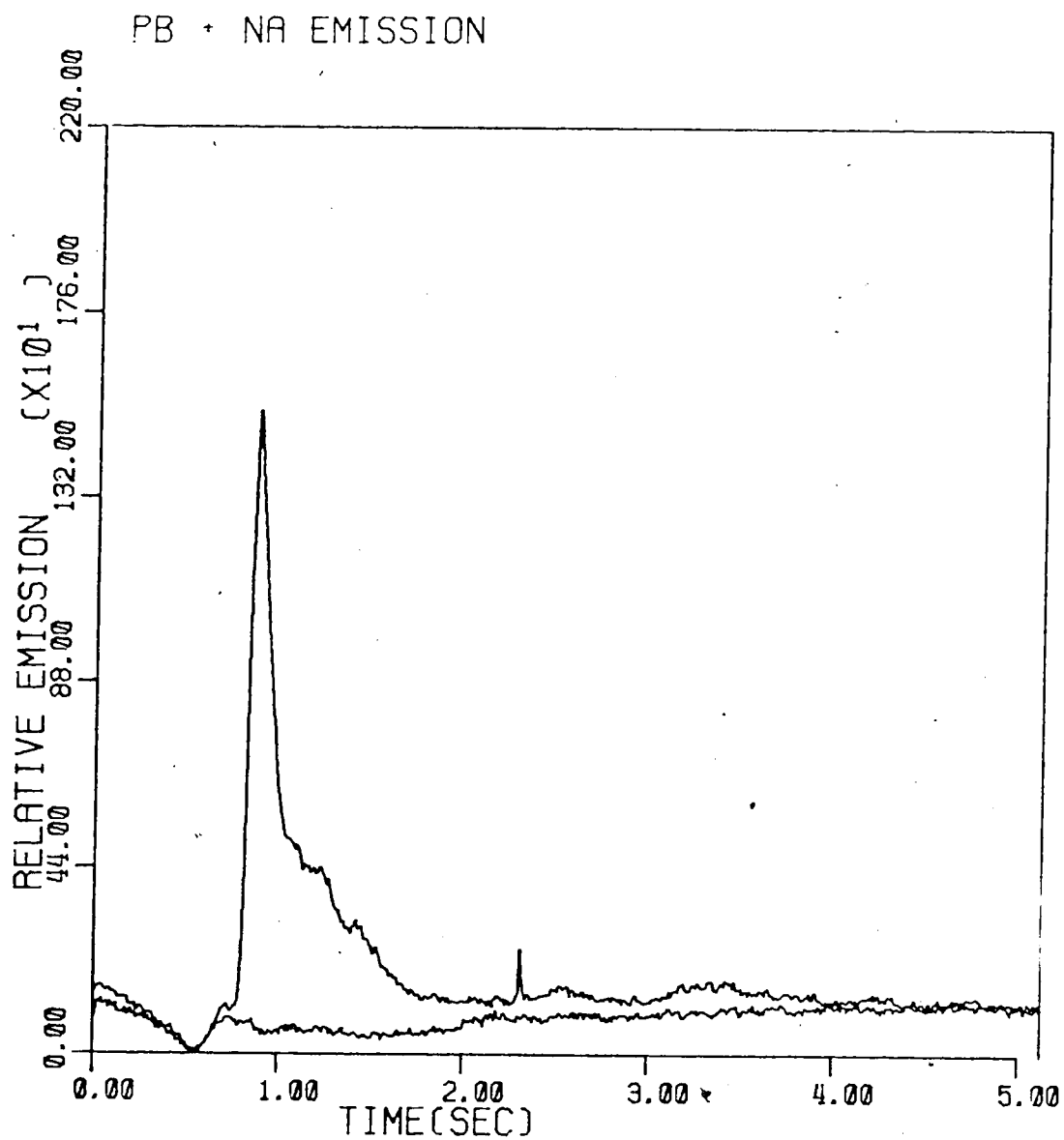
Figure 47. Temporal profile, 100 ng Pb(II) - 220.353 nm.
Matrix of 200,000 ng of Na$^+$ as NaCl.

reducing the peak emission and extending the time of emission.

Table XVIII gives the Pb emission intensity data for a series of solutions containing zero to 20,000 ppm of added sodium as NaCl which is greater than the concentration of NaCl in sea water. The data given is background connected, where the background is for a blank solution containing the same concentration of NaCl as the Pb solution. The sample size was 10 μL, therefore the Pb quantity was 100 ng and the sodium quantity ranged from 0 to 200,000 ng (0.2 mg). The results are shown graphically in Figure 48. Although the plot shows a slight rise in Pb emission intensity with increasing NaCl concentration this increase is not significant. This increase in intensity is probably due to instrumental drift during the four hours required for this experiment.

B. Matrix Effects on Pb(II) Spatial Emission Profiles

In Chapter II the use of a photodiode array mounted vertically in the focal plane of the monochromator was introduced as a tool for measuring vertical spatial emission intensity profiles. References 50 and 51 are examples of how this technique has been used. Data given in Reference 59 for Ca(II) emission at 393.3 nm and Cr(II) emission at 283.5 nm show that as the ratio of an easily ionized matrix material to analyte increases the emission

Table XVIII

Effect of Sodium on Pb(II) - 220.353 nm Emission

All Samples 100 ng Pb

Wt. Na as NaCl ng	$\overline{\int E_t dt}$	RSD %
0	43,992	3.4
2	46,110	13.1
20	38,729	13.1
200	43,754	4.3
2,000	43,653	4.7
20,000	48,629	5.0
200,000	46,820	25.9

EFFECT OF NA-PB(II)-220.353NM
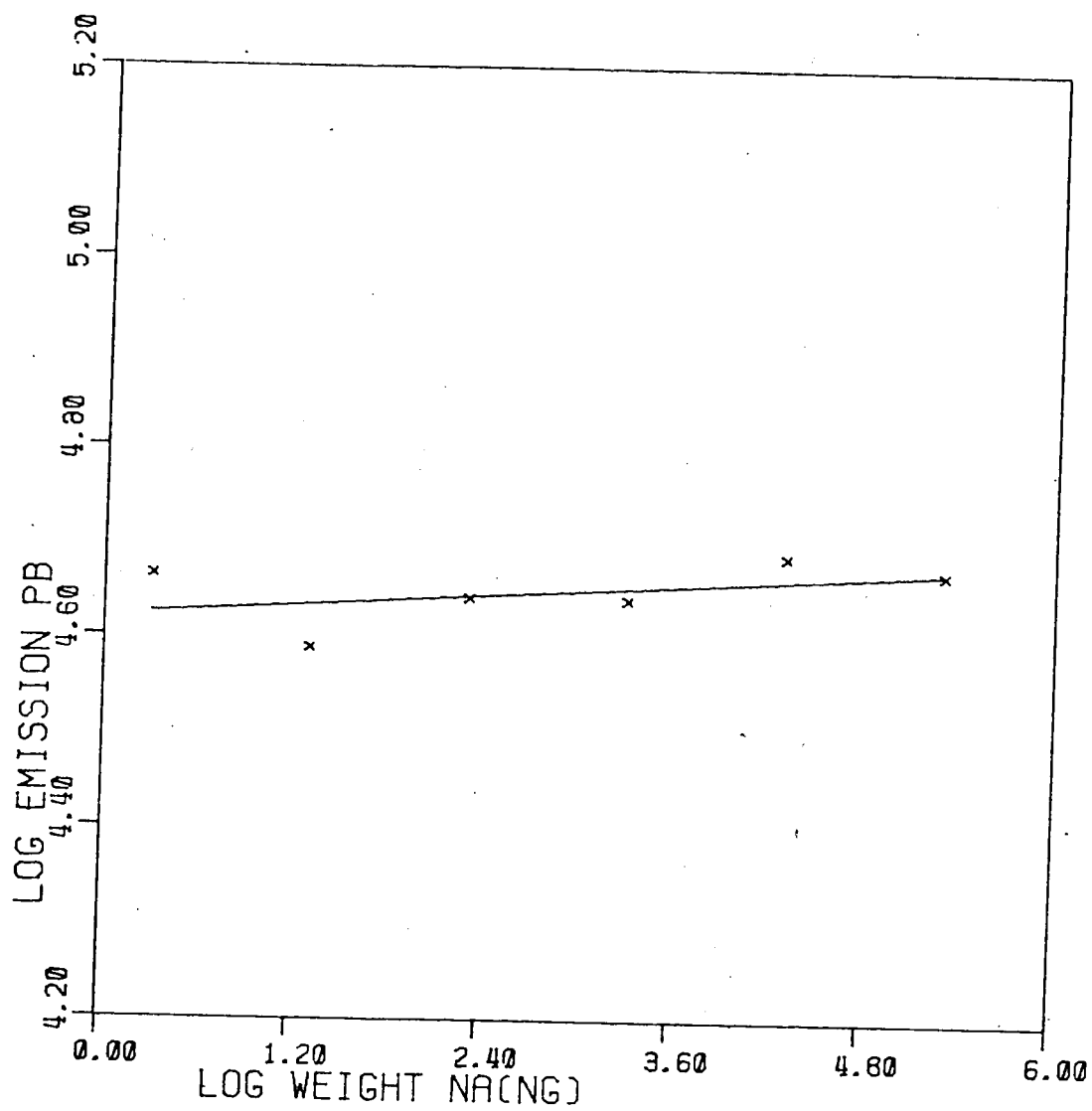
Figure 48. Effect of Sodium ion Pb(II) - 220.353 nm emission.

profile of the analyte shifts lower in the plasma. In order to check for this type of behavior 5 µL samples of 1000 ppm Pb in distilled water were vaporized both with and without 5 or 10 µL additions of 20,000 ppm sodium as NaCl. The vertical spatial emission profiles obtained for the Pb(II) emission line at 220.353 nm for ratios of Na/Pb = 0 and Na/Pb = 20 are given in Figure 49 and 50. The results obtained are consistant with the results shown for Ca(II) and Cr(II) in Reference 51 in that the emission shows an increase at lower heights above the coil and a decrease in emission at higher heights. The point of maximum emission has also shifted from 14.7 mm above the load coil to 12.2 mm. This spatial shift would be expected to increase as the ratio of matrix material to analyte increases, therefore, the choice of slit height and the height of observation can be very important. As an example, if the slit height were chosen to be small, for instance 1 mm or 2 mm, and centered at about 15 mm above the load coil then a large excess of matrix could cause the measured signal to decrease. On the other hand if the slit was centered at 12 mm above the load coil the emission intensity could increase under the same conditions. In the measurement described in section B a slit height of 12 mm centered at about 17 above the coil and an image magnification of -0.5 meant that the height observed was from about 5 mm to 30 mm above the load coil.
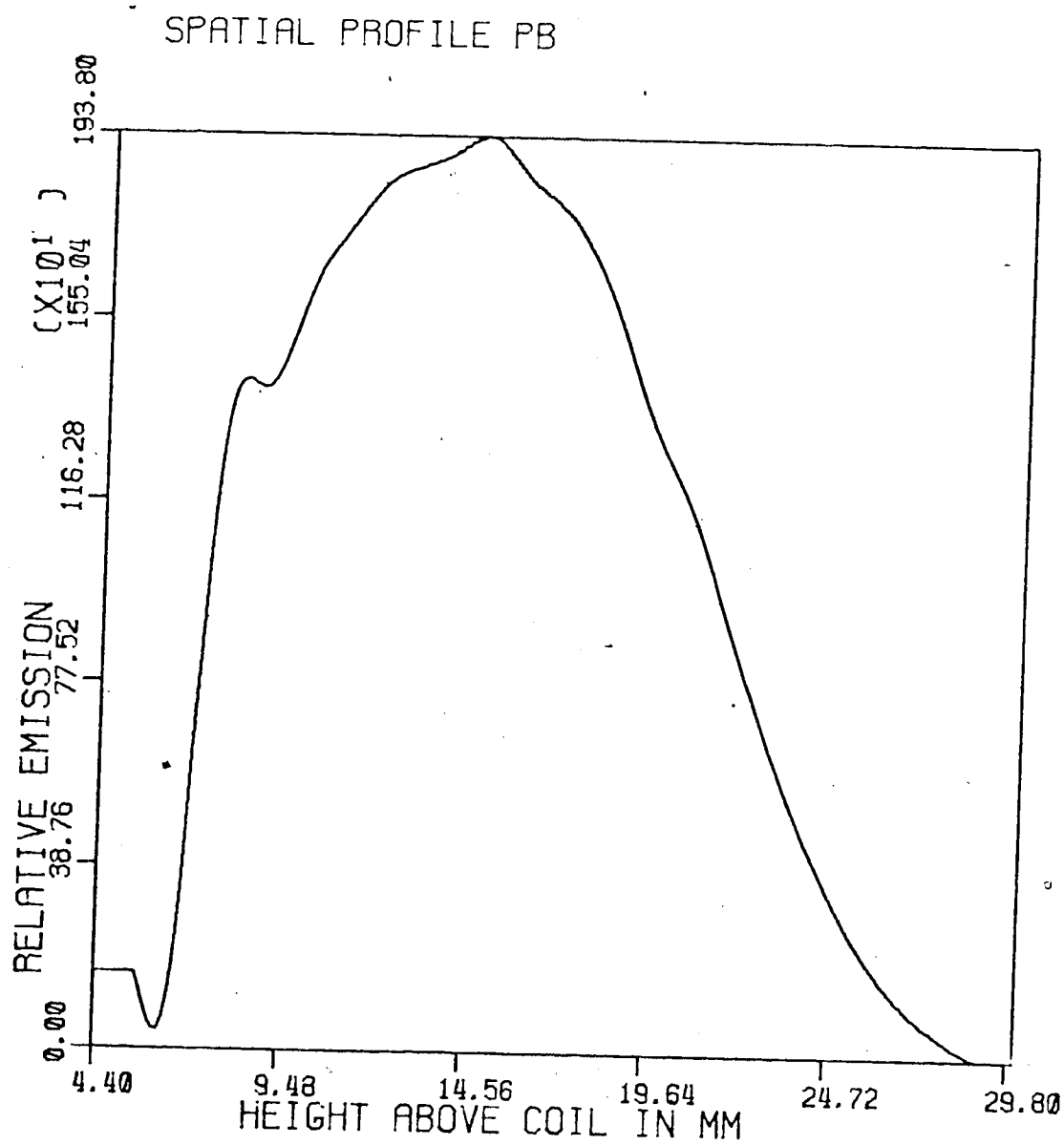
Figure 49. Vertical emission profile, Na/Pb = 0.

SPATIAL PROFILE PB + NA
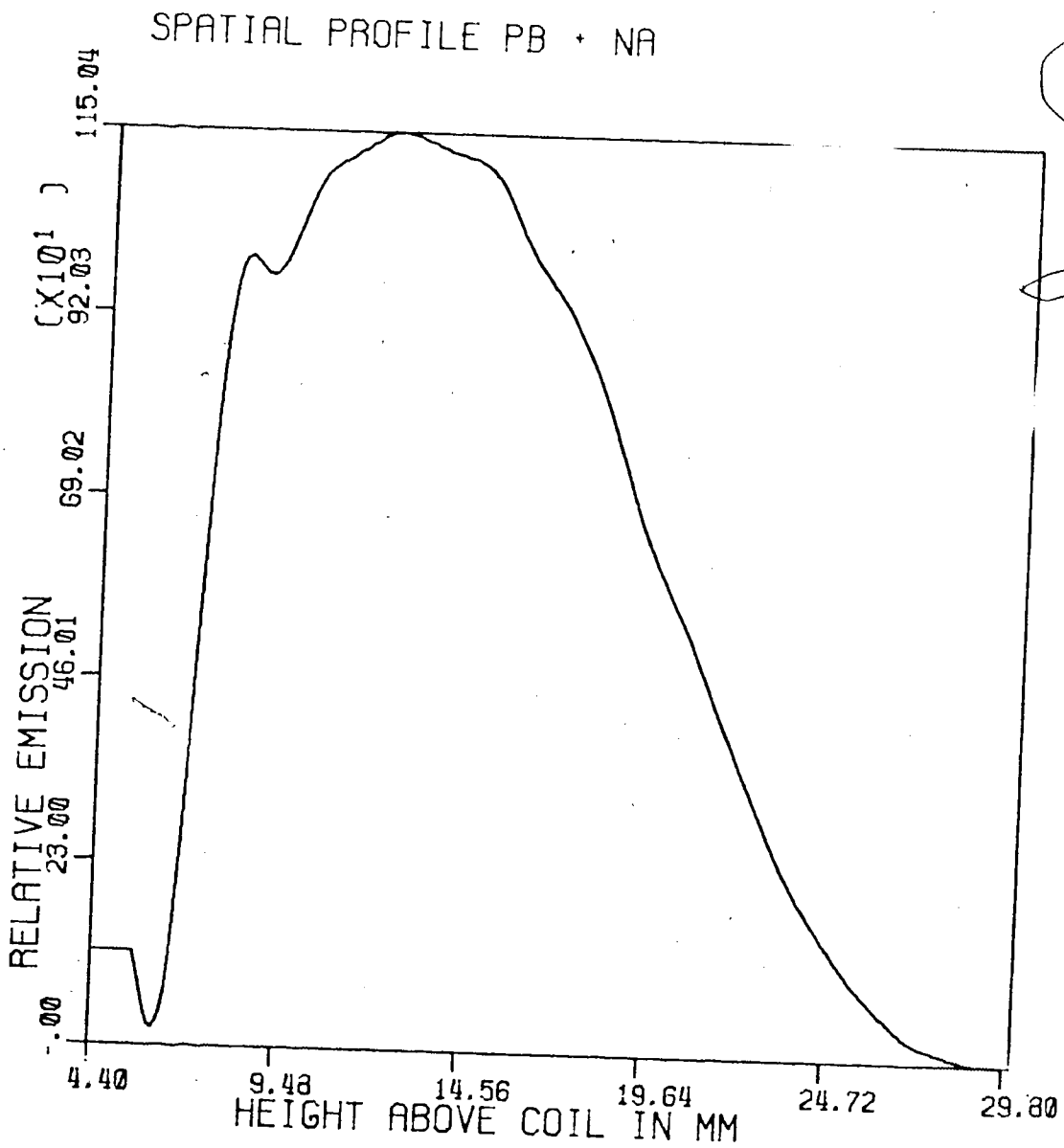
Figure 50. Vertical emission profile, Na/Pb = 20.

With these conditions spatial shifts would be expected to
cause little change in measured emission intensity as
observed in the work reported in section A.

CHAPTER V

Direct Solids Analysis by EA-ICAP-OES Using a

Computer Coupled Photodiode Array

Direct Reading Spectrometer

One of the main objectives of this experimental work
was to test the graphite furnace EA-ICAP-PES technique as a
direct solids analysis technique. Direct solids analysis
is in many ways the most difficult type of analysis to
perform. The matrix is frequently complex and the elements
being analyzed for are generally only present in small
amounts, frequently at the ppm level. Volatilization be-
havior can vary because of inhomogeneous particle sizes if
powders are analyzed and in almost all cases there is an
inhomogeneous distribution of analyte. This last problem is
particularly difficult or impossible to overcome and can be
a limiting factor in direct solids analysis when sample size
reaches the level of about 2 mg or less. In the review
entitled "Direct Analysis of Solids by Atomic-absorption
Spectrophotometry", Langmyhr (60) summarizes this problem:

> "Brittle inorganic materials are usually analyzed in
> the form of powders. The errors introduced by the
> sampling of powders for trace analysis vary consid-
> erably with the distribution pattern of the analyte."

and

> "In the sampling and treatment of solid materials of
> human, animal and plant origin, the diversity of the
> samples and the widely differing properties of the

analytes make it difficult to give any general pro-
cedure. The amount of material available is often
small and the elements to be determined may be in-
homogeneously distributed, and consequently sampling
errors may occur."

The fact that d.c. arc analysis and graphite furnace
AAS analysis are widely used for the direct analysis of
solids clearly demonstrates that the above problems can be
overcome to an acceptable degree. It must be noted, how-
ever, that in direct solids analysis a much higher RSD is
generally acceptable than in the analysis of solutions by
such techniques as flame AAS.

One technique which has been successfully used in d.c.
arc analysis to minimize or eliminate the problems en-
countered in direct solids analysis is the use of an internal
standard. In this technique a known amount of a material
not normally present is added to the sample and the analysis
is based on the ratio of the analyte emission intensity to
that of the internal standard. This technique assume that
the internal standard and the sample will behave in a similar
manner during sample volatization, excitation, and emis-
sion, therefore the choice of internal standard can be very
important.

The use of an internal standard requires the sim-
ultaneous measurement of the analyte and internal standard
emission and thus requires multielement analysis capability.
It was felt that the use of an internal standard might be

helpful in this experimental work therefore it was decided to use the photodiode array direct reading spectrograph developed in this laboratory over the last 8 years. This instrument also has the advantages of allowing quick checking for spectral interference by other elements present in the sample matrix and allows the measurement of the plasma background emission at a wavelength adjacent to that of the analyte. This was felt to be a very useful feature in view of the fact that the background emission was found to vary with the matrix as shown in the previous chapter.

A. Analysis of Spex G-Standard Mixture

The Spex G-Standards manufactured by Spex Industries, Meluchen, N.J., are commonly used as standards for d.c. arc emission spectroscopy. These standards consist of a graphite matrix containing a known amount (0.0001% to 0.1%) of 49 elements and 0.1% of In as the internal standard. These standards were chosen as model solids for a test of EA-ICAP-OES direct solids analysis.

Analyte emission te poral behavior has been shown earlier to be affected by the matrix therefore it is obvious that a time study of emission with direct solids analysis would be necessary. The PDA direct reading spectrometer has been shown to be useful for such studies (44) with d.c. arc emission and while the temporal resolution is much less than

with the PMT system it was felt that it would be adequate for this purpose. The results are seen in Figure 51. The PDA integration time was set to approximately 0.4 seconds and each scan is stored and then plotted separately. The wavelength region covered is from about 250 nm at diode number 0 to about 195 nm at diode number 1024. Some of the emission lines shown are identified in Figure 52. Examination of Figure 51 will show, for instance, that Cd and Zn, present at the 0.001% level, show emission between 1.2 and 2.8 seconds with their maximum emission occurring in the integration period between 1.2 and 1.6 seconds. The internal standard In which is present at 0.1% shows emission starting at 1.2 seconds, reaching a maximum at 2.0 seconds, and is still showing emission at 2.8 seconds, the last scan plotted. The results of this time study are that the emission of Cd and Zn show similar, but not identical, behavior to that of the internal standard, and that the PDA signals must be time-averaged for about 3 seconds to include all the emission due to Cd, Zn, or In. The calibration data and curves for Cd(I) and Zn(I) in the G-Standards are shown in Tables XIX and XX and Figures 53 through 56 where concentration of Cd and Zn are plotted vs. the ratio of the analyte emission to the sample weight and to the internal standard emission. Acceptable calibration plots can be prepared from either of these types of data but in all

Table XIX

Calibration Data for Cd(I) - 228.802 nm

in Spex G-Standards

Amount Cd %	$\int E_t dt$ (Cd)/Spl.Wt.	RSD %	$\int E_t dt$ (Cd)/$\int E_t dt$ (In)	RSD %
0.00033	56.5	19.6	0.0182	23.8
0.001	1,004.5	14.8	0.288	11.5
0.010	23,440.1	36.4	4.273	31.3

$\int E_t dt$ (Cd)/Spl.Wt.:

Slope = 1.7

R = 1.0

$\int E_t dt$ (cd)/$\int E_t dt$ (In):

Slope = 1.5

R = 1.0

Table XX

Calibration Data for Zn(I) - 213.856 nm

in Spex G-Standards

Amount Zn %	$\overline{\int E_t dt}$(Zn)/Spl.Wt.	RSD %	$\overline{\int E_t dt}$(Zn)/$\overline{\int E_t dt}$(In)	RSD %
0.00033	237.2	11	0.0756	6.5
0.001	897.8	11	0.258	12.9
0.01	24,324.5	26	4.439	1.0

$\overline{\int E_t dt}$(Zn)/Spl.Wt.:

Slope = 1.4

R = 1.0

$\overline{\int E_t dt}$(Zn)/$\overline{\int E_t dt}$(In):

Slope = 1.2

R = 1.0
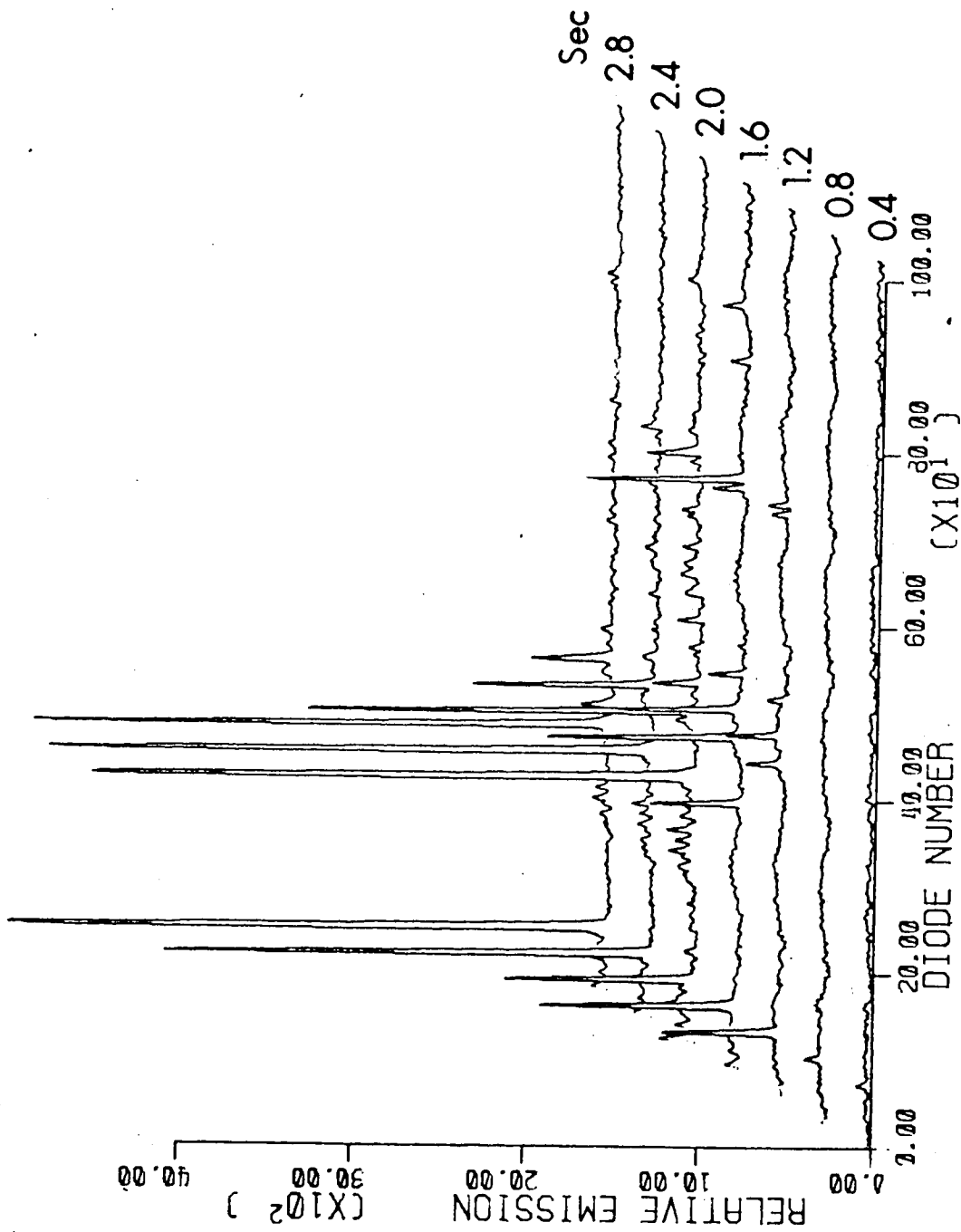
Figure 51. Time study of 5.2 mg of Spex G3 Standard Containing 49 elements at 0.001% level and 0.1% In.
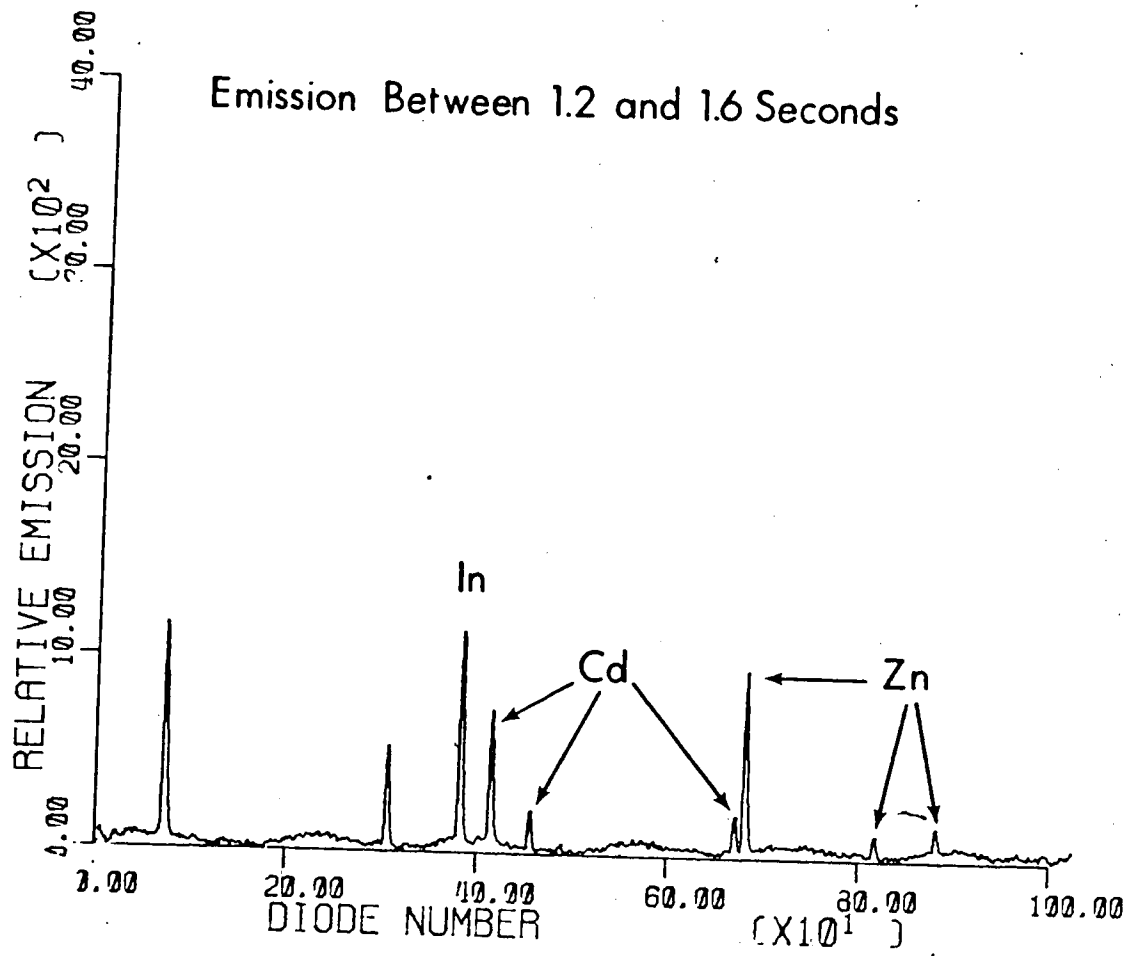
Figure 52. Spectrum taken between 1.2 and 1.6 second from Spex G3 Standard time study, Figure 51.

SPEX STANDARDS CD(I)-228.802NM
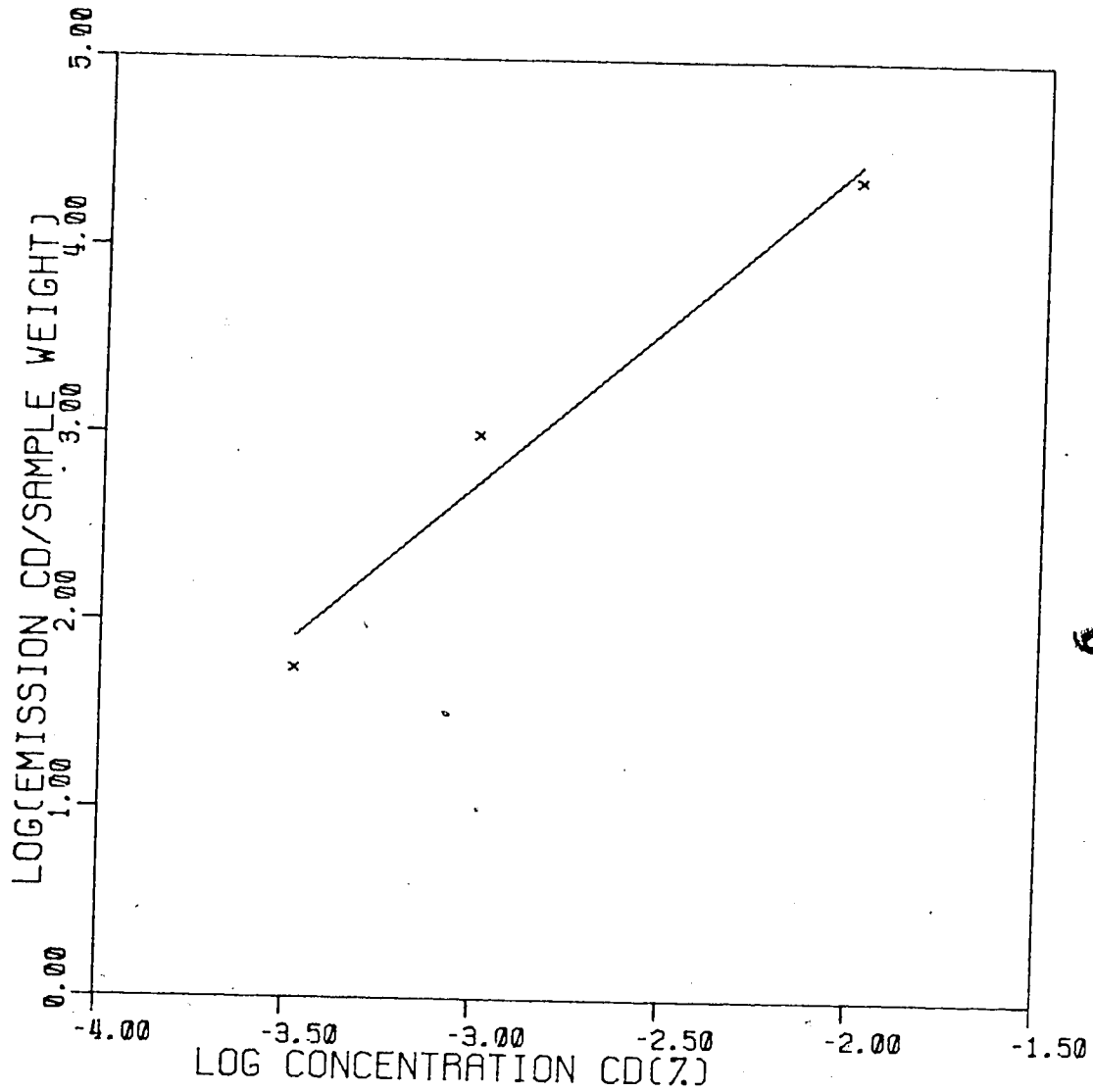
Figure 53.   Log-log calibration plot for Spex G-Standards
             Cd(I) - 228.802 nm/sample weight.

Figure 54. Log-log calibration plot for Spex G-Standards
(Cd(I) − 228.802 nm)/(In(II) − 230.606 nm).
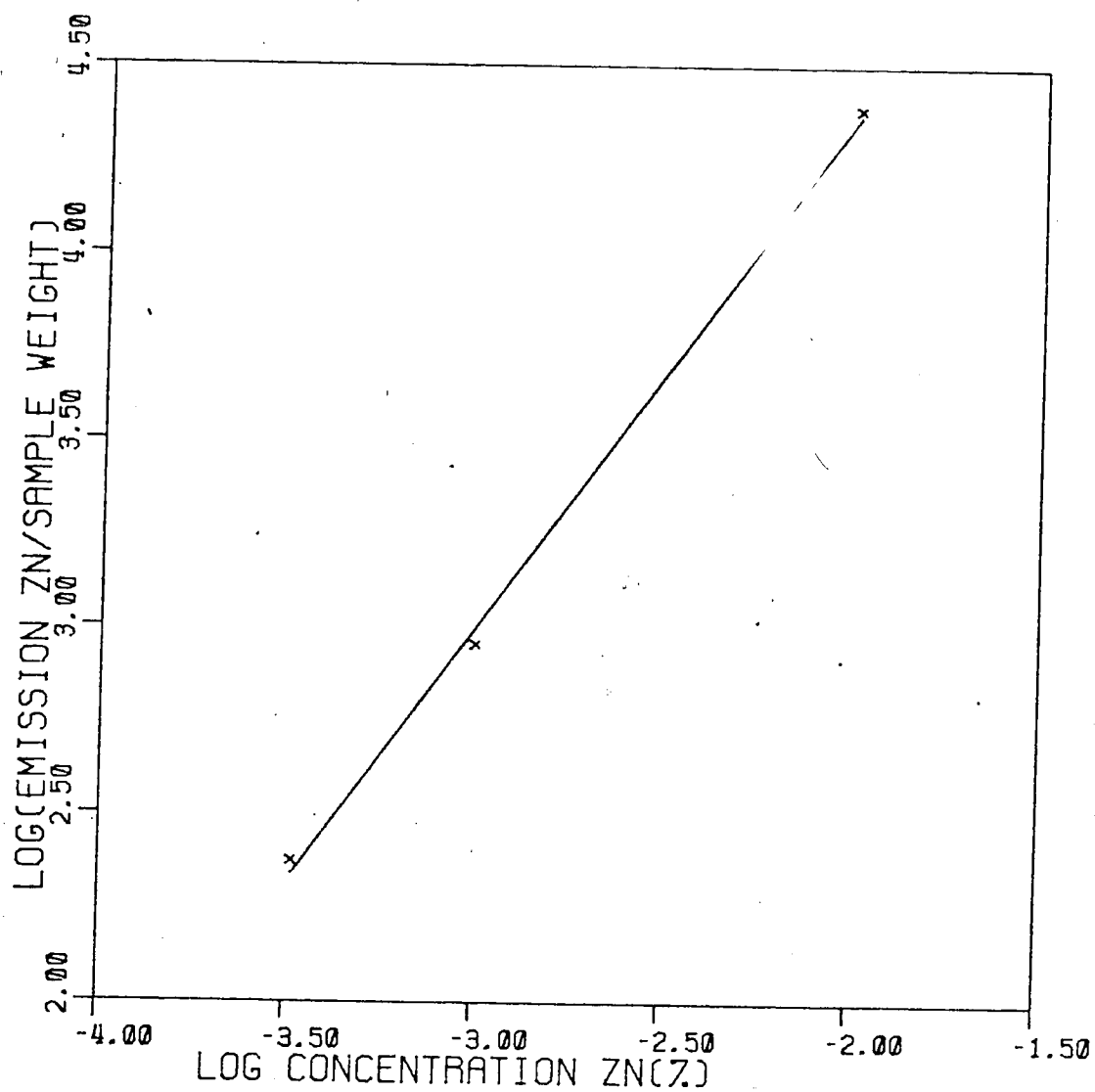
Figure 55. Log-log calibration plot for Spex G-Standards Zn(I) - 213.856 nj/sample weight.

SPEX G STANDARDS ZN(I)-213.856NM
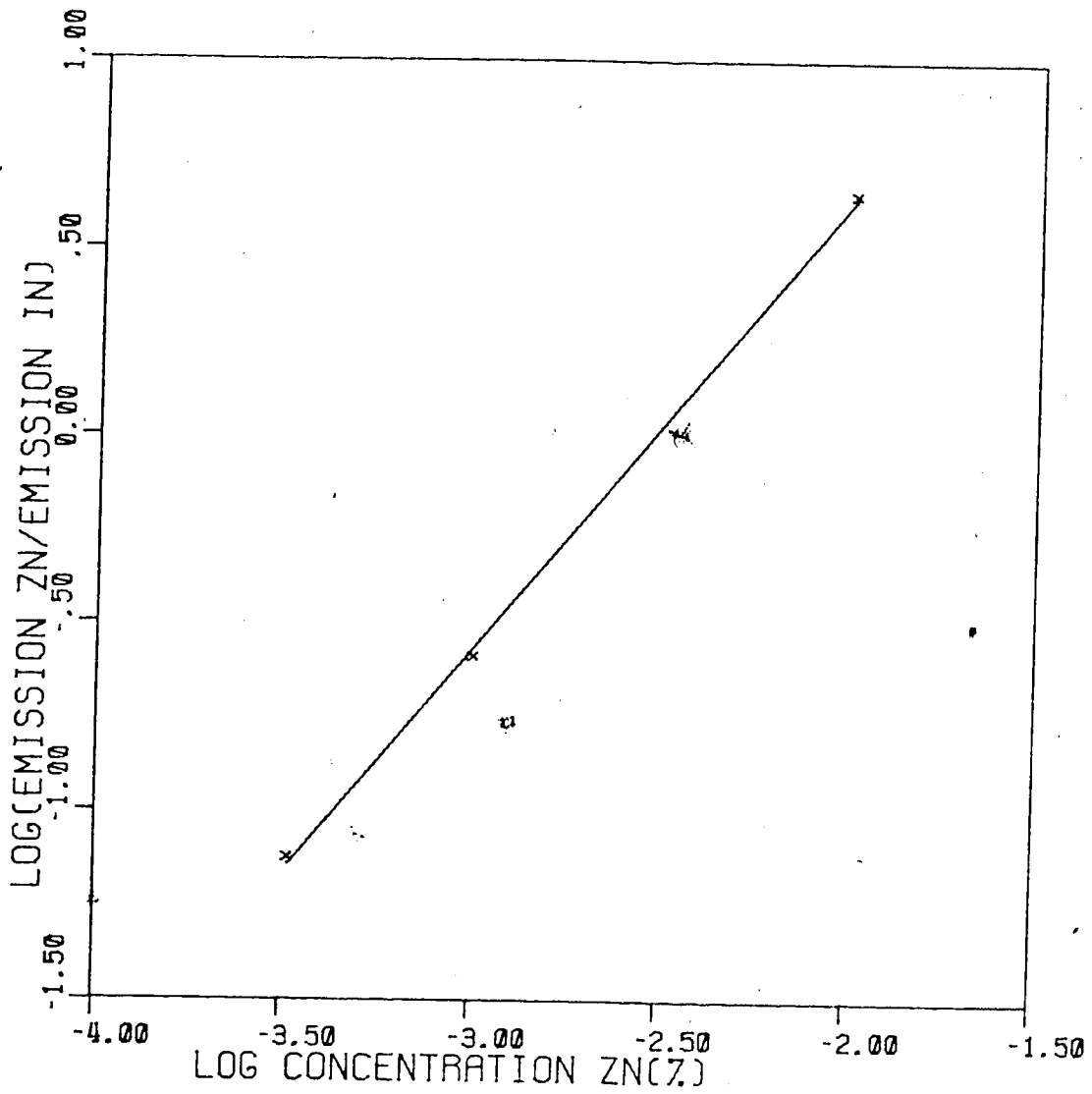
Figure 56. Log-log calibration plot for Spex G-Standards
(Zn(I) - 213.856 nm)/(In(II) - 230.606 nm).

cases the slopes of the log-log plots indicate that a matrix effect is present. The slopes of the log-log plots of the ratio of Mn emission to that of In, the internal standard plots, are closer to 1 therefore these show the least matrix effect. The RSD values for the Cd(I) and Zn(I) emission lines vs. weight of sample or the internal standard In(II) emission are quite similar. This indicates that with these Spex G-Standards the major cause of analytical error was variations in the sample vaporization, and was not due sampling errors.

The linear range covered with these curves is only from 0.00033% (3.3 ppm) to 0.01% (100 ppm). The use of an OD 1 filter would have allowed extention to higher analyte concentration but this was felt to be unnecessary since this was only a preliminary test of the system. Extention of the analytical curve to a lower concentration was not found to be possible with this PDA based direct reading spectrometer system since the integration time was limited to abo t 0.4 seconds by the need to keep the In emissio rom saturating the array. At longer integration time. he Cd(I) and Zn(I) emission could be detected but the saturation of the In(I) emission line meant that its emission could not be accurately recorded.

B.   Analysis of NBS Standard Reference Materials

Several U.S. National Bureau of Standards-Standard
Reference Materials (NBS-SRM) were used to test how well direct
solids analysis of "real" materials could be performed with
EA-ICAP-OES.   These materials were four botanicals, two
coal samples, and one coal fly ash sample representing a
wide range of sample matrices.

The NBS-SRM's were prepared for analysis by grinding in
a vibrating ball mill a mixture of 100 mg of the SRM and
100 mg of spec⁺ ⌐s. ⌐c graphite containing 0.2% In.   The
spectroscopic gra⌐ ⌐⌐ ⌐ntaining 0.2% In was prepared by
grinding together 48.4 mg of finely powdered In_2O_3 and 10 g
of the spectroscopic grade graphite powder.   The grinding
containers and balls were plastic to keep contamination of
the sample as low as possible during this process and all
materials were ground together for at least 10 minutes to
ensure that mixing was as thorough as possible.

It must be noted at this point that the amount of In_2O_3
dispersed in the graphite is quite small and there exists
a large chance for non-homogeneous distribution.   The amount
of SRM used is also quite small and sampling of the SRM may
also be non-homogeneous.   These problem, are emphasized by
the fact that only 2 to 3 mg of the mixture were vaporized
during these experiments.   As will be seen, the results in-
dicate that there is indeed a problem with non-homogeneous

distribution.

Because of the complexity of the matrices, another problem was encountered in analyzing these "real" solid samples, that of spectral interference. The resolution available with the PDA based direct reading spectrometer places the lower limit on the resolution obtainable. In order to maximize the resolution the monochromator entrance slit was set to about 8 μm and all electronic filtering of the PDA signals was eliminated. Under these conditions a strong emission peak forms an image about 14 diodes FWHM which means that emission lines 0.67 nm apart could be baseline resolved.

Figure 57 is a plot showing the emission spectrum produced by 300 ng each of manganese and zinc. The samples were in the form of single element solutions and 3 μL each of their 100 ppm solutions were used with the EA-ICAP-OES system. The Mn(II) emission peaks are at 260.569 nm, 259.373 nm, and 257.610 nm and the Zn(I) and Zn(II) emission peaks are at 213.856 nm and 206.191 nm respectively. The 257.610 nm Mn(II) line and the 213.856 nm Zn(I) line were chosen for the analytical lines because they are strongest and had the least spectral interference from overlapping emission lines.

Figure 58 is the spectrum for 2000 ng of Fe while Figure 59 is for 10,000 ng of Si. These materials are present in
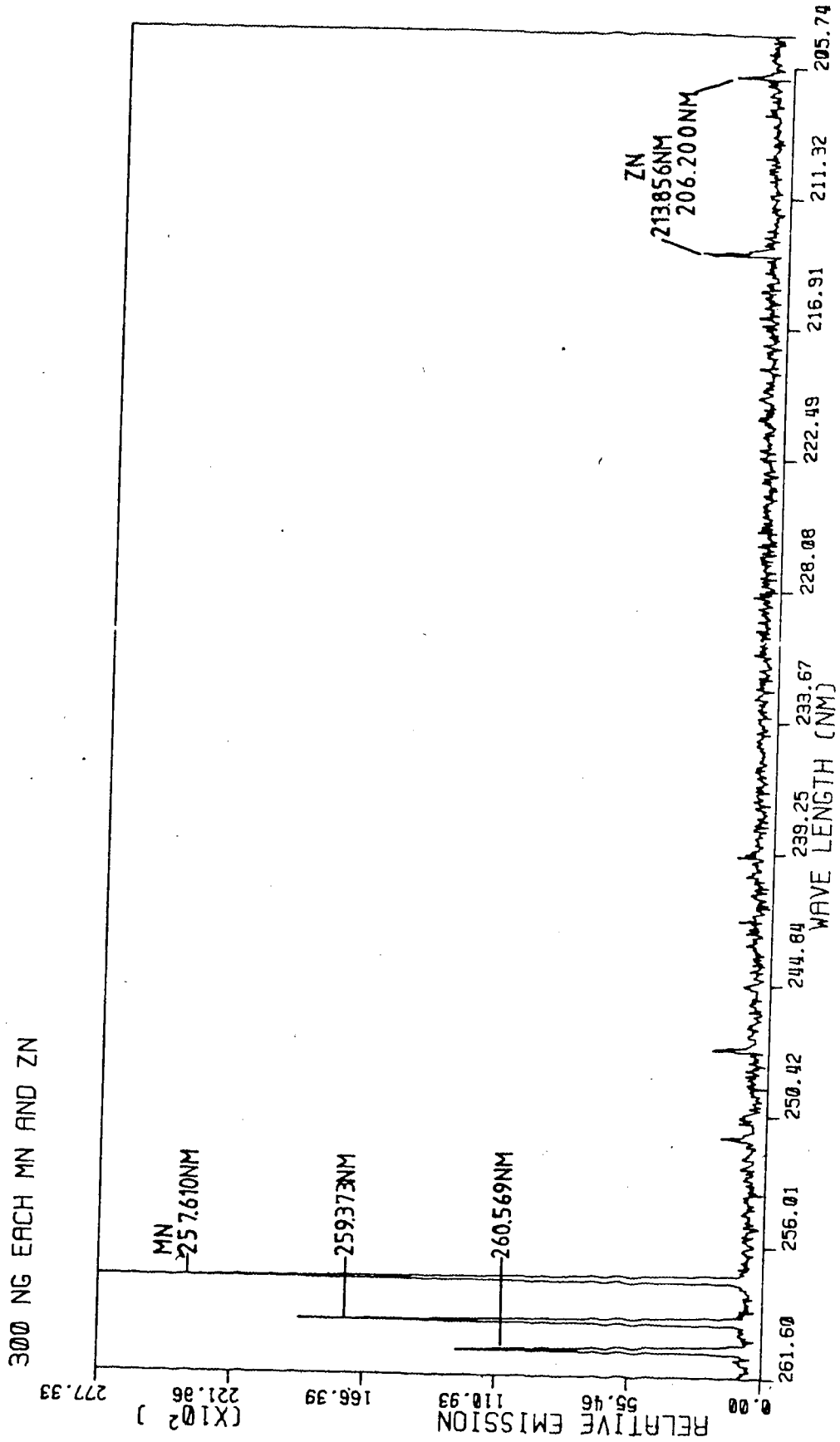
Figure 57. Spectrum from 300 ng each of Mn and Zn.
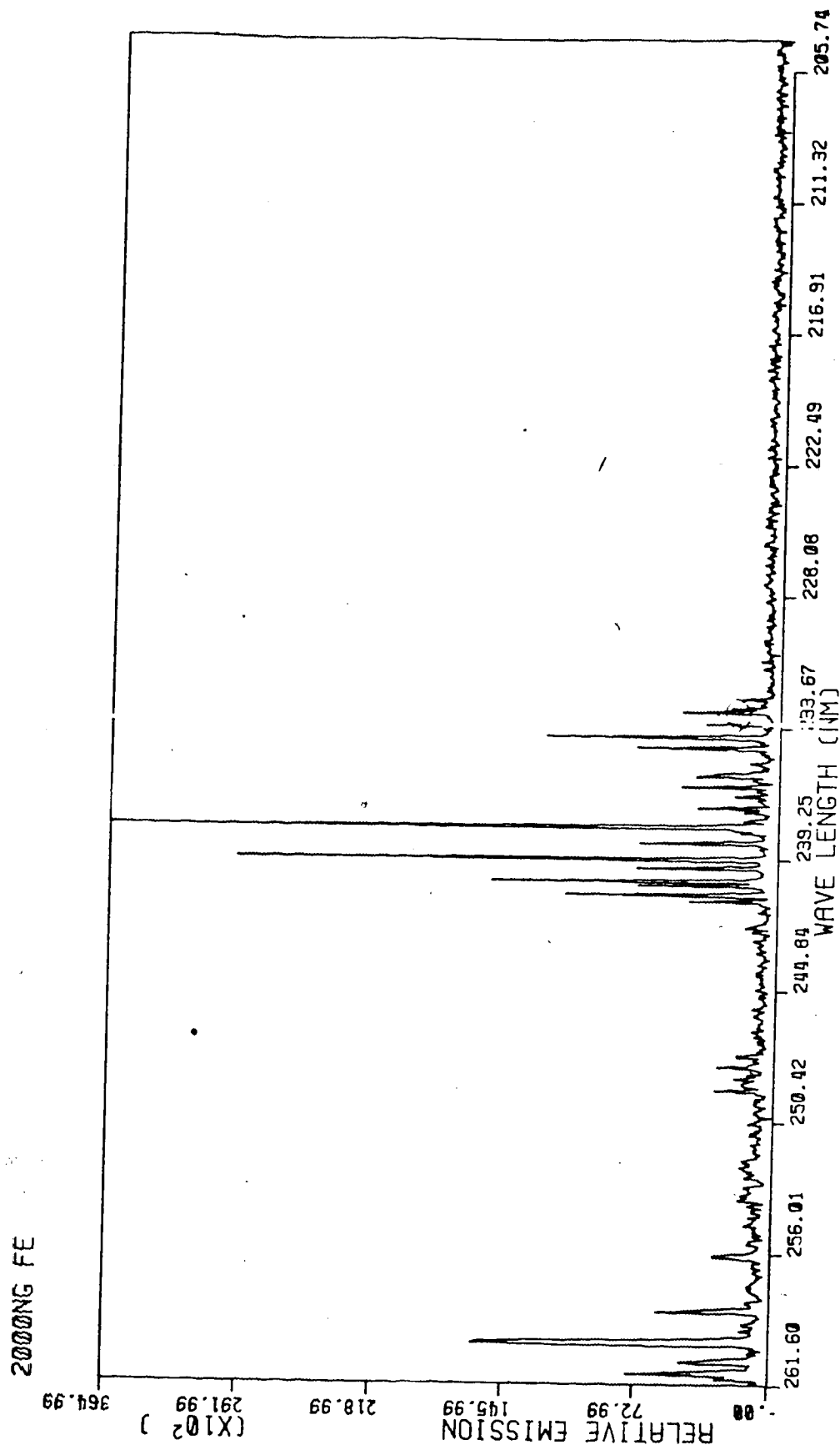
Figure 58. Spectrum from 2000 ng of Fe.

133
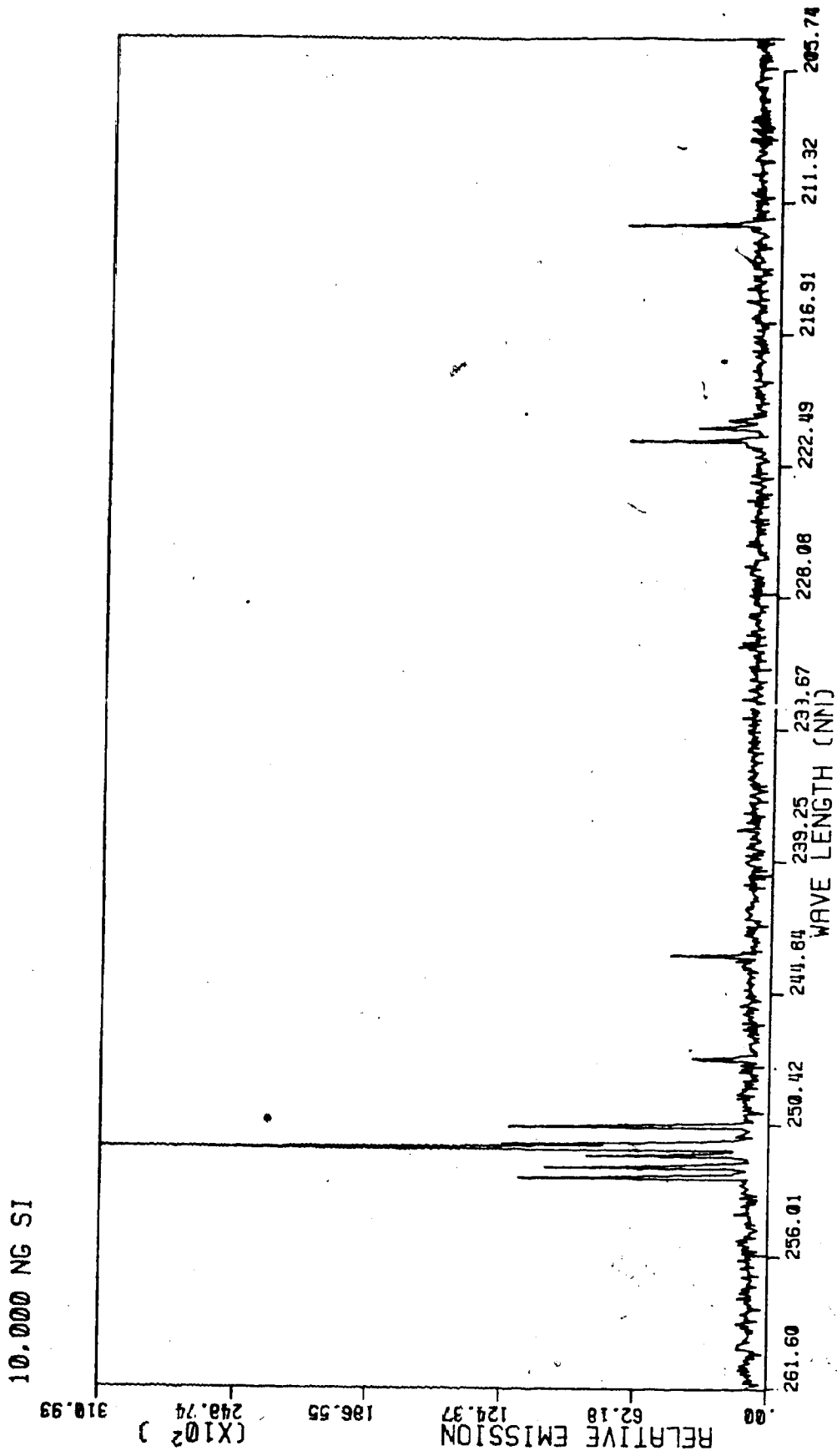
Figure 59. Spectrum from 10,000 ng of Si.

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very high concentration in several of the NBS-SRM's. An example of spectral overlap interference can be seen in the Fe spectrum where several small lines overlap the 260.569 nm and 259.373 nm Mn(II) emission lines.

Figures 60 through 66 are the spectra recorded for the seven NBS-SRM's used. The plots have been scaled to keep the Mn(II), In(I), and Zn(I) emission lines on scale. With the exception of the Pine Needle spectrum the spectra are quite complex and it is easy to see why spectral inter-ferences are common and why the choice of an analytical line can be very important.

The sample vaporization time was 3 seconds but to insure that all sample emission was recorded the PDA was clocked at 15 KHz and 75 scans of 0.137 seconds each were time-averaged together for a total integration time of 10.24 seconds. Plasma background and PDA fixed pattern clocking noise were also integrated and subtracted from the emission signals. Emission values were obtained by summing up the values recorded at the 5 diodes representing the peak of the em-ission line and subtracting the sum of 5 diodes reading background near the emission peak. The Mn(II) emission line at 257.610 nm appears to be clear of spectral interference however the Zn(I) line at 213.856 nm and the Zn(II) line at 206.191 nm both show spectral interference.

Table XXI lists the Mn and Zn concentrations in the
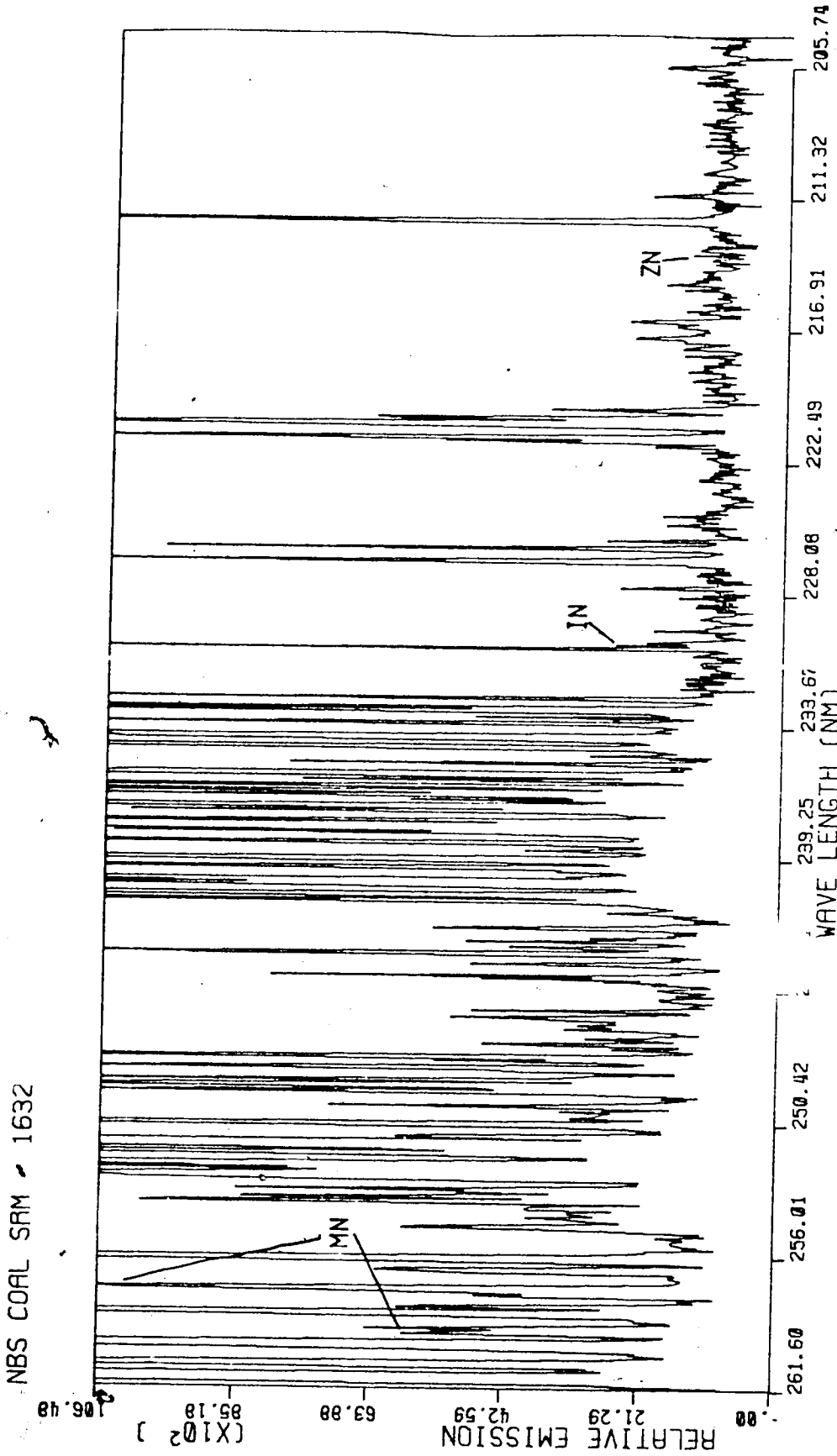
Figure 60. Spectrum from 2.6 mg of 50:50 mixture of NBS-SRM Coal #1632 and graphite (0.2% In).
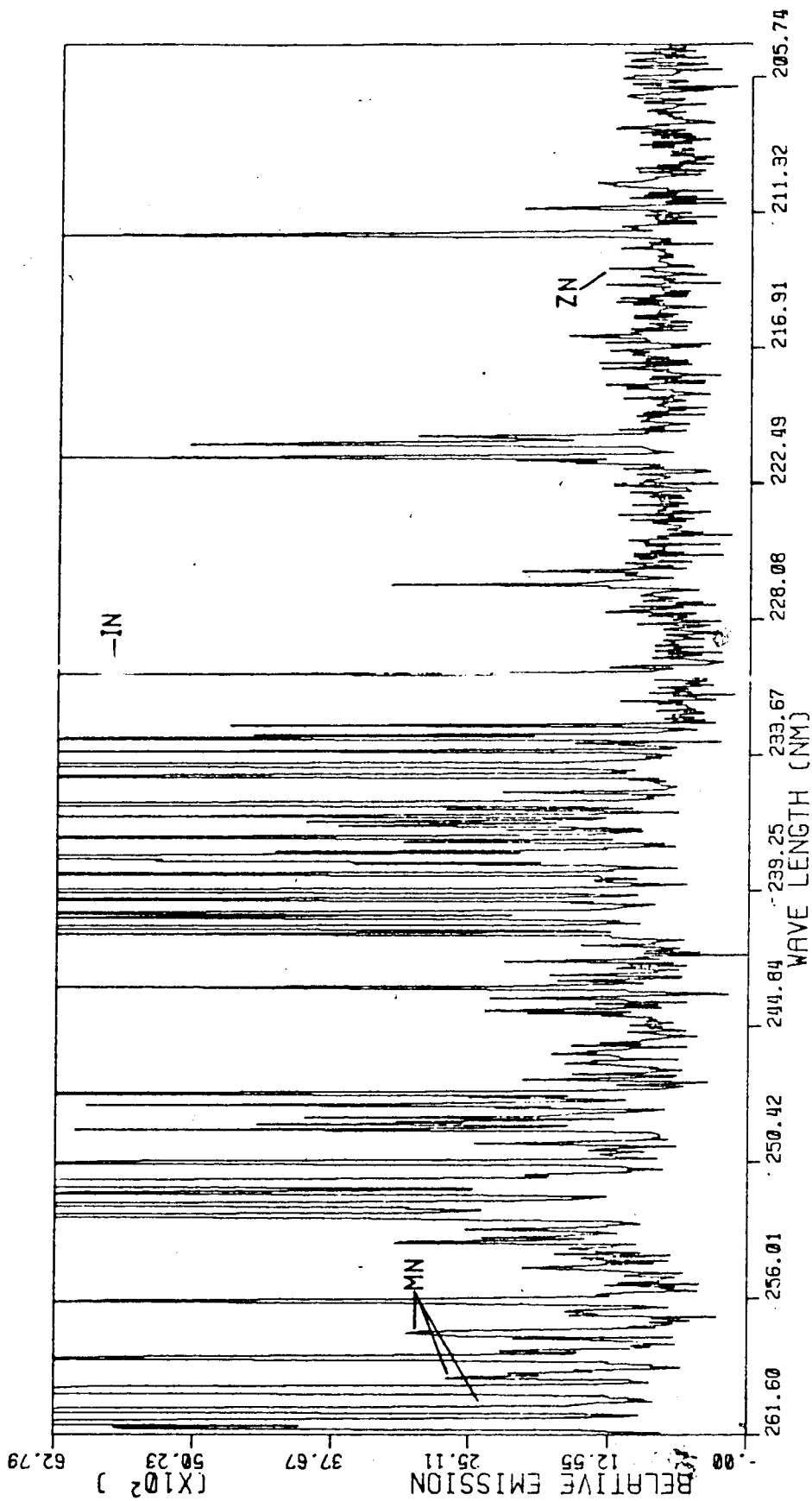
Figure 61.   Spectrum from 2.6 mg of 50:50 mixture of NBS-SRM Coal #1635 and graphite (0.2% In).

Figure 62. Spectrum from 2.5 mg of 50:50 mixture of NBS-SRM Coal Fly Ash #1633 and graphite (0.2% In).
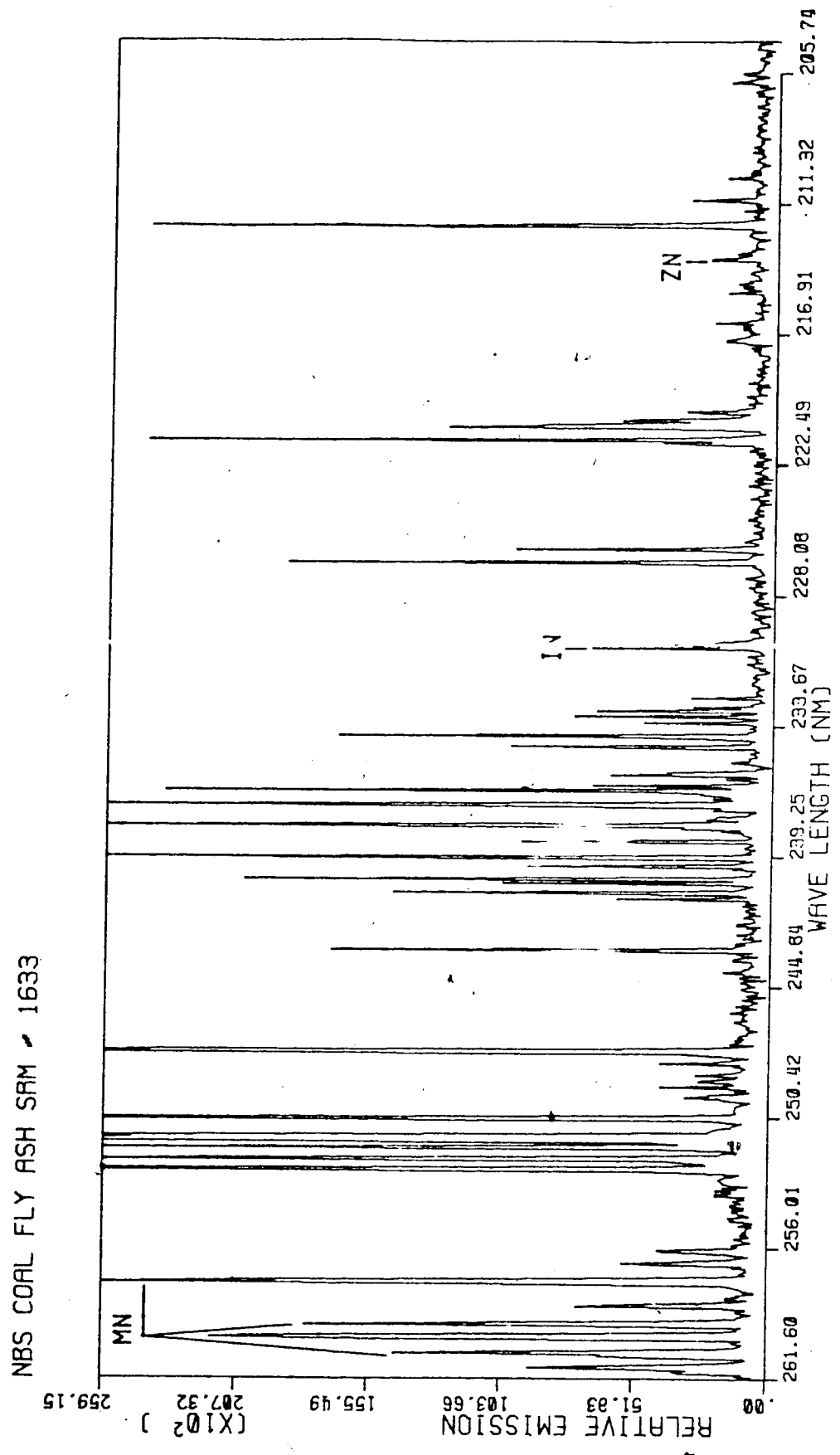
Figure 63. Spectrum from 2.8 mg of 50:50 mixture of NBS-SRM Spinach #1570 and graphite (0.2% In).

NBS SPINACH SRM - 1570

140
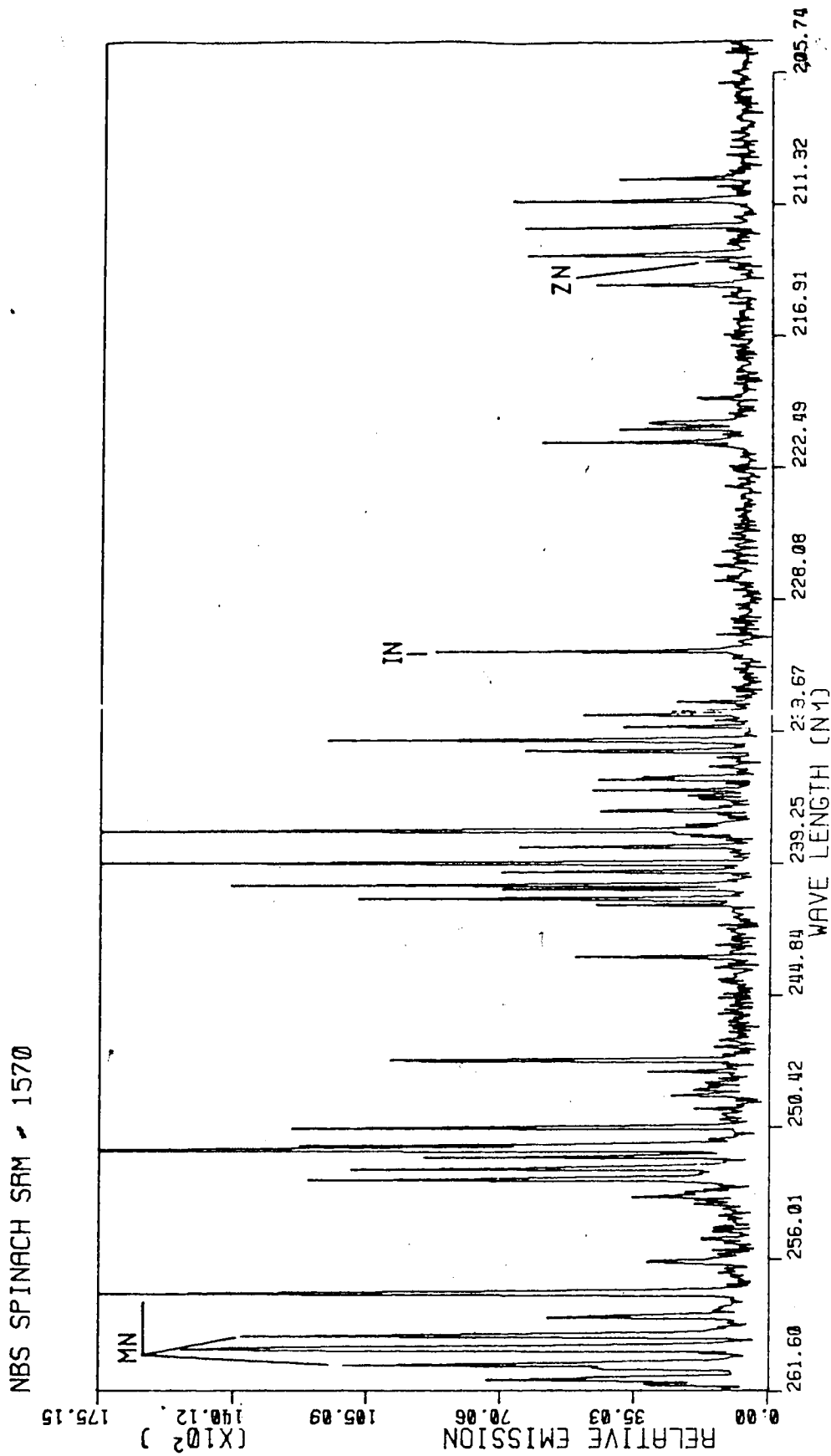
Figure 64. Spectrum from 2.1 mg of 50:50 mixture of NBS-SRM Orchard Leaves #1571 and graphite (0.2% In).

NBS ORCHARD LEAVES SRM -1571
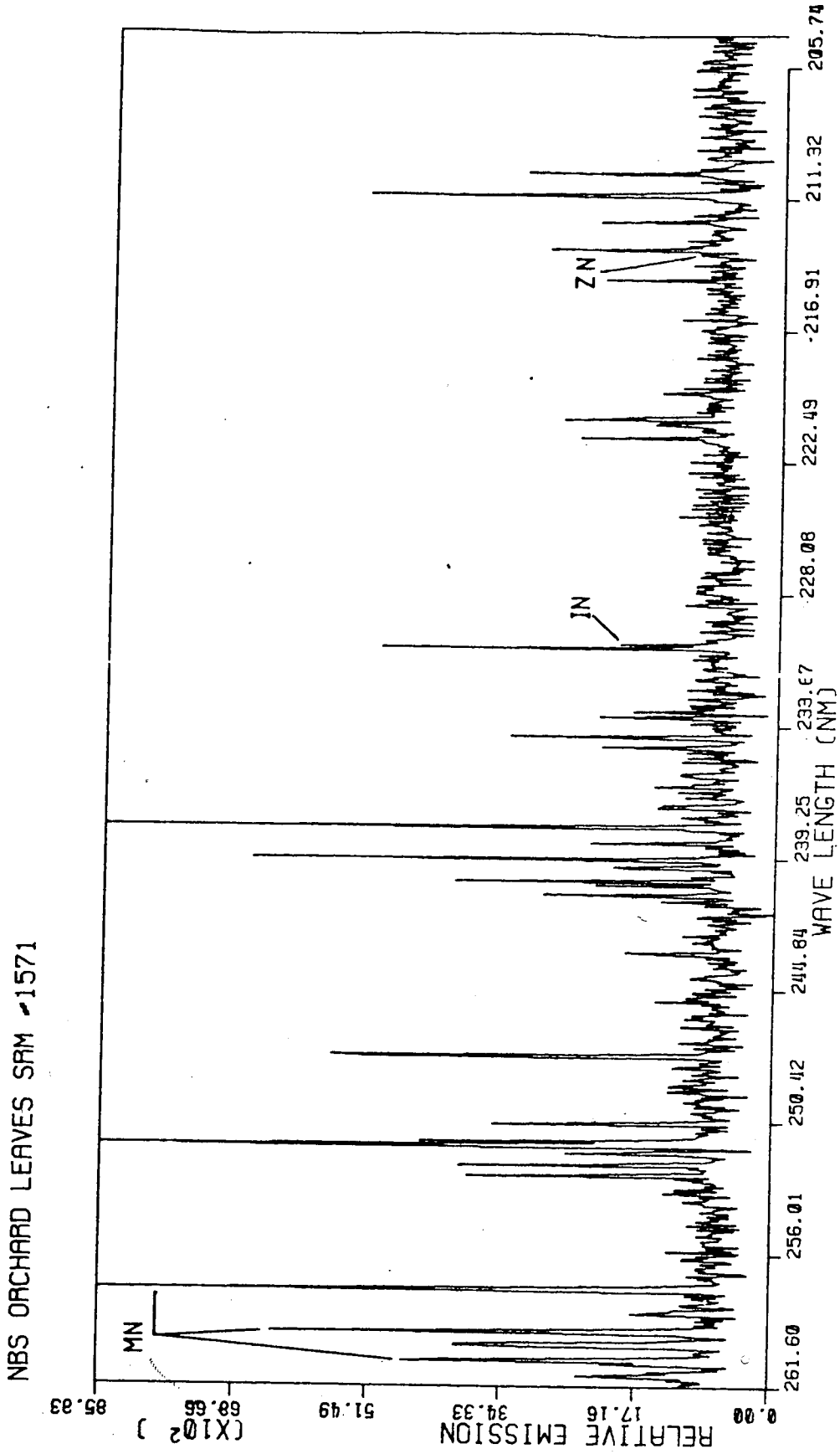
Figure 65. Spectrum from 2.3 mg of 50:50 mixture of NBS-SRM Tomato Leaves #1573 and graphite (0.2% In).
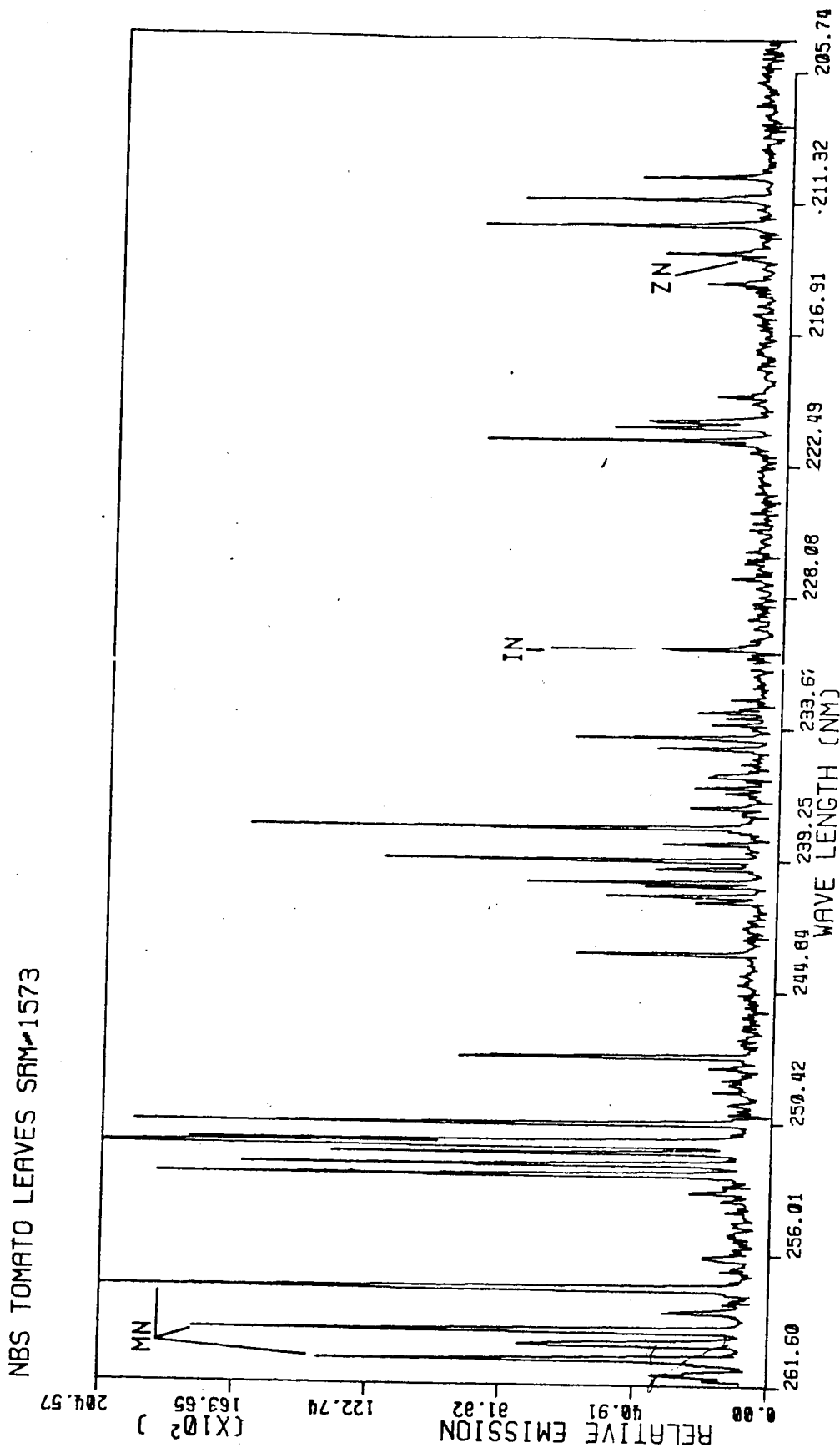
Figure 66. Spectrum from 2.4 mg of 50:50 mixture of NBS-SRM Pine Needles #1575 and graphite (0.2% In).
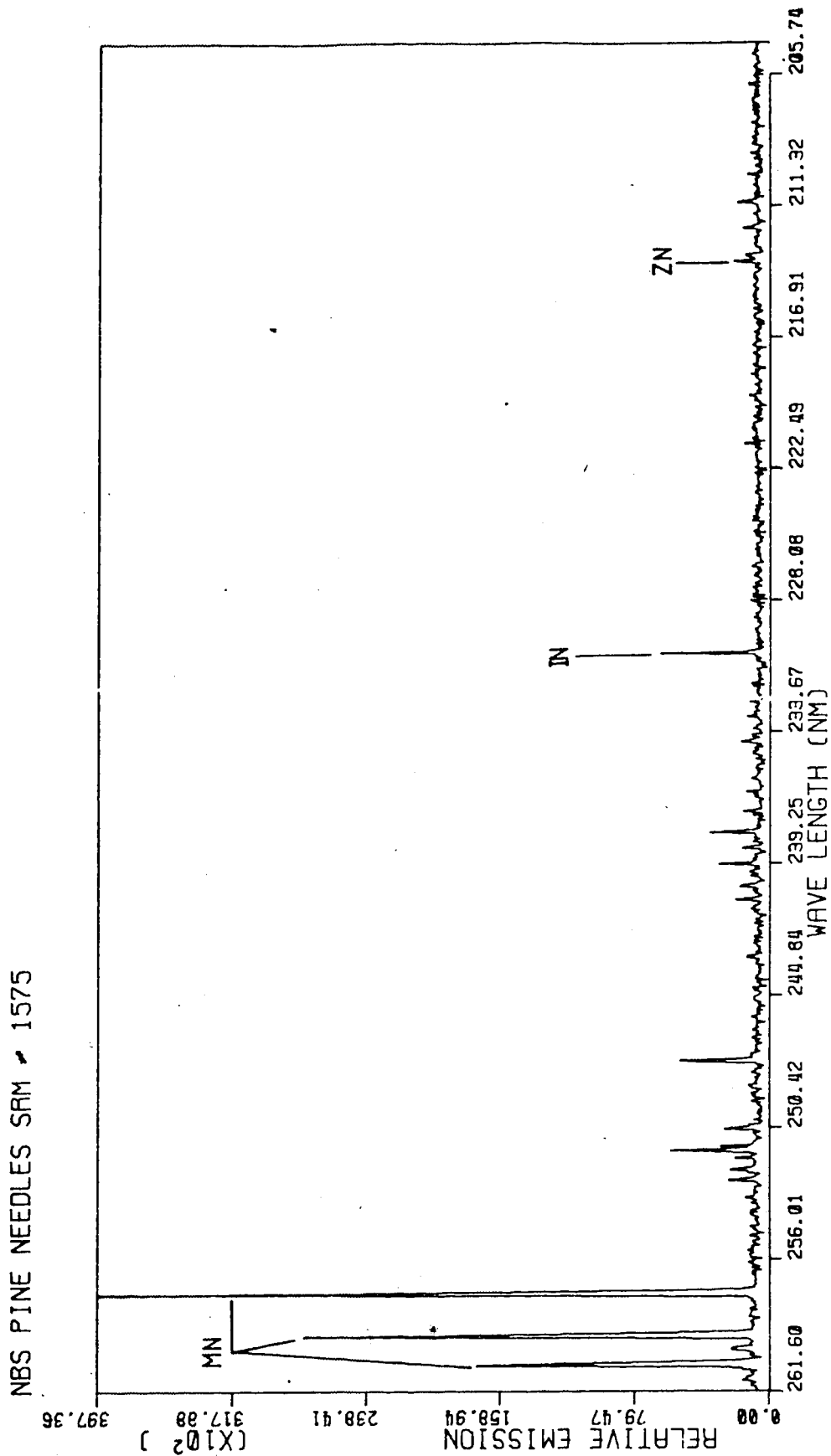
Table XXI

Concentrations of Mn and Zn in NBS-SRM

Material	SRM #	Concentration Mn	Concentration Zn
Coal	1632	40 ± 3	37 ± 4 ppm
Coal	1635	21.4±1.5	4.7±0.5 ppm
Coal Fly Ash	1633	493 ± 7	210 ± 20 ppm
Spinach	1570	165 ± 6	50 ± 2 ppm
Orchard Leaves	1571	91 ± 4	25 ± 3 ppm
Tomato Leaves	1573	238 ± 7	62 ± 6 ppm
Pine Needles	1575	675 ± 15	--

SRM's used and the analytical results are given in Table
XXII and Table XXIII for Mn(II) emission at 257.610 nm and
Zn(I) emission at 213.856 nm. The Zn(II) emission line at
206.191 nm is too weak to be recorded under these operating
conditions.

Log-log calibration curves are shown in Figures 67
through 70 for the Mn(II) and Zn(I) emission lines. The
plots are for the ratio of analyte emission to weight of
sample and for the ratio of analyte emission to internal
standard emission. In these cases the slopes of the log-log
plots show that matrix effects are present, however neither
type of plot is clearly preferable. The RSD values of the
emission vs sample weight or internal standard emission are
also similar, with neither being clearly better. These
results indicate that the major problem in these analyses
was sampling error, which may be impossible to overcome.

Table XXII

Calibration Data for Mn(II) - 257.610 nm Emission in NBS-SRM's

SRM #	Mn (ppm)	$\int E_t dt(Mn)$/Spl.Wt.	RSD %	$\int E_t dt(Mn)/\int E_t dt(In)$	RSD
1635	21.4	2,459.2	15.6	0.761	
1632	40.0	9,490.8	17.4	2.773	
1571	91.0	8,515.9	35.6	2.209	2.0
1570	165.0	15,998.2	34.9	3.278	23.0
1573	238.0	15,649.9	27.3	4.823	23.9
1633	493.0	25,364.6	34.5	.641	30.0
1575	675.0	50,962.0	19.4	12.149	38.0

$\int E_t dt(Mn)$/Spl.Wt.:

Slope = 0.7

R = 0.9

$\int E_t dt(Mn)/\int E_t dt(In)$:

Slope = 0.7

R = 0.9

Table XXIII

Calibration Data for Zn(I) - 213.856 nm Emission in NBS-SRM's

SRM #	Zn (ppm)	$\int E_t\, dt(Zn)/$Spl.Wt.	RSD %	$\int E_t\, dt(Zn)/\int E_t\, dt(In)$	RSD %
1635	4.7	322.0	50.6	0.098	53.0
1571	25.0	396.0	21.7	0.077	57.0
1632	37.0	421.3	59.2	0.105	83.0
1570	50.0	825.2	52.3	0.167	42.2
1573	62.0	1,247.6	17.8	0.392	22.7
1633	210.0	2,017.8	11.7	0.626	22.5

$\int E_t\, dt(Zn)/$Spl.Wt.:

Slope = 0.5

R = 0.9

$\int E_t\, dt(Zn)/\int E_t\, dt(In)$:

Slope = 0.5

R = 0.8

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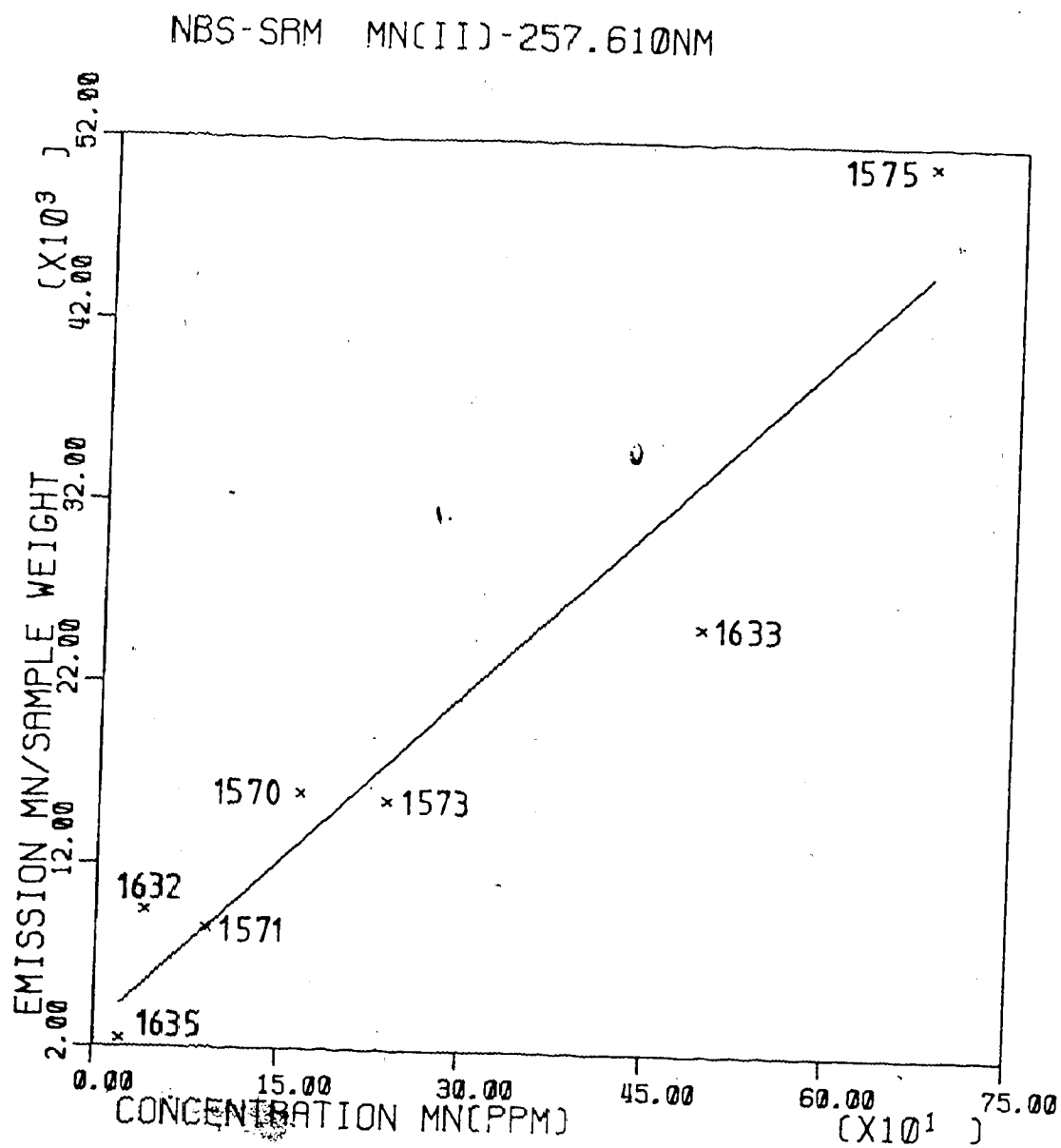
Figure 67. Calibration plot – Mn(II) emission/sample weight vs concentration of Mn in NBS-SRM.

NBS-SRM MN[II]-257.610NM
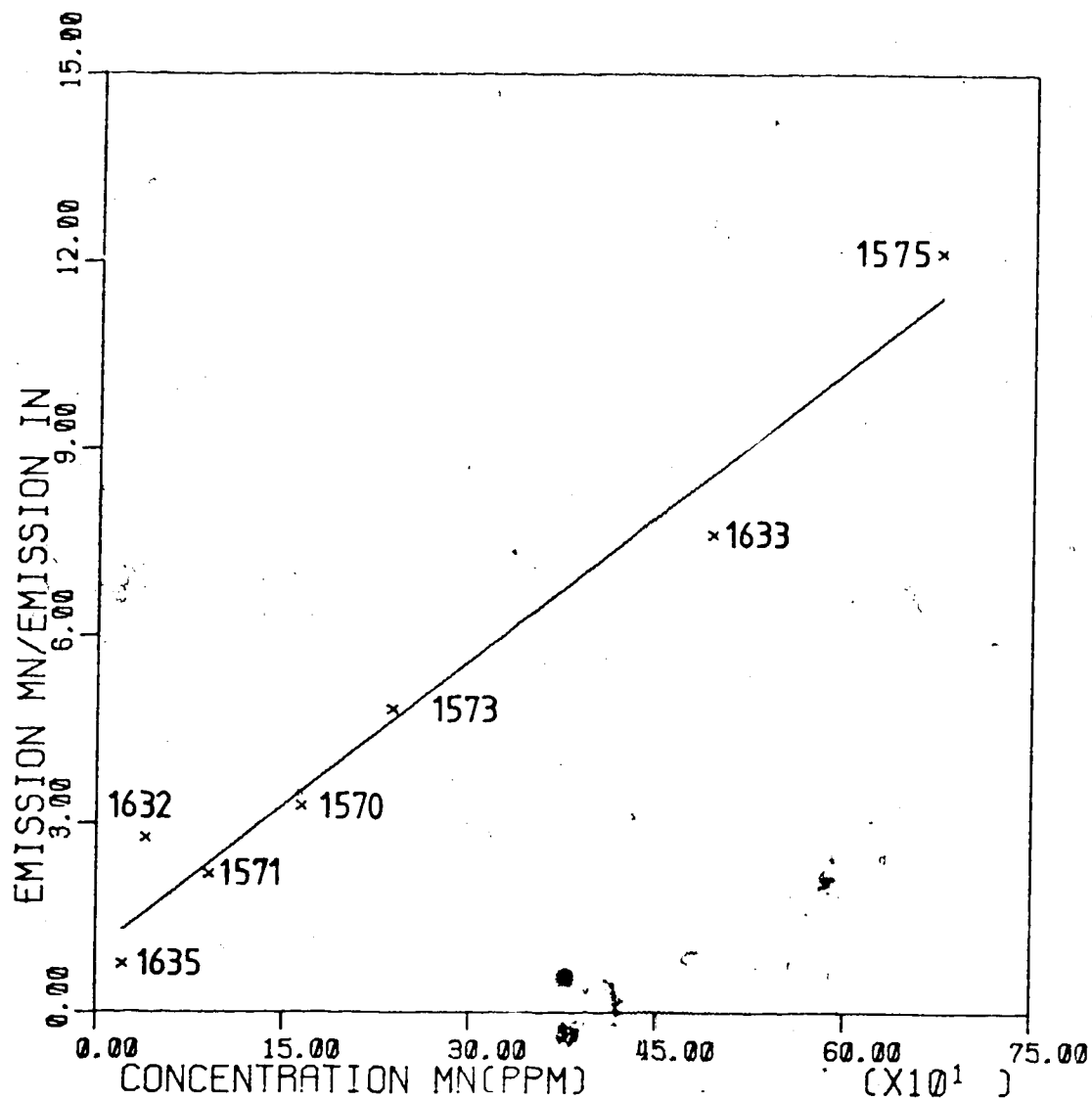
Figure 68. Calibration plot - Mn(II) emission/In(I) emission
vs concentration of Mn in NBS-SRM.
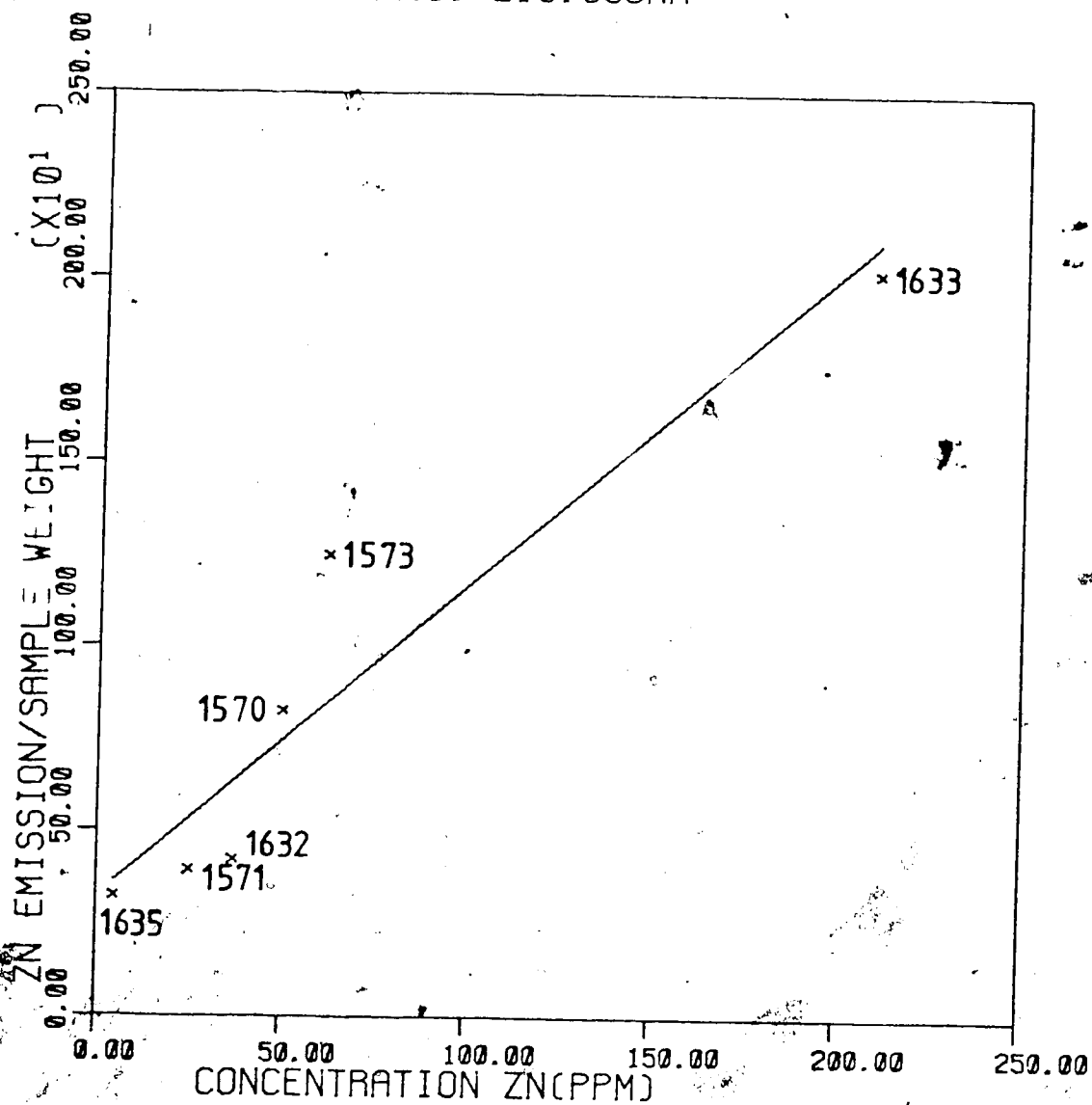
Figure 69. Calibration plot – Zn(I) emission/sample weight vs concentration of Zn in NBS-SRM.
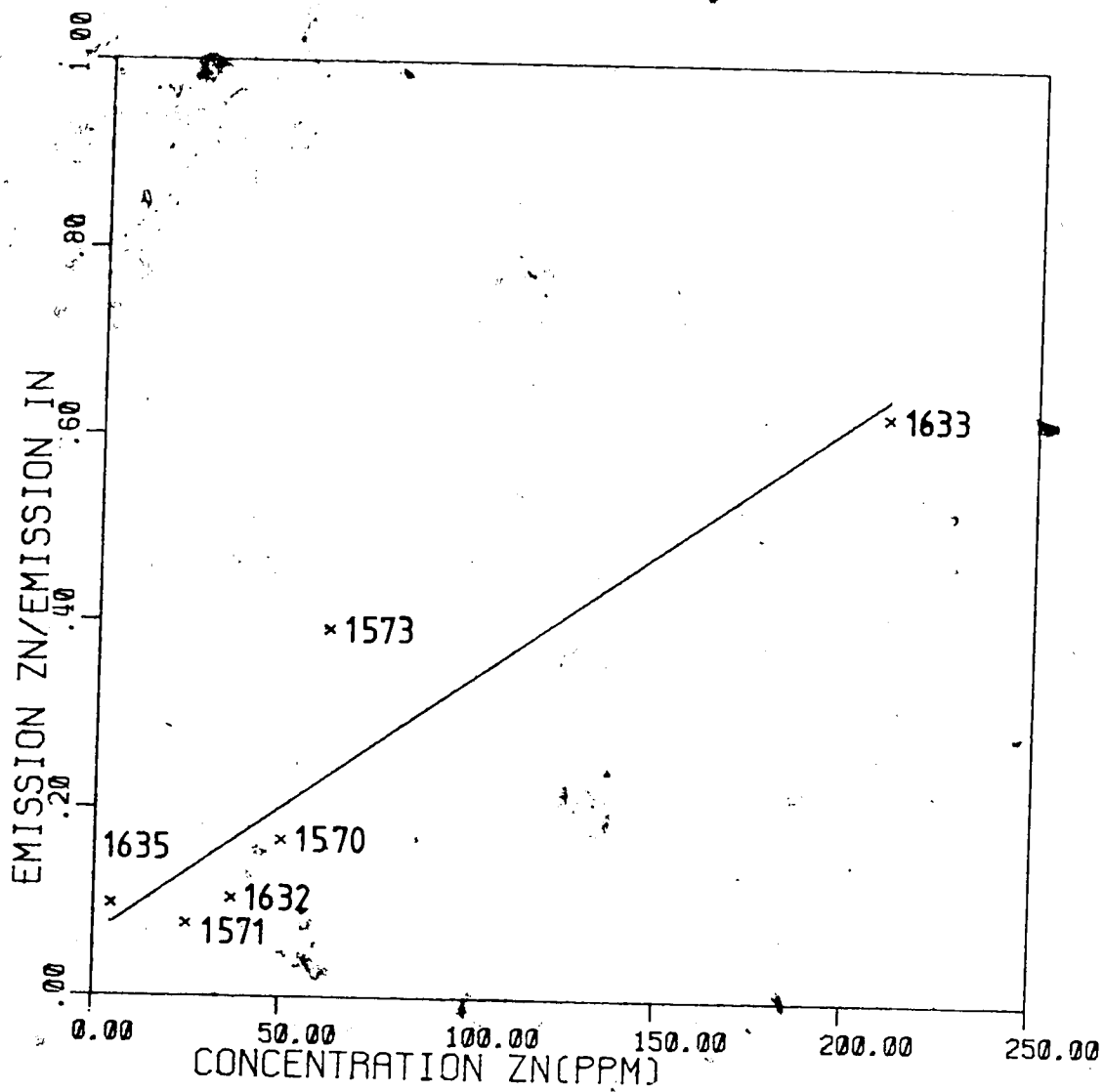
Figure 70. Calibration plot - Zn(I) emission/In(I) emission vs concentration of Zn in NBS-SRM.

The inductively coupled argon plasma was first introduced commercially as a source for optical emission spectroscopy in 1974 and its use has been growing rapidly ever since. The dominant sample introduction technique for plasma emission spectroscopy has been the nebulizer, requiring that samples be in solution and that several mL of solution be available. In our laboratory sample introduction techniques to allow the analysis of small volume (µL) samples in solution and the direct analysis of solid samples by ICAP-OES have been under investigation. In this work, the analytical aspects of the use of a graphite cup electrothermal atomizer in combination with the inductively coupled argon plasma for the analysis of small volume samples in solution and the direct analysis of solids has been studied.

The graphite cup electrothermal atomization device used for this work was constructed from a Varian Model 63 Carbon Rod Atomizer used for atomic absorption spectroscopy. The graphite carbon cup used was enclosed in a small quartz cell. Argon gas flowed through the cell to carry the vaporized sample material into the plasma.

Preliminary investigations of the temporal behavior and analytical capabilities of the EA-ICAP-OES technique were carried out with single element solutions and a single

channel monochromator-PMT detector system coupled to a

computer-based data acquisition system. The plasma emission

background was found to vary during the atomization, pro-

bably due to pressure/flow changes caused by the heating of

the argon inside the vaporization cell. The background

emission profile was found to vary in detail from atomization

to atomization, possibly due to small changes in the heating

during atomization, but the integrated emission during the

atomization was fairly constant.

Temporal studies of analyte emission during atomization

showed the emission profile to be peak shaped with a rise

time of about 0.1 second and a fall time of 1 to 3 seconds.

The emission rise and fall times were found to increase as

sample weight increased. Emission peak height measurements

had greater relative standard deviations (RSD) than back-

ground subtracted peak area measurements therefore peak

areas were used for analytical measurements. The analytical

results show that a linear dynamic range of three to four

orders of magnitude are possible with a RSD of 5 to 10% at

about 100 times the detection limit.

The analysis of lead is widely performed by carbon

furnace AAS but suffers from severe matrix interference

affects. A study of this effect of a NaCl matrix on EA-

ICAP-OES analysis of Pb showed that even at a NaCl con-

centration greater than in sea water only a small change in

emission peak area was found. This peak area change was mainly due to a change in the plasma background emission and compensation was possible by using a blank of similar NaCl concentration. A study of the vertical emission profile of Pb showed that the emission maximum shifted lower in the plasma with a high NaCl concentration. This finding meant that the choice of slit height and position was very important.

The study of direct solids analysis was carried out with the use of Spex G-standards and National Bureau of Standards-Standard Reference Materials. The use of a computer coupled photodiode array direct reading spectrometer allowed multichannel analysis so that the internal standard analysis technique and background subtraction were possible. Four botanical materials, two coal samples, and a sample of coal fly ash were used to provide a variety of sample matrices. These SRM's were mixed 50:50 with graphite containing indium as an internal standard and a sample size of about 3 mg was used. The results show that while there are matrix effects it was possible to construct reasonable calibration curves for Cd and Zn in the Spex G-Standards and for Mn and Zn in the NBS-SRM's.

Future work can be envisioned in all areas investigated in this experimental work. A recent article by Price, Dymott, and Whiteside (61) on the use of graphite cups for

introducing solid samples into a graphite furnace for AAS
shows one possible method for improving the atomization step.
Ramp atomization was rejected for this work because it
did not provide a long enough heating time for complete
vaporization, but the background emission changes were much
less than with step atomization. Modification of the power
supply so that ramp heating to a plateau several seconds
long and feedback control of the heating are certain to
improve the technique.

The use of a computer based system was found to be
excellent for the temporal studies, but the systems limited
dynamic range required the use of variable signal amplif-
ication which resulted in varying background levels, thus
complicating the analytical work. The use of a data ac-
quisition system with significantly larger dynamic range
so that the variable amplifier could be eliminated should
have a high priority. An excellent candidate would be the
use of an integrating digital voltameter system similar to
the Laboratory Data Acquisition System (52) developed by
M. Blades of our laboratory.

The present work has shown that combining a carbon
furnace for sample atomization with ICAP-OES analysis shows
good potential, but it has also shown that much work still
needs to be done.

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APPENDIX A

Software Developed for the Monochromator-Photomultiplier
Readout System

A.   Introduction

The software programs developed to interface the photo-multiplier detector system with the minicomputer and to allow manipulation, readout, and storage of this data are described in this section. Programming was done in Fortran 01C and Macro 01C languages under the RT11 02C operating system on a DEC PDP 11/10 16 bit minicomputer.

The programming philosophy in this program, and in the following ones, was to break each task into a separate module and to then select the desired task module from a menu. This type of programming has proven to be very efficient since modules can be easily used in several different programs with only small modifications if necessary.

Since Fortran programs are fairly easy to understand only descriptive headings are given at the start of each module. The data acquisition subroutines are written in Macro assembly language which is more difficult to understand therefore each line of the program is fully described. Refer to the appropriate DEC manuals for further information.

B. ADCPMT - Main Program for Monochromator Photomultiplier
Readout System

1. Purpose: This program provides an interface between the
system user and the data acquisition subroutine and
provides the means for obtaining readout or storing data
on the disk under user defined names.

2. Operation: This program consists of 9 task modules which
are menu selectable. This program is entered via menu
selection #4, RESTART(START), where the operator enters
the number of data points to be acquired, the data ac-
quisition rate (master clock rate ÷ number of master
clock pulses between samples), a delay after the start
pulse until the start of data acquisition, and the sample
name. The date and time are automatically read from the
operating system. After these entries data acquisition
takes place via subroutine GDPMT and then the menu is
entered.

From the menu task modules are selected to allow:

1. PLOT: Plot data acquired on the VT-55 screen.

2. LIST: List data acquired on the VT-55 screen.

3. STASTICS: Perform statistical analysis of the data,
i.e. calculate the mean value of a set of data, the
standard deviation within that set, and calculate the
signal to noise within that set.

4. RESTART: Restart data acquisition.

5. WRITE DISK: Write the data acquired on disk under a user selected name.

6. EXIT: Exit from the program.

7. TOTALS: Allows calculations of the totals for selected portions of the data thus providing a means of calculating the integrated signal intensity.

8. READ DISK: Allows a named data file to be read from disk.

9. SMOOTH: Allows a simplified least squares smoothing of the data based on the procedure of Savitzky and Golay.

```
C
C
C          PROGRAM ADCPMT.FOR(20-NOV-79)
C
C          PURPOSE:
C                   TO ACQUIRE AND PROCESS DATA FROM THE PHOTOMULTIPLIER TUBE.
C
C          SUBROUTINES NEEDED:
C                   PLOT55
C                   GDPMT
C                   SYSLIB
C                   /F
C
C          *************
C          *WRITTEN    *
C          *BY:        *
C          *DONALD HULL*
C          *************
C
C
           DIMENSION        TITLE(3),ANP(1),DAT(3),TIM(3),A1(30)
           INTEGER*2        A(1040),B(1040),C(520),DBLK(4),NDIOD(30),NDIODN(30)
           EQUIVALENCE(B(513),C(1))
           COMMON/DRH/A,NP,MCR,ISPLF,NDELAY
           INTEGER ATTACH, SELGR, STATUS, N, HGRD, VGRD, MARKER, ORIGIN,
          1 VECT, CURPOS, ERASCR, ERALIN, DISPLY, ESCCMD, UP, DOWN, HOME,
          1 ESCRN, ELIN, ENHOLD, DSHOLD, COPY, ENPRNT, DSPRNT, BELL
           DATA    ANP,TITLE,DAT,TIM/0.,3*0.,3*0.,3*0./
           DATA    DBLK/3RDK0,3RDAT,3RA ,3RDAT/
           DATA    ATTACH, SELGR, STATUS, N, HGRD, VGRD, MARKER, ORIGIN,
          1 VECT, CURPOS, ERASCR, ERALIN, DISPLY, ESCCMD, UP, DOWN, HOME,
          1 ESCRN, ELIN, ENHOLD, DSHOLD, COPY, ENPRNT, DSPRNT, BELL
          1/0,1,2,3,4,5,6,7,8,9,10,11,12,13,65,66,72,74,75,91,92,93,94,95,7/
           CALL DATE(DAT)
511        WRITE(7,51)DAT
51         FORMAT(1X,3A4)
           GO TO 6
400        WRITE(7,54)
54         FORMAT(' ','INPUT #POINTS.')
           READ(5,59,ERR=120,END=120)XNP
           WRITE(7,55)
55         FORMAT(' ','INPUT MASTER CLOCK RATE.'
          1,//,' ','1 MHZ=2',//,' ','100 KHZ=4',//,' ','10 KHZ=6'
          2,//,' ','1 KHZ=8'//,' ','100 HZ=10',//,' ','60 HZ=14')
           READ(5,59,ERR=120,END=120)XMCR
59         FORMAT(F10.0)
           WRITE(7,68)
68         FORMAT(' ','INPUT THE NUMBER OF MASTER CLOCK PULSES
          1 BETWEEN SAMPLES.')
           READ(5,59,ERR=120,END=120)XSPL
           IF(XSPL .EQ. 0)XSPL = 1.0
           WRITE(7,69)
69         FORMAT(' ','INPUT DELAY AFTER START PULSE UNTIL
          1 THE START OF DATA AQUISITION-F10.3')
           READ(5,59,ERR=120,END=120)XDELAY
           IF (XDELAY .EQ. 0)XDELAY = 0.001
440        MCR=IFIX(XMCR+257.)
           IF(XMCR .EQ. 2.)FREQ=1000000./XSPL
           IF(XMCR .EQ. 4.)FREQ=100000./XSPL
           IF(XMCR .EQ. 6)FREQ=10000./XSPL
           IF(XMCR .EQ. 8)FREQ=1000./XSPL
           IF(XMCR .EQ. 10)FREQ=100./XSPL
```

```fortran
      IF(XMCR .EQ. 14)FREQ=60./XSPL
      IFREQ=IFIX(FREQ)
      ISPLF=IFIX(XSPL)
      NP=IFIX(X      )
      NDELAY=           ELAY*1000)
      WRITE(7          )
53    FORMAT('  ','INPUT SAMPLE NAME IN 3A4-FORMAT.')
      READ(5,52,ERR=120,END=120)TITLE
52    FORMAT(3A4)
      CALL TIME(TIM)
      WRITE(7,170)TITLE,DAT,TIM,NP,IFREQ
      WRITE(7,171)
171   FORMAT('  ','STRIKE CARRAGE RETURN TO SET UP FOR DATA AQUISITION.')
      READ(5,59,ERR=120,END=120)TEMP
      DO 401  I=1,1040
401   A(I)=0
C
C
C     ACQUIRE DATA WITH SUBROUTINE GDPMT AND STORE ON DISK.
C
      CALL GDPMT
      CALL TIME(TIM)
C
C
C     CALCULATION OF MAXIMUM, MINIMUM, AND RANGE OF VALUES.
91    A(NP+1)=NP
      A(NP+2)=IFREQ
      A(NP+3)=A(4)
      A(NP+4)=1
      A(NP+5)=A(4)
      A(NP+6)=1
      DO 1000 I=5,NP
C
C
C     MAXIMUM AND SUBSCRIPT DETERMINATION.
C
      IF(A(NP+3) .LT. A(I))A(NP+3)=A(I)
      IF(A(NP+3) .EQ. A(I))A(NP+4)=I
C
C
C     MINIMUM AND SUBSCRIPT DETERMINATION.
C
      IF(A(NP+5) .GT. A(I))A(NP+5)=A(I)
1000  IF(A(NP+5) .EQ. A(I))A(NP+6)=I
C
C
C     RANGE DETERMINATION.
C
      A(NP+7)=A(NP+3)-A(NP+5)
      WRITE(7,170)TITLE,DAT,TIM,A(NP+1),A(NP+2)
      WRITE(7,56)(A(NP+I),I=3,7)
56    FORMAT('  ','MAX=',I6,2X,'SUB=',I6,' MIN=',
     1 I6,2X,'SUB=',I6,' RANGE=',I6,/)
C
C
C     PROCESSING REQUEST.
6     WRITE(7,57)
57    FORMAT('  ','PLOT=1, LIST=2, STATISTICS=3, RESTART=4,
     1 WRITE DISK=5',//,' EXIT=6, TOTALS=7, READ DISK=8, SMOOTH=9,
     2 REPEAT=10')
      READ(5,58,ERR=120,END=120)NTEMP
58    FORMAT(I2)
      CALL PLOT55(ESCCMD,HOME,0)
      CALL PLOT55(ESCCMD,ESCRN,0)
      GO TO(100,200,300,400,500,600,700,800,900,440),NTEMP
      GO TO 6
C
C
C     DISPLAY A PLOT OF DATA ON THE VT-55 SCREEN.
100   NPLOT=NP
```

```fortran
        WRITE(7,101)
101     FORMAT(' ','NORMALIZED PLOT? YES=1, NO=0')
        READ(5,59,END=120,ERR=100)XNORM
        IF(XNORM .EQ. 1.0)SCFAC=FLOAT(A(NP+7))
        IF(XNORM .EQ. 1.0)GO TO 102
        WRITE(7,103)
103     FORMAT(' ','ENTER SCALING FACTOR, F10.0')
        READ(5,59,END=120,ERR=100)SCFAC
102     CONTINUE
        CALL PLOT55(ESCCMD,HOME,0)
        CALL PLOT55(ESCCMD,ESCRN,0)
        CALL PLOT55(CURPOS,0,0)
        WRITE(7,170)TITLE,DAT,TIM,A(NP+1),A(NP+2)
        WRITE(7,56)(A(NP+I),I=3,7)
        D2=FLOAT(A(NP+5))
        DO      150    I=1,NP
        D1=FLOAT(A(I))
        D=((D1-D2)*100.)/SCFAC
150     B(I)=IFIX(D)
        CALL PLOT55(STATUS,547,476)
        CALL PLOT55(SELGR,0,0)
        CALL PLOT55(CURPOS,0,0)
        CALL PLOT55(HGRD,1,0,0)
        IF(NPLOT .LE. 512)GO TO 151
        CALL PLOT55(STATUS,551,472)
        CALL PLOT55(SELGR,1,0)
        CALL PLOT55(HGRD,1,101)
151     IF(NP .GT. 512)NPLOT=512
        CALL PLOT55(SELGR,0,0)
        CALL PLOT55(ORIGIN,0,0)
        CALL PLOT55(N,-NPLOT,B)
        IF(NP .LE. 512)GO TO 153
        NPLOT=NP-512
        CALL PLOT55(SELGR,1,0)
        DO 156   I=1,NPLOT
156     C(I)=C(I)+101
        CALL PLOT55(N,-NPLOT,C)
153     CALL PLOT55(DISPLY,0,BELL)
        READ(5,58,END=120,ERR=120)NSTOP
120     CALL PLOT55(ESCCMD,HOME,0)
        CALL PLOT55(ESCCMD,ESCRN,0)
        CALL PLOT55(STATUS,0,1023)
        GO TO 6
C
C
C       THIS SECTION LISTS THE DATA ON THE VT-55 COPIER.
200     CALL PLOT55(ESCCMD,HOME,0)
        CALL PLOT55(ESCCMD,ESCRN,0)
        CALL PLOT55(DISPLY,0,BELL)
        WRITE(7,170)TITLE,DAT,TIM,A(NP+1),A(NP+2)
170     FORMAT(' ',3A4,3X,3A4,'/',3A4,3X,'   NP=',I6,3X,'SPL. FREQ.=',I6,/)
        DO 250  I=1,NP+7,200
        DO 251  J=I,I+190,10
        WRITE(7,63)J,(A(K),K=J,J+9)
63      FORMAT(' ',I4,2X,'>',10(I5,1X))
        IF(K .GT. (NP+7))GO TO 252
251     CONTINUE
        READ(5,58,ERR=120,END=120)NSTOP
253     CALL PLOT55(ESCCMD,HOME,0)
        CALL PLOT55(ESCCMD,ESCRN,0)
250     CONTINUE
252     CALL PLOT55(ESCCMD,HOME,0)
        CALL PLOT55(DISPLY,0,BELL)
        READ(5,58,ERR=120,END=120)NSTOP
        GO TO 120
C
```

```
C        ...IS SECTION CALCULATES THE MEAN VALUE OF A SET OF DATA,
C        ...ULATES THE  STANDARD DEVIATION WITHIN THAT SET, AND
C        ...CULATES THE SIGNAL TO NOISE RATIO FOR THAT SET.
C        ...IS IS REPEATED AS DESIRED.
300      CALL PLOT55(ESCCMD,HOME,0)
         CALL PLOT55(ESCCMD,ESCRN,0)
         WRITE(7,301)
301      FORMAT(' ',',ENTER STARTING DATA POINT, THE STOPPING DATA POINT,'
     1,//,' ','AND THE NUMBER OF DATA POINTS PER SET OF DATA.  3F10.0')
         READ(5,302,END=120,ERR=120)START,STOP,SET
302      FORMAT(3F10.0)
         ISTART=IFIX(START)
         ISTOP=IFIX(STOP)
         ISET=IFIX(SET)
         WRITE(7,170)TITLE,DAT,TIM,A(NP+1),A(NP+2)
         WRITE (7,56)(A(NP+I),I=3,7)
         WRITE(7,66)
66       FORMAT(' ',' POINT NOS.                 MEAN
     1    STD. DEV.          S/N')
         DO 310  I=ISTART,ISTOP,ISET
         SUM=0.
         SQUARE=0.
         DO 309  J=I,(I+ISET-1)
         SUM=SUM+FLOAT(A(J))
         SQUARE=SQUARE+((FLOAT(A(J)))**2)
         IF(J .LT. ISTOP)GO TO 308
         J=J+1
         SET=FLOAT(J-I)
         GO TO 303
308      CONTINUE
309      CONTINUE
303      XMEAN=SUM/(SET)
         STDEV=SQRT((SQUARE-((SUM**2)/(SET)))/(SET-1))
         IF(STDEV .GT. 0)GO TO 304
         WRITE(7,305)I,(J-1),XMEAN,STDEV
305      FORMAT(I4,' TO ',I4,1X,2(4X,F10.4),10X,'XXXX')
         GO TO 310
304      SNR=XMEAN/STDEV
         WRITE(7,67)I,(J-1),XMEAN,STDEV, SNR
67       FORMAT(I4,' TO ',I4,1X,3(4X,F10.4))
310      CONTINUE
         CALL PLOT55(ESCCMD,HOME,0)
         CALL PLOT55(DISPLY,0,BELL)
         READ(5,58,END=120,ERR=120)NSTOP
         GO TO 120
C
C
C        THIS SECTION WRITES THE PROGRAM ON DISK WITH THE CHOOSEN NAME.
500      REWIND  1
         WRITE(7,170)TITLE,DAT,TIM,A(NP+1),A(NP+2)
         WRITE(7,56)(A(NP+I),I=3,7)
         ANP(1)=FLOAT(NP)
         CALL ASSIGN(1,'DK:FTN1.DAT',-1,'NEW','NC',1)
         WRITE(1)(ANP(1))
         WRITE(1)(TITLE(I),I=1,3)
         WRITE(1)(DAT(I),I=1,3)
         WRITE(1)(TIM(I),I=1,3)
         WRITE(1)(A(I),I=1,NP+7)
         ENDFILE 1
         CALL CLOSE(1)
         GO TO 120

C
C
C        THIS SECTION CALCULATES THE TOTALS FOR SELECTED
C        PORTIONS OF THE DATA.
```

```
700        DO 705  J=1,30
           A1(J)=0
           NDIOD(J)=0
           NDIOND(J)=0
705        CONTINUE
           CALL PLOT55(ESCCMD,HOME,0)
           CALL PLOT55(ESCCMD,ESCRN,0)
           WRITE(7,170)TITLE,DAT,TIM,A(NP+1),A(NP+2)
           WRITE(7,56)(A(NP+I),I=3,7)
           JR=0
           WRITE(7,782)
782        FORMAT(' ','ENTER THE STARTING POINT # AND # OF POINTS.',/,
          1 ' ENTER EXTRA CARRAGE RETURN TO COMMENCE PROCESSING.')
701        READ(5,781,END=120,ERR=701)DIODE,DIODEN
781        FORMAT(2F10.0)
           IF(DIODE .EQ. 0)GO TO 710
           JR=JR+1
           NDIOD(JR)=IFIX(DIODE)
           NDIODN(JR)=IFIX(DIODEN)
           IF(JR .GE. 30)GO TO 710
           GO TO 701
710        CALL PLOT55(ESCCMD,HOME,0)
           CALL PLOT55(ESCCMD,ESCRN,0)
           WRITE(7,170)TITLE,DAT,TIM,A(NP+1),A(NP+2)
           WRITE(7,740)
740        FORMAT(' ','  START      NP       TOTAL')
           DO 716  K=1,JR
           DO 718  L=NDIOD(K),(NDIOD(K)+NDIODN(K)-1)
718        A1(K)=A1(K)+A(L)
           WRITE(7,755)NDIOD(K),NDIODN(K),A1(K)
755        FORMAT(3X,I4,3X,I4,F12.0)
716        CONTINUE
           READ(5,58,END=120,ERR=120)NSTOP
           GO TO 120
C
C
C          THIS SECTION READS A FILE FROM THE DISK
C
800        WRITE(7,810)
810        FORMAT(' ',' ENTER DATA FILE NAME AS *------.DAT.',/)
           CALL ASSIGN(1,'DK:FTN1.DAT',-1,'OLD','NC',1)
           READ(1)(ANP(1))
           NP=IFIX(ANP(1))
           READ(1)(TITLE(I),I=1,3)
           READ(1)(DAT(I),I=1,3)
           READ(1)(TIM(I),I=1,3)
           READ(1)(A(I),I=1,NP+7)
           ENDFILE 1
           CALL CLOSE(1)
           GO TO 120
C
C
C          THIS SECTION DOES SMOOTHING OF DATA BY SIMPLIFIED LEAST
C          SQUARES PROCEDURE FROM SAVITZKY AND GOLAY,
C          ANAL. CHEM.,36(8),P1627(1964)
C
900        WRITE(7,999)
999        FORMAT(' ','INPUT FILTER SIZE:',/,/,' 1=5 POINT FILTER',
          1 /,' 2=7 POINT FILTER',/,' 3=9 POINT FILTER',
          2 /,' 4=11 POINT FILTER',
          3 /,' 5=13 POINT FILTER',/,' 6=15 POINT FILTER',
          4 /,' 7=17 POINT FILTER',/,' 8=19 POINT FILTER',/,
          5 ' 9=21 POINT FILTER')
           READ(5,58,ERR=900,END=120)NGO
           GO TO (910,920,930,940,950,960,970,980,990),NGO
910        DO 915  I=3,(NP-2)
915        B(I)=IFIX(((-FLOAT(A(I-2)+A(I+2)))*3+(FLOAT(A(I-1)+A(I+1)))*12
          1 +(FLOAT(A(I)))*17)/35)
```

```
        DO 916  I=3,(NP-2)
916     A(I)=B(I)
        A(1)=A(3)
        A(2)=A(3)
        A(NP-1)=A(NP-2)
        A(NP)=A(NP-2)
        GO TO 91
920     DO 925  I=4,(NP-3)
925     B(I)=IFIX(((-FLOAT(A(I-3)+A(I+3)))*2+(FLOAT(A(I-2)+A(I+2)))*3
     1 +(FLOAT(A(I-1)+A(I+1)))*6+(FLOAT(A(I)))*7)/21)
        DO 926  I=4,(NP-3)
926     A(I)=B(I)
        A(1)=A(4)
        A(2)=A(4)
        A(3)=A(4)
        A(NP-2)=A(NP-3)
        A(NP-1)=A(NP-3)
        A(NP)=A(NP-3)
        GO TO 91
930     DO 935  I=5,(NP-4)
935     B(I)=IFIX(((-FLOAT(A(I-4)+A(I+4)))*21
     1 +(FLOAT(A(I-3)+A(I+3)))*14
     2 +(FLOAT(A(I-2)+A(I+2)))*39+(FLOAT(A(I-1)+A(I+1)))*54
     3 +(FLOAT(A(I)))*59)/231)
        DO 936  I=5,(NP-4)
936     A(I)=B(I)
        DO 937  I=1,4
        A(I)=A(5)
937     A(NP-I+1)=A(NP-4)
        GO TO 91
940     DO 945  I=6,(NP-5)
945     B(I)=IFIX(((-FLOAT(A(I-5)+A(I+5)))*36
     1 +(FLOAT(A(I-4)+A(I+4)))*9+(FLOAT(A(I-3)+A(I+3)))*44
     2 +(FLOAT(A(I-2)+A(I+2)))*69
     2 +(FLOAT(A(I-1)+A(I+1)))*84+(FLOAT(A(I)))*89)/429)
        DO 946  I=6,(NP-5)
946     A(I)=B(I)
        DO 947  I=1,5
        A(I)=A(6)
947     A(NP-I+1)=A(NP-5)
        GO TO 91
950     DO 955  I=7,(NP-6)
955     B(I)=IFIX(((-FLOAT(A(I-6)+A(I+6)))*11
     1 +(FLOAT(A(I-4)+A(I+4)))*9+(FLOAT(A(I-3)+A(I+3)))*16
     2 +(FLOAT(A(I-2)+A(I+2)))*21+(FLOAT(A(I-1)+A(I+1)))*24
     3 +(FLOAT(A(I)))*25)/143)
        DO 956  I=7,(NP-6)
956     A(I)=B(I)
        DO 957  I=1,6
        A(I)=A(7)
957     A(NP-I+1)=A(NP-6)
        GO TO 91
960     DO 965  I=8,(NP-7)
965     B(I)=IFIX(((-FLOAT(A(I-7)+A(I+7)))*78-(FLOAT(A(I-6)+A(I+6)))*13
     1 +(FLOAT(A(I-5)+A(I+5)))*42+(FLOAT(A(I-4)+A(I+4)))*87
     2 +(FLOAT(A(I-3)+A(I+3)))*122+(FLOAT(A(I-2)+A(I+2)))*147
     3 +(FLOAT(A(I-1)+A(I+1)))*162+(FLOAT(A(I)))*167)/1105)
        DO 966  I=8,(NP-7)
966     A(I)=B(I)
        DO 967  I=1,7
        A(I)=A(8)
967     A(NP-I+1)=A(NP-7)
        GO TO 91
970     DO 975  I=9,(NP-8)
975     B(I)=IFIX(((-FLOAT(A(I-8)+A(I+8)))*21+(-FLOAT(A(I-7)+A(I+7)))*6
     1 +(FLOAT(A(I-6)+A(I+6)))*7+(FLOAT(A(I-5)+A(I+5)))*18
```

```
      2 +(FLOAT(A(I-4)+A(I+4)))*27+(FLOAT(A(I-3)+A(I+3)))*34
      3 +(FLOAT(A(I-2)+A(I+2)))*39+(FLOAT(A(I-1)+A(I+1)))*42
      4 +(FLOAT(A(I)))*43)/323)
        DO 976  I=9,(NP-8)
976     A(I)=B(I)
        DO 977  I=1,8
        A(I)=A(9)
977     A(NP-I+1)=A(NP-8)
        GO TO 91
984     DO 985  I=10,(NP-9)
985     B(I)=IFIX((((-FLOAT(A(I-9)+A(I+9)))*136-(FLOAT(A(I-8)+A(I+8)))*51
      1 +(FLOAT(A(I-7)+A(I+7)))*24+(FLOAT(A(I-6)+A(I+6)))*89
      2 +(FLOAT(A(I-5)+A(I+5)))*144+(FLOAT(A(I-4)+A(I+4)))*189
      3 +(FLOAT(A(I-3)+A(I+3)))*224+(FLOAT(A(I-2)+A(I+2)))*249
      4 +(FLOAT(A(I-1)+A(I+1)))*264+(FLOAT(A(I)))*269)/2261)
        DO 986  I=10,(NP-9)
986     A(I)=B(I)
        DO 987  I=1,9
        A(I)=A(10)
987     A(NP-I+1)=A(NP-9)
        GO TO 91
        DO 995  I=11,(NP-10)
995     B(I)=IFIX((((-FLOAT(A(I-10)+A(I+10)))*171
      1 -(FLOAT(A(I-9)+A(I+9)))*76
      2 +(FLOAT(A(I-8)+A(I+8)))*9+(FLOAT(A(I-7)+A(I+7)))*84
      3 +(FLOAT(A(I-6)+A(I+6)))*149+(FLOAT(A(I-5)+A(I+5)))*204
      4 +(FLOAT(A(I-4)+A(I+4)))*249+(FLOAT(A(I-5)+A(I+5)))*204
      5 +(FLOAT(A(I-2)+A(I+2)))*309+(FLOAT(A(I-3)+A(I+3)))*284
      6 +(FLOAT(A(I)))*329)/3059)
        DO 996  I=11,(NP-10)
996     A(I)=B(I)
        DO 997  I=1,10
        A(I)=A(11)
997     A(NP-I+1)=A(NP-10)
        GO TO 91
C
C
C       THIS SECTION CAUSES AN EXIT FROM THE PROGRAM.
600     STOP
        END
```

C. GDPMT - Data Acquisition Subroutine

1. This subroutine acquires the data from the Photomultiplier
    Readout System via A/D conversion by the LPS 11 unit and
    transfers the acquired data to the main program ADCPMT.
    Data acquisition is started by a signal from the carbon
    furnace power supply and clocked by the LPS 11 internal
    clock.

```
;       PROGRAM GDPMT.MAC(4-JAN-78)
;
;
;       PURPOSE:
;               TO ACQUIRE DATA FROM A PMT WITH THE
;               DEC LPS UNIT, AND TO TRANSFER
;               THE DATA TO THE MAIN PROGRAM.
;
;
;       *************
;       *           *
;       *WRITTEN BY:*
;       *           *
;       *DONALD HULL*
;       *           *
;       *WITH HELP  *
;       *           *
;       *FROM:      *
;       *           *
;       *ROBERT HALL*
;       *           *
;       *************
;
;
;
;
;
;
;
;
;
        .TITLE   GET DATA FROM A PMT WITH THE LPS UNIT
        .MCALL   ..V2..,.REGDEF,.FETCH,.CLOSE,.PRINT
        .MCALL   .EXIT,.WRITW,.SRESET,.ENTER,.TTYOUT,.TTYIN
        ..V2..
        .REGDEF
        .GLOBL   GDPMT


        STR=170400              ;SET ADDRESS A/D STATUS REGISTER
        ADB=170402              ;SET ADDRESS A/D BUFFER
        DIBUF=170412            ;SET ADDRESS DIGITAL INPUT BUFFER
        CLK=170404              ;SET ADDRESS CLOCK STATUS REGISTER
        BUFP=170406             ;SET ADDRESS LPSKW BUFFER/PRESET
        KBRD=177562             ;SET ADDRESS KEY BOARD

        .CSECT

GDPMT:  NEG     ISPLF           ;NEGATE # MCR PULSES BETWEEN SPLS
        NEG     NDELAY          ;NEGATE DELAY TIME

RESTRT: MOV     #1040.,R1       ;SET POINT COUNTER
        MOV     #A,R3           ;SET ADDRESS OF ARRAY(A)
LP0:    MOV     #0,(R3)+        ;CLEAR ARRAY(A)
        DEC     R1              ;DECREMENT POINT COUNTER
        BNE     LP0             ;RETURN IF POINT COUNTER NOT ZERO
        MOV     #0,CLK

; SET UP FOR DATA ACQUISITION ,

        .PRINT  #WAIT
STRT1:  MOV     NP,R1           ;SET POINT COUNTER
        MOV     #A,R3           ;SET ADDRESS ARRAY(A)
        MOV     DIBUF,R4        ;CLEAR DIGITAL BUFFER
```

```
          MOV     R4,DIBUF
LP2:      MOV     DIBUF,R4        ;CHECK DIGITAL BUFFER FOR
          BIT     #2,R4           ;START PULSE ON BIT 1
          BEQ     LP2             ;RETURN IF NO START PULSE
          MOV     #0,BUFP         ;CLEAR BUFFER/PRESET
          MOV     NDELAY,BUFP     ;MOVE IN DELAY TO BUFFER/PRESET
          MOV     #11,CLK         ;SET CLOCK FREQUENCY AT 1KHZ,NON-REPEAT
LP3:      TSTB    CLK             ;TEST FOR END OF COUNT FLAG
          BPL     LP3
DATA:     MOV     #0,BUFP         ;CLEAR BUFFER/PRESET
          MOV     #0,CLK          ;CLEAR CLOCK PRIOR TO LOADING.BUFP
          MOV     ISPLF,BUFP      ;SET UP BUFFER/PRESET FOR SPL FREQUENCY
          MOV     #40,STR         ;SET UP TRIGGER ON A/D STATUS REGISTER
          MOV     MCR,CLK         ;SET UP MASTER CLOCK RATE

; BEGIN DATA ACQUISITION

SPL:      TSTB    STR             ;TEST FOR A/D END OF CONVERSION
          BPL     SPL             ;ON BIT 7 OF A/D STATUS REGISTER
          MOV     ADB,(R3)+       ;STORE SAMPLE DATA
          DEC     R1              ;DECREMENT POINT COUNTER
          BNE     SPL             ;RETURN FOR ANOTHER POINT IF NOT FINISHED

; FINISHED.  EXIT FROM SUBROUTINE.

          RTS     PC

          .EVEN
.CSECT DRH
A:        .BLKW   1040.
NP:       .WORD   0
MCR:      .WORD   0
ISPLF:    .WORD   0
NDELAY:   .WORD   0
          .CSECT
          .EVEN
WAIT:     .ASCIZ  /WAITING FOR START PULSE/
END:      .END    GDPMT
```

APPENDIX B

Software Developed to Plot the Monochromator-
Photomultiplier Readout System Data on a
Zeta Incremental Plotter

A. This program consists of 5 menu selectable task modules and allow the data acquired with the Photomultiplier Readout System to be plotted. The sections are:

1. READ DISK: Reads data from a named file on disk.

2. AXIS: Draws the plot axis using operator defined axis names, sizes, and dimensions.

3. PLOT: Plots the data within the axis drawn by Module 2.

4. RESTART: Restarts program to allow a new data file to be read for plotting.

5. EXIT: Exits from program.

```
C
C
C            PROGRAM PMTPLT.FOR(22-OCT-79)
C
C            PURPOSE:
C                    TO PLOT, WITH THE XY-PLOTTER, DATA STORED ON DISK.
C
C
C            SUBROUTINES NEEDED:
C                    XYLIB
C                    SYSLIB
C                    /F
C
C            ************
C            *WRITTEN   *
C            *BY:       *
C            *DONALD HULL*
C            ************
C
C
C
             DIMENSION      ANP(1),TITLE(3),DAT(3),TIM(3),X(1040),Y(1040)
             DIMENSION      XAXIS(5),YAXIS(5),TITPLT(5)
             INTEGER*2      DBLK(4),A(1040),B(1040)
             DATA     DAT,TITLE,TIM/3*0.,3*0.,3*0./
             DATA     DBLK/3RDK0,3RDAT,3RA  ,3RDAT/
C
C            THIS SECTION RESTARTS PROGRAM BY CLEARING X & Y ARRAYS.
C
700          WRITE(7,110)
110          FORMAT(' ',' ENTER THE NUMBER OF PAGES TO ADVANCE THE PEN.')
             READ (5,111)PAGES
111          FORMAT(F10.0)
             ADV=PAGES*8.5
             CALL PLOTST(0.005,'IN')
             CALL PLOT(ADV,0.0,-3)
             CALL PLOTND
             DO 701  I=1,1040
             X(I)=FLOAT(I)
701          Y(I)=0.0
C
C            THIS SECTION SELECTS THE PART OF THE PROGRAM TO BE EXICUTED.
C
1            WRITE(7,50)
50           FORMAT(' ','READ DISK=1, AXIS=2, PLOT=3, RESTART=4, SMOOTH=5
     1 ,EXIT=6')
             READ(5,51)NTEMP
51           FORMAT(I2)
             IF(NTEMP .LT. 1 .OR. NTEMP .GT. 8)GO TO 1
             GO TO(100,500,600,700,900,800),NTEMP
C
C            THIS SECTION READS DATA FILE FROM DISK.
C
100          WRITE(7,120)
120          FORMAT(' ',' ENTER DATA FILE NAME AS *------,DAT.',/)
             CALL ASSIGN(1,'DK:FTN1.DAT',-1,'OLD','NC',1)
             READ(1)(ANP(1))
             NP=IFIX(ANP(1))
             READ(1)(TITLE(I),I=1,3)
             READ(1)(DAT(I),I=1,3)
             READ(1)(TIM(I),I=1,3)
             READ(1)(A(I),I=1,NP+7)
             ENDFILE 1
```

```fortran
         CALL CLOSE(1)

C
C        THIS SECTION DOES BOOK KEEPING ON THE DATA ARRAY.
C
470      DO 480  I=1,NP+7
480      Y(I)=FLOAT(A(I))
490      DO 491  I=7,1,-1
491      Y(NP+2+I)=Y(NP+I)
C
C        THIS SECTION SETS THE MINIMUM VALUE TO 0.0 AND
C        THE MAXIMUM VALUE TO BE EQUAL TO THE RANGE FOR
C        PLOTTING PURPOSES
C
C
C        CALCULATION OF MAXIMUM, MINIMUM, AND RANGE OF VALUES.
C
         Y(NP+5)=Y(5)
         Y(NP+6)=FLOAT(5)
         Y(NP+7)=Y(5)
         Y(NP+8)=FLOAT(5)
C
C        MAXIMUM AND SUBSCRIPT DETERMINATION.
C
         DO 1000 I=6,NP
         IF(Y(NP+5) .LT. Y(I))Y(NP+5)=Y(I)
         IF (Y(NP+5) .EQ. Y(I))Y(NP+6)=FLOAT (I)
C
C        MINIMUM AND SUBSCRIPT DETERMINATION.
C
         IF(Y(NP+7) .GT. Y(I))Y(NP+7)=Y(I)
1000     IF(Y(NP+7) .EQ. Y(I))Y(NP+8)=FLOAT(I)
C
C        RANGE DETERMINATION.
C
         Y(NP+9)=Y(NP+5)-Y(NP+7)
         DO 492  I=1,NP
492      Y(I)=Y(I)-Y(NP+7)
         Y(NP+5)=Y(NP+5)-Y(NP+7)
         Y(NP+7)=0.0
         WRITE(7,493)TITLE,DAT,TIM,Y(NP+3),Y(NP+4)
493      FORMAT(' ',3A4,3A4,'/',3A4,3X,'NP=',F4.0,3X,'FREQ=',F4.0)
         WRITE(7,494)(Y(NP+I),I=5,9)
494      FORMAT(' ','MAX=',F10.0,'@',F4.0,'  MIN=',F10.0,
     1 '@',F4.0,'  RANGE=',F10.0)
         GO TO 1
C
C        THIS SECTION DRAWS THE AXIS OF THE PLOT.
C
500      WRITE(7,501)
501      FORMAT(' ',' NEW X&Y TITLES AND AXIS LENGTHS? YES=1,NO=0')
         READ(5,111,ERR=500,END=500)XNEW
         IF(XNEW .EQ.0)GO TO 521
502      FORMAT(5A4)
         WRITE(7,510)
510      FORMAT(' ',' ENTER THE TITLE FOR THE XAXIS, 20 CHARACTERS MAX.')
         READ(5,502)XAXIS
         WRITE(7,503)
503      FORMAT(' ','ENTER THE TITLE FOR THE Y AXIS, 20 CHARACTERS MAX.')
         READ(5,502)YAXIS
         WRITE(7,520)
520      FORMAT(' ',' ENTER X AND Y AXIS LENGTHS, 2F10.0.')
         READ(5,525)XLONG,YLONG
521      WRITE(7,504)
504      FORMAT(' ','ENTER THE TITLE FOR THE PLOT, 20 CHARACTERS MAX.')
         READ(5,502)TITPLT
```

```
                XMIN=0.0
                XMAX=Y(NP+3)
                YMIN=0.0
                YMAX=Y(NP+5)
     525        FORMAT(2F10.0)
                WRITE(7,494)(Y(NP+I),I=5,9)
                WRITE(7,620)
     620        FORMAT(' ',' NORMALIZED PLOT=1, SCALED PLOT=0.')
                READ(5,51)NTEMP
                IF(NTEMP .EQ. 1)GO TO 550
                WRITE(7,625)
     625        FORMAT(' ',' ENTER NEW VALUE FOR Y RANGE, F10.0.')
                READ(5,111)YMAX
     550        X(NP+1)=XMIN
                X(NP+2)=(XMAX-XMIN)/XLONG
                X(NP+9)=X(NP+2)/Y(NP+4)
                Y(NP+1)=YMIN
                Y(NP+2)=(YMAX-YMIN)/YLONG
                CALL PLOTST(0.005,'IN')
                CALL PLOT(1.5,1.0,-3)
                CALL AXIS(0.0,0.0,XAXIS,-20,XLONG,0.0,X(NP+1),X(NP+9))
                CALL AXIS(0.0,0.0,YAXIS,+20,YLONG,90.0,Y(NP+1),Y(NP+2))
                TITLNG=(XLONG-2.8)/2
                CALL PLOT(TITLNG,(YLONG+0.5),3)
                CALL SYMBOL(TITLNG,(YLONG+0.5),0.14,TITPLT,0,20)
                CALL PLOT (0.0,YLONG,+3)
                CALL PLOT(XLONG,YLONG,+2)
                CALL PLOT(XLONG,0.0,+2)
                CALL PLOT(0.0,0.0,+3)
                CALL PLOT(-1.5,-1.0,-3)
                CALL PLOTND
                GO TO 1
     C
     C
     C          THIS SECTION PLOTS THE DATA.
     C
     600        X(NP+1)=XMIN
                X(NP+2)=(XMAX-XMIN)/XLONG
                Y(NP+1)=YMIN
                Y(NP+2)=(YMAX-YMIN)/YLONG
                CALL PLOTST(0.005,'IN')
                CALL PLOT(1.5,1.0,-3)
                CALL LINE(X,Y,NP,1,0,0)
                CALL PLOT(0.0,0.0,+3)
                CALL PLOT(-1.5,-1.0,-3)
                CALL PLOTND
                GO TO 1
     C
     C
     C          THIS SECTION DOES SMOOTHING OF DATA BY SIMPLIFIED LEAST
     C          SQUARES PROCEDURE FROM SAVITZKY AND GOLAY,
     C          ANAL. CHEM.,36(8),P1627(1964)
     C
     900        WRITE(7,999)
     999        FORMAT(' ','INPUT FILTER SIZE:',/,/,' 1=5 POINT FILTER',
          1 /,' 2=7 POINT FILTER',/,' 3=9 POINT FILTER',
          2 /,' 4=11 POINT FILTER',
          3 /,' 5=13 POINT FILTER',/,' 6=15 POINT FILTER',
          4 /,' 7=17 POINT FILTER',/,' 8=19 POINT FILTER',/,
          5 ' 9=21 POINT FILTER')
                READ(5,51,ERR=900,END=1)NGO
                GO TO (910,920,930,940,950,960,970,980,990),NGO
     910        DO 915  I=3,(NP-2)
     915        B(I)=IFIX(((-FLOAT(A(I-2)+A(I+2)))*3+(FLOAT(A(I-1)+A(I+1)))*12
          1 +(FLOAT(A(I)))*17)/35)
                DO 916  I=3,(NP-2)
     916        A(I)=B(I)
                A(1)=A(3)
```

```
         DO 976   I=9,(NP-8)
976      A(I)=B(I)
         DO 977   I=1,8
         A(I)=A(9)
977      A(NP-I+1)=A(NP-8)
         GO TO 470
980      DO 985   I=10,(NP-9)
985      B(I)=IFIX(((-FLOAT(A(I-9)+A(I+9)))*136-(FLOAT(A(I-8)+A(I+8)))*51
     1   +(FLOAT(A(I-7)+A(I+7)))*24+(FLOAT(A(I-6)+A(I+6)))*89
     2   +(FLOAT(A(I-5)+A(I+5)))*144+(FLOAT(A(I-4)+A(I+4)))*189
     3   +(FLOAT(A(I-3)+A(I+3)))*224+(FLOAT(A(I-2)+A(I+2)))*249
     4   +(FLOAT(A(I-1)+A(I+1)))*264+(FLOAT(A(I)))*269)/2261)
         DO 986   I=10,(NP-9)
986      A(I)=B(I)
         DO 987   I=1,9
         A(I)=A(10)
987      A(NP-I+1)=A(NP-9)
         GO TO 470
990      DO 995   I=11,(NP-10)
995      B(I)=IFIX(((-FLOAT(A(I-10)+A(I+10)))*171
     1   -(FLOAT(A(I-9)+A(I+9)))*76
     2   +(FLOAT(A(I-8)+A(I+8)))*9+(FLOAT(A(I-7)+A(I+7)))*84
     3   +(FLOAT(A(I-6)+A(I+6)))*149+(FLOAT(A(I-5)+A(I+5)))*204
     4   +(FLOAT(A(I-4)+A(I+4)))*249+(FLOAT(A(I-3)+A(I+3)))*284
     5   +(FLOAT(A(I-2)+A(I+2)))*309+(FLOAT(A(I-1)+A(I+1)))*324
     6   +(FLOAT(A(I)))*329)/3059)
         DO 996   I=11,(NP-10)
996      A(I)=B(I)
         DO 997   I=1,10
         A(I)=A(11)
997      A(NP-I+1)=A(NP-10)
         GO TO 470
C
C
C        THIS SECTION CAUSES AN EXIT FROM THE PROGRAM.
C
800      CALL PLOTST(0.005,'IN')
         CALL PLOT(8.5,0.0,-3)
         CALL PLOTND
         STOP
         END
```

APPENDIX C

Software Developed for the Computer Coupled
Photodiode Array Readout Systems

A. ADCFUR - This main program is much like that described in
Appendix A, Section B and contains several of the same
task modules although they may be slightly modified.
The task modules are:

1. PLOT

2. LIST

3. PEAK LOCATE: Searches for and lists the value and diode
number for all peaks.

4. RESTART

5. EXIT

6. WRITE DISK

7. READ DISK

8. TOTALS

```
C
C
C       PROGRAM ADCFUR.FOR(31-DEC-79)
C
C       PURPOSE:
C               TO ACQUIRE AND PROCESS DATA FROM THE PHOTO-DIODE ARRAY.
C
C       SUBROUTINES NEEDED:
C               PLOT55
C               FGDFUR
C               SYSLIB/F
C
C       *************
C       *WRITTEN    *
C       *BY:        *
C       *DONALD HULL*
C       *************
C
C
        DIMENSION       TITLE(3),DAT(3),C(1040),A1(30)
        INTEGER*4       A(1040)
        INTEGER*2       B(1040),D(520),NDIOD(30),NDIODN(30)
        EQUIVALENCE(B(513),D(1))
        EQUIVALENCE(A(1),C(1))
        COMMON/DRH/A,NS,NP,IBKD
        INTEGER ATTACH, SELGR, STATUS, N, HGRD, VGRD, MARKER, ORIGIN,
     1 VECT, CURPOS, ERASCR, ERALIN, DISPLY, ESCCMD, UP, DOWN, HOME,
     1 ESCRN, ELIN, ENHOLD, DSHOLD, COPY, ENPRNT, DSPRNT, BELL
        DATA    DAT,TITLE/3*0.,3*0./
        DATA    ATTACH, SELGR, STATUS, N, HGRD, VGRD, MARKER, ORIGIN,
     1 VECT, CURPOS, ERASCR, ERALIN, DISPLY, ESCCMD, UP, DOWN, HOME,
     1 ESCRN, ELIN, ENHOLD, DSHOLD, COPY, ENPRNT, DSPRNT, BELL
     1/0,1,2,3,4,5,6,7,8,9,10,11,12,13,65,66,72,74,75,91,92,93,94,95,7/
        CALL DATE(DAT)
        WRITE(7,52)DAT
400     DO 91   I=1,1040
        C(I)=0.
91      B(I)=0
52      FORMAT(' ',3A4)
        WRITE(7,53)
53      FORMAT(' ','INPUT SAMPLE NAME IN 3A4-FORMAT.')
        READ(5,51,END=120)TITLE
51      FORMAT(3A4)
        WRITE(7,54)
54      FORMAT(' ','INPUT #SCANS.')
        READ(5,59,END=120)XNS
        WRITE(7,55)
55      FORMAT(' ','INPUT #POINTS.')
        READ(5,59,END=120)XNP
59      FORMAT(F10.0)
        WRITE(7,68)
68      FORMAT(' ','DO YOU WISH BACKGROUND SUBTRACTION? YES=1, NO=0')
        READ(5,59,END=120)BKD
        NS=IFIX(XNS)
        NP=IFIX(XNP)
        IBKD=IFIX(BKD)
        NP=NP+4
C
C       ACQUIRE DATA WITH SUBROUTINE FGDFUR.
C
        CALL FGDFUR
```

```
C
C          CONVERSION OF DATA FROM INTEGER*4 TO REAL
C
           DO 90    J=5,NP
90         C(J-4)=AJFLT(A(J))
           NP=NP-4
           C(NP+1)=XNS
           C(NP+2)=XNP
           C(NP+3)=BKD
C
C          CALCULATION OF MAXIMUM, MINIMUM, AND RANGE OF VALUES.
C
           C(NP+4)=C(1)
           C(NP+5)=1.
           C(NP+6)=C(1)
           C(NP+7)=1.
           DO 1000 I=2,NP
C
C          MAXIMUM AND SUBSCRIPT DETERMINATION.
C
           IF(C(NP+4) .LT. C(I))C(NP+4)=C(I)
           IF(C(NP+4) .EQ. C(I))C(NP+5)=FLOAT(I)
C
C          MINIMUM AND SUBSCRIPT DETERMINATION.
C
           IF(C(NP+6) .GT. C(I))C(NP+6)=C(I)
1000       IF(C(NP+6) .EQ. C(I))C(NP+7)=FLOAT(I)
C
C          RANGE DETERMINATION.
C
           C(NP+8)=C(NP+4)-C(NP+6)
           WRITE(7,56)(C(NP+I),I=4,8)
56         FORMAT(' ','MAX=',F10.0,2X,'@',F5.0,' MIN=',F10.0,
      1 2X,'@',F5.0,' RANGE=',F10.0)
C
C          PROCESSING REQUEST.
C
6          WRITE(7,57)
57         FORMAT(' ','PLOT=1, LIST=2, PEAK LOCATE=3, RESTART=4,',/,
      1 ' EXIT=5, WRITE DISK=6, READ DISK=7, TOTALS=8')
           CALL PLOT55(DISPLY,0,BELL)
           READ(5,58,END=120)NTEMP
58         FORMAT(I2)
           CALL PLOT55(ESCCMD,HOME,0)
           CALL PLOT55(ESCCMD,ESCRN,0)
           GO TO(100,200,300,400,500,600,700,800),NTEMP
           GO TO 6
C
C          DISPLAY A PLOT OF DATA ON THE VT-55 SCREEN.
C
100        NPLOT=NP
           WRITE(7,101)
101        FORMAT(' ','NORMALIZED PLOT? YES=1, NO=0')
           READ(5,59,END=120)XNORM
           IF(XNORM .EQ. 1.0)SCFAC=C(NP+8)
           IF(XNORM .EQ. 1.0)GO TO 102
           WRITE(7,103)
103        FORMAT(' ','ENTER SCALING FACTOR, F10.0')
           READ(5,59,END=120)SCFAC
102        CONTINUE
           DO 150  I=1,NP
           B(I)=IFIX(((C(I)-C(NP+6))*100.)/SCFAC)
           IF(B(I) .GT. 100)B(I)=100
150        CONTINUE
           CALL PLOT55(ESCCMD,HOME,0)
           CALL PLOT55(ESCCMD,ESCRN,0)
```

```
              CALL PLOT55(STATUS,547,476)
              CALL PLOT55(SELGR,0,0)
              CALL PLOT55(CURPOS,0,0)
              WRITE(7,170)TITLE,DAT,C(NP+1),C(NP+2),C(NP+3)
              WRITE(7,56)(C(NP+I),I=4,8)
              CALL PLOT55(HGRD,1,0,0)
              IF(NPLOT .LE. 512)GO TO 151
              CALL PLOT55(STATUS,551,472)
              CALL PLOT55(SELGR,1,0)
              CALL PLOT55(HGRD,1,101)
151           IF(NP .GT. 512)NPLOT=512
              CALL PLOT55(SELGR,0,0)
              CALL PLOT55(ORIGIN,0,0)
              CALL PLOT55(N,-NPLOT,B)
              IF(NP .LE. 512)GO TO 153
              NPLOT=NP-512
              CALL PLOT55(SELGR,1,0)
              DO 156  I=1,NPLOT
156           D(I)=D(I)+101
              CALL PLOT55(N,-NPLOT,D)
153           CALL PLOT55(DISPLY,0,BELL)
              READ(5,58,END=120)NSTOP
120           CALL PLOT55(ESCCMD,HOME,0)
              CALL PLOT55(ESCCMD,ESCRN,0)
              CALL PLOT55(STATUS,0,1023)
              GO TO 6
C
C
C             THIS SECTION LISTS THE DATA ON THE VT-55 COPIER.
C
200           CALL PLOT55(ESCCMD,HOME,0)
              CALL PLOT55(ESCCMD,ESCRN,0)
              CALL PLOT55(DISPLY,0,BELL)
              WRITE(7,170)TITLE,DAT,C(NP+1),C(NP+2),C(NP+3)
              WRITE(7,56)(C(NP+I),I=4,8)
170.          FORMAT(' ',3A4,3A4,3X,'NS=',F10.0,3X,'NP=',F10.0,
     1        3X,'BKGD=',F10.0)
              DO 250  I=1,NP+8,100
              DO 251  J=I,I+95,5
              WRITE(7,63)J,(C(K),K=J,J+4)
              IF(K .GT. (NP+8))GO TO 252
251           CONTINUE
              READ(5,58,END=120)NSTOP
253           CALL PLOT55(ESCCMD,HOME,0)
              CALL PLOT55(ESCCMD,ESCRN,0)
250           CONTINUE
65            FORMAT(' ',I4,2X,'>',5(F10.0,1X))
252           CALL PLOT55(ESCCMD,HOME,0)
              CALL PLOT55(DISPLY,0,BELL)
              READ(5,58,END=120)NSTOP
              GO TO 120
C
C
C             THIS SECTION DETERMINES PEAK LOCATIONS AND DISPLAYS
C             THE LOCATION AND PEAK VALUE ON THE VT-55.
C
300           CALL PLOT55(ESCCMD,HOME,0)
              CALL PLOT55(ESCCMD,ESCRN,0)
              WRITE(7,170)TITLE,DAT,C(NP+1),C(NP+2),C(NP+3)
              WRITE(7,56)(C(NP+I),I=4,8)
              WRITE(7,64)
64            FORMAT(' ','ENTER THE THRESHOLD',F10.0')
              READ(5,59,END=120)THRES
66            FORMAT(' ','POINT NO.   AMPLITUDE')
              DO 320  J=1,NP
              NCNT=0
              WRITE(7,66)
              DO 310  I=J,NP
```

```
                     IF(C(I) .LT. THRES)GO TO 310
                     IF(C(I+1) .GT. C(I))GO TO 310
                     IF(C(I) .LE. C(I-1))GO TO 310
                     WRITE(7,67)I,C(I)
                     NCNT=NCNT+1
                     J=I
                     IF(I .GE. NP)GO TO 320
                     IF(NCNT .EQ. 20)GO TO 311
      310            J=I.
                     IF(I .GE. NP)GO TO 320
      311            READ(5,58,END=120)NSTOP
                     CALL PLOT55(ESCCMD,HOME,0)
                     CALL PLOT55(ESCCMD,ESCRN,0)
      320            CONTINUE
      67             FORMAT(5X,I4,6X,F10.0)
                     CALL PLOT55(ESCCMD,HOME,0)
                     CALL PLOT55(DISPLY,0,BELL)
                     READ(5,58,END=120)NSTOP
                     CALL PLOT55(ESCCMD,ESCRN,0)
                     GO TO 120
      C
      C              THIS SECTION WRITES THE DATA ON DISK AND NAMES THE DATA FILE.
      C
      600            REWIND 1
                     WRITE(7,170)TITLE,DAT,C(NP+1),C(NP+2),C(NP+3)
                     WRITE(7,56)(C(NP+I),I=4,8)
                     WRITE(7,720)
                     CALL ASSIGN(1,'DK:FTN1.DAT',-1,'NEW','NC',1)
                     WRITE(1)(DAT(I),I=1,3)
                     WRITE(1)(TITLE(I),I=1,3)
                     WRITE(1)(C(I),I=1,NP+8)
                     ENDFILE 1
                     CALL CLOSE(1)
                     GO TO 120
      C
      C              THIS SECTION READS DATA FILE FROM DISK.
      C
      700            WRITE(7,720)
      720            FORMAT(' ',' ENTER DATA FILE NAME AS *------(.DAT).',/)
                     CALL ASSIGN(1,'DK:FTN1.DAT',-1,'OLD','NC',1)
                     READ(1)(DAT(I),I=1,3)
                     READ(1)(TITLE(I),I=1,3)
                     READ(1)(C(I),I=1,NP+8)
                     ENDFILE 1
                     CALL CLOSE(1)
                     GO TO 120
      C
      C              THIS SECTION CALCULATES THE TOTALS FOR SELECTED
      C              PORTIONS OF THE DATA.
      C
      800            DO 805  J=1,30
                     A1(J)=0
                     NDIOD(J)=0
                     NDIOND(J)=0
      805            CONTINUE
                     CALL PLOT55(ESCCMD,HOME,0)
                     CALL PLOT55(ESCCMD,ESCRN,0)
                     WRITE(7,170)TITLE,DAT,C(NP+1),C(NP+2),C(NP+3)
                     WRITE(7,56)(C(NP+I),I=4,8)
                     JR=0
                     WRITE(7,882)
      882            FORMAT(' ','ENTER THE STARTING POINT # AND # OF POINTS.',//,
             1       ' ENTER EXTRA CARRAGE RETURN TO COMMENCE PROCESSING.')
      801            READ(5,881,END=120,ERR=801)DIODE,DIODEN
      881            FORMAT(2F10.0)
                     IF(DIODE .EQ. 0)GO TO 810
```

```
          JR=JR+1
          NDIOD(JR)=IFIX(DIODE)
          NDIODN(JR)=IFIX(DIODEN)
          IF(JR .GE. 30)GO TO 810
          GO TO 801
810       CALL PLOT55(ESCCMD,HOME,0)
          CALL PLOT55(ESCCMD,ESCRN,0)
          WRITE(7,170)TITLE,DAT,C(NP+1),C(NP+2),C(NP+3)
          WRITE(7,56)(C(NP+I),I=4,8)
          WRITE(7,840)
840       FORMAT(' ',' START        NP      . TOTAL')
          DO 816   K=1,JR
          DO 818   L=NDIOD(K),(NDIOD(K)+NDIODN(K)-1)
818       A1(K)=A1(K)+C(L)
          WRITE(7,855)NDIOD(K),NDIODN(K),A1(K)
855       FORMAT(3X,I4,3X,I4,F12.0)
816       CONTINUE
          READ(5,58,END=120,ERR=120)NSTOP
          GO TO 120
C
C
C         THIS SECTION CAUSES AN EXIT FROM THE PROGRAM.
C
500       STOP
          END
*
```

B. FGDFUR - This subroutine acquires time-averaged data from
    the Computer Coupled Photodiode Array Readout system via
    A/D conversion by the LPS 11 unit and transfers the
    acquired data to the main program ADCFUR. Data may be
    background subtracted before transfer to ADCFUR if desired.
    Data acquisition is started by the combination of the
    start signal from the carbon furnace power supply and the
    photodiode array start signal. Data acquisition is
    clocked by the photodiode array clock.

```
;       PROGRAM FGDFUR.MAC(1-OCT-79)
;
;
;       PURPOSE:
;               TO ACQUIRE DATA WITH THE DEC LPS UNIT,
;               DO AVERAGING OF THE DATA, AND TO TRANSFER
;               THE DATA TO THE MAIN PROGRAM.
;
;
;       **************
;       *            *
;       *WRITTEN BY:*
;       *            *
;       *DONALD HULL*
;       *            *
;       *WITH HELP   *
;       *            *
;       *FROM:       *
;       *            *
;       *ROBERT HALL*
;       *            *
;       **************
;
;
;
;
;
;
;

        .TITLE  FAST GET DATA FROM LPS UNIT
        .MCALL  ..V2..,,.REGDEF,.FETCH,.CLOSE,.PRINT
        .MCALL  .EXIT,.WRITW,.SRESET,.ENTER,.TTYOUT,.TTYIN
        ..V2..
        .REGDEF
        .GLOBL  FGDFUR


        STR=170400              ;SET ADDRESS A/D STATUS REGISTER
        ADB=170402              ;SET ADDRESS A/D BUFFER
        DIBUF=170412            ;SET ADDRESS DIGITAL INPUT BUFFER
        KBRD=177562             ;SET ADDRESS KEY BOARD

        .CSECT

FGDFUR: MOV     #1,BKD          ;SET UP BACKGROUND FLAG

RESTRT: MOV     #2080.,R1       ;SET POINT COUNTER
        MOV     #A,R3           ;SET ADDRESS OF ARRAY(A)
LPO:    MOV     #0,(R3)+        ;CLEAR ARRAY(A)
        DEC     R1              ;DECREMENT POINT COUNTER
        BNE     LPO             ;RETURN IF POINT COUNTER NOT ZERO

; WAIT FOR KEY BOARD FLAG TO BEGIN DATA ACQUISITION

        .PRINT  #DATAQ          ;ASK FOR KEY BOARD FLAG
LP1:    .TTYIN                  ;GET CHARACTER FROM TTY
        BCS     LP1             ;WAIT FOR INPUT
        CMPB    R0,#12          ;WAS LAST CHARACTER=LF?
        BNE     LP1             ;RETURN IF NOT FINISHED

; SET UP FOR DATA ACQUISITION
```

```
            MOV     DIBUF,R4        ;CLEAR DIGITAL INPUT BUFFER
            MOV     R4,DIBUF
LP10:       MOV     DIBUF,R4        ;TEST FOR ASH CYCLE FINISH FLAG
            BIT     #2,R4           ;ON BIT 1
            BEQ     LP10            ;RETURN IF NO FLAG
STRT2:      MOV     NS,R2           ;SET SCAN COUNTER
STRT1:      MOV     NP,R1           ;SET POINT COUNTER
            MOV     #B,R3           ;SET ADDRESS ARRAY(B)
            MOV     R2,R0           ;MOVE VALUE OF NS TO BCD-INPUT

;     BEGIN DATA ACQUISITION

DATA:       MOV     DIBUF,R4        ;CLEAR DIGITAL INPUT BUFFER
            MOV     R4,DIBUF
LP2:        MOV     DIBUF,R4        ;TEST FOR START FLAG ON
            BIT     #1,R4           ;BIT 0
            BEQ     LP2             ;RETURN IF NO FLAG

            MOV     #20,STR         ;SET UP TRIGGER ON A/D STATUS REGISTER
SPL:        TSTB    STR             ;TEST FOR A/D END OF CONVERSION
            BPL     SPL             ;ON BIT 7 OF A/D STATUS REGISTER
            MOV     ADB,(R3)+       ;STORE SAMPLE DATA
            DEC     R1              ;DECREMENT POINT COUNTER
            BNE     SPL             ;RETURN FOR ANOTHER POINT IF NOT FINISHED

;     DOUBLE WORD ADD

            MOV     NP,R1           ;SET UP POINT COUNTER
            MOV     #A,R3           ;SET ADDRESS ARRAY(A)
            MOV     #B,R0           ;SET ADDRESS ARRAY(B)
LP3:        ADD     (R0)+,(R3)+     ;LOW-ORDER WORD ADD
            ADC     (R3)+           ;CARRY BIT ADD
            DEC     R1              ;DECREMENT POINT COUNTER
            BNE     LP3             ;RETURN FOR ANOTHER POINT IF NOT FINISHED
            DEC     R2              ;DECREMENT SCAN COUNTER
            BNE     STRT1           ;RETURN FOR ANOTHER SCAN IF NOT FINISHED
            TST     IBKD            ;TEST BACKGROUND FLAG AND
            BEQ     FIN

;     WAIT FOR KEY BOARD FLAG TO START BACKGROUND SUBTRACTION

BKGD:       .PRINT  #BKDAQ
LP4:        .TTYIN                  ;ASK FOR KEY BOARD FLAG
            BCS     LP4             ;GET CHARACTER FROM TTY
            CMPB    R0,#12          ;CHECK FOR INPUT
            BNE     LP4             ;WAS LAST CHARACTER=LF?
            MOV     #0,BKD          ;RETURN IF NOT
                                    ;CLEAR BACKGROUND FLAG

;     SET UP FOR BACKGROUND SUBTRACTION

STRT4:      MOV     NS,R2           ;SET SCAN COUNTER
STRT3:      MOV     NP,R1           ;SET POINT COUNTER
            MOV     #B,R3           ;SET ADDRESS OF ARRAY(B)
            MOV     R2,R0           ;MOVE VALUE OF NS TO BCD-INPUT
;     BEGIN BACKGROUND SUBTRACTION

BKG:        MOV     DIBUF,R4        ;CLEAR DIGITAL INPUT BUFFER
            MOV     R4,DIBUF
LP5:        MOV     DIBUF,R4        ;TEST FOR START FLAG ON
            BIT     #1,R4           ;BIT 0
            BEQ     LP5             ;RETURN IF NO FLAG
            MOV     #20,STR         ;SET UP A/D STATUS REGISTER
LP6:        TSTB    STR             ;TEST FOR A/D END OF CONVERSION
            BPL     LP6             ;AT BIT 7 A/D STATUS REGISTER
            MOV     ADB,(R3)+       ;STORE BACKGROUND DATA
```

```
                DEC     R1              ;DECREMENT POINT COUNTER
                BNE     LP6             ;RETURN FOR ANOTHER POINT IF NOT FINISHED
        ; DOUBLE WORD SUBTRACTION
        ;
                MOV     NP,R1           ;SET UP POINT COUNTER
                MOV     #A,R3           ;SET ADDRESS ARRAY(A)
                MOV     #B,R0           ;SET ADDRESS ARRAY(B)
        SUBK:   SUB     (R0)+,(R3)+     ;LOW-ORDER WORD SUBTRACTION
                SBC     (R3)+           ;CARRY SUBTRACTION
                DEC     R1              ;DECREMENT POINT COUNTER
                BNE     SUBK            ;RETURN FOR ANOTHER POINT IF NOT FINISHED
                DEC     R2              ;DECREMENT SCAN COUNTER
                BNE     STRT3           ;RETURN FOR ANOTHER SCAN IF NOT FINISHED
        ;
        ; FINISHED.  EXIT FROM SUBROUTINE.
        ;
        FIN:    RTS     PC
        ;
        ;
        ;
                .EVEN
        .CSECT DRH
        A:      .BLKW   2080.
        NS:     .WORD   0
        NP:     .WORD   0
        IBKD:   .WORD   0
        .CSECT
        .EVEN
        BKD:    .WORD   0
        B:      .BLKW   1040.
        DATAQ:  .ASCIZ  /STRIKE CR TO START DATA ACQUISITION./
        BKDAQ:  .ASCIZ  /STRIKE CR TO START BACKGROUND ACQUISITION./
        END:    .END    FGDFUR
```

APPENDIX D

Software Developed to Plot the Computer-Controlled

Photodiode Array Readout System Data on a

Zeta Incremental Plotter

A. This program consists of 6 menu selectable task modules
and allow plotting of the data acquired with the photo-
diode array-based systems. The task modules are:

1. READ DISK

2. AXIS

3. PLOT

4. RESTART

5. SMOOTH: A Smoothing routine based on the simplified
least squares smoothing procedure of Savitzky and Golay.

6. EXIT

```
C
C
C       PROGRAM PDAPLT.FOR(5-DEC-79)
C
C       PURPOSE:
C               TO PLOT, WITH THE XY-PLOTTER, FLOATING POINT PHOTO DIODE ARRAY
C               DATA STORED ON DISK.
C
C
C       SUBROUTINES NEEDED:
C               XYLIB
C               SYSLIB
C               /F
C
C       *************
C       *WRITTEN    *
C       *BY:        *
C       *DONALD HULL*
C       *************
C
C
        DIMENSION       TITLE(3),DAT(3),X(1040),Y(1040),F(1040)
        DIMENSION       XAXIS(7),YAXIS(7),TITP(7)
        INTEGER*2       DBLK(4)
        DATA    DAT,TITLE/3*0.,3*0./
        DATA    DBLK/3RDK0,3RDAT,3RA  ,3RDAT/
C
C       THIS SECTION RESTARTS PROGRAM BY CLEARING X & Y ARRAYS.
C
700     CALL PLOTST(0 ,05,'IN')
        CALL PLOT(8. ,0.  -3)
        CALL PLOTND
        DO 701  I=1,1040
        X(I)=FLOAT(I)
701     Y(I)=0.0
        WRITE(7,110)
110     FORMAT(' ','INF IT ' DATA POINTS.')
        READ(5,111)XNP
111     FORMAT(F10.0)
        NP=IFIX(XNP)
C
C       THIS SECTION SELECTS THE PART OF THE PROGRAM TO BE EXICUTED.
C
1       WRITE(7,50)
50      FORMAT(' ','READ DISK=1, AXIS=2, PLOT=3, RESTART=4,
     1 ,SMOOTH=5, EXIT=6')
        READ(5,51)NTEMP
51      FORMAT(I2)
        IF(NTEMP .LT. 1 .OR. NTEMP .GT. 6)GO TO 1
        GO TO(100,500,600,700,900,800),NTEMP
C
C       THIS SECTION READS DATA FILE FROM DISK.
C
100     WRITE(7,120)
120     FORMAT(' ',' ENTER DATA FILE NAME AS *------,DAT.',/)
        CALL ASSIGN(1,'DK:FTN1.DAT',-1,'OLD','NC',1)
        READ(1)(DAT(I),I=1,3)
        READ(1)(TITLE(I),I=1,3)
        READ(1)(Y(I),I=1,NP+8)
        ENDFILE 1
        CALL CLOSE(1)
```

```
C
C
C            THIS SECTION DOES BOOK KEEPING ON THE DATA ARRAY.
490          DO 491  I=8,1,-1
491          Y(NP+2+I)=Y(NP+I)
C
C            THIS SECTION SETS THE MINIMUM VALUE TO 0.0 AND
C            THE MAXIMUM VALUE TO BE EQUAL TO THE RANGE FOR
C            PLOTTING PURPOSES
C
C            CALCULATION OF MAXIMUM, MINIMUM, AND RANGE OF VALUES.
C
91           Y(NP+6)=Y(1)
             Y(NP+7)=FLOAT(1)
             Y(NP+8)=Y(1)
             Y(NP+9)=FLOAT(1)
             DO 1000  I=2,NP
C
C            MAXIMUM AND SUBSCRIPT DETERMINATION.
C
             IF(Y(NP+6) .LT. Y(I))Y(NP+6)=Y(I)
             IF(Y(NP+6) .EQ. Y(I))Y(NP+7)=FLOAT(I)
C
C            MINIMUM AND SUBSCRIPT DETERMINATION.
C
             IF(Y(NP+8) .GT. Y(I))Y(NP+8)=Y(I)
1000         IF(Y(NP+8) .EQ. Y(I))Y(NP+9)=FLOAT(I)
C
C            RANGE DETERMINATION.
C
             Y(NP+10)=Y(NP+6)-Y(NP+8)
             IF(NTEMP .EQ. 5)GO TO 495
             DO 492  I=1,NP
492          Y(I)=Y(I)-Y(NP+8)
             Y(NP+6)=Y(NP+6)-Y(NP+8)
             Y(NP+8)=0.0
495          WRITE(7,493)TITLE,DAT,Y(NP+3),Y(NP+4),Y(NP+5)
493          FORMAT(' ',3A4,3A4,3X,'NS=',F4.0,3X,'NP=',F4.0,3X,'BKGD=',F4.0)
             WRITE(7,494)(Y(NP+I),I=6,10)
494          FORMAT(' ','MAX=',F10.0,'@',F4.0,' MIN=',F10.0,
     1       '@',F4.0,' RANGE=',F10.0)
             GO TO 1
C
C            THIS SECTION DRAWS THE AXIS OF THE PLOT.
C
500          CONTINUE
502          FORMAT(7A4)
             WRITE(7,510)
510          FORMAT(' ',' ENTER THE TITLE FOR THE XAXIS, 28 CARACTERS MAX.')
             READ(5,502)XAXIS
             WRITE(7,503)
503          FORMAT(' ','ENTER THE TITLE FOR THE Y AXIS, 28 CARACTERS MAX')
             READ(5,502)YAXIS
             WRITE(7,504)
504          FORMAT(' ','ENTER THE TITLE FOR THE PLOT, 28 CARACTERS MAX.')
             READ(5,502)TITP
             XMIN=0.0
             XMAX=Y(NP+4)
             WRITE (7,505)
505          FORMAT(' ','XMIN=0 & XMAX=NP.',/
     1       '  ENTER 1 TO CHANGE, CARRAGE RETURN IF NO CHANGE DESIRED.')
             READ(5,51)NTEMP
             IF (NTEMP .NE. 1)GO TO 506
             WRITE(7,507)
507          FORMAT(' ','ENTER NEW VALUES FOR XMIN AND XMAX, 2F10.0.')
```

```
              READ(5,525)XMIN,XMAX
506           YMIN=0.0
              YMAX=Y(NP+6)
              WRITE(7,520)
520           FORMAT(' ',' ENTER X AND Y AXIS LENGTHS, 2F10.0,')
              READ(5,525)XLONG,YLONG
525           FORMAT(2F10.0)
621           WRITE(7,494)(Y(NP+I),I=6,10)
              WRITE(7,620)
620           FORMAT(' ',' NORMALIZED PLOT=1, SCALED PLOT=0.')
              READ(5,51)NTEMP
              IF(NTEMP .EQ. 1)GO TO 550
              WRITE(7,625)
625           FORMAT(' ',' ENTER NEW VALUE FOR Y RANGE, F10.0.')
              READ(5,111)YMAX
550           X(NP+1)=XMIN
              X(NP+2)=(XMAX-XMIN)/XLONG
              Y(NP+1)=YMIN
              Y(NP+2)=(YMAX-YMIN)/YLONG
              CALL PLOTST(0.005,'IN')
              CALL PLOT(1.5,1.0,-3)
              CALL AXIS(0.0,0.0,XAXIS,-28,XLONG,0.0,X(NP+1),X(NP+2))
              CALL AXIS(0.0,0.0,YAXIS,+28,YLONG,90.0,Y(NP+1),Y(NP+2))
              CALL PLOT(XLONG,0,+3)
              CALL PLOT(XLONG,YLONG,+2)
              CALL PLOT(0,YLONG,+2)
              CALL PLOT(0,(YLONG+0.5),+3)
              CALL SYMBOL(0,(YLONG+0.5),0.14,TITP,0,28)
              CALL PLOT(0.0,0.0,+3)
              CALL PLOT(-1.5,-1.0,-3)
              CALL PLOTND
              GO TO 1
C
C             THIS SECTION PLOTS THE DATA.
C
600           WRITE(7,610)
610           FORMAT(' ',' CHANGE Y-RANGE? YES=1, NO=CARRAGE RETURN')
              READ(5,51)NQ
              IF(NQ .EQ. 0)GO TO 611
              WRITE(7,625)
              READ(5,111)YMAX
611           X(NP+1)=0.0
              X(NP+2)=XNP/XLONG
              Y(NP+1)=YMIN
              Y(NP+2)=(YMAX-YMIN)/YLONG
              CALL PLOTST(0.005,'IN')
              CALL PLOT(1.5,1.0,-3)
              CALL LINE(X,Y,NP,1,0,0)
              CALL PLOT(0.0,0.0,+3)
              CALL PLOT(-1.5,-1.0,-3)
              CALL PLOTND
              GO TO 1
C
C             THIS SECTION DOES SMOOTHING OF DATA BY SIMPLIFIED LEAST
C             SQUARES PROCEDURE FROM SAVITZKY AND GOLAY,
C             ANAL. CHEM.,36(8),P1627(1964)
C
900           WRITE(7,999)
999           FORMAT(' ','INPUT FILTER SIZE:',/,/,' 1=5 POINT FILTER',
     1       /,' 2=7 POINT FILTER',/,' 3=9 POINT FILTER',
     2       /,' 4=11 POINT FILTER',
     3       /,' 5=13 POINT FILTER',/,' 6=15 POINT FILTER',
     4       /,' 7=17 POINT FILTER',/,' 8=19 POINT FILTER',/,
     5       ' 9=21 POINT FILTER')
              READ(5,58,ERR=900,END=1)NGO
58            FORMAT(I2)
```

```
         GO TO (910,920,930,940,950,960,970,980,990),NGO
910      DO 915  I=3,(NP-2)
915      F(I)=(((-(Y(I-2)+Y(I+2)))*3+((Y(I-1)+Y(I+1)))*12
     1 +((Y(I)))*17)/35)
         DO 916  I=3,(NP-2)
916      Y(I)=F(I)
         Y(1)=Y(3)
         Y(2)=Y(3)
         Y(NP-1)=Y(NP-2)
         Y(NP)=Y(NP-2)
         GO TO 91
920      DO 925  I=4,(NP-3)
925      F(I)=(((-(Y(I-3)+Y(I+3)))*2+((Y(I-2)+Y(I+2)))*3
     1 +((Y(I-1)+Y(I+1)))*6+((Y(I)))*7)/21)
         DO 926  I=4,(NP-3)
926      Y(I)=F(I)
         Y(1)=Y(4)
         Y(2)=Y(4)
         Y(3)=Y(4)
         Y(NP-2)=Y(NP-3)
         Y(NP-1)=Y(NP-3)
         Y(NP)=Y(NP-3)
         GO TO 91
930      DO 935  I=5,(NP-4)
935      F(I)=(((-(Y(I-4)+Y(I+4)))*21
     1 +((Y(I-3)+Y(I+3)))*14
     2 +((Y(I-2)+Y(I+2)))*39+((Y(I-1)+Y(I+1)))*54
     3 +((Y(I)))*59)/231)
         DO 936  I=5,(NP-4)
936      Y(I)=F(I)
         DO 937  I=1,4
         Y(I)=Y(5)
937      Y(NP-I+1)=Y(NP-4)
         GO TO 91
940      DO 945  I=6,(NP-5)
945      F(I)=(((-(Y(I-5)+Y(I+5)))*36
     1 +((Y(I-4)+Y(I+4)))*9+((Y(I-3)+Y(I+3)))*44
     2 +((Y(I-2)+Y(I+2)))*69
     2 +((Y(I-1)+Y(I+1)))*84+((Y(I)))*89)/429)
         DO 946  I=6,(NP-5)
946      Y(I)=F(I)
         DO 947  I=1,5
         Y(I)=Y(6)
947      Y(NP-I+1)=Y(NP-5)
         GO TO 91
950      DO 955  I=7,(NP-6)
955      F(I)=(((-(Y(I-6)+Y(I+6)))*11
     1 +((Y(I-4)+Y(I+4)))*9+((Y(I-3)+Y(I+3)))*16
     2 +((Y(I-2)+Y(I+2)))*21+((Y(I-1)+Y(I+1)))*24
     3 +((Y(I)))*25)/143)
         DO 956  I=7,(NP-6)
956      Y(I)=F(I)
         DO 957  I=1,6
         Y(I)=Y(7)
957      Y(NP-I+1)=Y(NP-6)
         GO TO 91
960      DO 965  I=8,(NP-7)
965      F(I)=(((-(Y(I-7)+Y(I+7)))*78-((Y(I-6)+Y(I+6)))*13
     1 +((Y(I-5)+Y(I+5)))*42+((Y(I-4)+Y(I+4)))*87
     2 +((Y(I-3)+Y(I+3)))*122+((Y(I-2)+Y(I+2)))*147
     3 +((Y(I-1)+Y(I+1)))*162+((Y(I)))*167)/1105)
         DO 966  I=8,(NP-7)
966      Y(I)=F(I)
         DO 967  I=1,7
         Y(I)=Y(8)
967      Y(NP-I+1)=Y(NP-7)
```

```
      GO TO 91
970   DO 975  I=9,(NP-8)
975   F(I)=(((-(Y(I-8)+Y(I+8)))*21+(-(Y(I-7)+Y(I+7)))*6
    1 +((Y(I-6)+Y(I+6)))*7+((Y(I-5)+Y(I+5)))*18
    2 +((Y(I-4)+Y(I+4)))*27+((Y(I-3)+Y(I+3)))*34
    3 +((Y(I-2)+Y(I+2)))*39+((Y(I-1)+Y(I+1)))*42
    4 +((Y(I)))*43)/323)
      DO 976  I=9,(NP-8)
976   Y(I)=F(I)
      DO 977  I=1,8
      Y(I)=Y(9)
977   Y(NP-I+1)=Y(NP-8)
      GO TO 91
980   DO 985  I=10,(NP-9)
985   F(I)=(((-(Y(I-9)+Y(I+9)))*136-((Y(I-8)+Y(I+8)))*51
    1 +((Y(I-7)+Y(I+7)))*24+((Y(I-6)+Y(I+6)))*89
    2 +((Y(I-5)+Y(I+5)))*144+((Y(I-4)+Y(I+4)))*189
    3 +((Y(I-3)+Y(I+3)))*224+((Y(I-2)+Y(I+2)))*249
    4 +((Y(I-1)+Y(I+1)))*264+((Y(I)))*269)/2261)
      DO 986  I=10,(NP-9)
986   Y(I)=F(I)
      DO 987  I=1,9
      Y(I)=Y(10)
987   Y(NP-I+1)=Y(NP-9)
      GO TO 91
990   DO 995  I=11,(NP-10)
995   F(I)=(((-(Y(I-10)+Y(I+10)))*171
    1 -((Y(I-9)+Y(I+9)))*76
    2 +((Y(I-8)+Y(I+8)))*9+((Y(I-7)+Y(I+7)))*84
    3 +((Y(I-6)+Y(I+6)))*149+((Y(I-5)+Y(I+5)))*204
    4 +((Y(I-4)+Y(I+4)))*249+((Y(I-3)+Y(I+3)))*284
    5 +((Y(I-2)+Y(I+2)))*309+((Y(I-1)+Y(I+1)))*324
    6 +((Y(I)))*329)/3059)
      DO 996  I=11,(NP-10)
996   Y(I)=F(I)
      DO 997  I=1,10
      Y(I)=Y(11)
997   Y(NP-I+1)=Y(NP-10)
      GO TO 91
C
C
C     THIS SECTION CAUSES AN EXIT FROM THE PROGRAM.
C
800   CALL PLOTST(0.005,'IN')
      CALL PLOT(8.5,0.0,-3)
      CALL PLOTND
      STOP
      END
```

APPENDIX E

Software Developed for Time Studies with the Computer-Coupled Photodiode Array Readout Systems

A. MULTFR - This main program is much like those described
in Appendix A and C except that the individual photodiode
array scans are not time averaged but are stored seq-
uentially on disk as individual scans by the subroutine
MULFUR and each individual scan may then be read from the
disk by menu selection #4, READ DISK. The task modules
are:

1. PLOT

2. LIST

3. PEAK LOCATE

4. READ DISK: Reads any selected scan from the sequential
file stored on disk by MULFUR.

5. RESTART

6. WRITE DISK: Writes the selected file on disk under the
operator selected name.

7. TOTALS

8. EXIT

```
C
6          WRITE(7,170)TITLE,DAT,XNS,XNP,C(NP+3)
           WRITE(7,56)(C(NP+I),I=4,8)
           WRITE(7,57)
57         FORMAT(' ','PLOT=1, LIST=2, PEAK LOCATE=3, READ DISK=4',/,
    1' ','RESTART=5, WRITE DISK=6, TOTALS=7, EXIT=8')
           CALL PLOT55(DISPLY,0,BELL)
           READ(5,58,END=120)NTEMP
58         FORMAT(I2)
           CALL PLOT55(ESCCMD,HOME,0)
           CALL PLOT55(ESCCMD,ESCRN,0)
           GO TO(100,200,300,400,500,600,700,800),NTEMP
           GO TO 6
C
C          READ INDIVIDUAL SCANS FROM DATA.DAT FILE ON DISK.
C
400        WRITE(7,68)NS
68         FORMAT(' ',I2,' SCANS AQUIRED.  WHICH SCAN DO YOU WISH?  ENTER
    1 # IN I2 FORMAT.')
           READ (5,58,END=120)NUMSET
720        XNUMST=FLOAT(NUMSET)
           NBLK=(5*(NUMSET-1))
           DO 91   I=1,1040
           C(I)=0.
91         B(I)=0
           ICD=LOOKUP(0,DBLK)
           ICODE=IREADW(NPX,B,NBLK,0)
           CALL CLOSEC(0)
           CALL IFREEC(0)
C
C          CONVERSION OF DATA FROM INTEGER*2 TO REAL
C
           DO 90   J=5,NPX
90         C(J-4)=FLOAT(B(J))
           C(NP+1)=XNS
           C(NP+2)=XNP
           C(NP+3)=XNUMST
           IF(NTEMP .EQ. 7)GO TO 715
C
C          CALCULATION OF MAXIMUM, MINIMUM, AND RANGE OF VALUES.
C
           C(NP+4)=C(1)
           C(NP+5)=1.
           C(NP+6)=C(1)
           C(NP+7)=1.
           DO 1000 I=2,NP
C
C          MAXIMUM AND SUBSCRIPT DETERMINATION.
C
           IF(C(NP+4) .LT. C(I))C(NP+4)=C(I)
           IF(C(NP+4) .EQ. C(I))C(NP+5)=FLOAT(I)
C
C          MINIMUM AND SUBSCRIPT DETERMINATION.
C
           IF(C(NP+6) .GT. C(I))C(NP+6)=C(I)
1000       IF(C(NP+6) .EQ. C(I))C(NP+7)=FLOAT(I)
C
C          RANGE DETERMINATION.
C
           C(NP+8)=C(NP+4)-C(NP+6)
56         FORMAT(' ','MAX=',F10.0,2X,'@',F5.0,' MIN=',F10.0,
    1 2X,'@',F5.0,' RANGE=',F10.0,/)
           GO TO 120
C
C          DISPLAY A PLOT OF DATA ON THE VT-55 SCREEN.
C
```

```
100       NPLOT=NP
          WRITE(7,101)
101       FORMAT(' ','NORMALIZED PLOT? YES=1, NO=0')
          READ(5,59,END=120)XNORM
          IF(XNORM .EQ. 1.0)SCFAC=C(NP+8)
          IF(XNORM .EQ. 1.0)GO TO 102
          WRITE(7,103)
103       FORMAT(' ','ENTER SCALING FACTOR, F10.0')
          READ(5,59,END=120)SCFAC
102       CONTINUE
          DO 150  I=1,NP
150       B(I)=IFIX(((C(I)-C(NP+6))*100.)/SCFAC)
          CALL PLOT55(ESCCMD,HOME,0)
          CALL PLOT55(ESCCMD,ESCRN,0)
          CALL PLOT55(STATUS,547,476)
          CALL PLOT55(SELGR,0,0)
          CALL PLOT55(CURPOS,0,0)
          WRITE(7,170)TITLE,DAT,C(NP+1),C(NP+2),C(NP+3)
          WRITE(7,56)(C(NP+I),I=4,8)
          CALL PLOT55(HGRD,1,0,0)
          IF(NPLOT .LE. 512)GO TO 151
          CALL PLOT55(STATUS,551,472)
          CALL PLOT55(SELGR,1,0)
          CALL PLOT55(HGRD,1,101)
151       IF(NP .GT. 512)NPLOT=512
          CALL PLOT55(SELGR,0,0)
          CALL PLOT55(ORIGIN,0,0)
          CALL PLOT55(N,-NPLOT,B)
          IF(NP .LE. 512)GO TO 153
          NPLOT=NP-512
          CALL PLOT55(SELGR,1,0)
          DO 156  I=1,NPLOT
156       D(I)=D(I)+101
          CALL PLOT55(N,-NPLOT,D)
153       CALL PLOT55(DISPLY,0,BELL)
          READ(5,58,END=120)NSTOP
120       CALL PLOT55(ESCCMD,HOME,0)
          CALL PLOT55(ESCCMD,ESCRN,0)
          CALL PLOT55(STATUS,0,1023)
          GO TO 6
C
C
C         THIS SECTION LISTS THE DATA ON THE VT-55 COPIER.
C
200       CALL PLOT55(ESCCMD,HOME,0)
          CALL PLOT55(ESCCMD,ESCRN,0)
          CALL PLOT55(DISPLY,0,BELL)
          WRITE(7,170)TITLE,DAT,C(NP+1),C(NP+2),C(NP+3)
          WRITE(7,56)(C(NP+I),I=4,8)
170       FORMAT(' ',3A4,3A4,3X,'NS=',F10.0,3X,'NP=',F10.0,
     1 3X,'SCAN #=',F10.0)
          DO 250  I=1,NP+8,100
          DO 251  J=I,I+95,5
          WRITE(7,63)J,(C(K),K=J,J+4)
          IF(K .GT. (NP+8))GO TO 252
251       CONTINUE
          READ(5,58,END=120)NSTOP
253       CALL PLOT55(ESCCMD,HOME,0)
          CALL PLOT55(ESCCMD,ESCRN,0)
          WRITE(7,170)TITLE,DAT,C(NP+1),C(NP+2),C(NP+3)
          WRITE(7,56)(C(NP+I),I=4,8)
250       CONTINUE
63        FORMAT(' ',I4,2X,'>',5(F10.0,1X))
252       CALL PLOT55(DISPLY,0,BELL)
          READ(5,58,END=120)NSTOP
          GO TO 120
C
```

```
C           THIS SECTION DETERMINES PEAK LOCATIONS AND DISPLAYS
C           THE LOCATION AND PEAK VALUE ON THE VT-55.
C
300         CALL PLOT55(ESCCMD,HOME,0)
            CALL PLOT55(ESCCMD,ESCRN,0)
            WRITE(7,170)TITLE,DAT,C(NP+1),C(NP+2),C(NP+3)
            WRITE(7,56)(C(NP+I),I=4,8)
            WRITE(7,64)
64          FORMAT(' ','ENTER THE THRESHOLD,F10.0')
            READ(5,59,END=120)THRES
66          FORMAT(' ','POINT NO.   AMPLITUDE')
            CALL PLOT55(ESCCMD,HOME,0)
            CALL PLOT55(ESCCMD,ESCRN,0)
            WRITE(7,170)TITLE,DAT,C(NP+1),C(NP+2),C(NP+3)
            WRITE(7,56)(C(NP+I),I=4,8)
            DO 320   J=1,NP
            NCNT=0
            WRITE(7,66)
            DO 310   I=J,NP
            IF(C(I) .LT. THRES)GO TO 310
            IF(C(I+1) .GT. C(I))GO TO 310
            IF(C(I) .LE. C(I-1))GO TO 310
            WRITE(7,67)I,C(I)
            NCNT=NCNT+1
            J=I
            IF(I .GE. NP)GO TO 320
            IF(NCNT .EQ. 20)GO TO 311
310         J=I
            IF(I .GE. NP)GO TO 320
311         READ(5,58,END=120)NSTOP
            CALL PLOT55(ESCCMD,HOME,0)
            CALL PLOT55(ESCCMD,ESCRN,0)
            WRITE(7,170)TITLE,DAT,C(NP+1),C(NP+2),C(NP+3)
            WRITE(7,56)(C(NP+I),I=4,8)
320         CONTINUE
67          FORMAT(5X,I4,6X,F10.0)
            CALL PLOT55(DISPLY,0,BELL)
            READ(5,58,END=120)NSTOP
            GO TO 120
C
C           THIS SECTION WRITES THE DATA ON DISK AND NAMES THE DATA FILE.
C
600         REWIND  1
            WRITE(7,170)TITLE,DAT,C(NP+1),C(NP+2),C(NP+3)
            WRITE(7,56)(C(NP+I),I=4,8)
            CALL ASSIGN(1,'DK:FTN1.DAT',-1,'NEW','NC',1)
            WRITE(1)(DAT(I),I=1,3)
            WRITE(1)(TITLE(I),I=1,3)
            WRITE(1)(C(I),I=1,NP+8)
            ENDFILE 1
            CALL CLOSE(1)
            GO TO 120
C
C           THIS SECTION READS DATA FROM THE DISK, AND CALCULATES THE
C           TOTALS FOR SELECTED PORTIONS OF THAT DATA.
C
700         DO 705   J=1,100
705         A(J)=0
            DO 706   J=1,30
706         A1(J)=0
            CALL PLOT55(EXCCMD,HOME,0)
            CALL PLOT55(EXCCMD,ESCRN,0)
            WRITE(7,170)TITLE,DAT,XNS,XNP
            WRITE(7,780)
780         FORMAT(' ',/,'WHICH SETS DO YOU WISH TO USE FOR TOTALS
          1 CALCULATIONS?'
```

```
                1,/,/,' ','ENTER THE # OF THE STARTING SCAN AND THE # OF SCANS.')
                READ(5,781,END=120)START,XLENTH              ()
  781           FORMAT(2F10.0)
                NSTART=IFIX(START)
                NLENTH=IFIX(XLENTH)
                WRITE(7,798)
  798           FORMAT(' ',1X,'RAW DATA OUT=1, NOT=ANYTHING ELSE')
                READ(5,58)IOPT
                JR=0
                TDIOD=0
                WRITE(7,782)
  782           FORMAT(' ','ENTER THE STARTING DIODE # AND # OF DIODES.',/,/,
               1' ','ENTER 0,0 TO COMMENCE PROCESSING.')
  701           READ(5,781,END=120)DIODE,DIODEN
                TDIOD=TDIOD+DIODEN
                IF(TDIOD .GT. 100)GO TO 710
                IF(DIODE .EQ. 0)GO TO 710
                JR=JR+1
                NDIOD(JR)=IFIX(DIODE)
                NDIODN(JR)=IFIX(DIODEN)
                GO TO 701
  710           CALL PLOT55(ESCCMD,HOME,0)
                CALL PLOT55(ESCCMD,ESCRN,0)
                IF(IOPT .NE. 1)GO TO 711
                NC=0
                WRITE(7,170)TITLE,DAT,C(NP+1),C(NP+2)
                WRITE(7,794)
  794           FORMAT(' ',1X,'SCAN',5X,'DIODE',7X,'VALUE')
  711           DO 725  NUMSET=NSTART,(NSTART+NLENTH-1)
                GO TO 720
  715           N=0
                IF(IOPT .NE. 1)GO TO 797
  793           FORMAT(' ',3X,I2,6X,I4,2X,F10.0)
                DO 797  K=1,JR
                DO 796  L=NDIOD(K),(NDIOD(K)+NDIODN(K)-1)
                NC=NC+1
                IF(L .EQ. NDIOD(K))WRITE(7,793)NUMSET,L,C(L)
                IF(L .NE. NDIOD(K))WRITE(7,795)L,C(L)
  795           FORMAT(12X,I4,2X,F10.0)
                IF(NC .LT. 20)GO TO 796
                NC=0
                READ(5,58,END=120)NSTOP
                CALL PLOT55(ESCCMD,HOME,0)
                CALL PLOT55(ESCCMD,ESCRN,0)
                WRITE(7,170)TITLE,DAT,C(NP+1),C(NP+2)
                WRITE(7,794)
  796           CONTINUE
  797           CONTINUE
                DO 716  K=1,JR
                DO 718  L=NDIOD(K),(NDIOD(K)+NDIODN(K)-1)
                N=N+1
                A(N)=A(N)+C(L)
  718           A1(K)=A1(K)+C(L)
  716           CONTINUE
  725           CONTINUE
                READ(5,58,END=120)NSTOP
                CALL PLOT55(ESCCMD,HOME,0)
                CALL PLOT55(ESCCMD,ESCRN,0)
                WRITE(7,756)TITLE,DAT,START,XLENTH
                WRITE(7,740)
  740           FORMAT(' ',1X,'DIODE',9X,'TOTAL',4X,'GROUP TOTAL')
                N=0
                NC=0
                DO 760  K=1,JR
                NCOUNT=NDIOD(K)+NDIODN(K)-1
                DO 750  L=NDIOD(K),(NDIOD(K)+NDIODN(K)-1)
```

```
       1,/,/,' ','ENTER THE # OF THE STARTING SCAN AND THE # OF SCANS.')
         READ(5,781,END=120)START,XLENTH
781      FORMAT(2F10.0)
         NSTART=IFIX(START)
         NLENTH=IFIX(XLENTH)
         WRITE(7,798)
798      FORMAT(' ',1X,'RAW DATA OUT=1, NOT=ANYTHING ELSE')
         READ(5,58)IOPT
         JR=0
         TDIOD=0
         WRITE(7,782)
782      FORMAT(' ','ENTER THE STARTING DIODE # AND # OF DIODES.',/,/,
       1' ','ENTER 0,0 TO COMMENCE PROCESSING.')
701      READ(5,781,END=120)DIODE,DIODEN
         TDIOD=TDIOD+DIODEN
         IF(TDIOD .GT. 100)GO TO 710
         IF(DIODE .EQ. 0)GO TO 710
         JR=JR+1
         NDIOD(JR)=IFIX(DIODE)
         NDIODN(JR)=IFIX(DIODEN)
         GO TO 701
710      CALL PLOT55(ESCCMD,HOME,0)
         CALL PLOT55(ESCCMD,ESCRN,0)
         IF(IOPT .NE. 1)GO TO 711
         NC=0
         WRITE(7,170)TITLE,DAT,C(NP+1),C(NP+2)
         WRITE(7,794)
794      FORMAT(' ',1X,'SCAN',5X,'DIODE',7X,'VALUE')
711      DO 725 NUMSET=NSTART,(NSTART+NLENTH-1)
         GO TO 720
715      N=0
         IF(IOPT .NE. 1)GO TO 797
793      FORMAT(' ',3X,I2,6X,I4,2X,F10.0)
         DO 797 K=1,JR
         DO 796 L=NDIOD(K),(NDIOD(K)+NDIODN(K)-1)
         NC=NC+1
         IF(L .EQ. NDIOD(K))WRITE(7,793)NUMSET,L,C(L)
         IF(L .NE. NDIOD(K))WRITE(7,795)L,C(L)
795      FORMAT(12X,I4,2X,F10.0)
         IF(NC .LT. 20)GO TO 796
         NC=0
         READ(5,58,END=120)NSTOP
         CALL PLOT55(ESCCMD,HOME,0)
         CALL PLOT55(ESCCMD,ESCRN,0)
         WRITE(7,170)TITLE,DAT,C(NP+1),C(NP+2)
         WRITE(7,794)
796      CONTINUE
797      CONTINUE
         DO 716 K=1,JR
         DO 718 L=NDIOD(K),(NDIOD(K)+NDIODN(K)-1)
         N=N+1
         A(N)=A(N)+C(L)
718      A1(K)=A1(K)+C(L)
716      CONTINUE
725      CONTINUE
         READ(5,58,END=120)NSTOP
         CALL PLOT55(ESCCMD,HOME,0)
         CALL PLOT55(ESCCMD,ESCRN,0)
         WRITE(7,756)TITLE,DAT,START,XLENTH
         WRITE(7,740)
740      FORMAT(' ',1X,'DIODE',9X,'TOTAL',4X,'GROUP TOTAL')
         N=0
         NC=0
         DO 760 K=1,JR
         NCOUNT=NDIOD(K)+NDIODN(K)-1
         DO 750 L=NDIOD(K),(NDIOD(K)+NDIODN(K)-1)
```

```
        N=N+1
        NC=NC+1
        IF(L .EQ. NCOUNT)GO TO 755
        WRITE(7,751)L,A(N)
        GO TO 753
755     WRITE(7,752)L,A(N),A1(K)
753     IF(NC .LT. 20)GO TO 750
        NC=0
        READ(5,58,END=120)NSTOP
        CALL PLOT55(ESCCMD,HOME,0)
        CALL PLOT55(ESCCMD,ESCRN,0)
        WRITE(7,756)TITLE,DAT,START,XLENTH
        WRITE(7,740)
750     CONTINUE
760     CONTINUE
751     FORMAT(' ',1X,I5,2X,F12.0)
752     FORMAT(' ',1X,I5,2X,2(F12.0,3X))
756     FORMAT(' ',3A4,3A4,3X,'STARTING SCAN#=',F4.0,3X,'# SCANS=',F4.0)
        CALL PLOT55(DISPLY,0,BELL)
        READ(5,58,END=120)NSTOP
        GO TO 120
C
C
C       THIS SECTION CAUSES AN EXIT FROM THE PROGRAM.
800     STOP
        END
```

B. MULFUR - This subroutine first acquires a background scan
and stores this. The individual scans are then added to
a negative background to give individual background
subtracted scans which are sequentially written into the
file DATA.DAT. Data acquisition is started by the com-
bination of the furnace start signal and the photodiode
array start signal. Data acquisition is clocked by the
photodiode array clock.

```
;       PROGRAM MULFUR.MAC(6-NOV-78)
;
;
;       PURPOSE:
;               TO ACQUIRE MULTIPLE SCANS WITH THE PHOTO-DIODE
;               ARRAY AND TO TRANSFER THESE SCANS INDIVIDUALLY
;               TO THE DISK(IN BLOCKS) FOR TRANSFER TO
;               THE MAIN FORTRAN PROGRAM FOR FURTHER PROCESSING.
;
;
;       **************
;       *            *
;       *WRITTEN BY:*
;       *            *
;       *DONALD HULL*
;       *            *
;       *WITH HELP  *
;       *            *
;       *FROM:      *
;       *            *
;       *ROBERT HALL*
;       *            *
;       **************
;
;
;
;
;
;
;
                ,TITLE  MULTIPLE SCANS OF FURNACE DATA
                .MCALL  ..V2..,.REGDEF,.FETCH,.CLOSE,.PRINT
                .MCALL  .EXIT,.WRITW,.SRESET,.ENTER,.TTYOUT,.TTYIN
                ..V2..
                .REGDEF
                .GLOBL  MULFUR
;
;
                STR=170400              ;SET ADDRESS A/D STATUS REGISTER
                ADB=170402              ;SET ADDRESS A/D BUFFER
                DIBUF=170412            ;SET ADDRESS DIGITAL INPUT BUFFER
                KBRD=177562             ;SET ADDRESS KEY BOARD

                .CSECT

MULFUR: MOV     (R5)+,R1                                ;RECEIVE DATA FROM FORTRAN
        MOV     @(R5)+,NS
        MOV     @(R5)+,NP
        MOV     @(R5)+,NBLK
        MOV     #0,BLK
        .SRESET
        .FETCH  #CORSPC,#FPRT
        BCC     GO1
        JMP     BADFET
GO1:    .ENTER  #AREA,#0,#FPRT,NBLK
        BCC     RESTRT
        JMP     BADENT

RESTRT: MOV     #1040.,R1       ;SET POINT COUNTER
        MOV     #B,R3           ;SET ADDRESS OF ARRAY(B)
LP0:    MOV     #0,(R3)+        ;CLEAR ARRAY(A)
        DEC     R1              ;DECREMENT POINT COUNTER
```

```
                BNE      LP0                     ;RETURN IF POINT COUNTER NOT ZERO
;
;       WAIT FOR KEY BOARD FLAG TO BEGIN DATA ACQUISITION
;
                .PRINT   #DATAQ                  ;ASK FOR KEY BOARD FLAG
        LP1:    .TTYIN                           ;GET CHARACTER FROM TTY
                BCS      LP1                     ;WAIT FOR INPUT
                CMPB     R0,#12                  ;WAS LAST CHARACTER=LF?
                BNE      LP1                     ;RETURN IF NOT FINISHED
;
;       SET UP FOR DATA ACQUISITION
;
        STRT2:  MOV      NS,R2                   ;SET SCAN COUNTER
                MOV      DIBUF,R4                ;CLEAR DIGITAL INPUT BUFFER
                MOV      R4,DIBUF
        LP10:   MOV      DIBUF,R4                ;TEST FOR ATOMIZE FLAG ON
                BIT      #2,R4                   ;BIT 1
                BEQ      LP10                    ;RETURN IF NO FLAG
        STRT1:  MOV      NP,R1                   ;SET POINT COUNTER
                MOV      #B,R3                   ;SET ADDRESS ARRAY(B)
;
;       BEGIN DATA ACQUISITION
;
        DATA:   MOV      DIBUF,R4                ;CLEAR DIGITAL INPUT BUFFER
                MOV      R4,DIBUF
        LP2:    MOV      DIBUF,R4                ;TEST FOR START FLAG ON
                BIT      #1,R4                   ;BIT 0
                BEQ      LP2                     ;RETURN IF NO FLAG

                MOV      #20,STR                 ;SET UP TRIGGER ON A/D STATUS REGISTER
        SPL:    TSTB     STR                     ;TEST FOR A/D END OF CONVERSION
                BPL      SPL                     ;ON BIT 7 OF A/D STATUS REGISTER
                MOV      ADB,(R3)+               ;STORE SAMPLE DATA
                DEC      R1                      ;DECREMENT POINT COUNTER
                BNE      SPL                     ;RETURN FOR ANOTHER POINT IF NOT FINISHED
;
;       WRITE A ON DISK AS DATA,DAT FILE
;
                .WRITW   #AREA,#0,#B,NP,BLK
                BCC      GO2
                JMP      BADWRT
        GO2:    ADD      #5,BLK
                DEC      R2                      ;DECREMENT SCAN COUNTER
                BNE      STRT1                   ;RETURN FOR ANOTHER SCAN IF NOT FINISHED
;
;       FINISHED.  EXIT FROM SUBROUTINE.
;
                .CLOSE   #0
        FIN:    RTS      PC
;
;
;


                .EVEN
        B:      .BLKW    1040.
        NS:     .WORD    0
        NP:     .WORD    0
        NBLK:   .WORD    0
                .EVEN
        BADFET: .PRINT   #FMSG
                .EXIT
        BADENT: .PRINT   #EMSG
                .EXIT
        BADWRT: .PRINT   #WMSG
                .EXIT
        BLK:    .WORD    0
        FPRT:   .RAD50   /DK /
```

```
              .RAD50   /DATA  DAT/
AREA:         .BLKW    10
FMSG:         .ASCIZ   /BAD FETCH/
EMSG:         .ASCIZ   /BAD ENTER/
WMSG:         .ASCIZ   /BAD WRITE/
              .EVEN
CORSPC:       .BLKW    400.
DATAQ:        .ASCIZ   /STRIKE CR TO START DATA ACQUISITION./
BKDAQ:        .ASCIZ   /STRIKE CR TO START BACKGROUND ACQUISITION./
END:          .END     MULFUR
```

APPENDIX F

Software Developed to Plot the Time Studies Obtained with

the Computer-Coupled Photodiode Array Readout System

A.   PLOT3D - This plotting program allows any of the selected

   individual scans acquired under MULTFR to be plotted as

   3-dimensional plots. The individual plots are separated

   by operator choosen x and y axis' values and the program

   is written to prevent lines being drawn through previously

   drawn lines. The task modules are:

1.   READ DISK: Reads the selected individual scan.

2.   AXIS

3.   PLOT: Plots the individual scans at operator choosen

   x, y increments.

4.   RESTART

5.   EXIT

```fortran
C
C
C         PROGRAM PLOT3D.FOR(7-JUL-79)
C
C         PURPOSE:
C                 TO PLOT IN 3-DIMENTIONS WITH THE X-Y PLOTTER, DATA
C                 STORED ON DISK BY THE PROGRAM MULTFR.
C
C         SUBROUTINES NEEDED:
C                 XYLIB
C                 SYSLIB
C                 /F
C
C         *************
C         *WRITTEN    *
C         *BY:        *
C         *DONALD HULL*
C         *************
C
C
          DIMENSION       ANP(1),X(1040),Y(1040),C(1040)
          DIMENSION       XAXIS(5),YAXIS(5),TITPLT(5)
          INTEGER*2       DBLK(4),A(1040)
          DATA      DBLK/3RDKO,3RDAT,3RA  ,3RDAT/
C
C
C         THIS SECTION RESTARTS PROGRAM BY CLEARING X & YDATA ARRAYS.
700       WRITE(7,110)
110       FORMAT(' ',' ENTER THE NUMBER OF PAGES TO ADVANCE THE PEN.')
          READ (5,111)PAGES
111       FORMAT(F10.0)
          WRITE(7,720)
720       FORMAT(' ','ENTER # SCANS.')
          READ(5,111)XNS
          WRITE(7,725)
725       FORMAT(' ','# POINTS = 1024.',/)
          XNP=1024.
          NS=IFIX(XNS)
          NP=IFIX(XNP+4.0)
          ADV=PAGES*8.5
          CALL PLOTST(0.005,'IN')
          CALL PLOT(ADV,0.0,-3)
          CALL PLOTND
          DO 701  I=1,1040
          X(I)=FLOAT(I)
701       Y(I)=0.0
C
C         THIS SECTION SELECTS THE PART OF THE PROGRAM TO BE EXICUTED.
1         WRITE(7,50)
50        FORMAT(' ','READ DISK=1, AXIS=2, PLOT=3, RESTART=4, EXIT=5')
          READ(5,51)NTEMP
51        FORMAT(I2)
          IF(NTEMP .LT. 1 .OR. NTEMP .GT. 8)GO TO 1
          GO TO(100,500,600,700,800),NTEMP
C
C         READ INDIVIDUAL SCANS FROM DATA.DAT FILE ON DISK.
C
100       WRITE(7,68)NS
68        FORMAT(' ',I2,'SCANS AQUIRED.  WHICH SCAN DO YOU WISH?  ENTER
```

```
       1 # IN I2 FORMAT.')
         READ (5,58)NUMSCN
  58     FORMAT(I2)
         XNUMSC=FLOAT(NUMSCN)
         NP=IFIX(XNP+4.)
         NBLK=IFIX(5*(XNUMSC-1))
         DO 91   I=1,1040
         C(I)=0.
  91     A(I)=0
         ICD=LOOKUP(0,DBLK)
         ICODE=IREADW(NP,A,NBLK,0)
         CALL CLOSEC(0)
         CALL IFREEC(0)
C
C
C        CONVERSION OF DATA FROM INTEGER*2 TO REAL
C
         DO 90    J=5,NP
  90     C(J-4)=FLOAT(A(J))
         NP=NP-4
         C(NP+1)=XNS
         C(NP+2)=XNP
         C(NP+3)=XNUMSC
C
C        CALCULATION OF MAXIMUM, MINIMUM, AND RANGE OF VALUES.
C
         C(NP+4)=C(1)
         C(NP+5)=1.
         C(NP+6)=C(1)
         C(NP+7)=1.
         DO 1000 I=2,NP
C
C        MAXIMUM AND SUBSCRIPT DETERMINATION.
C
         IF(C(NP+4) .LT. C(I))C(NP+4)=C(I)
         IF(C(NP+4) .EQ. C(I))C(NP+5)=FLOAT(I)
C
C        MINIMUM AND SUBSCRIPT DETERMINATION.
C
         IF(C(NP+6) .GT. C(I))C(NP+6)=C(I)
1000     IF(C(NP+6) .EQ. C(I))C(NP+7)=FLOAT(I)
C
C        RANGE DETERMINATION.
C
         C(NP+8)=C(NP+4)-C(NP+6)
C
C        THIS SECTION SETS THE MINIMUM VALUE TO 0.0 AND
C        THE MAXIMUM VALUE TO BE EQUAL TO THE RANGE FOR
C        PLOTTING PURPOSES
C
         DO 492  I=1,NP
492      C(I)=C(I)-C(NP+6)
         C(NP+4)=C(NP+4)-C(NP+6)
         C(NP+6)=0.0
         WRITE(7,493)C(NP+1),C(NP+2),C(NP+3)
493      FORMAT(' ',3X,'NS=',F10.0,3X,'NP=',F10.0,3X,'SCAN #=',F10.0)
         WRITE(7,494)(C(NP+I),I=4,8)
494      FORMAT(' ','MAX=',F10.0,'@',F4.0,' MIN=',F10.0,
     1   '@',F4.0,' RANGE=',F10.0)
         GO TO 1
C
C        THIS SECTION DRAWS THE AXIS OF THE PLOT.
C
500      CONTINUE
502      FORMAT(5A4)
         WRITE(7,510)
510      FORMAT(' ',' ENTER THE TITLE FOR THE XAXIS, 20 CHARACTERS MAX.')
```

```
            READ(5,502)XAXIS
            WRITE(7,503)
503         FORMAT(' ','ENTER THE TITLE FOR THE Y AXIS, 20 CHARACTERS MAX.')
            READ(5,502)YAXIS
            WRITE(7,504)
504         FORMAT(' ','ENTER THE TITLE FOR THE PLOT, 20 CHARACTERS MAX.')
            READ(5,502)TITPLT
            WRITE(7,601)
601         FORMAT(' ','ENTER X AND Y ORIGIN OFFSETS IN INCHES-2F10.0.')
            READ(5,602)XOFF,YOFF
602         FORMAT(2F10.0)
            OFF=0
            YOFFY=0
            XMIN=0.0
            XMAX=C(NP+2)
            YMIN=0.0
            YMAX=C(NP+4)
            WRITE(7,520)
520         FORMAT(' ',' ENTER X AND Y AXIS LENGTHS, 2F10.0.')
            READ(5,525)XLONG,YLONG
525         FORMAT(2F10.0)
            WRITE(7,494)(C(NP+I),I=4,8)
            WRITE(7,620)
620         FORMAT(' ',' NORMALIZED PLOT=1, SCALED PLOT=0.')
            READ(5,51)NTEMP
            IF(NTEMP .EQ. 1)GO TO 550
            WRITE(7,625)
625         FORMAT(' ',' ENTER NEW VALUE FOR Y RANGE, F10.0.')
            READ(5,111)YMAX
550         X(NP+1)=XMIN
            X(NP+2)=(XMAX-XMIN)/XLONG
            Y(NP+1)=YMIN
            Y(NP+2)=(YMAX-YMIN)/YLONG
            CALL PLOTST(0.005,'IN')
            CALL PLOT(1.5,1.0,-3)
            CALL AXIS(0.0,0.0,XAXIS,-20,XLONG,0.0,X(NP+1),X(NP+2))
            CALL AXIS(0.0,0.0,YAXIS,+20,YLONG,90.0,Y(NP+1),Y(NP+2))
            CALL PLOT(0.5,(YLONG+0.5),3)
            CALL SYMBOL(0.5,(YLONG+0.5),0.14,TITPLT,0,20)
            CALL PLOT(0.0,0.0,+3)
            CALL PLOT(-1.5,-1.0,-3)
            CALL PLOTND
            GO TO 1
C
C           THIS SECTION PLOTS THE DATA.
C
600         NOFFX=IFIX(XOFF*X(NP+2))
            OFFY=YOFFY*Y(NP+2)
            DO 605 I=1,NP
605         C(I)=C(I)+OFFY
            DO 610 I=1,(NP-NOFFX)
            IF(Y(I+NOFFX) .GT. C(I))C(I)=Y(I+NOFFX)
610         CONTINUE
            DO 615 I=1,NP
615         Y(I)=C(I)
            CALL PLOTST(0.005,'IN')
            CALL PLOT((1.5+OFF),1.0,-3)
            CALL LINE(X,Y,NP,1,0,0)
            CALL PLOT(0.0,0.0,+3)
            CALL PLOT(-(1.5+OFF),-1.0,-3)
            CALL PLOTND
            OFF=OFF+XOFF
            YOFFY=YOFFY+YOFF
            GO TO 1
C
C           THIS SECTION CAUSES AN EXIT FROM THE PROGRAM.
```

```
C
800     CALL PLOTST(0.005,'IN')
        CALL PLOT(8.5,0.0,-3)
        CALL PLOTND
        STOP
        END
```

APPENDIX G

Software Developed to Calculate the Linear Least Squares Best

Fit Equation for Emission Data and

Plot this Data and Calculated Line

A. LFIT - After entry of sample concentration and emission
    intensity values this program will calculate the linear
    least squares best fit equation for that data. The
    linear fitting may be performed on the data as entered
    or after the logarithm has been calculated for the data
    thereby allowing log-log linear fitting as well as the
    normal linear-linear fitting. This feature was fre-
    quently used in this work since the concentration-emission
    intensity data normally covered three to four orders of
    magnitude.

    The plotting section of this program allows plot-
    ting of the calculated line, average y values (emission
    intensity values), and 95% confidence limits within axis
    for which the operator may choose the size, ranges,
    and titles.

```
C
C
C          PROGRAM LFIT.FOR(17-JUL-80)
C
C
C          SUBROUTINES NEEDED:
C                  SYSLIB
C                  XYLIB
C                  VTLIB
C                  LPSLIB
C                  /F
C
C
C
C          ************
C          *WRITTEN BY:*
C          *          *
C          *BOB HALL   *
C          *          *
C          *REVISED BY:*
C          *          *
C          *DONALD HULL*
C          ************
C
C
           DIMENSION X(45),Y(45,32),YP(45),XAXIS(8),YAXIS(8),IX(1000)
           DIMENSION YAVE(45),YSS(45),NR(45),YPE(45),STAT(11),TITP(8)
           DIMENSION XGT(320),YGT(320),XS(45),YS(45,32)
           DATA STAT/12.706,4.303,3.182,2.776,2.571,2.447,2.365,2.306
       1   ,2.262,2.228,1.960/
           DATA    X,Y,YP,XAXIS,YAXIS,IX,YAVE,YSS,NR,YPE,TITP,XGT,YGT,
       1 XS,YS/45*0.0,1440*0.0,45*0.0,8*' ',8*' ',1000*0.
       1 45*0.0,45*0.0,45*0,45*0.0,8*' ',320*0.0,320*0.0,45*0.0,1440*0.0/
1          WRITE (5,500)
500        FORMAT (' ','LINEAR LEAST SQUARES FIT TO Y=AX + B ')
           WRITE (5,502)
502        FORMAT (' ','TO TERMINATE ENTER -CTRL Z',//)
504        FORMAT (I5)
           DO 130 JJ=1,45
119        WRITE(7,117)
117        FORMAT(' ','  INPUT #REPTS PER X VALUE ')
           READ(5,504,END=118)NRPTS
           N=JJ
           NR(JJ)=NRPTS
           WRITE(7,149)
149        FORMAT(' ',' INPUT X VALUE ')
           READ(5,121,END=119)XS(JJ)
           DO 120 IJ=1,NRPTS
           CALL LED(IJ,'I4')
           WRITE(7,159)
159        FORMAT(' ',' INPUT Y VALUE')
           READ(5,121,END=119)YS(JJ,IJ)
121        FORMAT(F10.0)
120        CONTINUE
           GO TO 130
118        JJ=JJ-1
           GO TO 131
130        CONTINUE
131        WRITE(7,505)
505        FORMAT(' ','LOG-LOG PLOT? Y=1,N=0')
           READ(5,504,END=131,ERR=131)JG
           DO 139 I=1,N
```

```
            YAVE(I)=0.
            YSS(I)=0.
139         YPE(I)=0.
            YTOT=0.
            NTOT=0
            SYS=0.0
            YT=0.0
            E=0.
            F=0.
            C=0.
            YSD=0.
            NT1=0
            DO 140 I=1,N
            KK=NR(I)
            X(I)=XS(I)
            IF(JG.EQ.1)X(I)=ALOG10(X(I))
            DO 129  J=1,KK
            Y(I,J)=YS(I,J)
            IF(JG.EQ.1)Y(I,J)=ALOG10(Y(I,J))
            YAVE(I)=Y(I,J)+YAVE(I)
            F=F+X(I)*Y(I,J)
            C=C+X(I)
            E=E+X(I)*X(I)
129       * YSS(I)=YSS(I)+Y(I,J)*Y(I,J)
            YT=YT+YAVE(I)
            YAVE(I)=YAVE(I)/FLOAT(NR(I))
            NTOT=NR(I)+NTOT
            SYS=SYS+YSS(I)
            IF(NR(I).EQ.1)GO TO 89
            YPE(I)=YSS(I)-(YAVE(I)**2*NR(I))
            YTOT=YPE(I)+YTOT
            YPE(I)=SQRT(YPE(I)/FLOAT(NR(I)-1))
            YSS(I)=(YPE(I))/(YAVE(I))*100.
            NT1=NR(I)-1+NT1
89          CONTINUE
140         CONTINUE
            IF(NT1.EQ.0)NT1=1
            XA=YTOT/FLOAT(NT1)
            IF(XA.EQ.0)XA=1.
B           AN=FLOAT(NTOT)
            G=0.0
            ANX=(AN*E-C*C)
            A=(AN*F-C*YT)/ANX
            B=(E*YT-C*F)/ANX
            WRITE(7,703)
703         FORMAT(' ','    N        X(I)',8X,'Y(I)...')
            DO 702 II=1,N
            KK=NR(II)
            DO 2000 NQ=1,KK,5
            WRITE(7,501)II,X(II),(Y(II,JJ),JJ=NQ,(NQ+4))
            IF(JJ .GT. KK)NQ=KK
2000        CONTINUE
501         FORMAT(I4,6(F12.3))
702         CONTINUE
            WRITE(7,800)
800         FORMAT(' ',' CHANGE X OR Y VALUES   Y=1,N=0')
            READ(5,504,END=702,ERR=702)NJ
            IF(NJ.EQ.0)GO TO 801
            WRITE(7,803)
803         FORMAT(' ','SPECIFY X(I),Y(I,K) TO CHANGE 2F10.0')
            READ(5,804,END=702,ERR=702)I,_
804         FORMAT(2F10.0)
            WRITE(7,805)
805         FORMAT(' ','INPUT X AND Y VALUES   2F110.0')
            READ(5,804,END=702,ERR=702)X(I),Y(I,J)
            XS(I)=X(I)
```

```
            YS(I,J)=Y(I,J)
            GO TO 131
  801       WRITE (5,508)
  508       FORMAT (' '//,3X,'N',11X,'X',8X,'YAVE',5X,'YSTDDEV',2X,'% REL S.D.
     1       ',5X,'YCALC',6X,'DIFF.',9X,'S/N')
            NJ=0
            AMVT=-1000000.
            ANVT=100000.
            XMIN=100000.
            XMAX=-100000.
            DO 13 I=1,N
            YP(I)=A*X(I)+B
            Q=YAVE(I)-YP(I)
            NN=NR(I)
            DO 113 J=1,NN
            NJ=NJ+1
            XGT(NJ)=X(I)
            IF(XMAX.LT.X(I))XMAX=X(I)
            IF(XMIN.GT.X(I))XMIN=X(I)
            YGT(NJ)=Y(I,J)
            IF(AMVT.LT.YGT(NJ))AMVT=YGT(NJ)
            IF(ANVT.GT.YGT(NJ))ANVT=YGT(NJ)
            QQ=Y(I,J)-YP(I)
  113       G=G+QQ*QQ
            IF(NR(I).EQ.1)YSS(I)=-1.
            WRITE (5,509) I,X(I),YAVE(I),YPE(I),YSS(I),YP(I),Q,(100./YSS(I))
  509       FORMAT (I4,7F12.3)
  13        CONTINUE
            SO=G/(AN-2.0)
            DO=SQRT(SO)
            SA=SO*AN/ANX
            DA=SQRT(SA)
            SB=SO*E/ANX
            DB=SQRT(SB)
            IF((NTOT-2-NT1).EQ.0)NT1=2
            XC=(G-YTOT)/FLOAT(NTOT-2-NT1)
            R=(AN*F-C*YT)/((SQRT(ANX))*(SQRT(AN*SYS-YT*YT)))
            WRITE (5,510) A,B
  510       FORMAT ('0','THE BEST FIT LINEAR EQUATION IS Y=',F12.3,' X +'
     1       ,F14.6)
            WRITE (5,511) DA,ABS((DA/A*100.))
  511       FORMAT (' ','THE STANDARD DEVIATION OF A=',E14.6,3X,'%= ',F8.3)
            WRITE (5,512) DB,ABS((DB/B*100.))
  512       FORMAT (' ','THE STANDARD DEVIATION OF B=',E14.6,3X,'%= ',F8.3)
            WRITE (5,513) DO
  513       FORMAT (' ','OVERALL STANDARD DEVIATION =',E14.6)
            WRITE(5,155)XA,XC,XC/XA
  155       FORMAT(' ','P.E. ',E14.4,' L.OF.FIT ',E14.4,'  F TEST <1',F10.5)
            WRITE (5,514) R
  514       FORMAT (' ','CORRELATION COEFFICIENT, R=',F10.6)
            CALL INIT(IX,1000)
            CALL SCROL(5,1020,5)
            CALL APNT(1.,1.,-1,5,-1,-1)
            CALL SCAL(XMIN,ANVT,XMAX,AMVT)
            YPN=1.E20
            YPM=-1.E20
            DO 215 JJ=1,N
            IF(YPM.LT.YP(JJ))YPM=YP(JJ)
            IF(YPN.GT.YP(JJ))YPN=YP(JJ)
  215       CONTINUE
            DO 115 JJ=1,NTOT
            XX=XGT(JJ)
            YY=YGT(JJ)
            CALL APNT(XX,YY)
  115       CONTINUE
            YP1=YPN
```

```
            XP1=XMIN
            YPN=YPM-YP1
            XPN=XMAX-XMIN
            CALL APNT(XP1,YP1,-1,3,-1,1)
            CALL LVECT(XPN,YPN)
            CALL APNT(XMIN,AMVT)
            CALL LVECT(0.,-(AMVT-ANVT))
            CALL LVECT((XMAX-XMIN),0.)
519         WRITE (5,520)
520         FORMAT ('0','DO YOU WISH A PLOT? Y=1,N=0')
            READ (7,504,END=519,ERR=519) JS
            IF (JS .NE. 1) GO TO 19
65          WRITE (5,600)
600         FORMAT (' ','ENTER TITLE FOR X AXIS, 32 CHARACTERS MAX.')
            READ (7,601,END=519,ERR=519) XAXIS
601         FORMAT (8A4)
            WRITE (5,602)
602         FORMAT (' ','ENTER TITLE FOR Y AXIS, 32 CHARACTERS MAX.')
            READ (7,601,END=519,ERR=519) YAXIS
            WRITE(7,711)
711         FORMAT(' ','INPUT TITLE FOR PLOT   32 CHARACTERS MAX.')
            READ(5,601,END=519,ERR=519)TITP
            WRITE (5,604)
604         FORMAT (' ','ENTER STARTING & FINISHING POINTS FOR X AXIS,2F12.0')
            READ (7,605,END=519,ERR=519) XMIN, XMAX
605         FORMAT (2F12.0)
            WRITE (5,606)
606         FORMAT (' ','ENTER STARTING & FINISHING POINTS FOR Y AXIS,2F12.0')
            READ (7,605,END=519,ERR=519) YMIN, YMAX
            WRITE (5,607)
607         FORMAT (' ','ENTER LENGTH OF X&Y AXIS IN INCHES,MAX=7.0, 2F12.0')
            READ (7,605,END=519,ERR=519) XLONG, YLONG
            X(N+1)=XMIN
            YAVE(N+1)=YMIN
            X(N+2)=(XMAX-XMIN)/XLONG
            YAVE(N+2)=(YMAX-YMIN)/YLONG
            WRITE (5,608)
608         FORMAT(' ','ENTER LINE START & FINISH X VALUES.',/,
     1      ' IF X1=X2 THEN NO LINE WILL BE PLOTTED.')
            READ (5,605) XA,XB
            IF(XA.EQ. XB)GO TO 675
            IF(XA .GE. XMIN .AND. XA .LT. XMAX)GO TO 60
            XA=XMIN
60          IF(XB .GT. XMIN .AND. XB .LE. XMAX)GO TO 61
            XB=XMAX
61          YA=A*XA + B
            YB=A*XB + B
            IF(YA .GE. YMIN .AND. YA .LT. YMAX)GO TO 62
            YA=YMIN
            XA=(YA-B)/A
62          IF (YB .GT. YMIN .AND. YB .LE. YMAX) GO TO 63
            YB=YMAX
            XB=(YB-B)/A
63          CONTINUE
            XGT(1)=XA
            XGT(2)=XB
            XGT(3)=X(N+1)
            XGT(4)=X(N+2)
            YGT(1)=YA
            YGT(2)=YB
            YGT(3)=YAVE(N+1)
            YGT(4)=YAVE(N+2)
675         CONTINUE
            DO 811 IK=1,N
            KK=NR(IK)
            IF(KK.EQ.1)GO TO 677
```

```
        NKK=KK-1
        IF(NKK.GT.10) NKK=11
        ST=YPE(IK)*STAT(NKK)/SQRT(FLOAT(KK))
        YSS(IK)=YAVE(IK)+ST
811     YPE(IK)=YAVE(IK)-ST
        WRITE(7,987)
987     FORMAT(' ',' THE 95 % CONFIDENCE INTERVAL ABOUT  THE MEAN',/,
     1  '      Y-HIGH           Y-AVE            Y-LOW')
        DO 988 I=1,N
        WRITE(7,989)I,YSS(I),YAVE(I),YPE(I)
988     CONTINUE
989     FORMAT(1X,I3,3(2X,F12.4))
        YSS(N+1)=YMIN
        YSS(N+2)=YAVE(N+2)
        YPE(N+1)=YMIN
        YPE(N+2)=YAVE(N+2)
677     CALL PLOTST (0.005,'IN')
        CALL PLOT (1.0,1.0,-3)
        CALL AXIS (0.0,0.0,XAXIS,-32,XLONG,0.0,X(N+1),X(N+2))
        CALL AXIS (0.0,0.0,YAXIS,+32,YLONG,90.0,YAVE(N+1),YAVE(N+2))
        CALL PLOT (0.0,YLONG,+3)
        CALL PLOT (XLONG,YLONG,+2)
        CALL PLOT (XLONG,0.0,+2)
        CALL PLOT (0.0,0.0,+3)
        IF(XA.EQ.XB) GO TO 678
        CALL LINE (XGT,YGT,2,1,0,0)
678     CALL PLOT (0.0,0.0,+3)
        IF(KK.EQ.1)GO TO 676
        CALL LINE(X,YSS,N,1,-1,17)
        CALL PLOT(0.,0.,3)
        CALL LINE(X,YPE,N,1,-1,18)
        CALL PLOT(0.,0.,3)
676     CALL LINE(X,YAVE,N,1,-1,4)
        TITLNG=(XLONG-4.48)/2.
        CALL PLOT (TITLNG,YLONG+0.5,3)
        CALL SYMBOL(TITLNG,(YLONG+0.5),0.14,TITP,0,32)
        CALL PLOT (7.5,-1.0,-3)
        CALL PLOTND
19      WRITE (5,518)
518     FORMAT (' ','TYPE 1 TO REPEAT CALCULATION OR 0 TO EXIT')
        READ (7,504) JK
        CALL SCROL(-1,-1,-1)
        CALL INIT
        CALL FREE
        IF (JK .EQ. 1) GO TO 131
        STOP
        END
```

APPENDIX H

Preparation of Solutions

All solutions used for this work were prepared from ACS Reagent-Grade Chemicals (or equivalent). The water used for dilution was the distilled water provided on tap by the Department of Chemistry. Distilled water blanks were run throughout this work and none of the elements tested analytically (Table VII) were present at detectable levels. Single element stock solutions of 1000 ppm of the elements were prepared from soluble salts and all other solutions were made by serial dilutions as necessary.

Stock Solutions

Element	Compound	Weight (g/L)	Solvent
Pb	$Pb(NO_3)_2$	1.5898	Water
Mg	$MgCl_2 \cdot 6H_2O$	8.3625	Water
Ag	$AgNO_3$	1.5746	Water
Cu	$Cu(NO_3)_2 \cdot 3H_2O$	3.8023	Water
Cd	$Cd(NO_3)_2 \cdot 4H_2O$	2.7444	Water
Zn	$Zn(NO_3)_2 \cdot 6H_2O$	4.5506	Water
Na[*]	NaCl	2.5421	Water

[*] Na was prepared as a 20,000 ppm solution.