

THE DESIGN AND SOME ABSORPTION CHARACTERISTICS
OF A TANTALUM BOAT ATOMIZING SYSTEM FOR
ATOMIC ABSORPTION SPECTROSCOPY

by

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Introduction

Since its development by Walsh in 1955, atomic absorption spectroscopy has played an important role in the analytical laboratory. The atomic absorption technique is useful in the quantitative determination of many metallic elements, as well as some non-metals. Atomic absorption spectroscopy is especially adapted to the quantitative rather than the qualitative aspect of analysis.

The basic theory of atomic absorption spectroscopy as developed by Walsh (64) is the following: to determine a certain element, light from a suitable source is passed through a flame. The source is generally a hollow cathode and contains the element that one wishes to determine. The flame is used to heat the sample to a high temperature, break the bonds of the molecules and convert them into the ground state atoms. In this condition the sample can absorb some of the radiation produced by the hollow cathode tube. This decrease in energy is detected and recorded and is proportional to the concentration of the element in the sample.

The flame as it is used in the conversion process, is relatively inefficient (48, 51, 15). This inefficiency in the atomization of samples has spurred scientists in the field to explore other means of introducing the sample into the optical path of the hollow cathode tube.

A number of persons have developed systems for this purpose, among them are King (29), who developed a graphite

furnace which was later modified by L'vov (35). L'vov achieved absolute sensitivities in the range of 10^{-8} to 5×10^{-11} grams of sample. Massman (37) reported the same results using a heated graphite cell in which electrical current was applied directly to the cell, and West and Williams (66) have used an unenclosed carbon rod. Donega and Burgess (16) used a heated tantalum boat, instead of a carbon rod, for the atomization process.

Among the advantages of a non-flame system, over the conventional flame, are the following (24):

1. The limits of detection are much better, sometimes as much as a million fold increase.
2. One can use a much smaller sample, 10 μ l is not uncommon, and some reports of a fraction of a μ l appear in the literature.
3. The non-flame system allows one to work in atmospheres which are controlled in composition and pressure.
4. Since it is a closed system, allows one to work in the vacuum UV.
5. The control of the background gas is impossible in the flame.

Purpose

The purpose of this thesis is twofold. The first is to investigate the possibilities of constructing a tantalum boat atomization system, as developed by Donega and Burgess (16), which produces a high degree of sensitivity and stability and one which is easy to operate and also economical to construct. The second purpose is to investigate the characteristics of such a device and its analytical utility.

Review of Non-Flame System Literature

Probably the first person to develop a non-flame system was the person who developed the process of atomic absorption. Walsh and Gatehouse (65) used a hollow cathode analyzer for direct analysis of solid metal samples. King (29) developed a graphite furnace which he heated with a flame. With the use of the flame in this manner, King eliminated all of the flame interferences that would be present if he aspirated the sample directly into the flame. This system was later modified by L'vov (35) who, instead of using a flame to heat the graphite furnace, used a carbon electrode. He placed his sample on the cold end of a carbon electrode and then inserted the carbon electrode through an opening in the graphite tube. When an arc was struck between the carbon electrode and the supplementary electrode the temperature was sufficient to atomize the sample. L'vov found that the electrode reached a temperature of between 2000 K and 3000 K. Although L'vov's system was quite similar to the one developed by King, L'vov made two important observations which later proved to be quite helpful. He first found that he could greatly decrease the amount of diffusion of sample vapor through the walls of the graphite tube if air originally in the tube was replaced with an inert gas such as argon or helium. The second observation was if he preheated the graphite tube before the atomization process occurred, he found the rate of diffusion of the vapor was again greatly decreased. L'vov found that if he heated the graphite tube with a ten kilowatt step-down transformer to approximately 1000 K the loss of

vapor due to diffusion through the walls of the graphite tube was less than four percent per second. He also found that a current of 40 to 60 amperes applied to the supplementary electrode was sufficient to vaporize a 100 μ l sample.

Massman (37) used L'vov's idea of heating the graphite tube with electrical power in his system. Massman placed electrical connections on both ends of the graphite tube and passed electrical current through the tube. The electrical current heated the graphite tube sufficiently to vaporize a sample placed in the tube. Massman however used much higher current, than did L'vov, to vaporize the sample. Around 500 amperes at 10 volts was needed to sufficiently heat the graphite tube.

West and Williams (65), instead of using a graphite tube, used an unenclosed solid carbon rod. They achieved success with this system and found it to be comparable to that of Massman's in terms of sensitivity. West and Williams believed their system was somewhat easier to operate than was Massman's because of the sample application of both systems. With the carbon rod system the sample is applied to the surface of the carbon rod, while with the graphite tube furnace the sample must be placed inside the graphite tube.

At this stage of development the non-flame systems seemed to divide into two distinct categories. One was the carbon rod analyzer, developed by West and Williams (65) and the graphite tube furnaces developed by King, L'vov, and Massman (29, 35, 37). The other idea was developed by Donega and

Burgess (16), referred to as a Tantalum Boat atomization system. They replaced the graphite tube or carbon rod with a tantalum boat or strip. Like Massman, Donega and Burgess used electrical current to heat the tantalum boat, but found they could use much less electrical energy than did Massman. Donega and Burgess found that 60 to 100 amperes at 12 volts was sufficient to heat the tantalum boat to approximately 2200 °C in less than 0.1 second. The procedure which Donega and Burgess followed was to place the sample on the tantalum boat, apply a low current, approximately five amperes, to dry the sample, pump an inert gas into the chamber, and apply a large current through the tantalum boat to atomize the sample.

Hwang and Ullucci (22) modified the system of Donega and Burgess to increase the sensitivities and detection limits of their system. Some of the sensitivities obtained with this system are the following: Cu; 1×10^{-11} g., Mg; 2×10^{-13} g., Mn; 2×10^{-11} g., Sn; 4×10^{-10} g., and Zn; 4×10^{-12} g. Later Hwang, Mokeler, and Ullucci (62) modified the design of the tantalum boat and considered some of the experimental parameters of the system to further improve the sensitivity.

Along with these two principal non-flame system categories, that is the graphite tube furnaces and carbon rod analyzers and the tantalum boat system, similar techniques have also been studied. One type system, developed by Kahn, Peterson, and Schallis (27) was that of the flame tantalum boat technique. 0.5 to 1.0 ml of sample is placed in the tantalum boat and then, using a specially designed holder, is dried by placing the boat near the flame. The tantalum boat is then pushed into

the flame and the sample heated and vaporized. The rapidly produced absorption signal is measured and recorded. The disadvantages with this type of system are that it can only be used for low melting metals and, because the boat temperature is lower than that of the flame, one incurs more interferences than normally are observed. However there is an increase in the sensitivity which outweighs the disadvantages in many cases. When using such metals as Hg, Ag, Te, and Pb an increase in sensitivity of approximately 25 times over the conventional flame and as much as a 65 fold increase in sensitivity in the case of Zn is observed.

Another semi non-flame technique was developed by Venghiattis (63) and is referred to as the solid pellet technique. A cylindrical pellet is made of solid propellant powder and the sample. The pellet is placed in the holder and into the flame. The pellet takes approximately ten seconds to burn which is sufficient time to obtain an accurate absorption reading. This technique is quite good for the determination of Au and Ag ores in the $\mu\text{g/g}$ range of concentration because no dissolving or separating of the sample is required. The interference effects of the solid propellant are quite small for Au and Ag.

Since the inception of non-flame techniques in atomic absorption spectroscopy much research has been done in the area of graphite tube furnaces and carbon rod analyzers, however a relatively small amount has been reported in the area of the tantalum boat atomizing system.

To try to review every paper published on the subject would be beyond the scope of this thesis. This discussion therefore will consider noteworthy contributions in the field of carbon rod analyzers and graphite tube furnaces.

New applications of non-flame systems were developed by King (30) who developed new uses for the graphite tube furnace. At the same time L'vov (33) reported progress in the area of the graphite cuvette technique. Later Mashireva and Seregin (36) simplified the technique of the cuvette for trace metal determination. Matousek (38) reported simplifications concerning the use of the carbon rod atomizer, and Segar and Gonzales (56) improved the flexibility of the Perkin-Elmer HGA-70 graphite tube furnace in selective volatilization analysis. They succeeded in detecting single elements from a mixture by a stepwise increase in the temperature of the graphite furnace. Woodruff and Shrader (68) were making improvements in the use of a graphite tube furnace by using a reference channel to reduce the interferences due to the optical system. In 1972 Steele and Buerin (58) developed a new graphite rod atomization system with the carbon rod exposed to the atmosphere and Fernadiz (18) experimented with the technique of "grooving" the inside of the graphite tube to increase the sensitivity. Molnar, Reeves, Winefordner, Glenn, Ahlstrom, and Savory (40) experimented with a graphite filament atomizer, using instead of a carbon rod, a thin graphite filament as the atomization apparatus.

With the many publications being presented in the field

of carbon rod and graphite tube atomization systems several reviews (5, 31, 34) covering the subject have appeared.

Since the carbon rod and graphite tube systems provide a much more sensitive approach to atomic absorption spectroscopy, a wide area of study has been in the detection of trace elements in a variety of media. Studies of trace elements in water (47, 54, 55, 60) have been made. Gold has been determined with the use of a graphite furnace (1) and with the use of a carbon filament atomizer (28) and in geological and metallurgical samples with the use of a carbon rod analyzer (10). Nickel (26) and manganese (17) have been detected with the use of a carbon rod atomizer. Calcium was determined in the one to ten nanogram region with the use of a heated graphite rod (12). Lead has been detected in air (44) and on human hair (49). With the use of the carbon rod analyzer trace amounts of selenium have been found in waste water (6), aluminum and calcium in high melting metals (41), chromium in urine samples (53), and beryllium in rock samples (57). Trace metal analysis with the use of the graphite rod system is also very diversified. Some of the varied applications include the determination of lead in fish (45), copper in fingernails (7), and vanadium in silicate rocks (13).

Along with the trace metal analysis, research has been stressed in trace impurities and matrix effects, such as impurities in metals (19) and in water (46). Matrix effects on the determination of chromium with the carbon rod analyzer (61) and those associated with the carbon filament atomization system (4) have been studied.

These non-flame systems, because of their low sensitivity range and ease of operation, adapt themselves quite well to diversified clinical applications, such as the determination of lead in blood with a graphite tube furnace (42) and also with the carbon rod atomizer (32, 39, 52). The determination of copper in blood using the carbon rod system (20, 59) and the determination of chromium in biological materials (14) have been studied.

Another area in which non-flame systems prove to be quite useful is the determination of wear metals in different types of oil. Many papers have been published in this area, dealing with the determination of wear metals in engine oil (50) and in petroleum products (11) using the carbon rod atomizer. More specifically, the determination of silver and copper in lubrication oil (3) and nickel and vanadium in mineral oil (43), all with the use of a carbon rod atomization system, have been studied.

Some work also has been done in the area of studying the effects of different types of organic solvents (2).

An area that has received little consideration is that of the different interference effects associated with these different systems. Interferences have been exhaustively studied in the flame, however, with the use of non-flame systems virtually no work has been reported. Baudin, Chapert, and Feve were the only people to study interferences concerning mainly with the King-type graphite furnace.

Atomic fluorescence, although increasing in popularity with the use of flame systems, is somewhat unadaptable to non-flame

systems. Winefordner has developed a non-flame cell (67) and a platinum furnace (9) for the use in atomic fluorescence spectroscopy.

Donega and Burgess (19) developed the first tantalum boat system. The system was modified by Hwang, Ullucci, and Malenfant (24) by simplifying its operation. Later work by these authors revealed some general applications (62) and more recently more specific applications have dealt with the determination of lead in blood (25). In 1972 Hwang, Mokeler, and Ullucci improved the sensitivity of the tantalum boat technique by redesigning the boat (23).

DEVELOPMENT OF THE ABSORPTION SYSTEM

Physical Construction of the Absorption System

The tantalum boat absorption chamber was constructed so the flameless atomic absorption technique could be utilized with operational ease and provide increased sensitivity over the conventional flame technique.

The construction of the unit was similar to an absorption chamber manufactured commercially by Instrumentation Laboratory Inc., Lexington, Mass. (Model Number IL 355), with revisions which improved the ease of operation.

The unit, as shown in Figure 1 and 1A, was constructed from $\frac{1}{4}$ " aluminum stock. The top, back, sides, and bottom were welded with the aid of a heliarc welder. The viewing window was constructed from $\frac{1}{4}$ " plexiglass and held into place by four bolts that tightened on to the front of the unit. An O-ring between the plexiglass window and the front of the unit, in a planed groove, supplied a vacuum seal between the window and the unit.

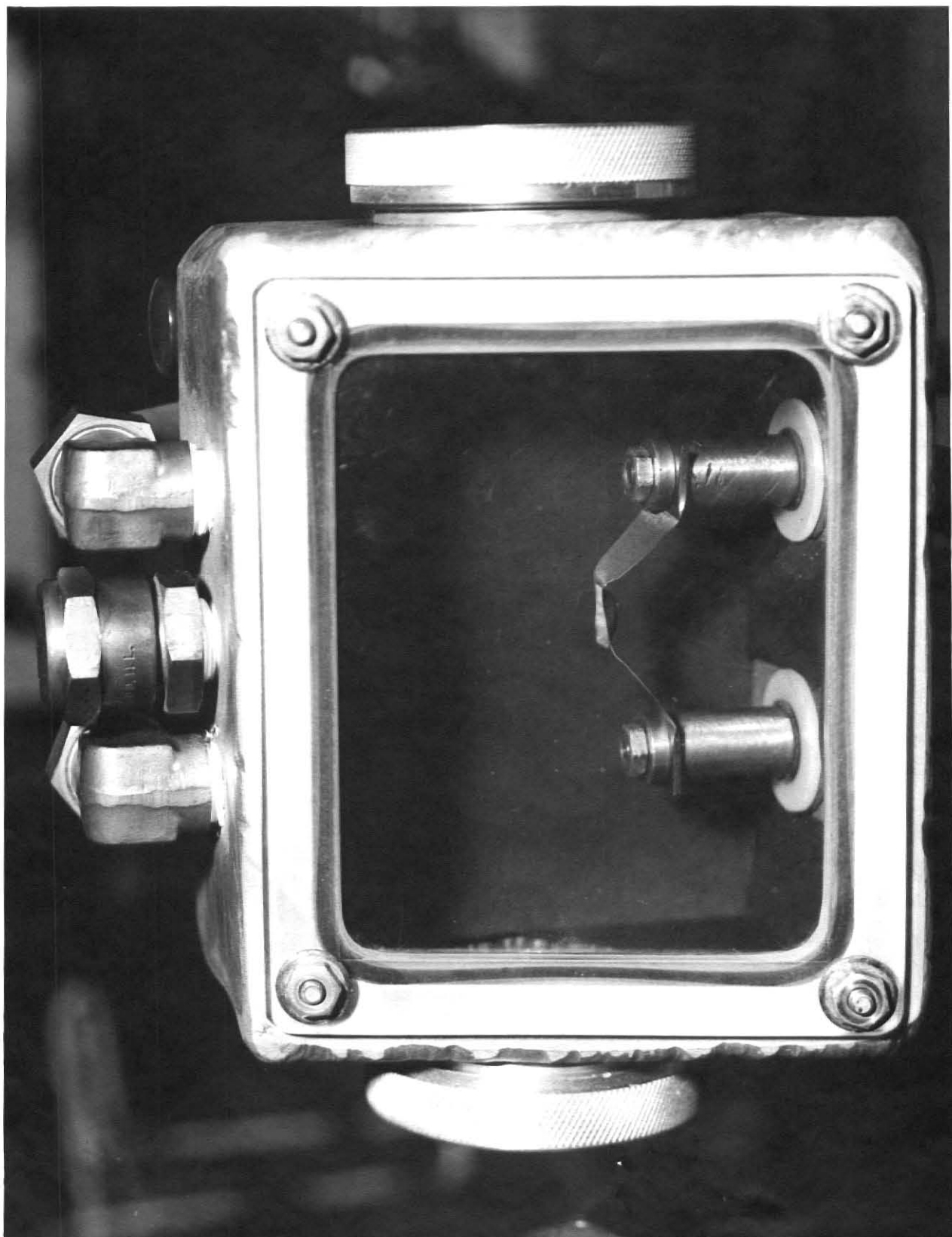
The quartz window holders, which allowed the light from the hollow cathode source to enter and exit the chamber directly above the tantalum boat, were constructed from aluminum pipe stock. They were threaded on the outside and welded into each end of the absorption unit. The outside diameter of the pipe was approximately $2\frac{1}{4}$ ", $\frac{1}{4}$ " larger than the diameter of the circular quartz windows used in the window holders. A groove was cut in the face of the aluminum pipe so that an O-ring could be secured in it. A cylindrical cap was constructed to screw unto the aluminum pipe. The quartz window was placed

EXPLANATION: FIG. 1.

Absorption unit assembly looking through the plexiglass viewing window at the tantalum boat itself.

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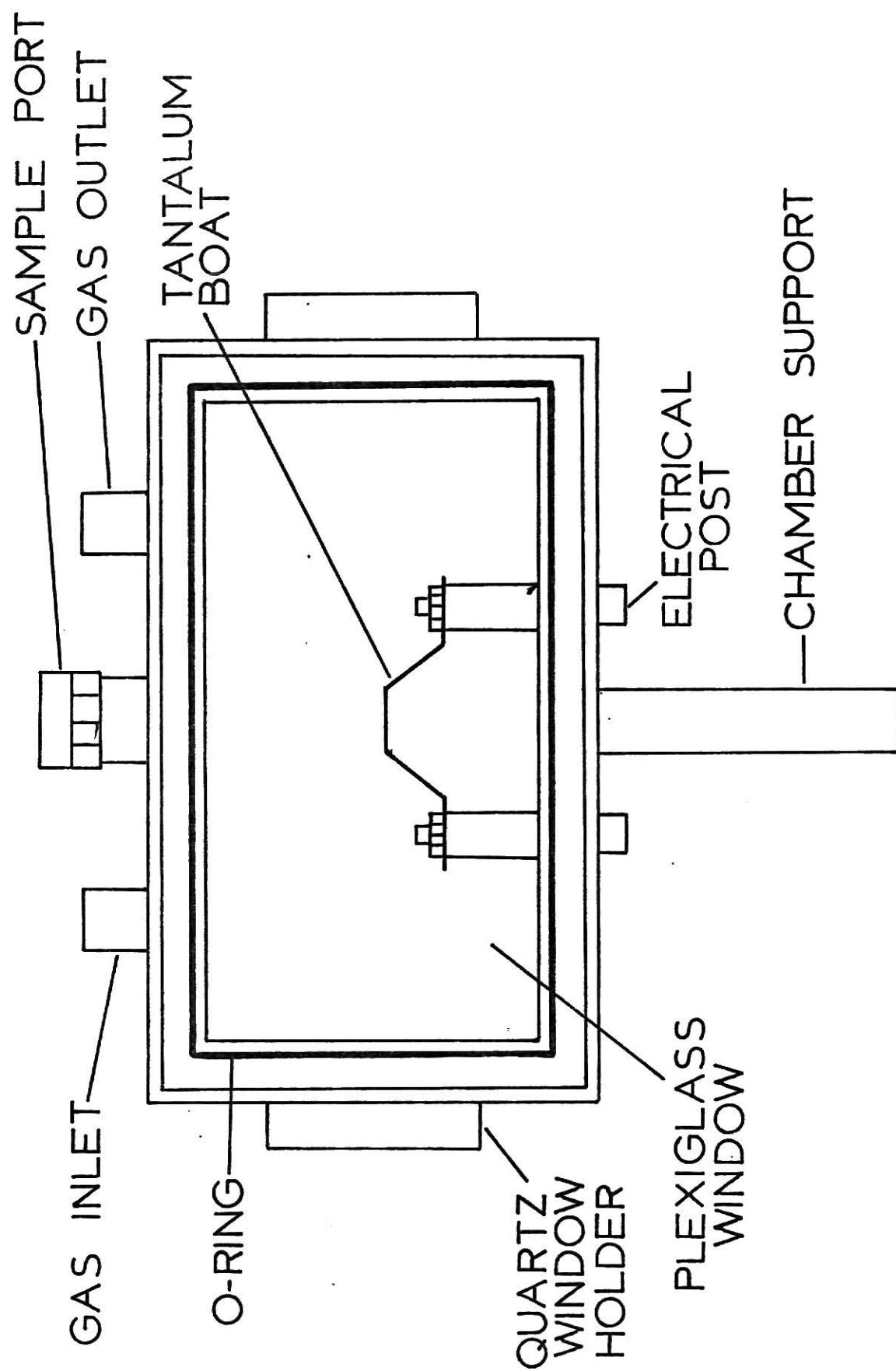


Figure 1A. Diagram of the front view of the absorption chamber

on the O-ring and the cap screwed unto the aluminum pipe. The cap secured the quartz window in place and provided a sufficient vacuum seal between the window and the absorption unit. Figure 2 shows a front configuration of the lens holder and also exhibits a view of the chamber looking through both quartz windows.

Construction of the electrical posts, which hold the tantalum boat, and their insulation, from the bottom of the unit, is shown in Figure 3. The brass electrical posts were inserted through holes drilled in the bottom of the absorption unit. Teflon washers insulated the brass electrical posts from the unit. O-rings between the posts and the teflon washers and between the teflon washers and the bottom of the unit provided a vacuum seal.

The sample injection port, Figure 4, provided a method of placing the sample in the tantalum boat without removing the plexiglass viewing window. A hole was tapped in the top of the unit directly above the tantalum boat and a brass pipe, approximately $3/4$ " in diameter was threaded into the hole. A cap was made to thread into the brass pipe and an O-ring groove planed into the face of the brass pipe. A sufficient vacuum seal was obtained when the cap was tightened into the brass pipe. A microliter syringe could be inserted through the brass pipe and a sample placed in the tantalum boat.

The tantalum boats were either purchased from Instrumentation Laboratory Inc., or constructed from five mil. tantalum foil m3N, (Ventron, Alpha Inorganics, catalog number 00331),

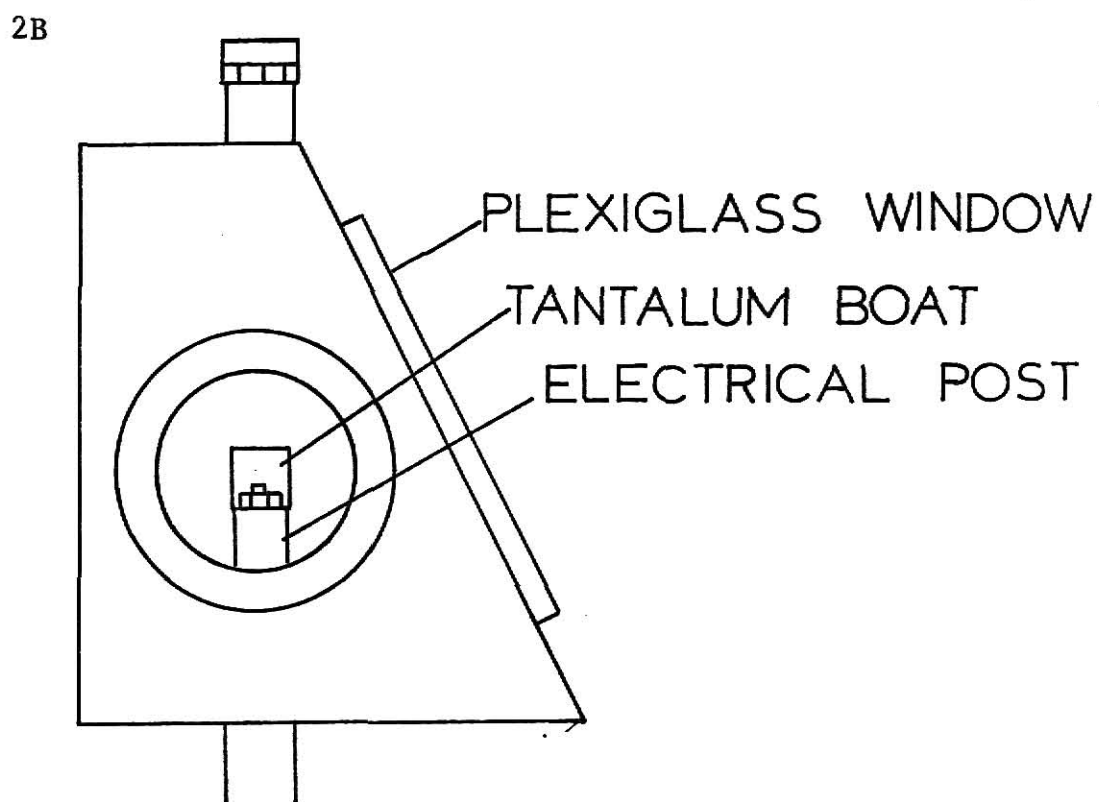
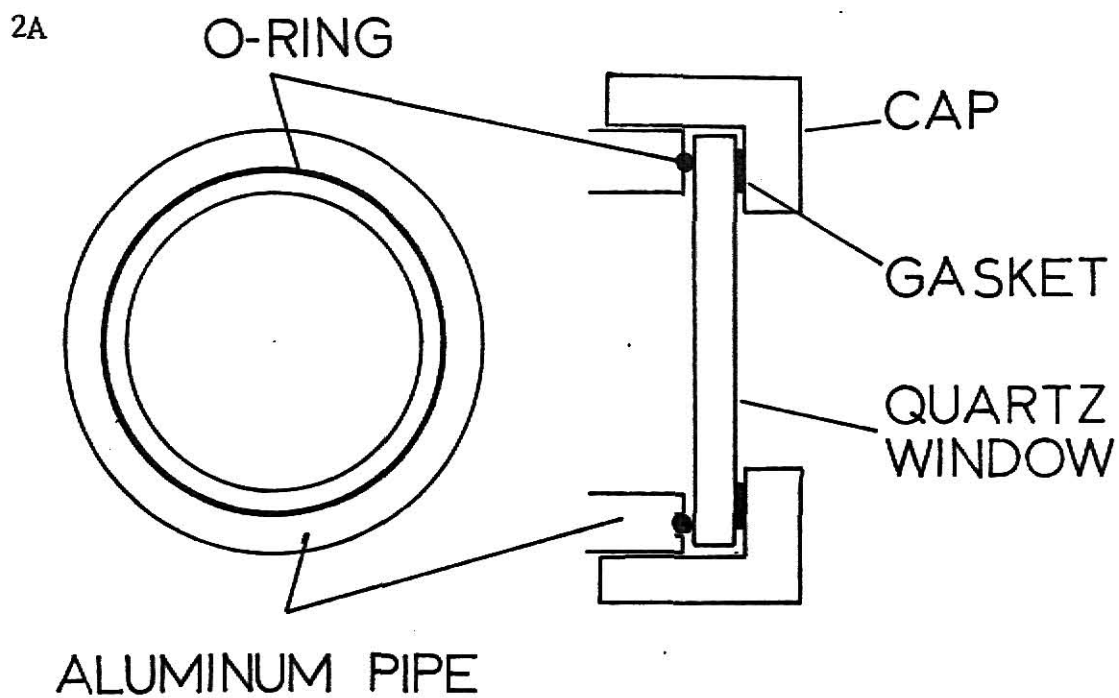


Figure 2. (A) Diagram of the quartz lens holder and
(B) view looking through the quartz windows.

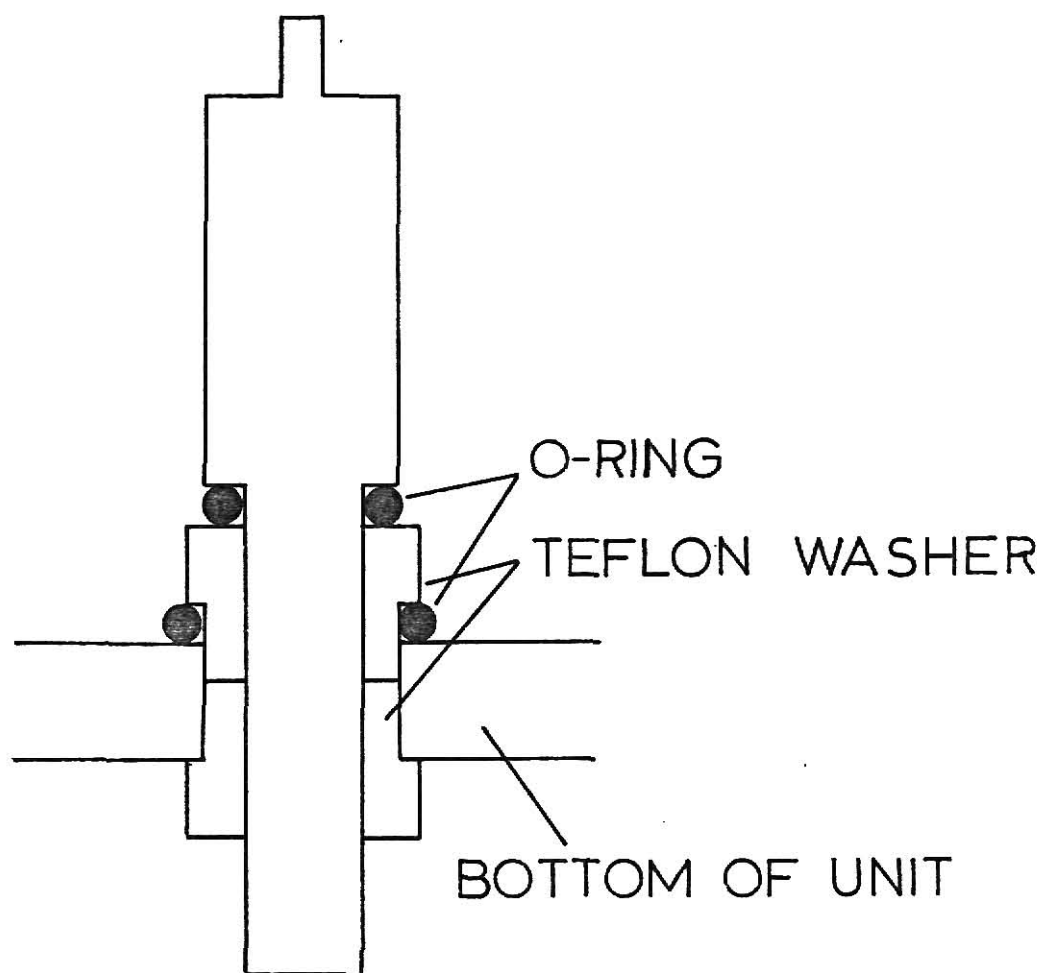


Figure 3. Cross-sectional diagram of the brass electrical posts.

with the use of a press that was especially designed to produce the shape of boat desired. When the tantalum foil was converted into the desired shape, excess tantalum was removed from the sides of the sample cavity to insure that most of the resistance and therefore most of the heating would occur in the sample area. The finished boat, as shown in Figure 5, was approximately 2" long and $\frac{1}{2}$ " wide. The sample cavity was large enough to hold approximately fifty microliters of liquid sample. A hole, approximately $\frac{1}{8}$ " from each end of the boat, was punched in the ends of the tantalum boat which enabled the boat to be placed on the electrical posts. Studs on the electrode posts allowed one to tighten the tantalum boat to the electrode posts. This insured that good electrical contact was made between the boat and the posts.

Purge Gas System

The tantalum boat atomization system was equipped with an inert gas purge system. This enabled the production of an inert atmosphere in the chamber and also permitted purging the system as desired.

A schematic diagram of the purge gas system is shown in Figure 6. All gases were obtained from commercially available sources. The gas from the cylinder (1), flowed through a regulator (2), into a calibrated flowmeter (3). A needle valve (4) regulated the flow rate and the toggle valve (5) was used as an ON-OFF switch for the gas flow. Rubber tubing connected the purge gas system to the absorption chamber. Toggle valve (6) connected the system to the vacuum pump (Duo-Seal, Welch

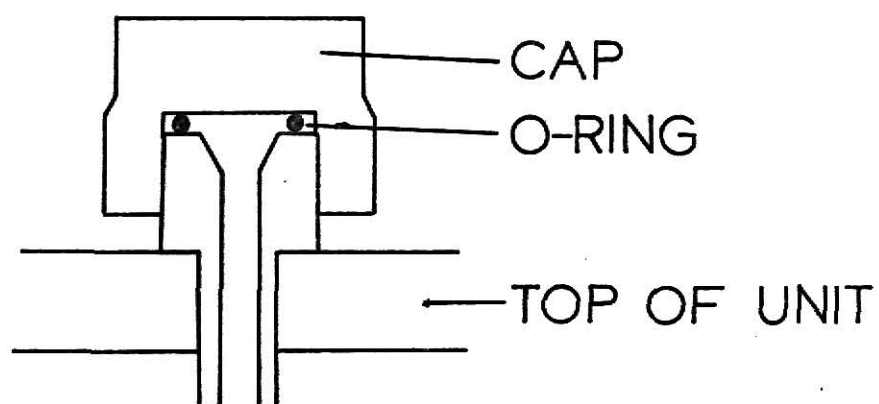


Figure 4. Cross-sectional diagram of the sample injection port.

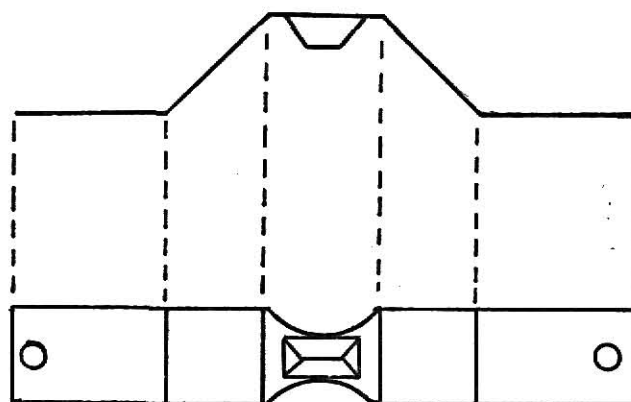


Figure 5. Diagram of the shape of the tantalum boats used.

Scientific Company, Model Number 1410), and toggle valve (7) allowed the system to be opened to the atmosphere. A closed end manometer was employed to monitor the pressure of the system and could be opened and closed to the system by using stopcock (8).

The construction of the gas system allowed one to:

(1) purge the system by allowing the inert gas to flow through the absorption chamber and escape into the atmosphere, (2) produce a static inert atmosphere in the absorption chamber, and to (3) create a pressure of less than atmosphere in the chamber with the use of the vacuum pump.

Electrical System

The electrical system consisted of three main components: (1) the transformer, (2) the variac, and (3) the timer. The transformer was a "boost and buck" Acme step-down type transformer (catalog number 11684) which was wired to produce a ten fold increase in the primary current with a maximum of 120 amperes at 12 volts.

The variac was a Powerstat (catalog number 2PF236B) which had a maximum power capacity of 2.8 KVA.

The timing system, Figures 7 and 8, was designed by Dr. Maarten VanSwaay and Mr. William Ryan of the Department of Chemistry, Kansas State University. The function of the timer was to allow the current to pass through the tantalum boat for a specified length of time. The timer was constructed so that one was able to predetermine the length of time that the current

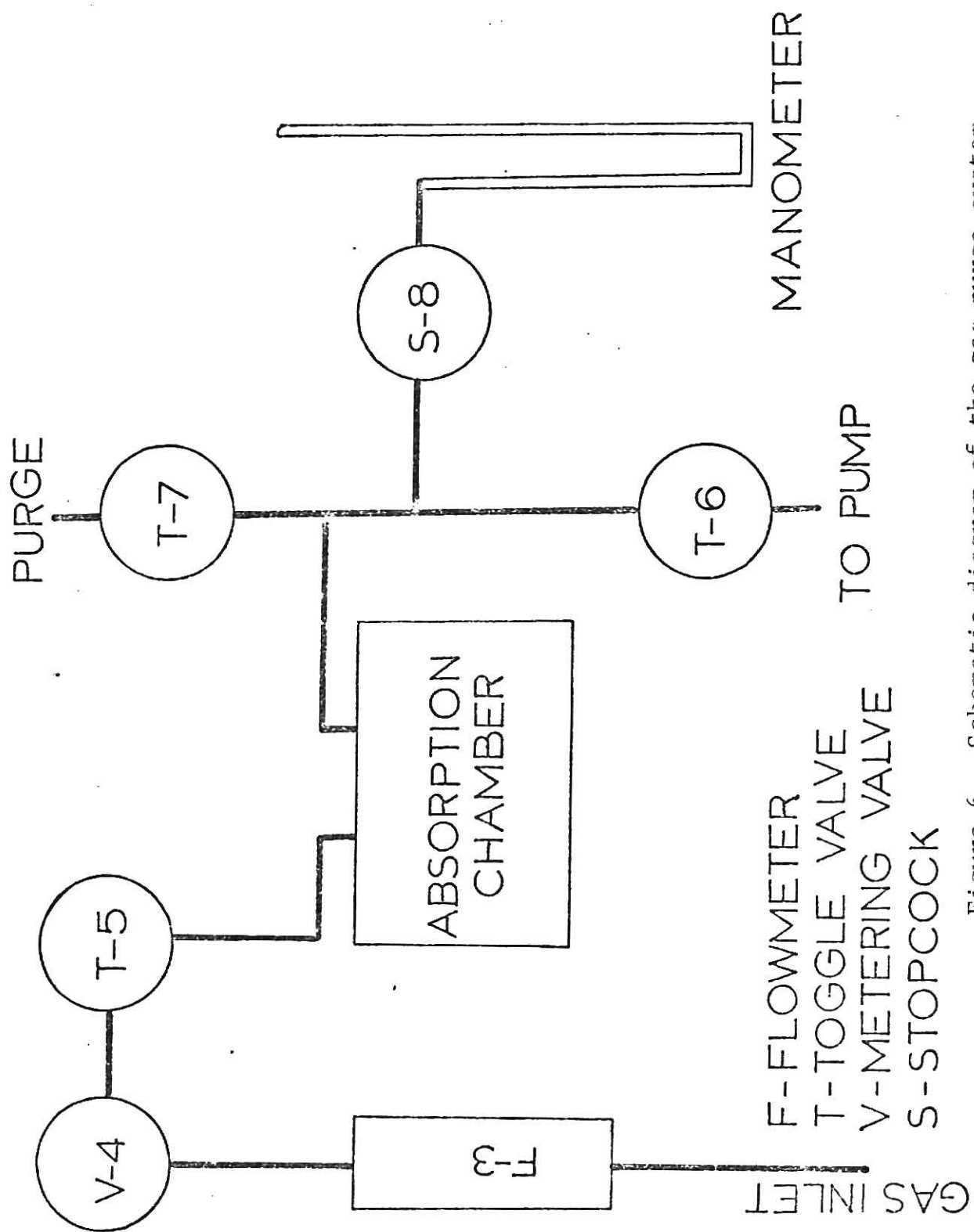
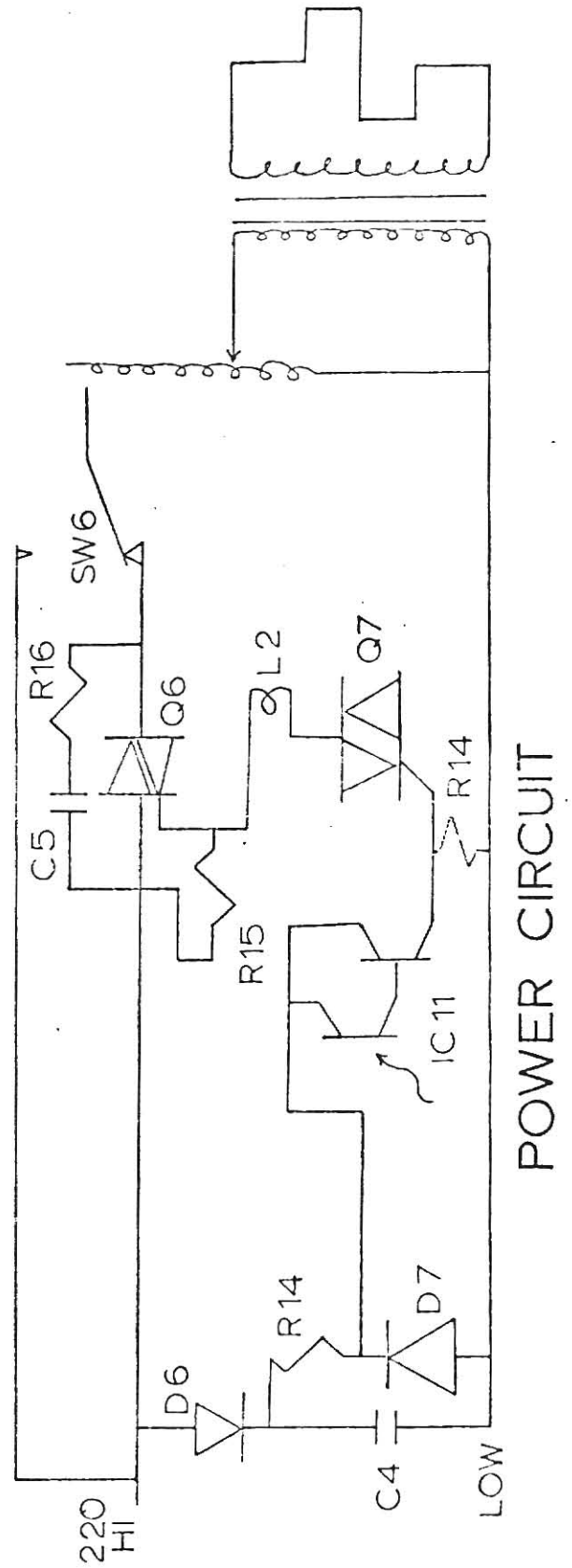
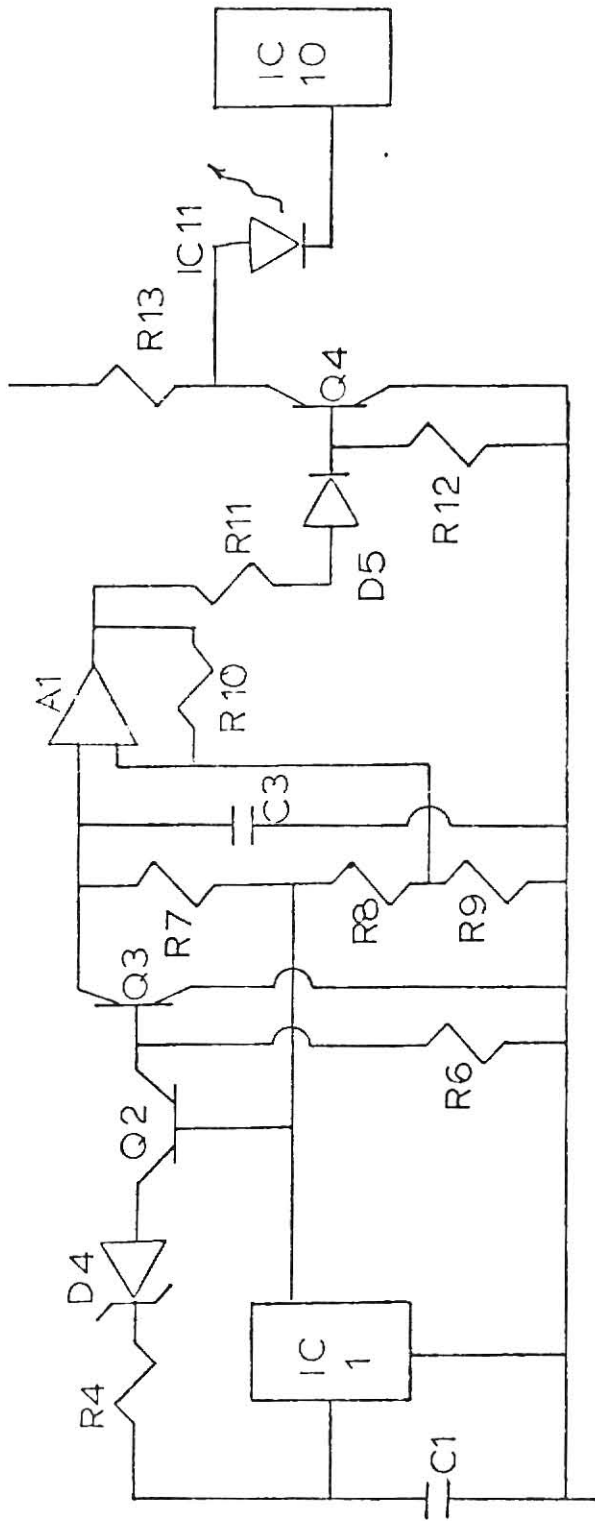


Figure 6. Schematic diagram of the gas purge system.

EXPLANATION: FIG. 7 & 8

Schematic diagrams used in the construction of the electrical timer. A complete list of components follow the diagrams.



ELECTRICAL COMPONENTS

COMPONENT	CATALOG NUMBER	DESCRIPTION
T1 - T2	F - 13X	110 V primary- 6.3 V secondary
SW1 - SW3	T - 205	Single deck rotary switch
SW4	8532B	Push button, momentary contact
SW5	35059	DPST
SW6		SPDT 12 A 220 V
D1 - D2	IN4001	Si Diode
D3	IN3070	Si Diode
D4	IN5221	2.4 V Zener
D5	IN4001	Si Diode
D6		1 A 1000 piv
D7	IN5233A	6.0 V Zener
Q1	2N5366	PNP Si
Q2, Q3	MPS 404	PNP Si
Q4, Q5	2N3417	NPN Si
Q6	40800	10 A Triac
Q7	40527	2.5 A Sensitive gate triac
Q8		NPN Ge
IC-1	LM309K	5 V regulator
IC-2	7473	Dual J-K
IC-3	7473	Dual J-K
IC-4, IC-5	7490	Decade counter
IC-6, IC-7	7442	4-10 line decoder
IC-8	7400	Quad Nand

IC-9	7404	Hex Inverter
IC-10	7476	Dual J-K
IC-11	MCT-2	Optical Isolator
A-1, A-2	741	Op Amp
C-1		2000 μ F, 20 V
C-2		10 μ F, 20 V
C-3		1 μ F, 600 V
C-4		50 μ F, 30 V
C-5		0.094 μ F, 400 V
C-6 - C-8		0.1 μ F, 50 V
C-9		0.047 μ F, 75 V
L-1	1050-C	110 V Indicator lite
L-2	1056-C	220 V, 10 W lite
B-1		Diode bridge
R-5		100
R-13		220
R-23		330
R-2, 15, 16, 4		1 K
R-1, 6, 8, 9, 11, 12, 17, 18, 19		10 K
R-21		4.7 K
R-22		2.2 K
R-14		24 K, 10W
R-3		47 K
R-20		100 K
R-7		220 K
R-10		1 M

was allowed to pass, and had a capability of allowing the current to pass from a minimum of 0.0166 seconds to a maximum of 6.60 seconds in 0.0166 second intervals.

A diagram of the timing and electrical system is shown in Figure 9. Electrical power from a common 220 volt wall outlet was supplied to the variac, which determined the amount of current allowed to pass, and then through the timing circuit. A by-pass switch permitted control of the current manually. The usefulness of this arrangement will become more apparent when the overall operation of the tantalum boat system is discussed. The transformer then increased the current by a factor of ten and this current then passed through the tantalum boat.

Instrumentation and Methods

Optical System

A schematic diagram of the optical system employed is shown in Figure 10. The monochromator was a Jarrell-Ash model 82-360 Ebert mounted one-half meter spectrometer with Jarrell-Ash electronics. The optical system external to the monochromator was arranged to allow emission from the hollow cathode to pass directly into the entrance slit of the monochromator. The entrance and exit slits widths were fixed at fifty microns.

Radiation sources for the atomic absorption measurements were hollow cathode lamps operated with a Jarrell-Ash power supply. The copper lamp (No. WL-22603A), manganese lamp

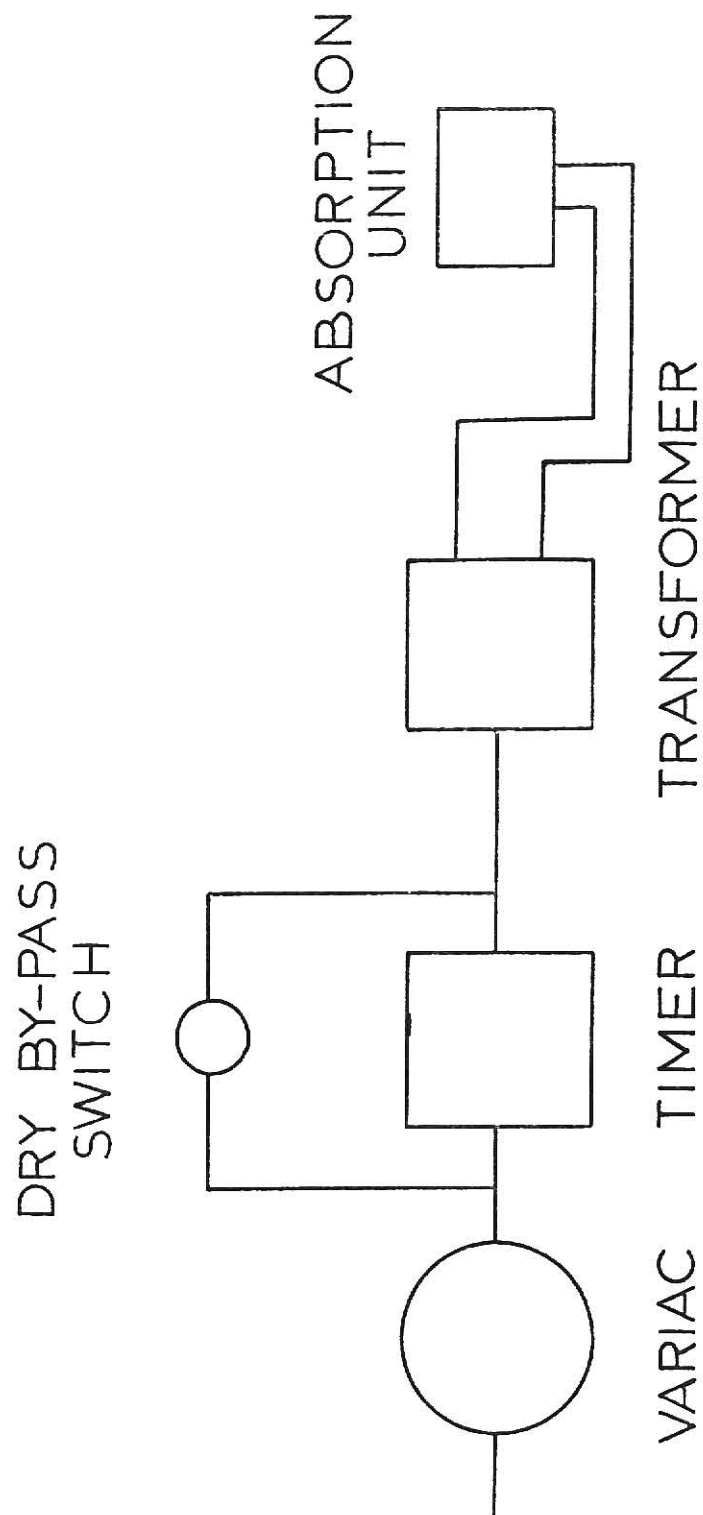


Figure 9. Schematic diagram of the entire electrical system.

(No. WL-22936A), zinc lamp (No. WL-22810A), magnesium lamp (No. WL-22968A), and the iron lamp (No. WL-22810A) all were manufactured by Westinghouse. The sodium lamp was a demountable hollow cathode arrangement constructed by Dr. Ronald Popham and designed from a model developed by G.I. Goodfellow (21).

Detection Limits

A schematic diagram of the detection system employed for the entire work presented is shown in Figure 10. The photomultiplier tube employed was a Hamamatsu R-106. A Jarrell-Ash regulated high voltage power supply was employed to supply the necessary high voltage to operate the photomultiplier tube. A PAR HR-8 amplifier, locked in phase with a mechanical chopper, was used to measure the photocurrent. The strip chart recorder was a Bristol model M-1 PH590 1 mv potentiometric type recorder with a 0.4 second pen response and a 0.5 second time constant. Two voltage dividers were used in the system. One divided the photomultiplier response in route to the amplifier by a factor of 10,000 and the other divided the amplifier signal going to the strip chart recorder by a factor of 100,000.

Solutions

Solutions of Cu^{++} , Mn^{++} , and Zn^{++} , for the detection limit study, were prepared from the pure metals. All standard stock solutions were 1×10^{-8} g/ μ l in concentration. Appropriate dilutions were made to obtain the working solutions.

Solutions for the Cu, Mn, and Zn compounds interference

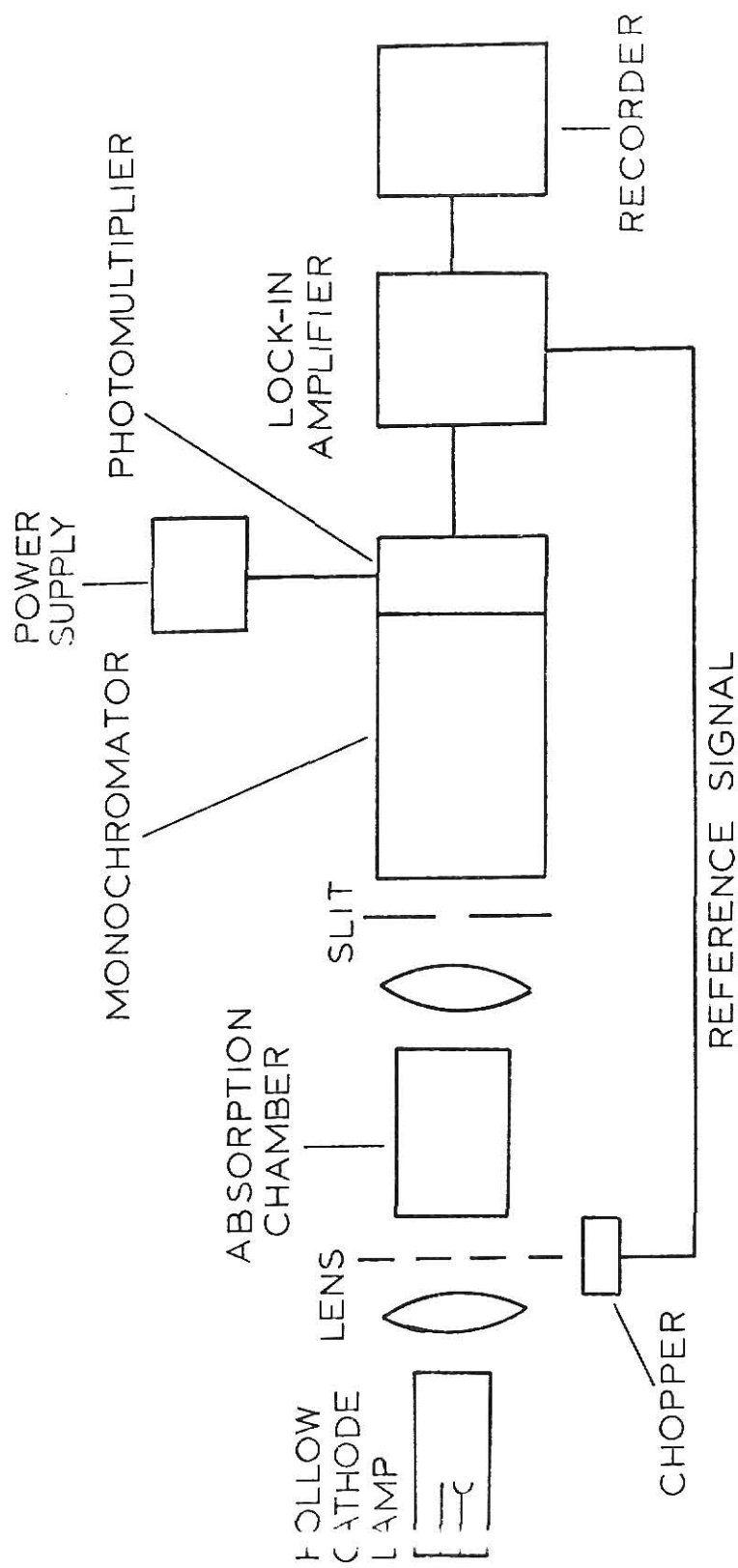


Figure 10. Schematic diagram of the optical system and electronic detection system.

study were prepared from their respective metal salt compounds. All stock solutions were 1×10^{-8} $\mu\text{g}/\text{l}$ in concentration and all metal salts were analytical grade reagents. Appropriate dilutions were made to obtain the working solutions.

The stock solutions used for the interfering cation studies were prepared in all cases, except magnesium, by dissolving the metal chloride in water or the metal carbonate in hydrochloric acid and diluting with water. The magnesium solution was prepared from the oxide by dissolving it in a minimum amount of hydrochloric acid and diluting to volume with water. Anion solutions for the interference studies were prepared directly from the corresponding acid of the anion.

Experimental Parameters

Optimum values for operating conditions of the absorption system were first determined. In all cases the resonance line was used in determination of the elements studied.

Photomultiplier voltage: A voltage of 500 volts to the photomultiplier tube was used for the entire study.

PAR HR-8 sensitivity: A sensitivity of either 500 uv or 1 mv full scale deflection was used for the entire work presented.

PAR HR-8 time constant: A time constant employed was 100 milliseconds.

Hollow Cathode lamp current: To determine the hollow cathode lamp current that would yield the best sensitivity, the current was increased until the scale on the amplifier showed twice the deflection of the strip chart recorder. This procedure expanded

the strip chart recorder scale by a factor of two and therefore the entire scale deflection of the recorder corresponded to a fifty percent absorption reading.

Inert Gas: Argon gas at a pressure of one atmosphere was used as the inert gas for the entire work presented.

Height of measurement: For all research presented in this thesis the center of the hollow cathode light source passed two millimeters above the center of the tantalum boat.

The drying time, drying current, analysis time, and analysis current varied with each particular study made.

Operating Procedure

The following operating procedure was used in the operation of the absorption process. Argon gas was allowed to flow through the system to flush out any air inside the chamber. The cap of the injection port could be removed without any unwanted air entering the chamber because of the positive pressure inside the chamber created by the gas flow. A sample was applied to the tantalum boat through the injection port with the use of a microliter syringe and the cap replaced. A small amount of current was passed through the tantalum boat. The inert gas flushed the water vapor out of the absorption chamber. The current used to dry the sample was shut off when the sample appeared dry and the gas flow also was shut off. This produced a static inert atmosphere in the absorption chamber. The timing circuit was employed in the electrical circuit with the use of a double pole double throw switch. The timer was set at a pre-

determined length of time and the variac also set at a predetermined value. The strip chart recorder was started and the firing button pushed. The firing button released the current to the tantalum boat. The current heated the tantalum boat to a certain temperature which vaporized the sample and converted it to ground state atoms. The absorption signal was observed on the strip chart recorder. To conserve chart paper the recorder was turned on immediately before each run and shut off after the absorption signal was recorded.

The signal obtained was quite different from the signal characteristics of the conventional flame absorption process. The signal produced in the tantalum boat process appears as a sharp spike rather than a continuous signal. This is due to the extremely fast atomization and decomposition of the sample into the light path of the hollow cathode and an equally fast diffusion of the sample atoms out of the light path. The height of the absorption peak determines the amount of the element present in the sample in our case. The height of the peak is proportional to the concentration of the ground state atoms.

EXPERIMENTAL RESULTS AND DISCUSSION

Operational Characteristics

The first experiments were performed to characterize the operating parameters of the absorption system.

The temperatures of various types of tantalum boats were determined by varying the variac settings and using an optical pyrometer (Leeds and Northrup, Model Number 1306) to measure the boat temperature. A distance of approximately six inches separated the optical pyrometer from the tantalum boat. To determine the temperature of the tantalum boat the variac was set at a predetermined value and the absorption chamber flushed with argon for approximately 30 seconds at a rate of two liters per minute. The gas flow was stopped and current was applied to the boat with the use of the manually operated "dry" switch. As soon as the determination of the temperature was made the current to the boat was discontinued. The chamber was operated at a pressure of approximately one atmosphere. Figure 11 shows the temperature of the tantalum boat with respect to the variac setting. The variac settings were changed from a value of 10 to 35. The temperature recorded was an average of the temperature of three different tantalum boats. The optical pyrometer was accurate to within $\pm 20^\circ \text{C}$ in the temperature range studied. The experiment showed that the temperature increased linearly with the variac settings and also that the used boat gave approximately the same temperature response as a new boat at a certain variac setting. The reason for the higher temperature of the commercial boat was due to the thinner tantalum foil

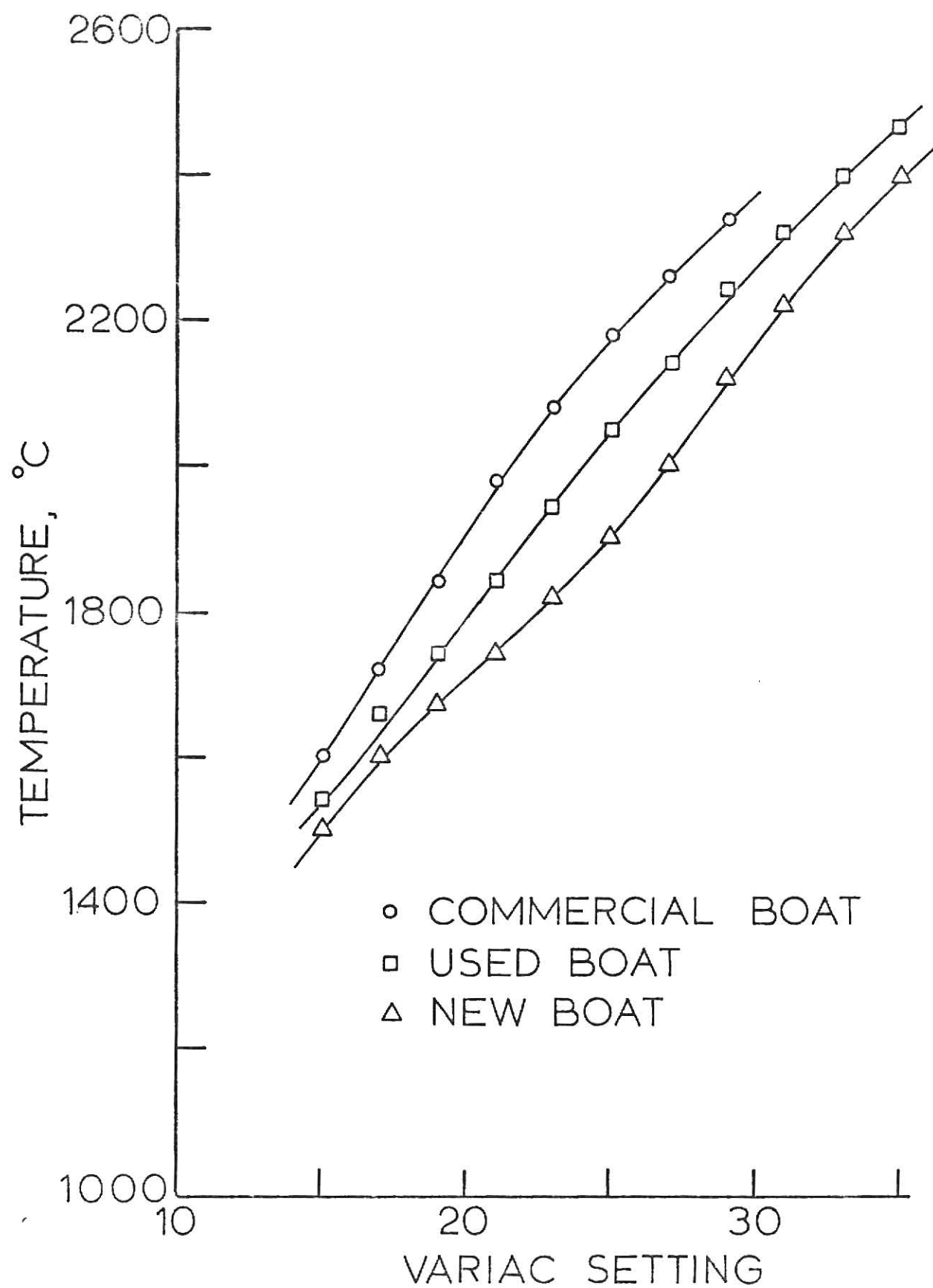


Figure 11. Temperature as a function of the variac setting.

used in its construction.

The current which passed through the tantalum boat at different variac settings also was measured. This was accomplished with the use of the Weston Electric ammeter (Model Number 633). Table 1 shows the results of this study.

Table 1. Amperage of different variac settings for different type tantalum boats.

Variac Setting	Amperes		
	Old	New	Commercial
4	20	24	31
5	23	27	34
7	30	34	41
10	38	41	49
12	42	47	55
14	47	53	61
16	52	58	66
18	56	61	71
20	60	66	75
22	63	69	79
24	67	72	83
26	69	76	88
28	72	79	91
30	74	82	94
32	76	85	
34	78	87	
36	81	89	

Accuracy and precision of the absorption system was next studied. One wanted to determine, with all experimental parameters held constant, if the same absorption signal could be

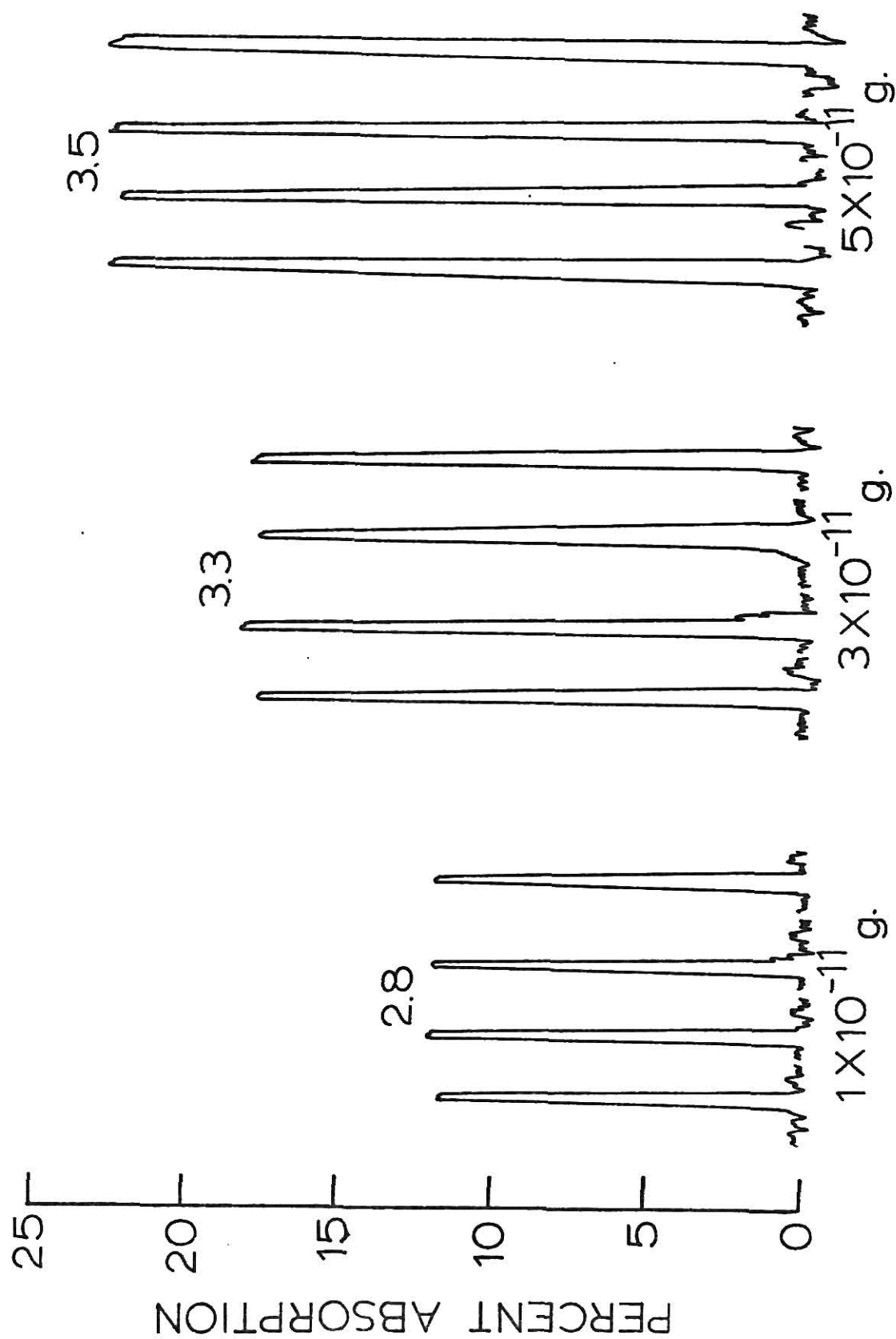
ed for the same size sample. The following experimental parameters were used:

Analyte:	Zn
Concentration (g/ μ l):	1×10^{-11}
Photomultiplier Voltage (volts):	500
Hollow Cathode Current (mA):	3.0
Analysis Time (sec):	2.0
Variac Setting for Analysis Time:	15
Dry Time (sec):	15
Variac Setting for Dry Time:	3
Purge Gas:	Argon
Purge Gas Pressure:	1 atm
Height above Boat (mm):	2.0
Wavelength (\AA):	2139

Figure 12 shows replicate recorder tracings of Zn samples. The number above each concentration represents the coefficient of variation (standard deviation expressed in relative percent) calculated from four consecutive absorption signals.

Optimum Temperature Conditions

As observed by Donega and Burgess (16) the absorption signal increases, reaches a maximum, and then decreases with increasing temperature of the tantalum boat. Optimum temperature parameters were investigated for certain elements. Also



REPLICATE RECORDER TRACINGS: Zn

Figure 12. Replicate recorder tracings of various Zn concentrations.

incorporated in this investigation was a time related study of the appearance and decay of the absorption peak. This study included four different element: Zn, Cu, Mn, and Fe.

An electrical system was attached to the timing system which produced a mark on the chart paper when the current, through the tantalum boat, started and stopped. This mark enabled one to determine when the absorption peak appeared with respect to the current application. Figure 13 through 16 show the results obtained for the four elements studied. Three different variac settings were investigated for each element. The experimental parameters appear in Table 2.

Table 2. Experimental parameters of the Time Study Analysis.

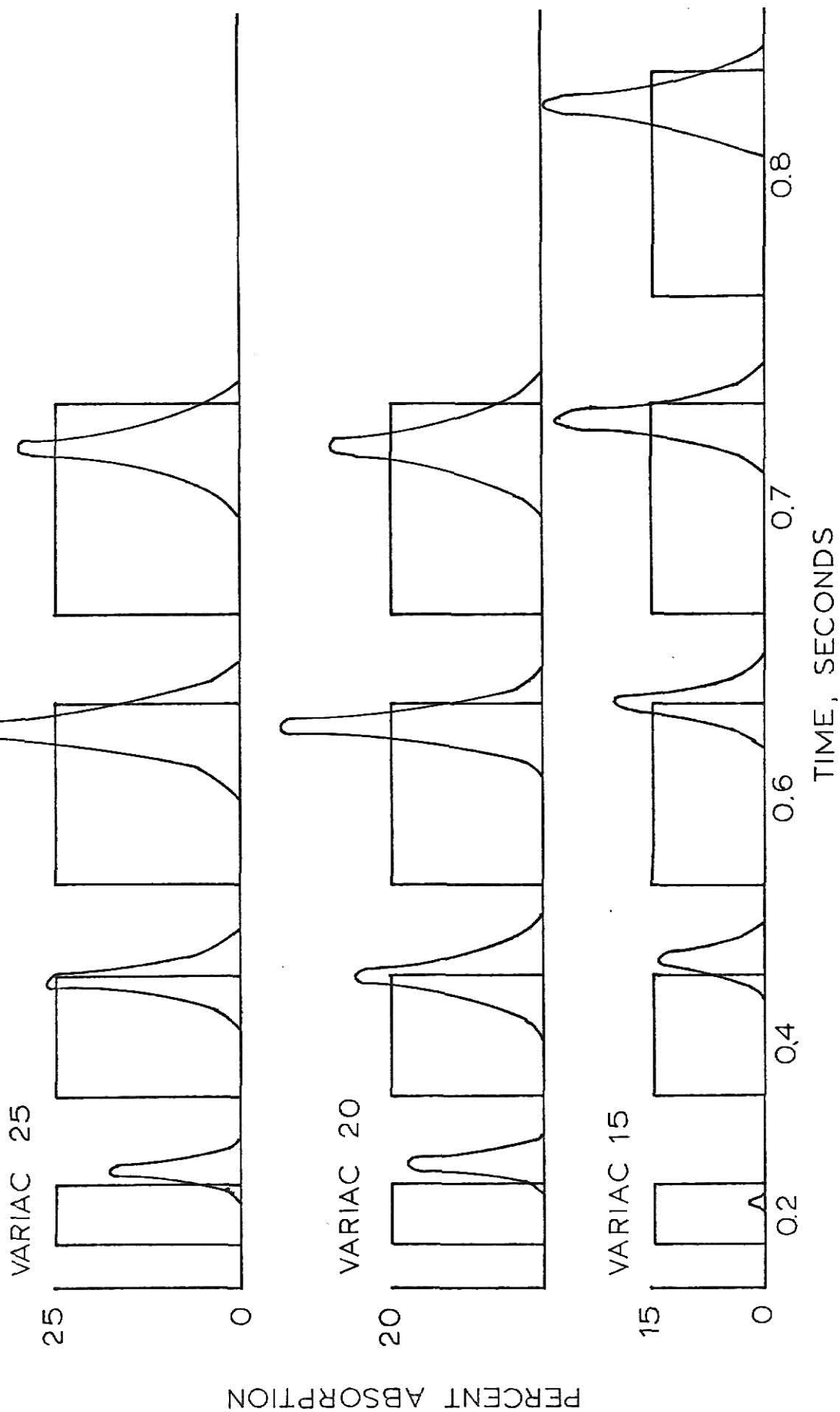
	Zn	Cu	Mn	Fe
Wavelength (Å):	2139	2347	2795	2482
PAR Sensitivity (μV):	500	500	500	500
Photomultiplier Voltage (volts):	500	500	500	500
Hollow Cathode Current (mA):	3.5	2.5	3.0	4.0
Purge Gas:	Argon	Argon	Argon	Argon
Purge Gas Pressure:	1 atm	1 atm	1 atm	1 atm
Analysis Time (sec):	Varied with each run			
Variac Setting for Analysis Time:	15-20-25	21-24-27	15-20-25	27-30-33
Dry Time (sec):	15	15	15	15
Variac Setting for Dry Time:	4	4	4	4
Height above Boat (mm):	2.0	2.0	2.0	2.0
Concentration of Analyte (g/μl):	1×10^{-11}	3×10^{-10}	4×10^{-11}	3×10^{-10}

EXPLANATION: FIG. 13-16

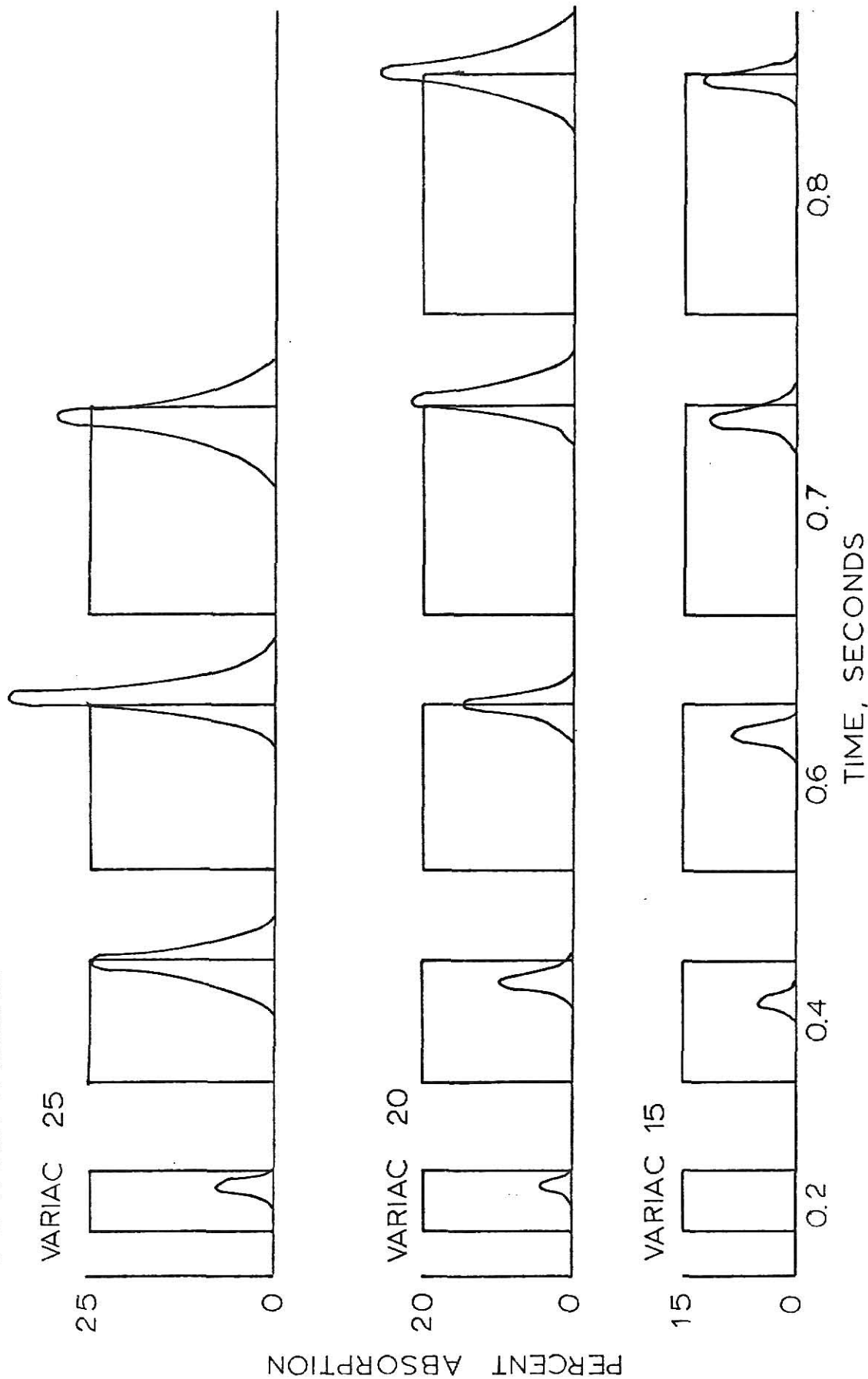
13: Zinc
14: Copper
15: Manganese
16: Iron

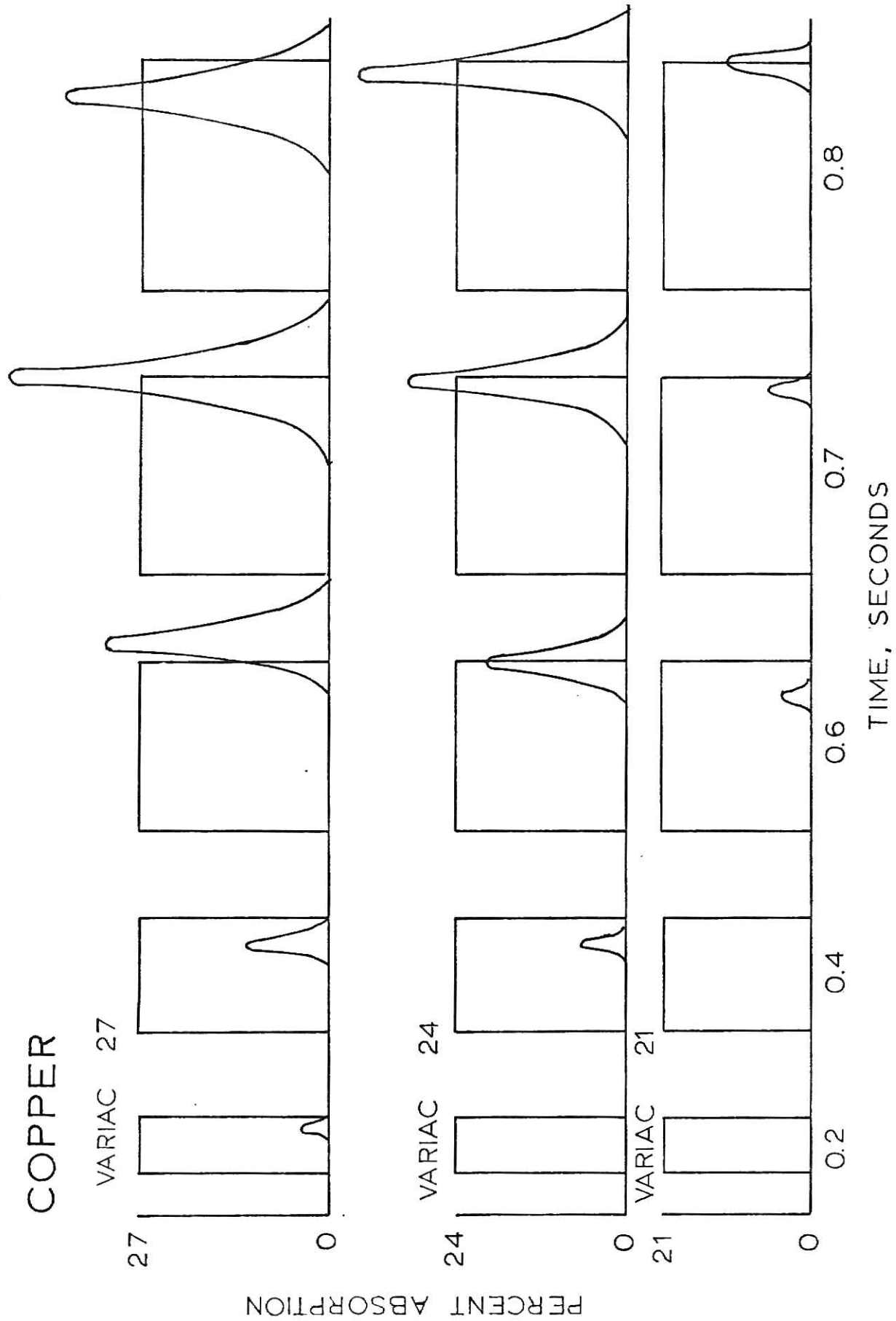
The X-axis represents the length of time the current was allowed to pass through the tantalum boat and the position of the peak occurs with respect to the application of the current. The Y-axis denotes the percent absorption and also the variac setting for each determination studied.

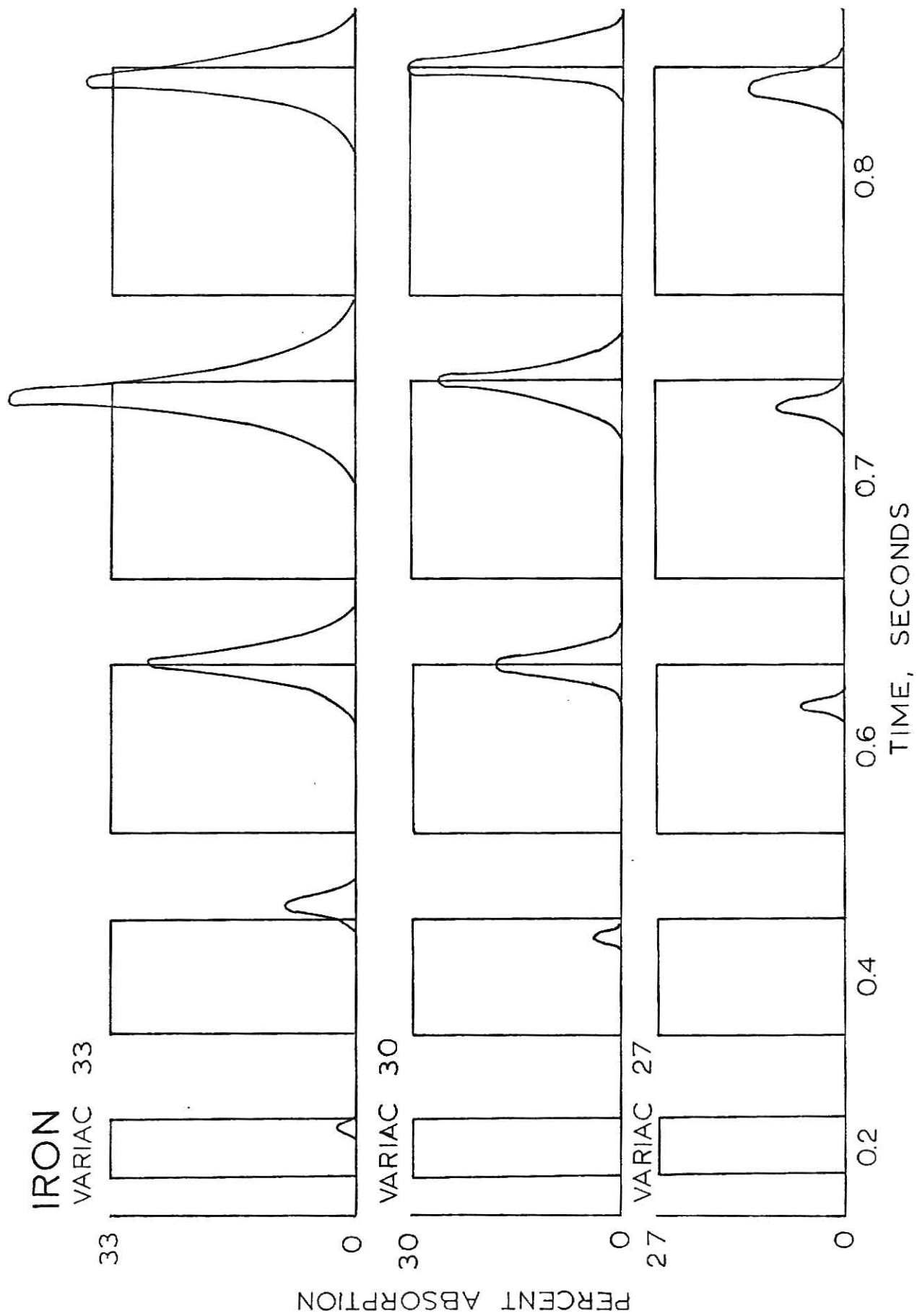
ZINC



MANGANESE







As the length of time the current passed through the boat increased, and the temperature also, the absorption peaks reached a maximum and then decreased. This is shown in Figures 17-20 where the absorption peak height was plotted versus the length of time the current was allowed to pass through the boat. This investigation revealed that a specific tantalum boat temperature was required to obtain the maximum absorption signal. Investigation of all four elements showed decreases in the magnitude of the absorption signal as the temperature of the tantalum boat increased. A possible explanation of the decrease in intensity as the temperature was increased was considered by Donega and Burgess (16) to be caused by the rapid diffusion of sample atoms through the light path of the hollow cathode at the increased temperature. To insure that all the sample was atomized from the tantalum boat before the next sample applied, the boat was heated manually to remove any remaining sample. For all determinations three samples were investigated at the same time setting and the average of the absorption signals used.

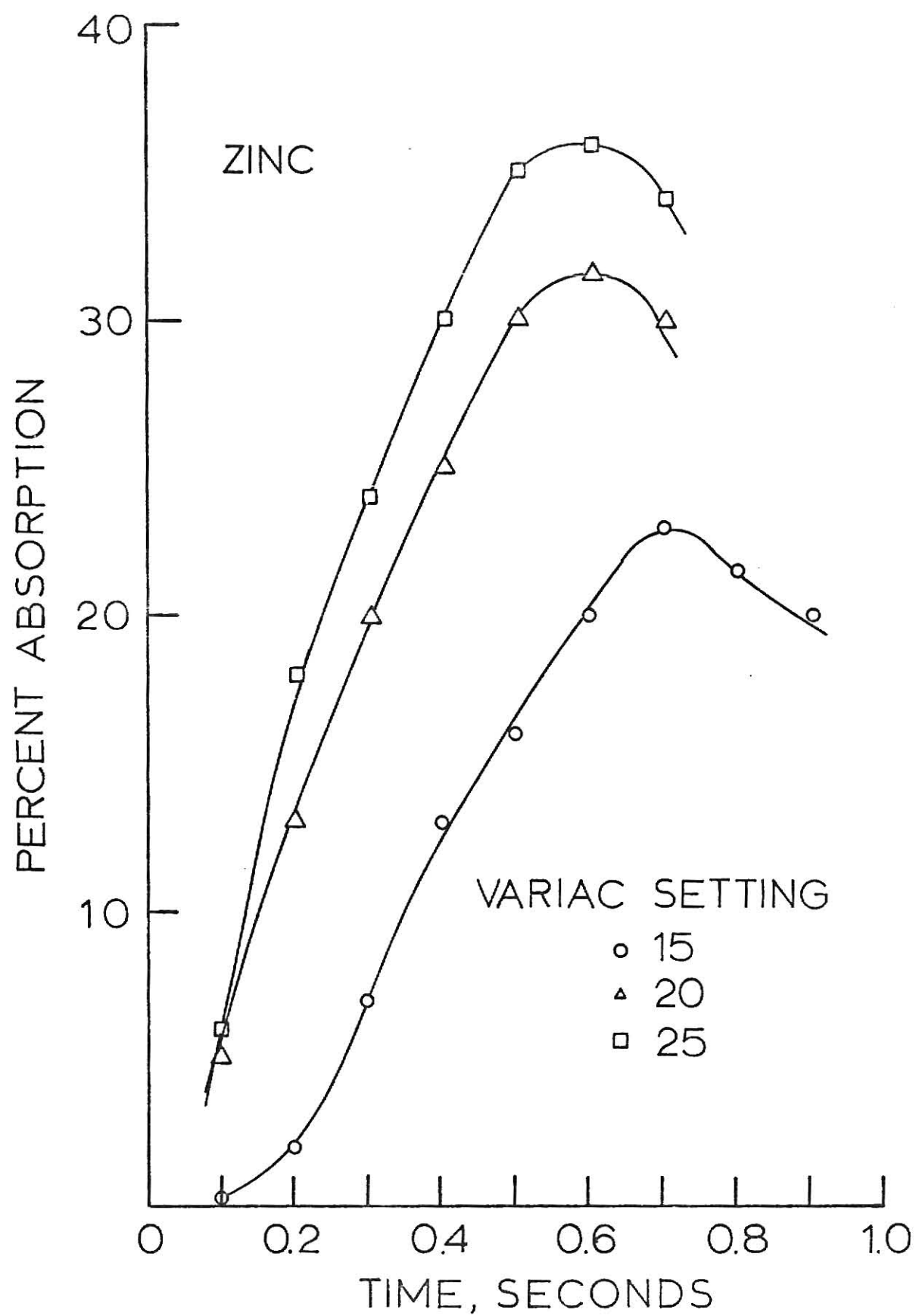
Sensitivity and Detection Limits

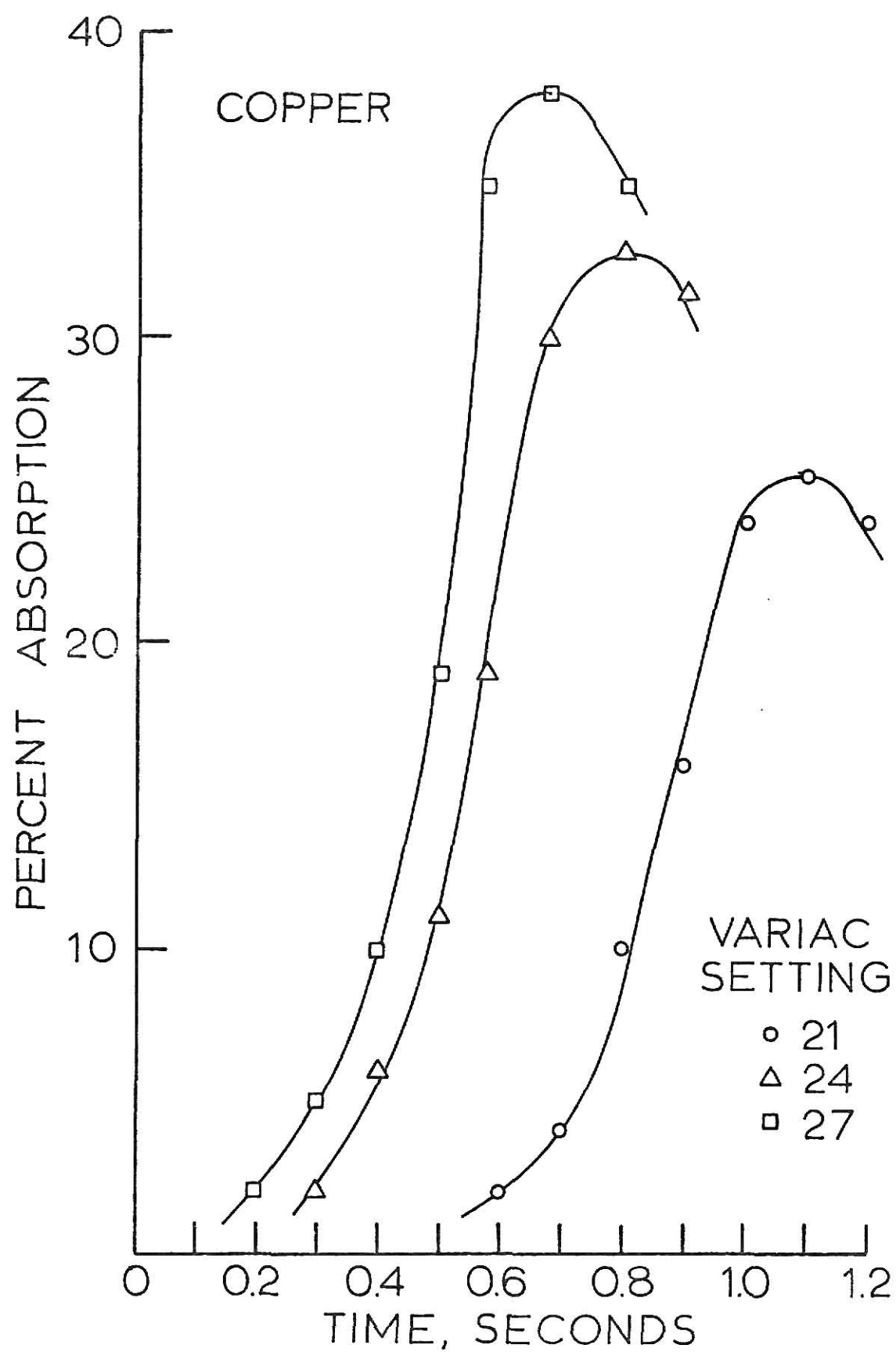
The response of Zn, Mn, and Cu as a function of the concentration was investigated. The sensitivities and detection limits of these elements were determined. Sensitivity is defined as the concentration of sample required to produce a one percent change in the absorption signal and the detection

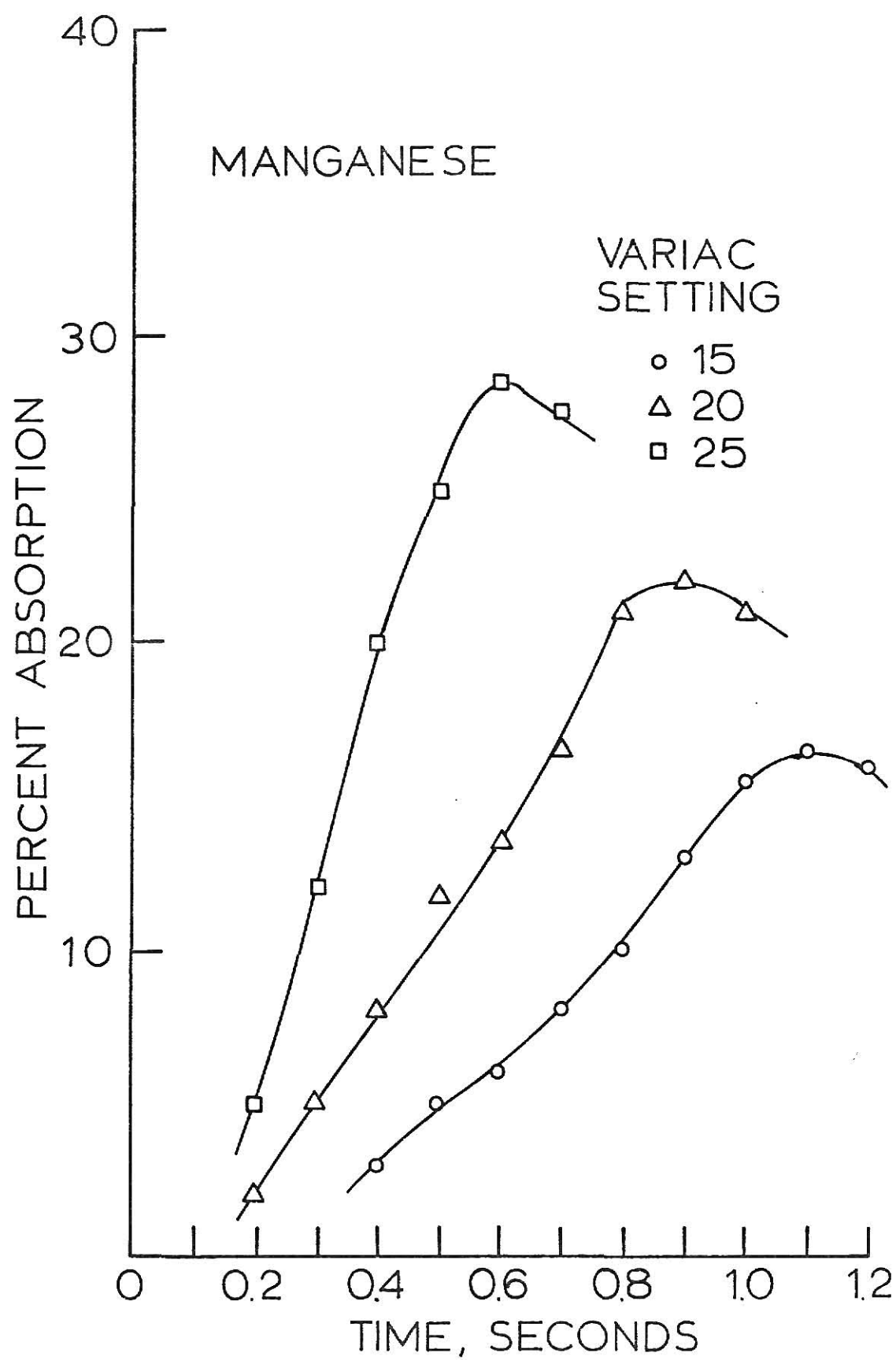
EXPLANATION: FIG. 17-20

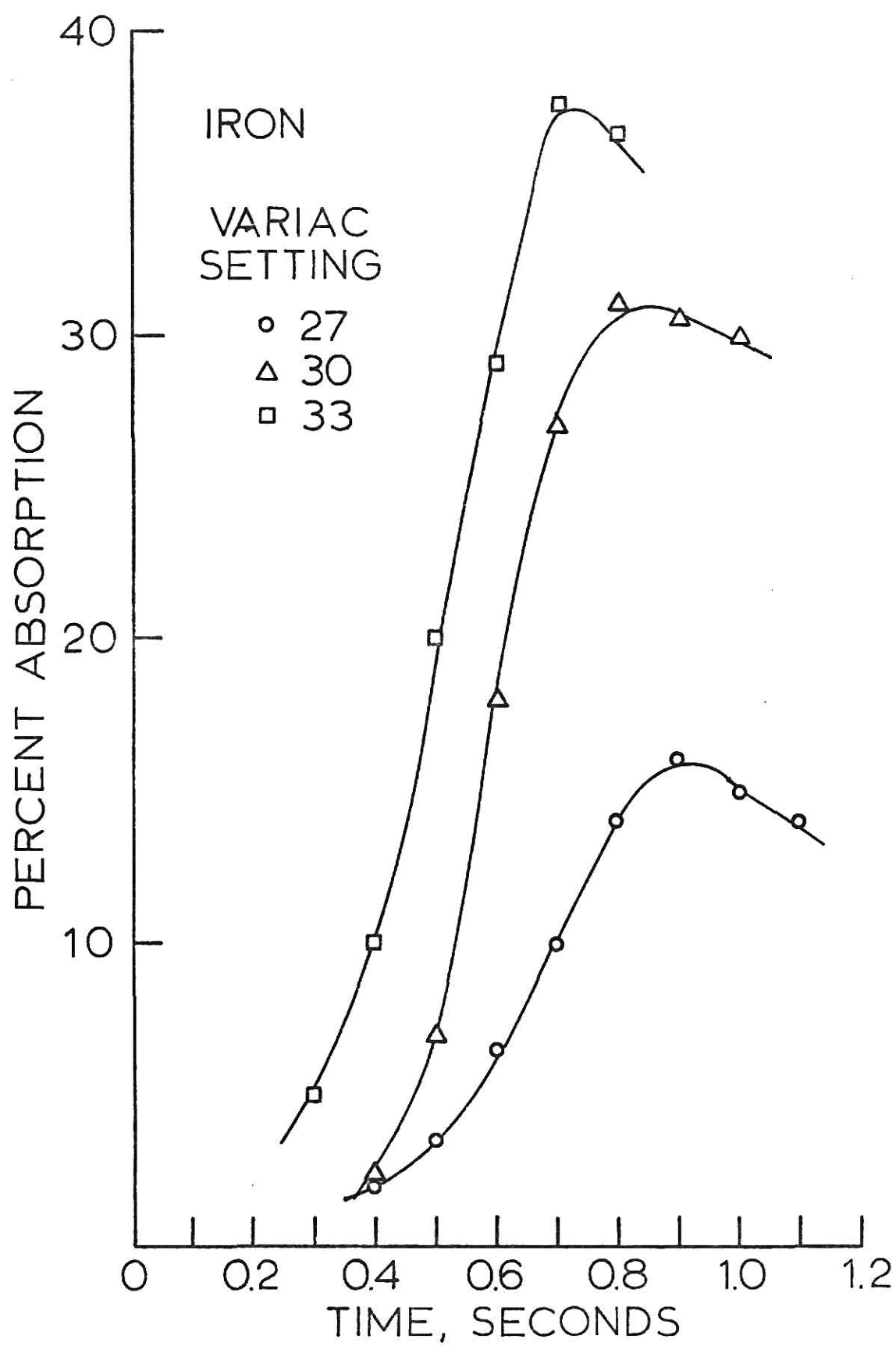
17: Zinc
18: Copper
19: Manganese
20: Iron

The absorption peak heights from figures 13-16 were plotted versus the length of time the current was allowed to pass through the tantalum boat. Each point denotes a separate sample run.









limit corresponds to the concentration required to produce a signal to noise ratio of two. Three samples were run at each concentration and the average absorbance plotted versus concentration. Figure 21 and 22 respectively, present the results. The experimental parameters used in this investigation are given in Table 3.

Table 3. Experimental Parameters for the Determination of Sensitivities and Detection Limits of Zinc, Copper, and Manganese.

	Zn	Cu	Mn
Wavelength (Å):	2139	3247	2795
PAR Sensitivity (μV):	500	500	500
Photomultiplier Voltage (volts):	4.0	2.5	6.9
Hollow Cathode Current (mA):	495	500	500
Purge Gas:	Argon	Argon	Argon
Purge Gas Pressure:	1 atm	1 atm	1 atm
Analysis Time (sec):	1.93	1.05	1.00
Variac Setting for Analysis Time (sec):	15	20	18
Dry Time (sec):	15	15	15
Variac Setting for Dry Time:	4	4	4
Height above Boat (mm):	2.0	2.0	2.0
Concentration of Analyte (g/μl):	Varied with each run		

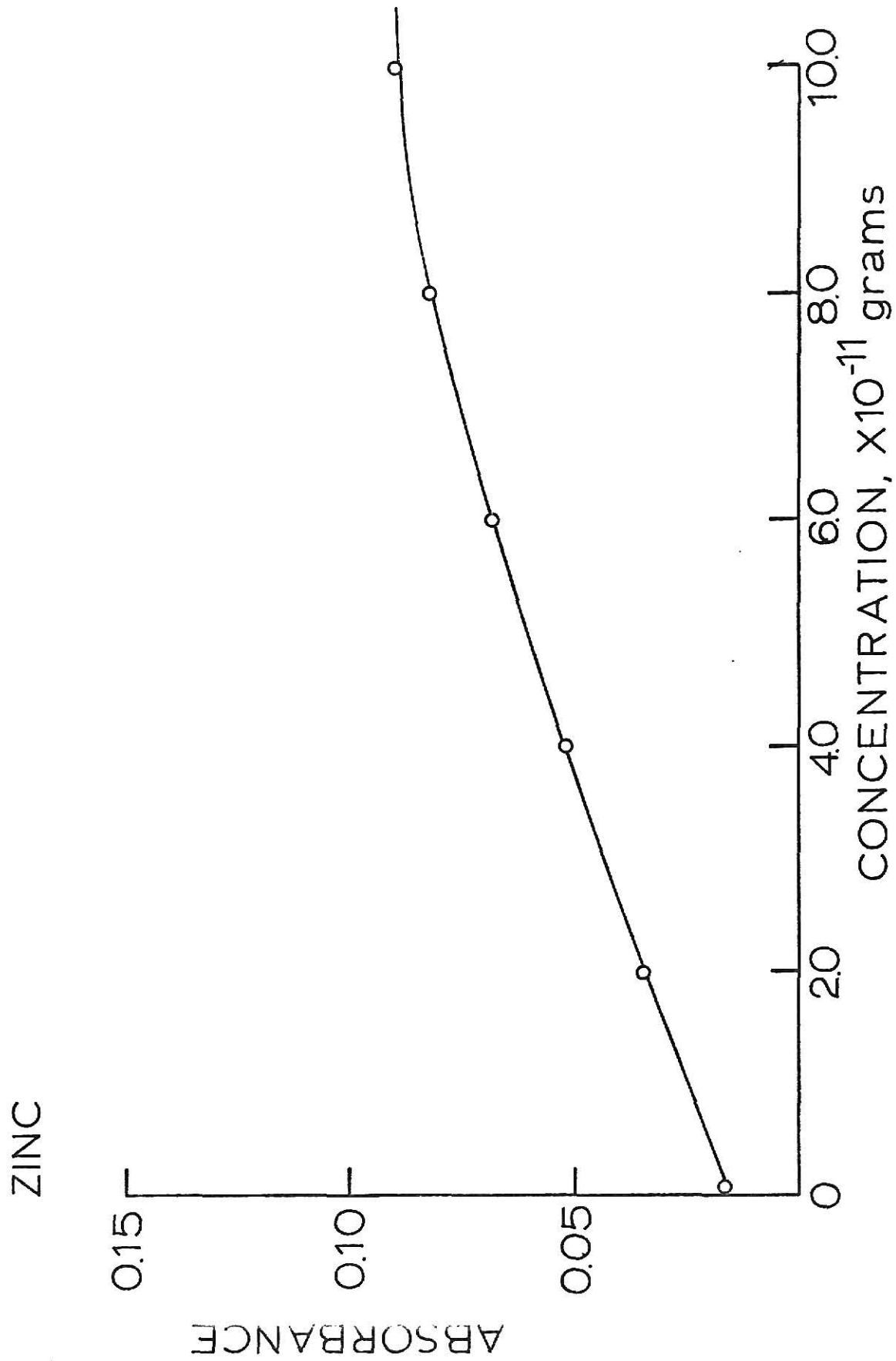


Figure 21. Calibration curve for Zinc.

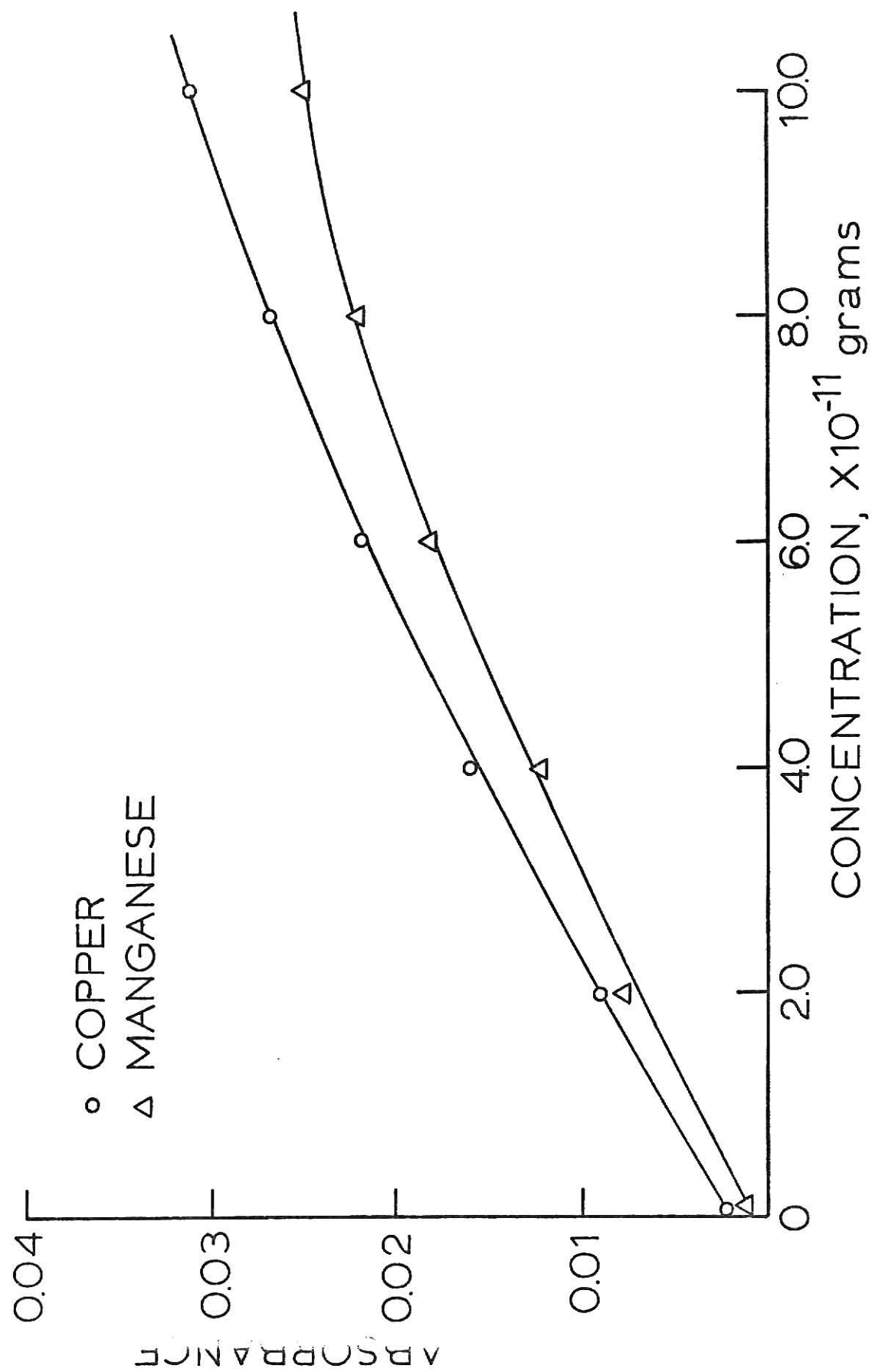


Figure 22. Calibration curve for Copper and Manganese.

The sensitivities and detection limits of the three elements studied are compiled in Table 4.

Table 4. Sensitivities and Detection Limits of Zn, Cu, and Mn.

	Sensitivity grams $\times 10^{-11}$	Detection Limit grams $\times 10^{-11}$
Zn	1.0	0.5
Cu	2.0	1.0
Mn	3.0	2.0

The absorbance signal of the elements increased linearly with the increase in concentration.

Interference Study

The remaining experiments dealt with interference effects associated with the tantalum boat atomization system.

Compound Interferences

The first interference effect investigated was the study of different compounds of the same element. The experiment consisted of studying compounds of the same element to investigate whether the absorption signal of different compounds, each with the same concentration of the cation, was the same. Compounds of Zn, Mg, and Cu were studied at three different variac settings. These settings corresponded to different temperatures of the tantalum boat. All samples were run in triplicate and an average of the absorption signal obtained. The experimental parameters are tabulated in Table 5. Figures 23-31 show the calibration curves of the different compounds. The calibration curves are quite linear, however, different

Table 5. Experimental Parameters for Cation Compound Effect.

	Zn	Cu	Mn
Wavelength (Å):	2139	3247	2852
PAR Sensitivity (μV):	500	500	500
Photomultiplier Voltage (volts):	505	500	500
Hollow Cathode Current (mA):	3.0	3.6	4.0
Purge Gas:	Argon	Argon	Argon
Purge Gas Pressure	1 atm	1 atm	1 atm
Analysis Time (sec):	1.0	1.0	1.0
Variac Setting for Analysis Time:	15-18-21	18-20-22	19-21-22
Dry Time (sec):	15	15	15
Variac Setting for Dry Time:	4	4	4
Height above Boat (mm):	2.0	2.0	2.0
Concentration of Analyte (g/ul):	Varied with each run		

compounds of the same element produced different absorption signals. As the temperature of the tantalum boat was increased (by increasing the variac setting) the curves moved closer together, probably due to the more effective atomization characterized by the higher temperature.

A possible explanation of this observation could be that the compounds were thermally decomposing into their respective elements, however compounds with oxygen available might be recombining to form oxides. The oxides may not thermally decompose at the same temperature. Compounds with a high percentage

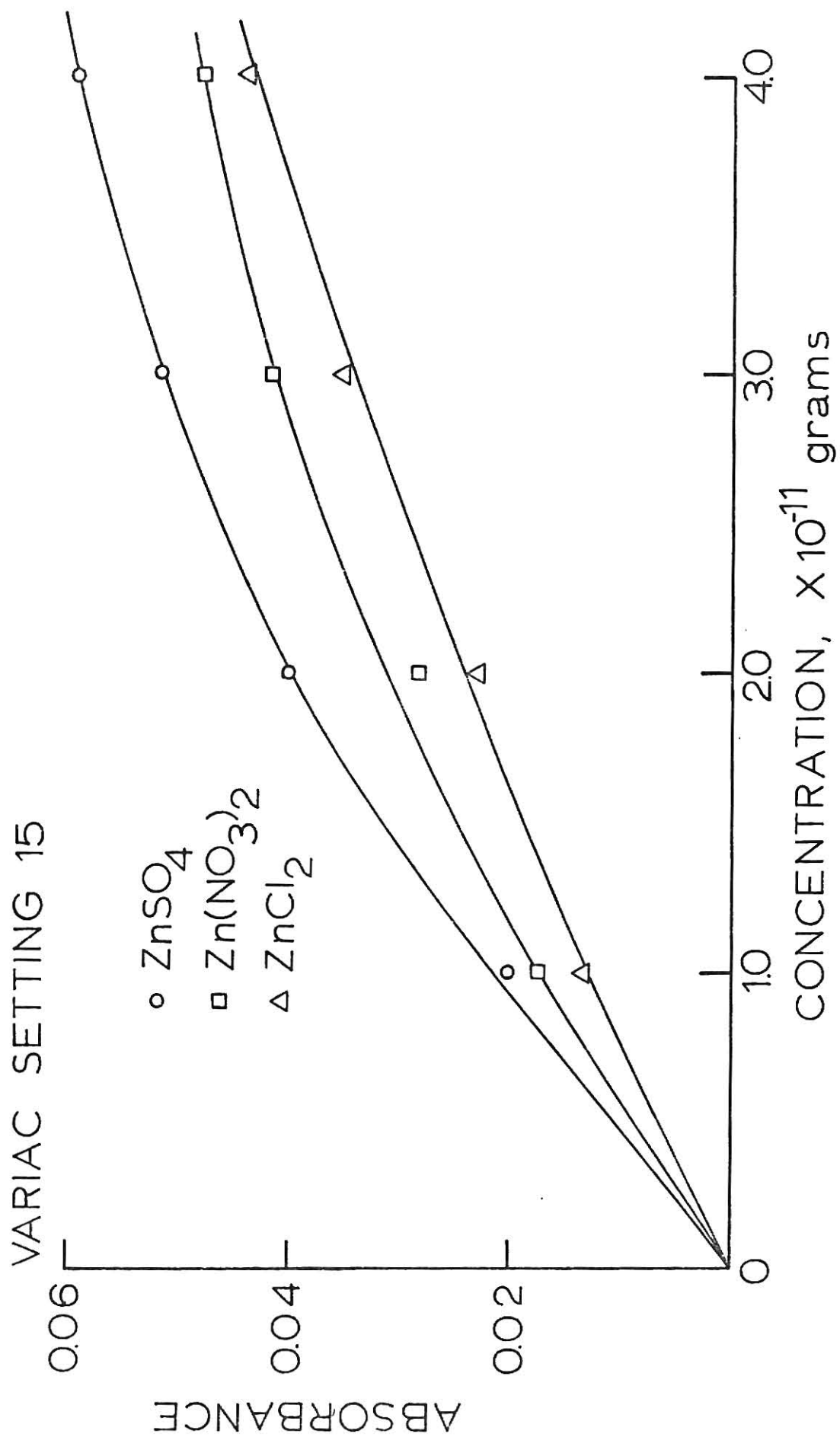
EXPLANATION: FIG. 23-25

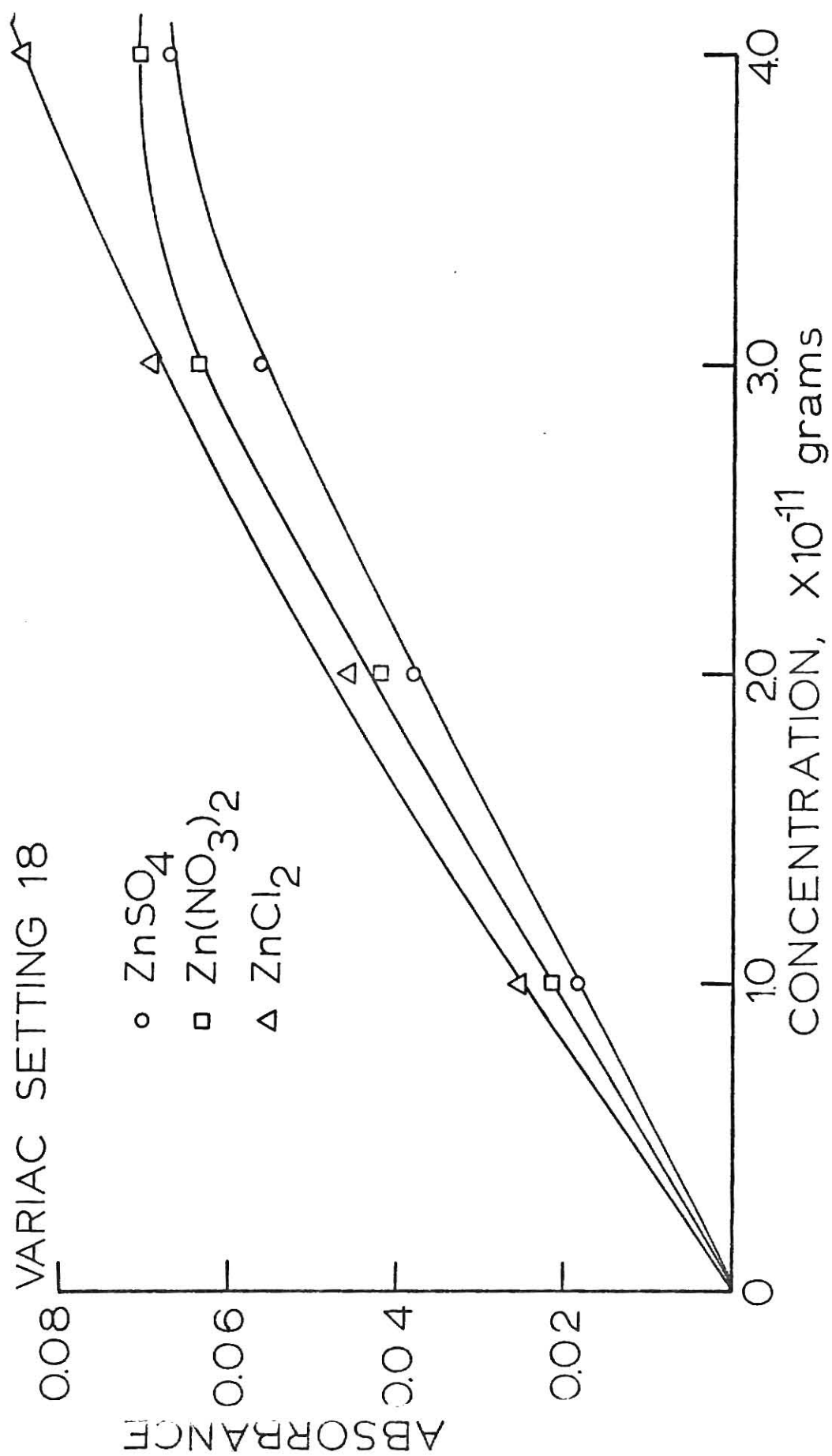
23: Variac Setting 15

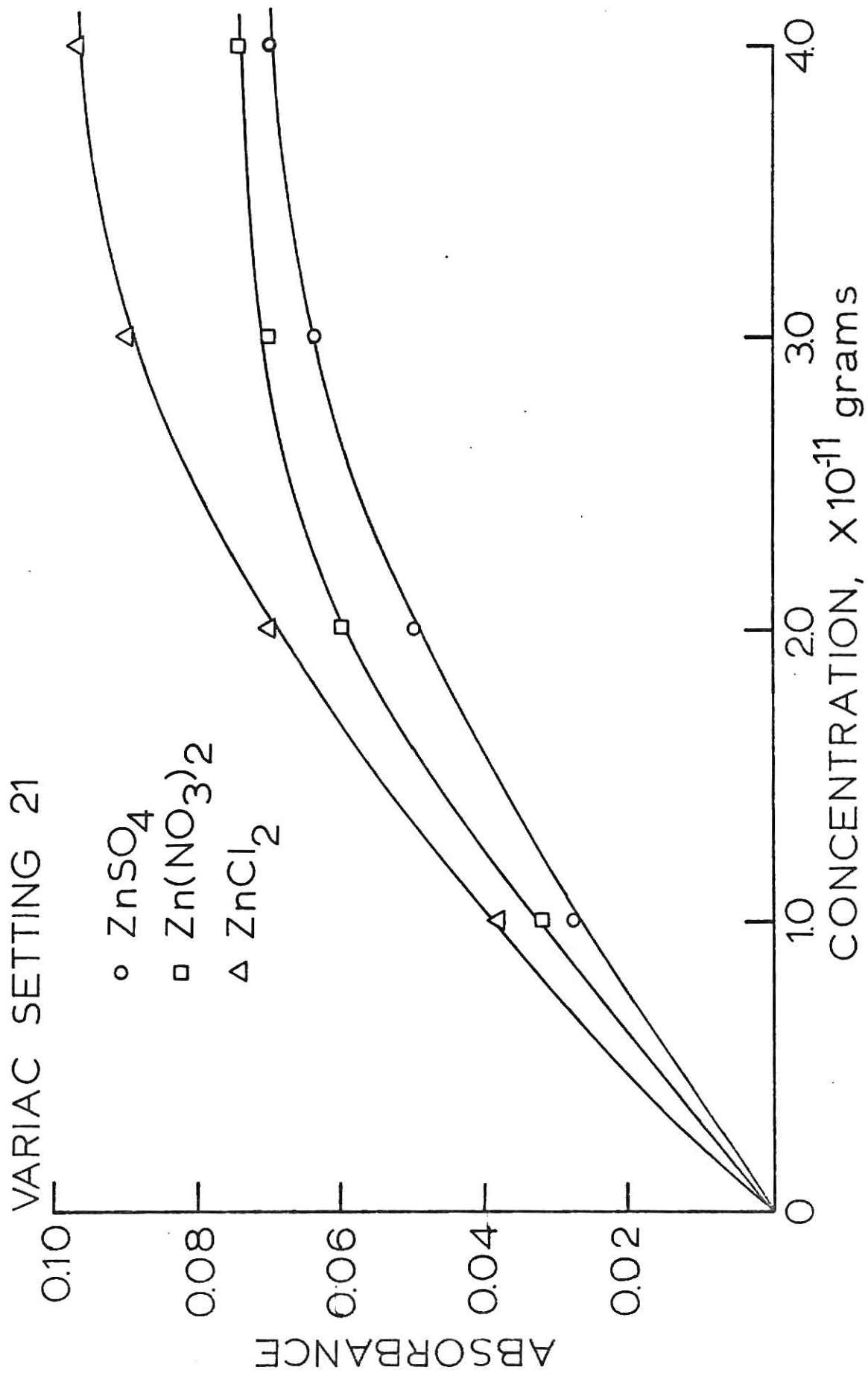
24: Variac Setting 18

25: Variac Setting 21

Calibration curves for the different Zinc Compounds
studied.



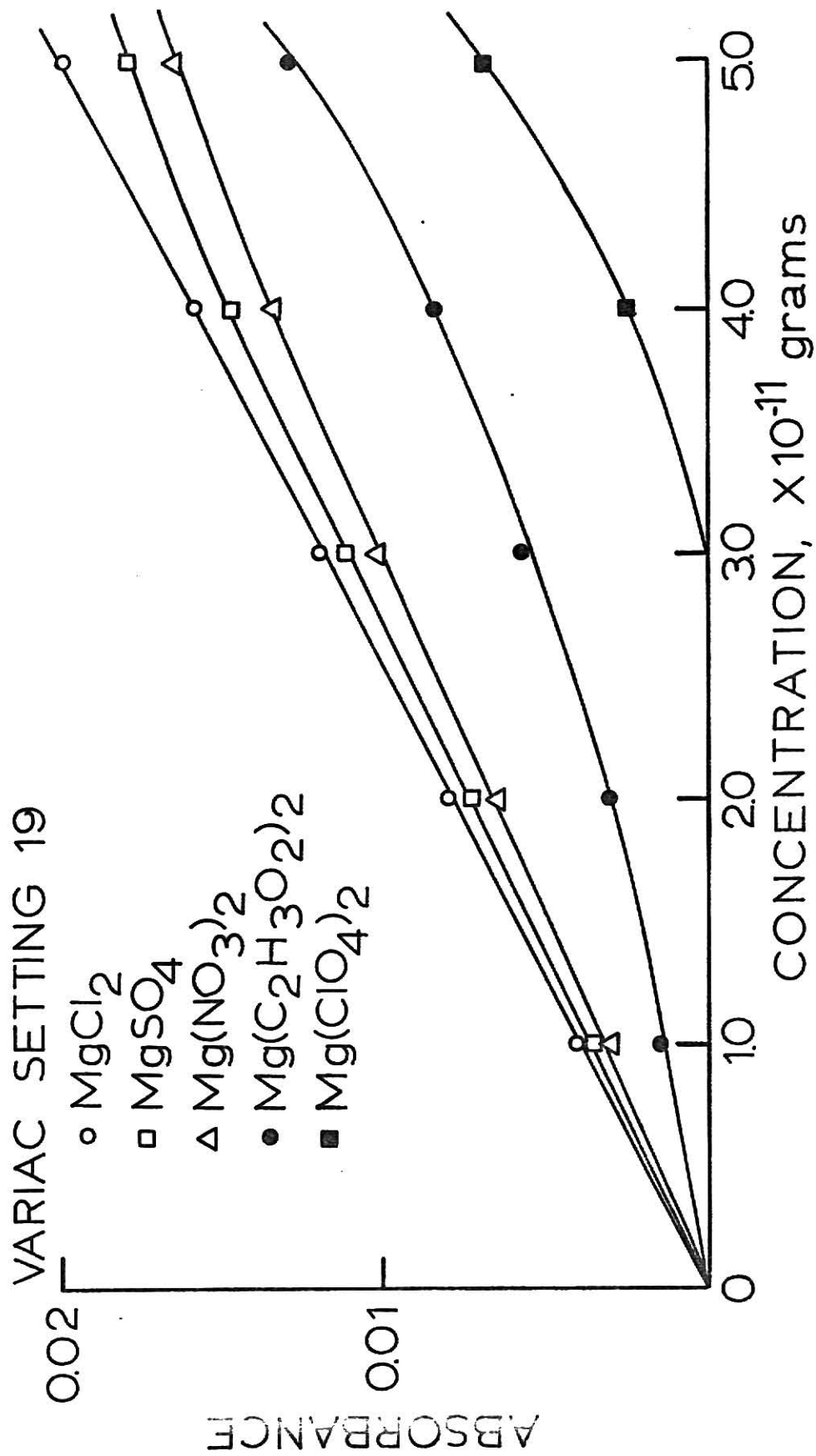


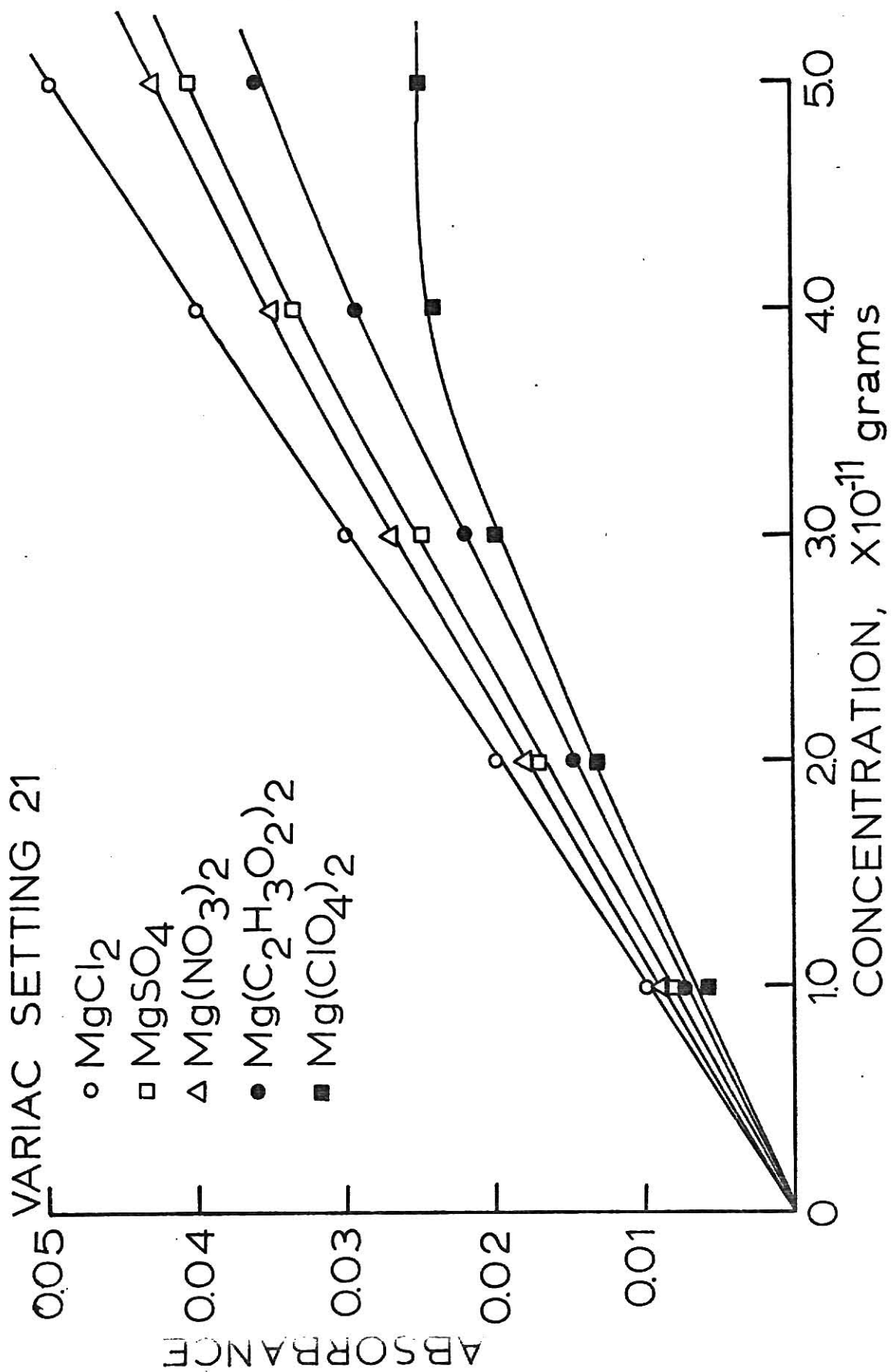


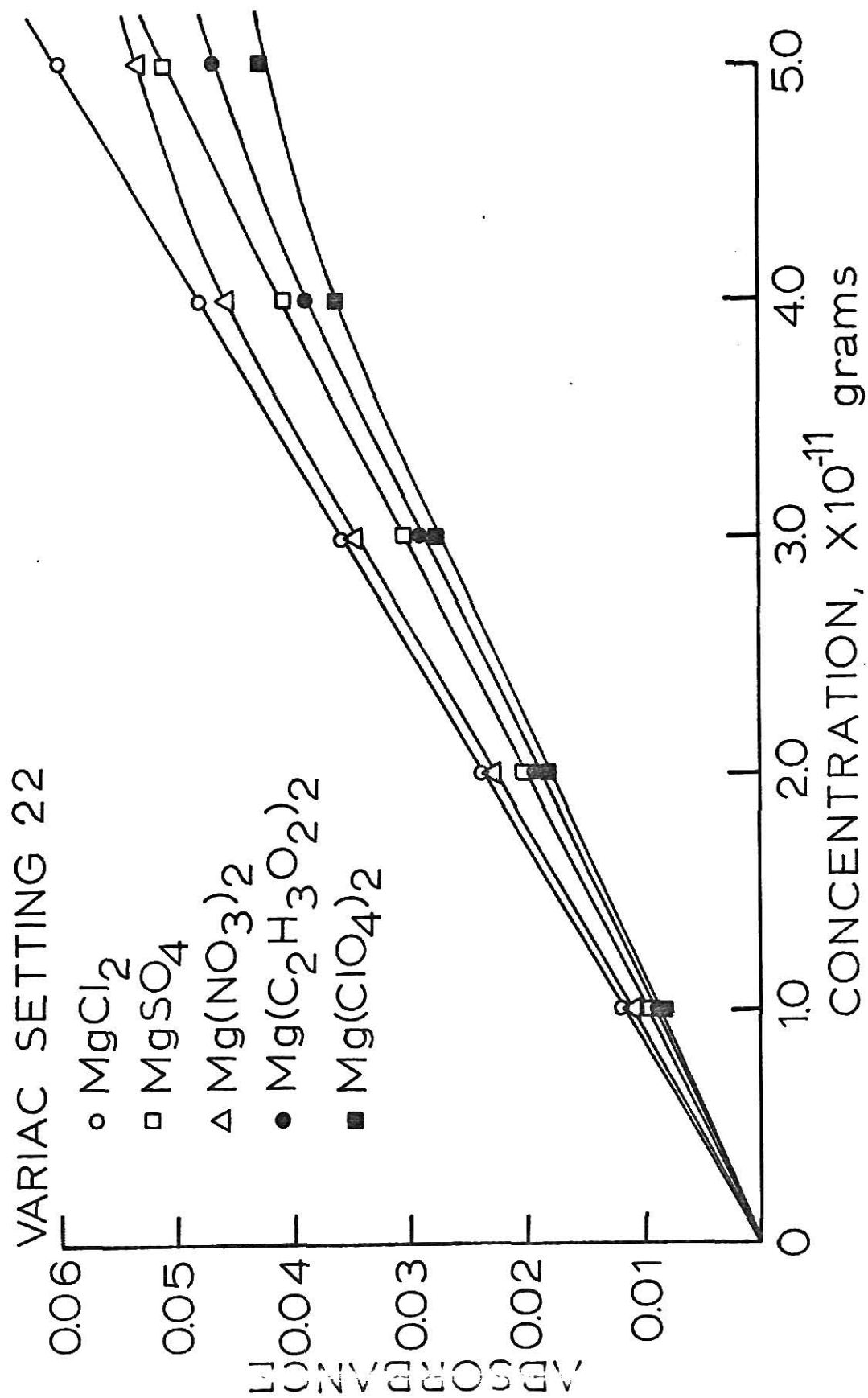
EXPLANATION: FIG. 26-28

26: Variac Setting 19
27: Variac Setting 21
28: Variac Setting 22

Calibration curves for the different Magnesium compounds
studied.



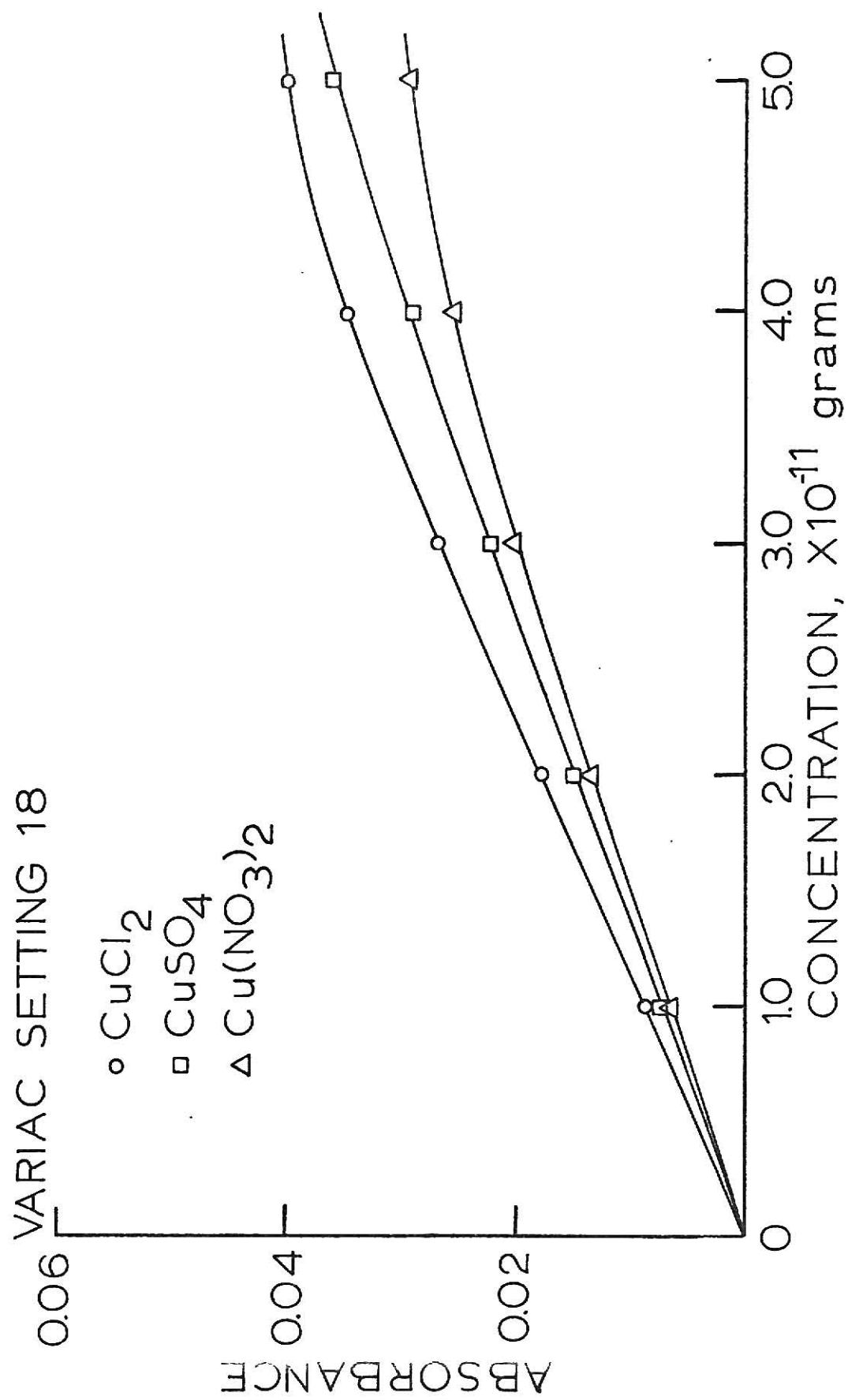


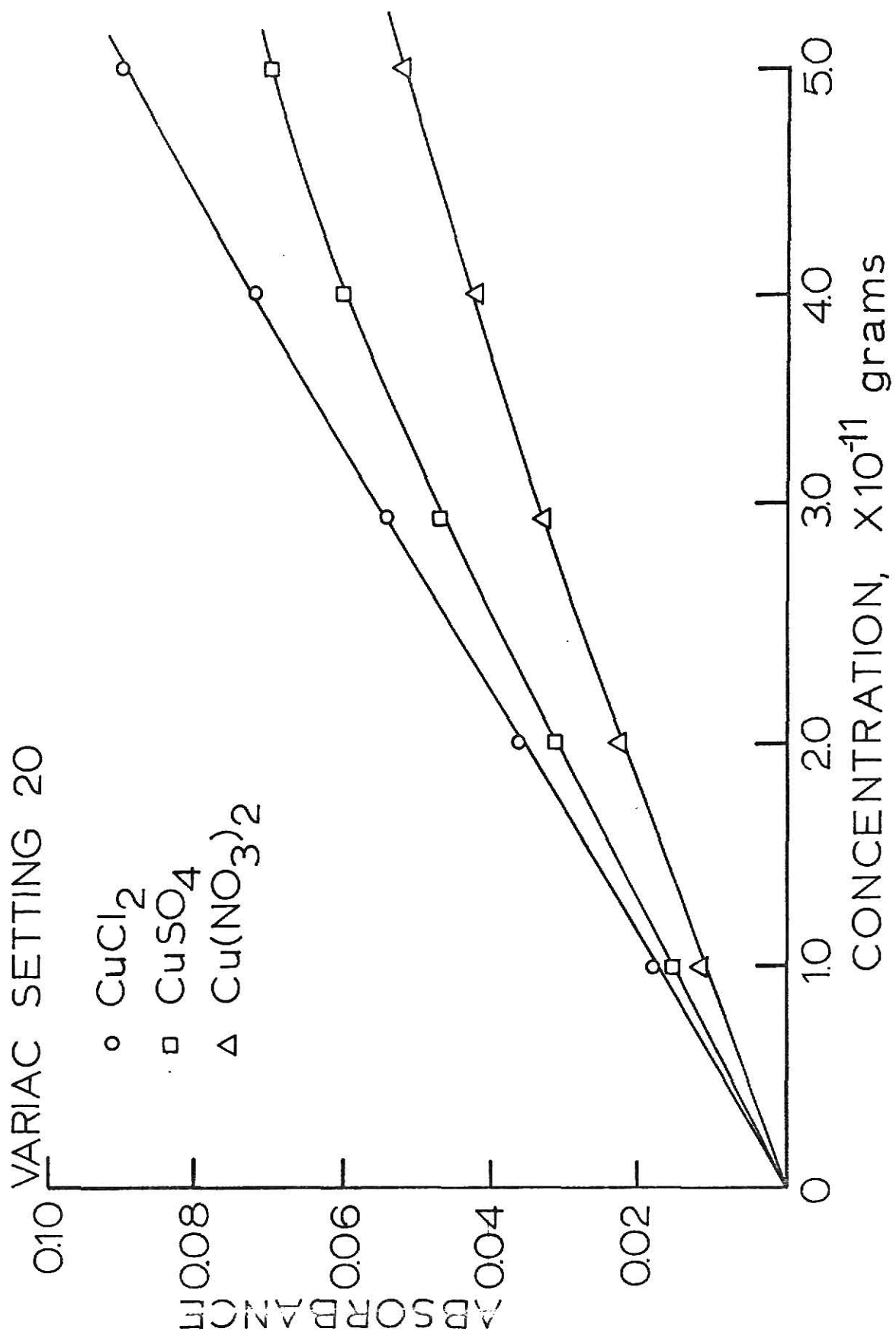


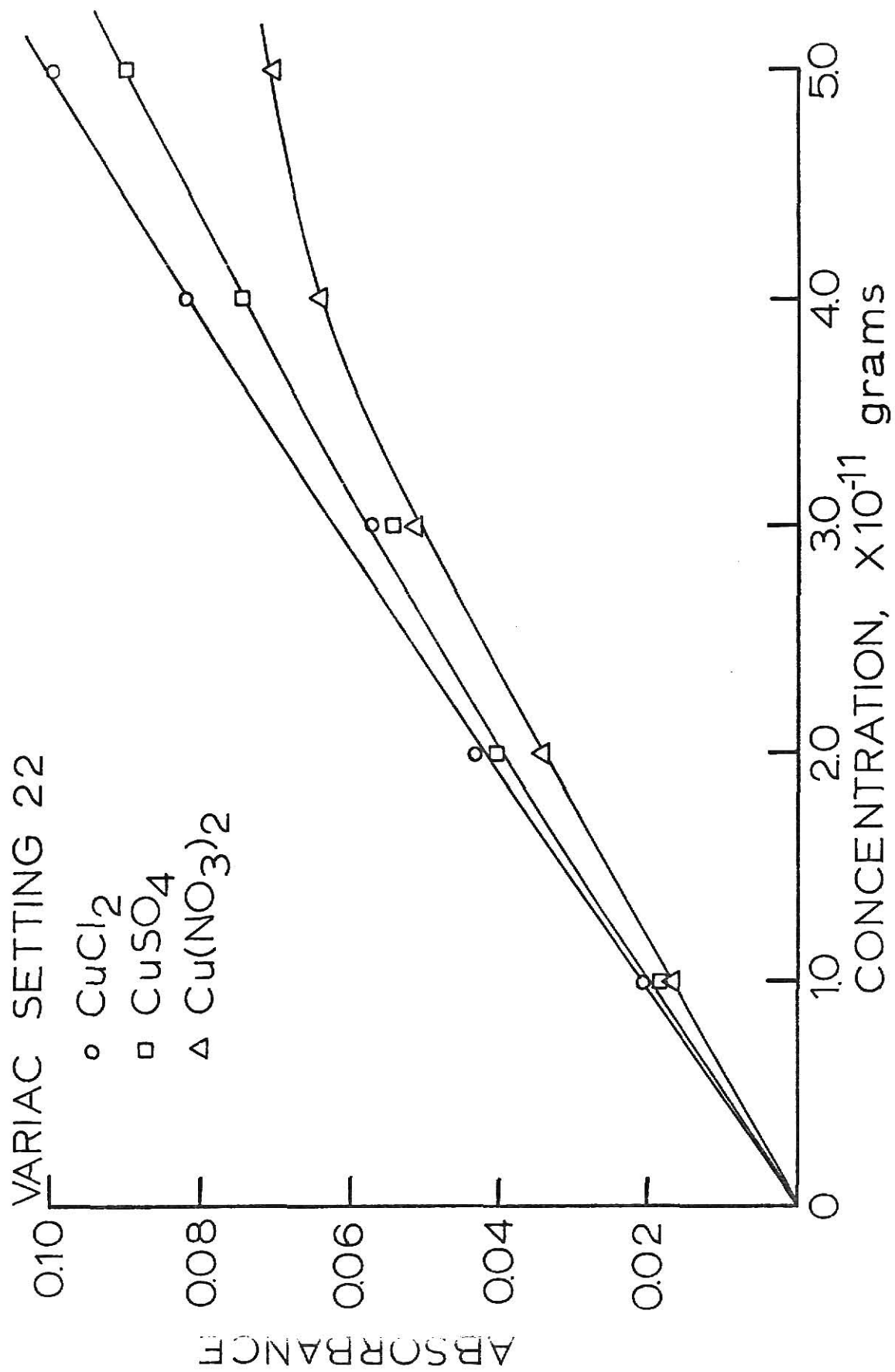
EXPLANATION: FIG. 29-31

29: Variac Setting 18
30: Variac Setting 20
31: Variac Setting 22

Calibration curves for the different Copper compounds
studied.







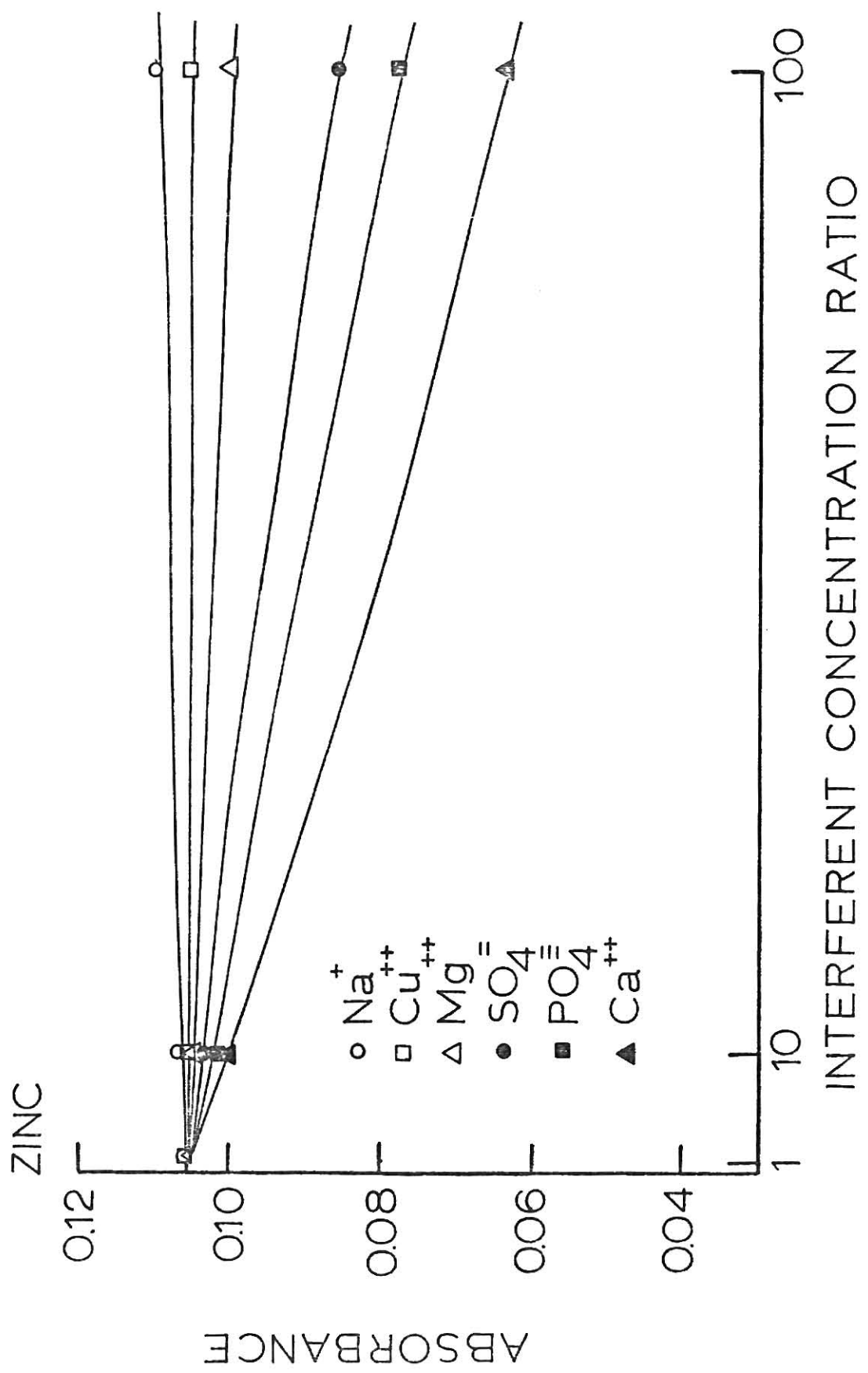
of oxygen exhibited a larger decrease in their absorption signals, probably because more oxygen was available to combine with the element. This was true for all the elements investigated in this experiment. Polarographic techniques were employed with the different stock solution to insure that they were all the same concentration.

Ionic Interferences

Absorption response as a function of different interfering elements added to the analyte was studied next. Zn, Cu, and Mn were used as the analytes and Ca^{++} , Cu^{++} , Mg^{++} , Na^+ , $\text{PO}_4^{=}$, and $\text{SO}_4^{=}$ were added to the analyte in ratios of 1, 10, and 100 times the concentration of the analyte ion. The experimental parameters for this study are shown in Table 6. The normalized results are shown in Figures 32 and 33. Only Ca^{++} , $\text{SO}_4^{=}$, and $\text{PO}_4^{=}$ affected the absorption of the analyte appreciably in all cases. The other interfering ions produced no more than a five percent change in the absorption response from when the interferents were absent. A decrease in the magnitude of the response was noted as the temperature of the tantalum boat was increased. That is, Mn displayed less of an interference effect when it was atomized at a high temperature than did Zn which was atomized at a lower temperature. Ca^{++} reduced the analytical signal as much as twenty percent in some cases.

EXPLANATION: FIG. 32-33

The Interferent Concentration Ratio is the ratio of the interferent to that of the analyte for the different elements studied.



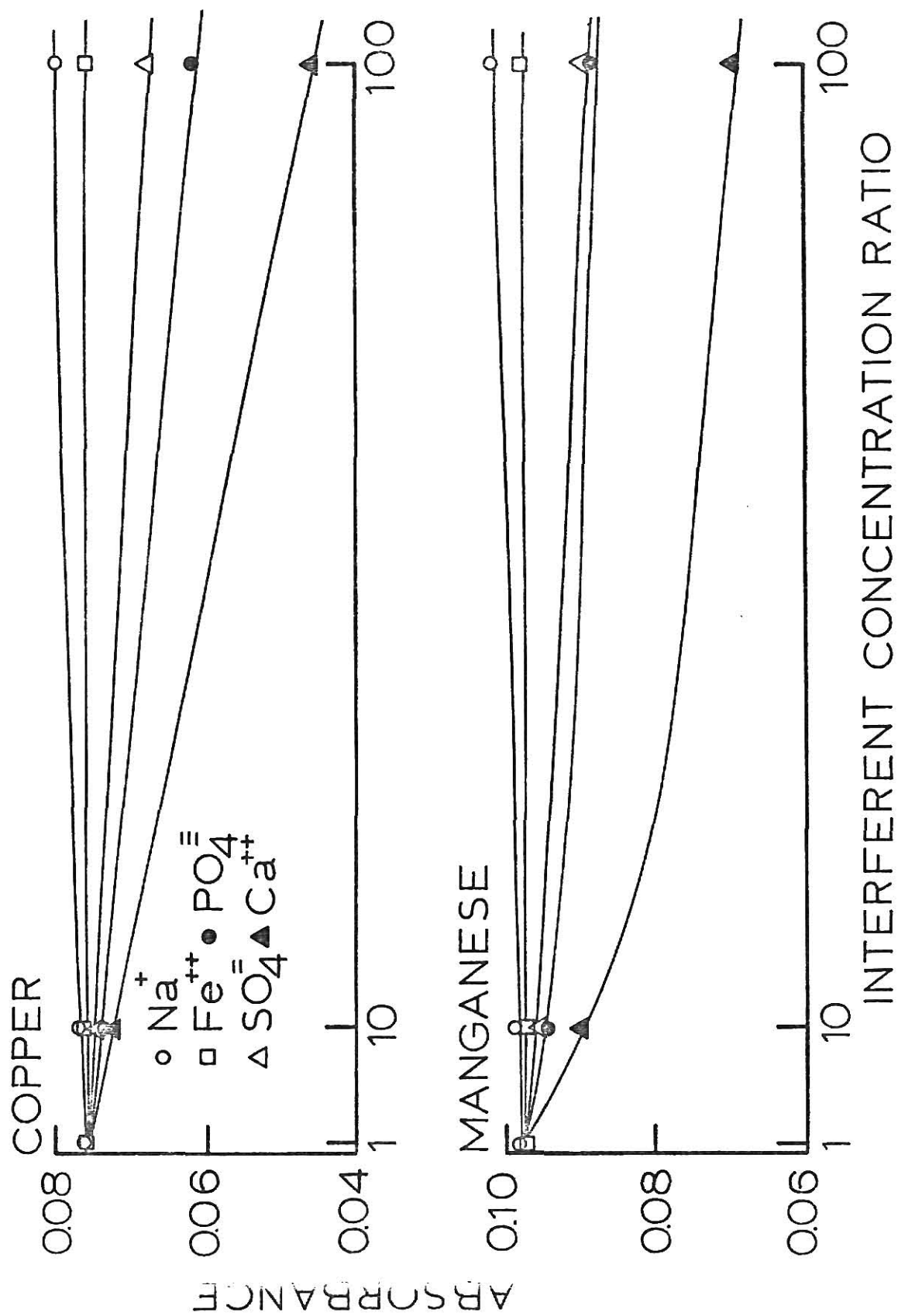


Table 6. Experimental Parameters for Ionic Interferences.

	Zn	Cu	Mn
Wavelength (Å):	2139	3246	2795
PAR Sensitivity (μV):	500	500	500
Photomultiplier Voltage (volts):	500	500	500
Hollow Cathode Current (mA):	4.1	2.0	3.0
Purge Gas:	Argon	Argon	Argon
Purge Gas Pressure:	1 atm	1 atm	1 atm
Analysis Time (sec):	2.0	0.58	0.50
Variac Setting for Analysis Time:	16	25	28
Dry Time (sec):	15	15	15
Variac Setting for Dry Time:	4	4	4
Height above Boat (mm):	2.0	2.0	2.0
Concentration of Analyte (g/μl):	3×10^{-11}	1×10^{-10}	1×10^{-10}

Bulk Effect

The next interference study investigated was that of a physical bulk effect of material on the tantalum boat. Different interfering elements were added to the analyte in ratios of 1000, 5000, and 10,000 times the concentration of the analyte. In this concentration the interferent acted more as a physical bulk interferent rather than one of a chemical nature. Experimental parameters are tabulated in Table 7.

Table 7. Experimental Parameters of the Bulk Effect.

	Zn	Cu	Mn
Wavelength (Å):	2139	3247	2795
PAR Sensitivity (μV):	500	500	500
Photomultiplier Voltage (volts):	500	500	500
Hollow Cathode Current (mA):	4.0	2.0	4.0
Purge Gas:	Argon	Argon	Argon
Purge Gas Pressure:	1 atm	1 atm	1 atm
Analysis Time (sec):	1.0	1.0	1.0
Variac Setting for Analysis Time:	19-22	22-26	26-30
Dry Time (sec):	15	15	15
Variac Setting for Dry Time:	4	4	4
Height above Boat (mm):	2.0	2.0	2.0
Concentration of Analyte (g/ul):	1×10^{-11}	3×10^{-11}	3×10^{-11}

The study, for each analyte, was investigated at two different variac settings which corresponded to two different temperatures. The lower temperature of the two was the optimum temperature obtained in earlier studies. Figures 34-39 show the results of this study. Again, as before, Ca^{++} interfered with the analyte to the largest extent. The absorption response was higher at the optimum temperature than at the higher temperature, however the percent change due to the interferent present was also more at this optimum temperature. This perhaps

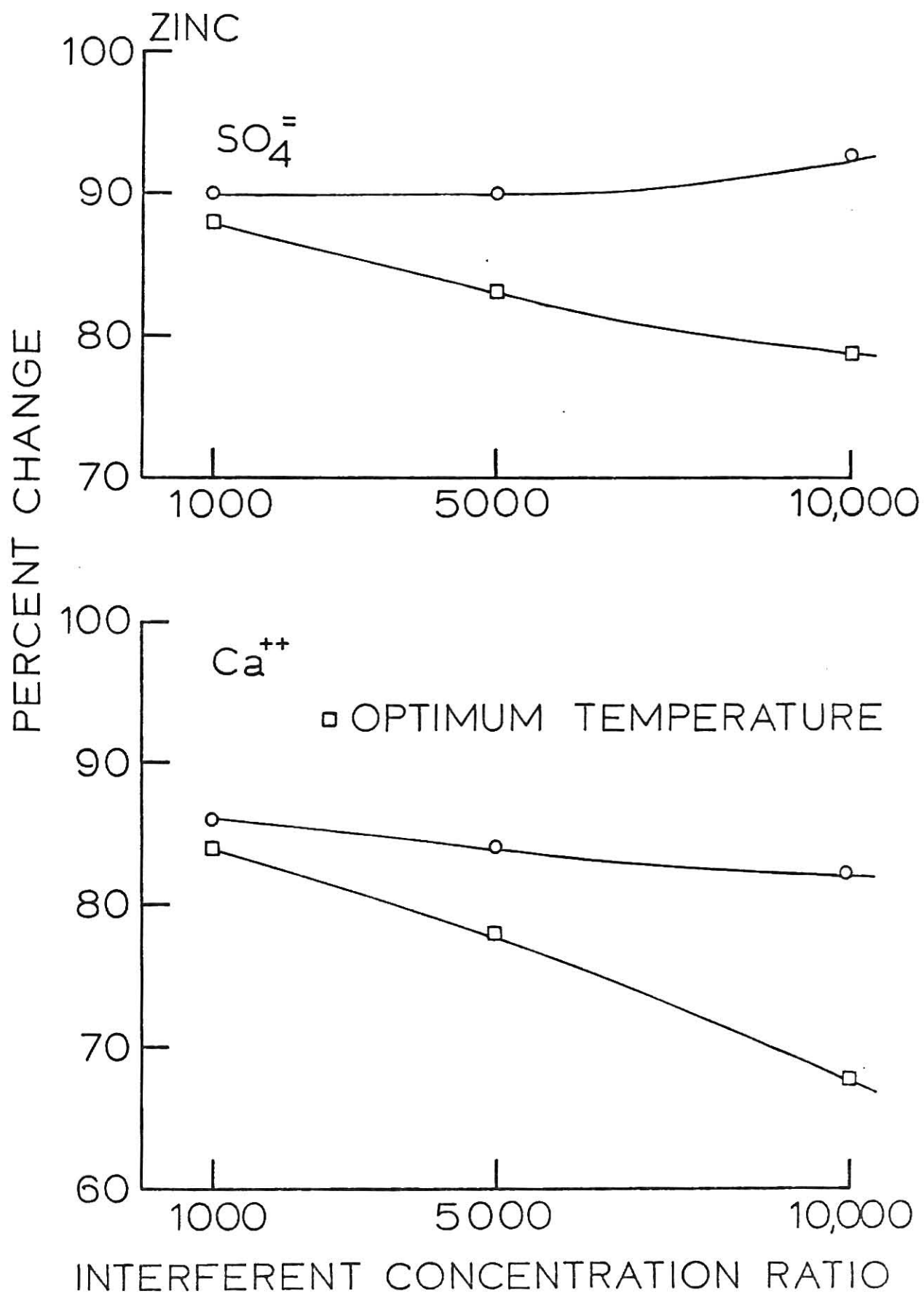
EXPLANATION: FIG. 34-39

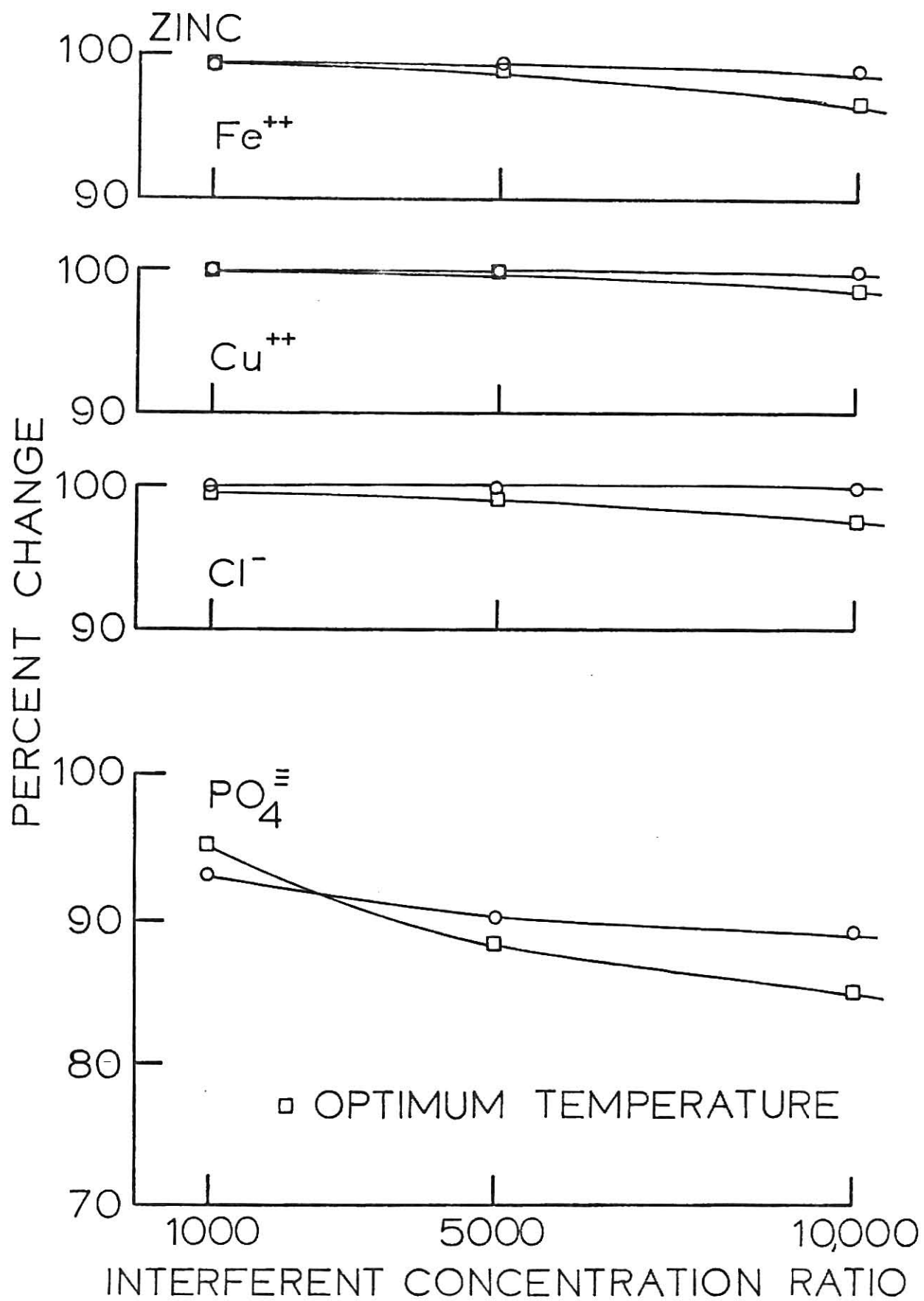
The Interferent Concentration Ratio is the ratio of the interferent to that of the analyte for the different elements studied.

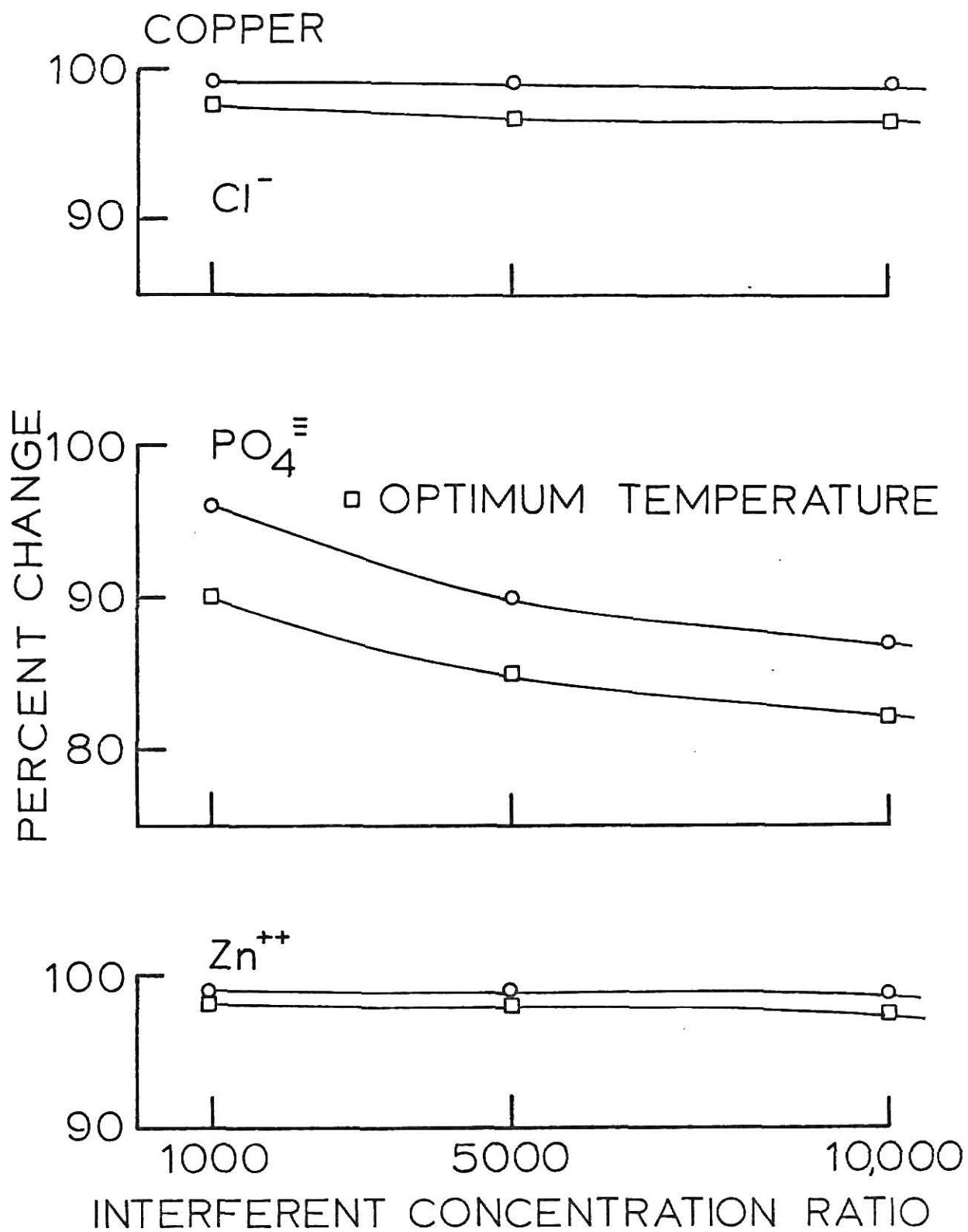
The Percent Change is the change in absorbance from when no interferent was present.

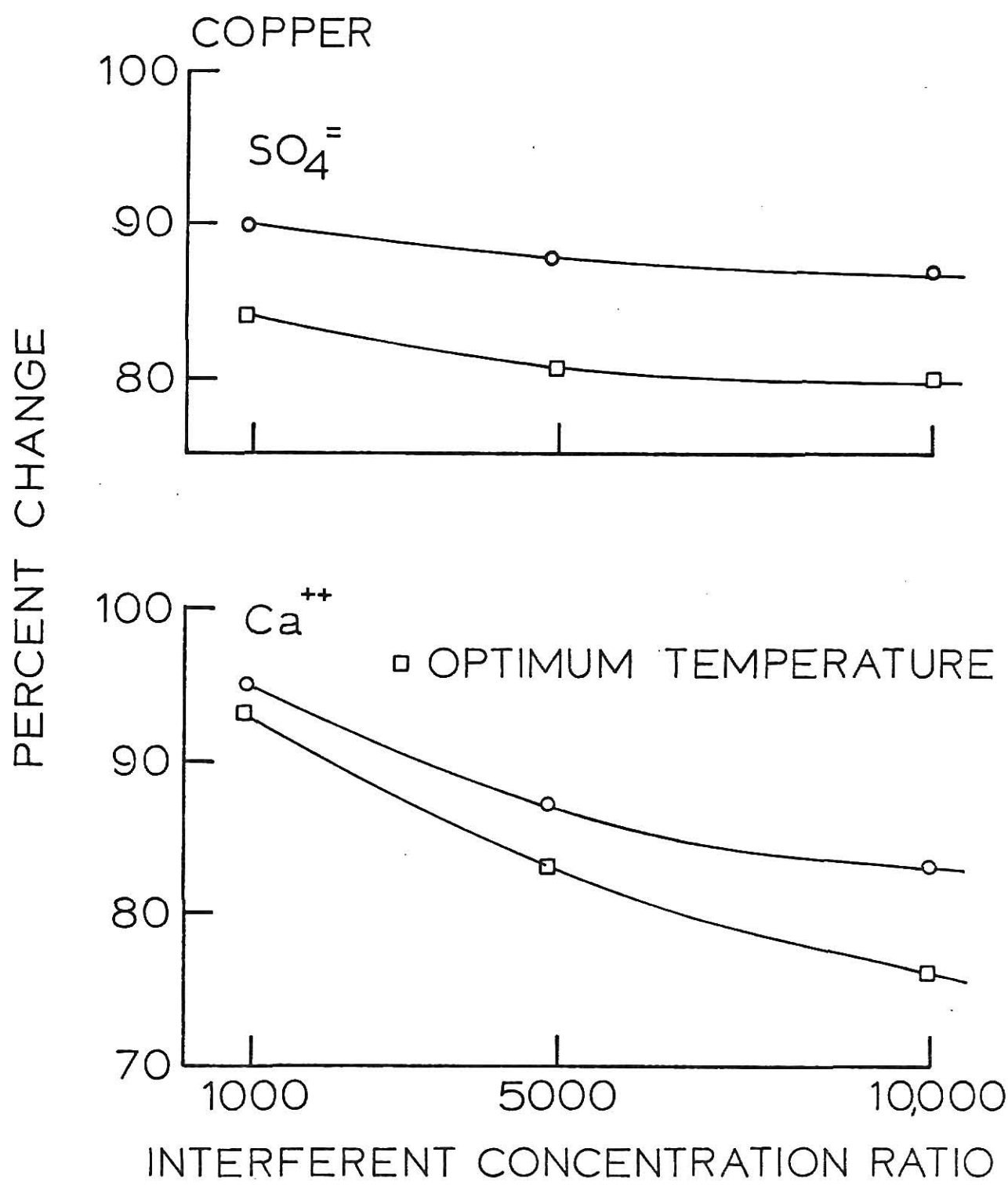
The Optimum Temperature is that temperature of the tantalum boat which produced the highest absorbance signal with no interferent present.

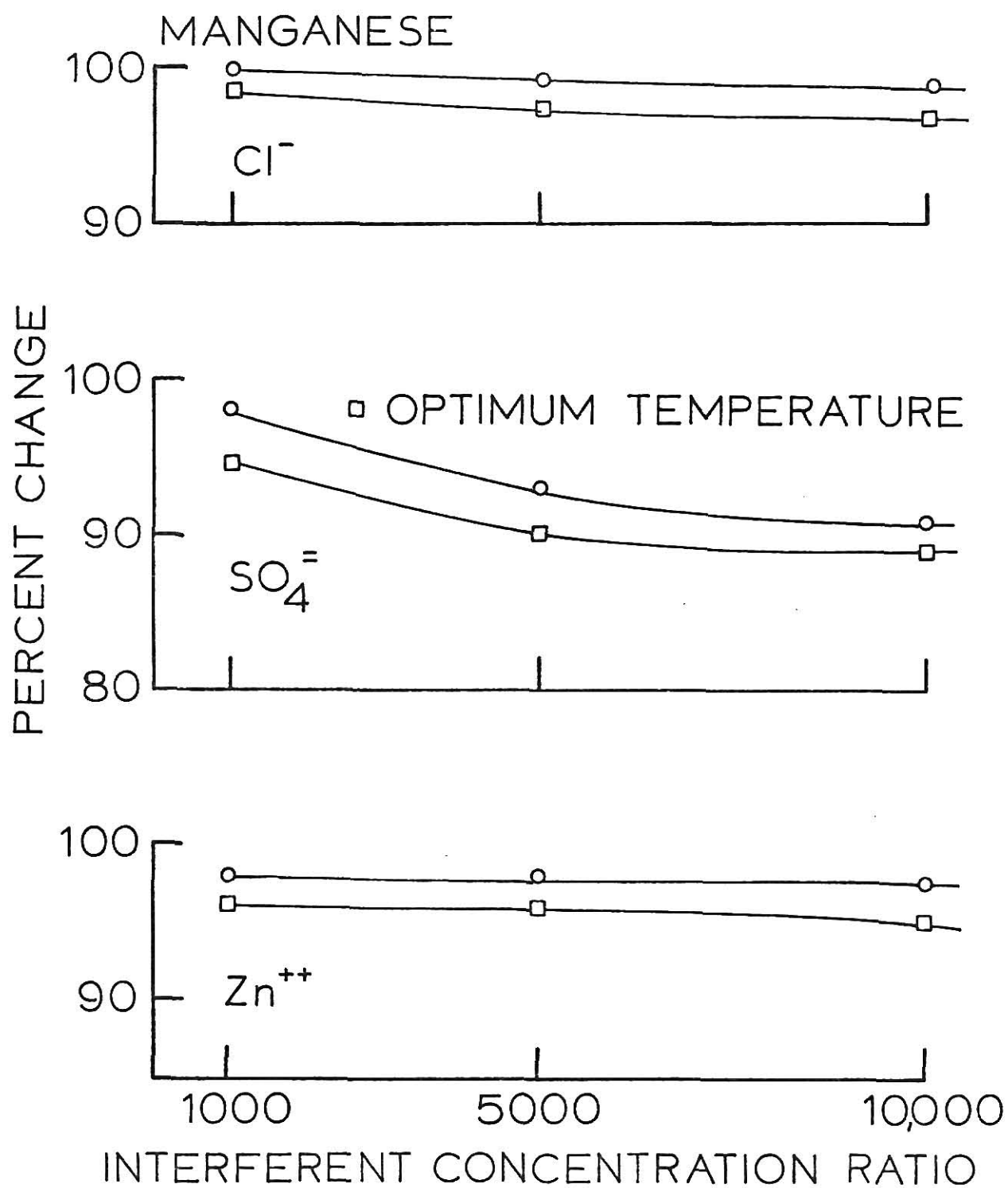
The other study in each case denotes a temperature higher than that of the optimum temperature.

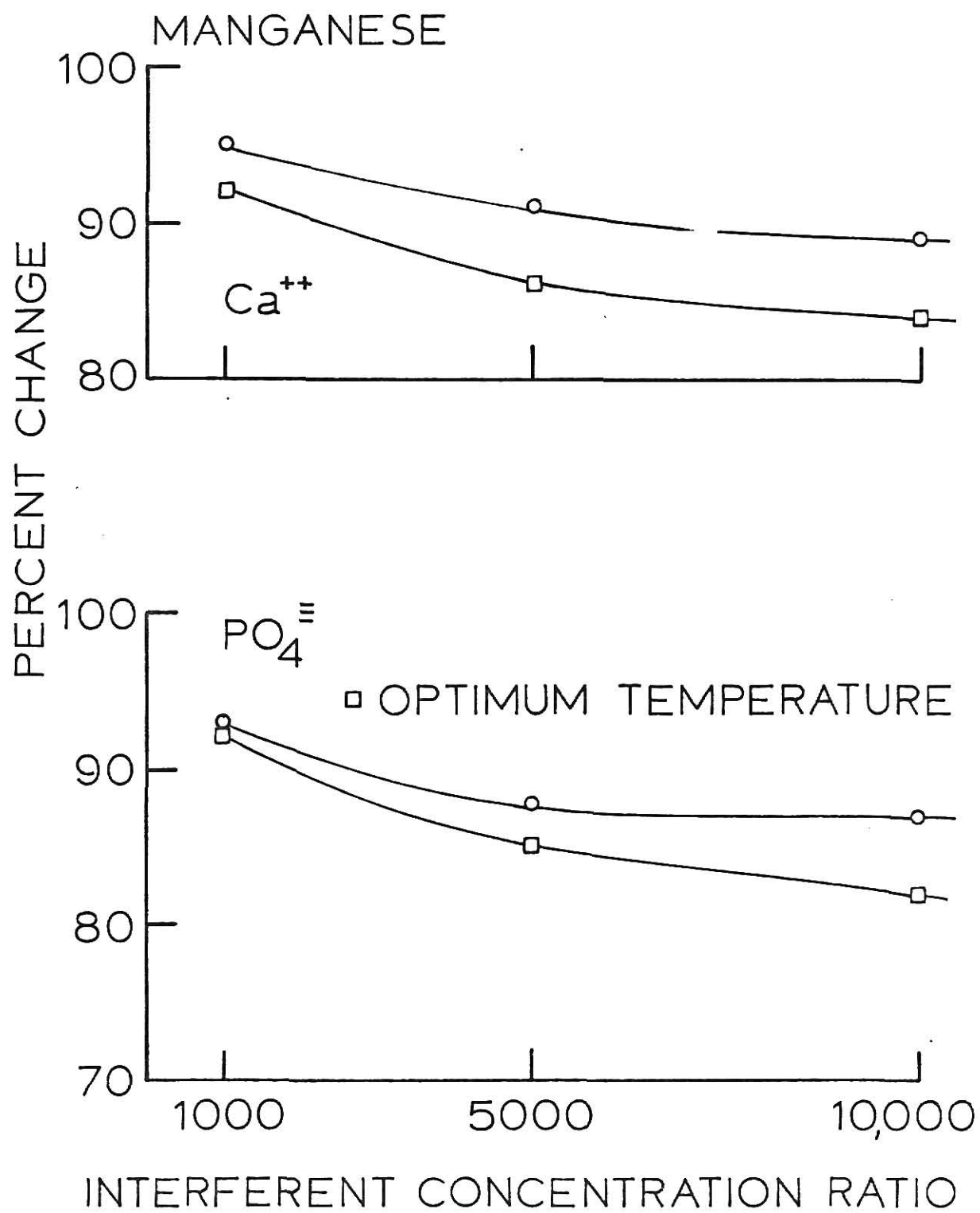












could be caused by incomplete atomization due to the interferent present. However at the higher temperature, it might be speculated that more of the interferent was also atomized reducing the bulk effect and decreasing the amount of change as more interferent was added. However the higher temperature may have caused the atoms to diffuse more rapidly through the optical path causing an overall decrease in the absorption signal (23).

Ionization Effect

The next experiment investigated was the interference effect of an easily ionizable element in the presence of another easily ionizable material. Sodium was chosen as the analyte and Li^+ , Rb^+ , and Cs^+ were used as the interferents.

Atomic emission techniques are usually used to determine Na, however, because of the small amount of sample used, the emission technique was not suitable.

Since a commercial sodium hollow cathode lamp was not available a demountable hollow cathode lamp was employed. Figure 40 illustrates the design of the tube used. The cathode consisted of a cylindrical piece of ultra pure carbon in which a hole was drilled in the center. The metal or salt of the desired element was placed in the cathode cavity.

Different sodium salts were investigated with the use of the demountable hollow cathode to determine which would be more stable and produce an intense sodium line emission. NaCO_3 was chosen for the cathode salt and Figure 41 represents the stability of this element's emission response.

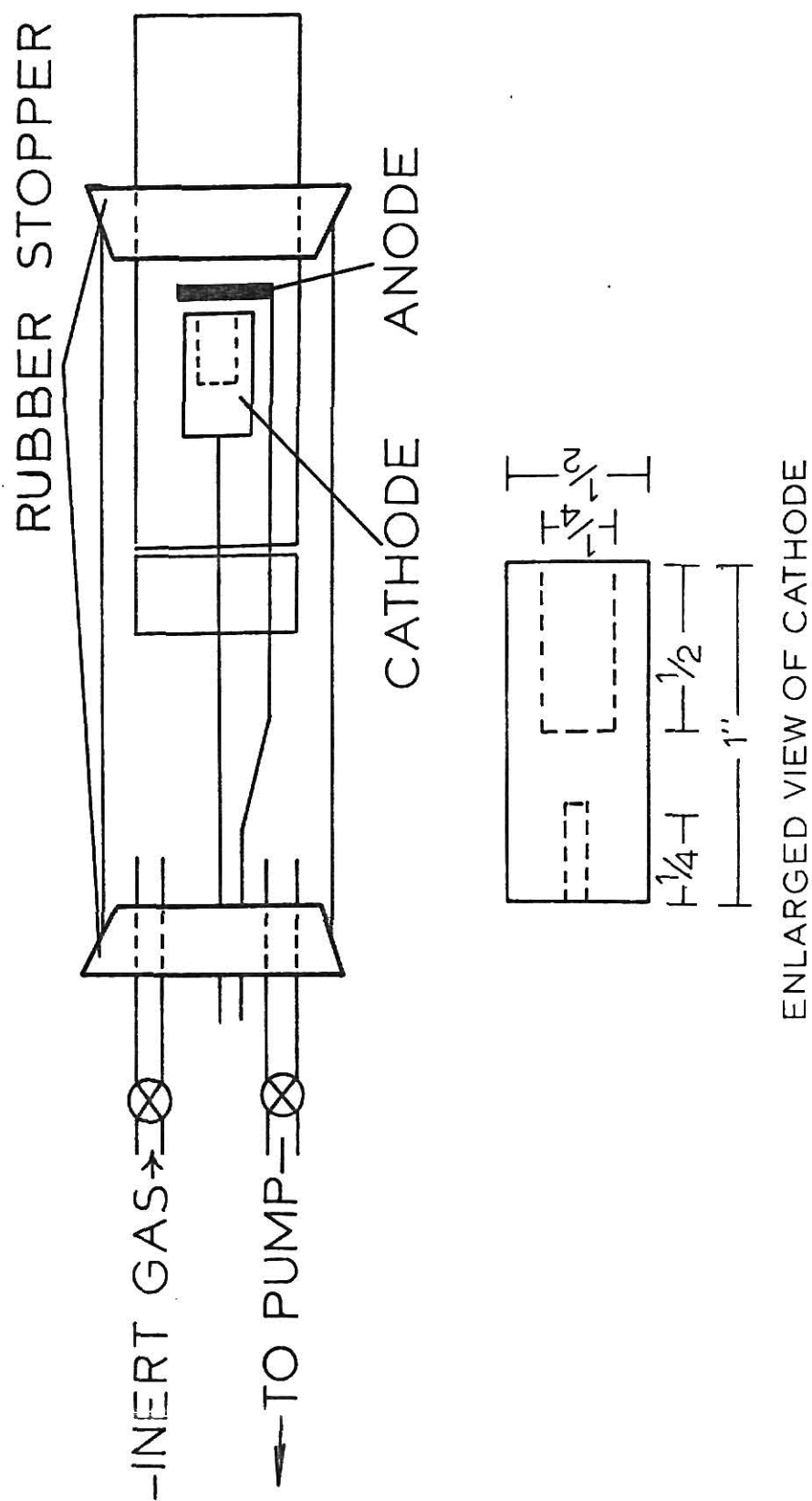


Figure 40. Schematic diagram of the demountable hollow cathode tube.

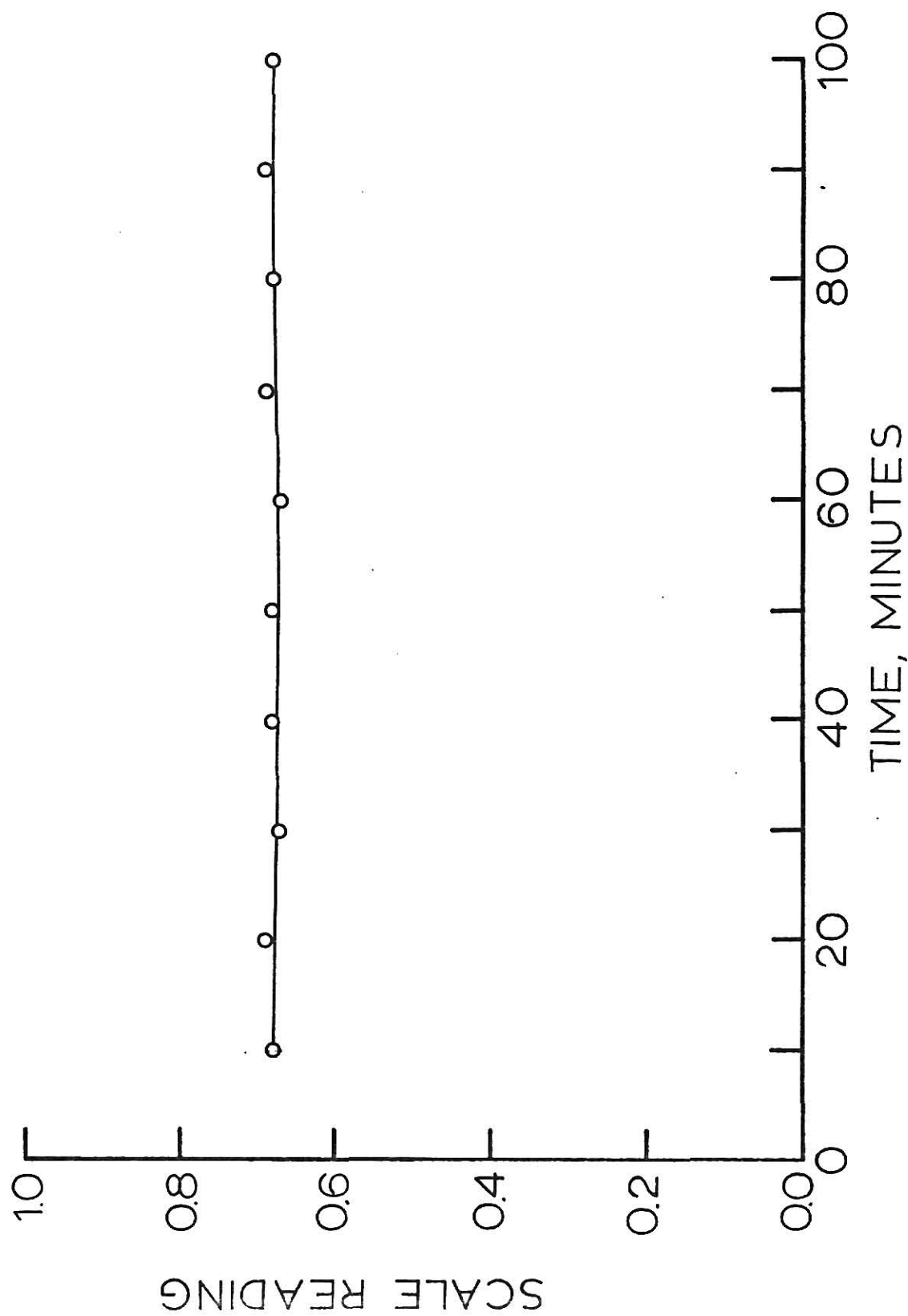


Figure 41. Stability of the Sodium demountable hollow cathode tube.

A calibration curve was constructed for sodium to insure that the demountable lamp and the system was functioning properly. Figure 42 shows the calibration curve was quite linear.

Li^+ , Rb^+ , and Cs^+ were added to solutions of Na in concentrations of 1, 10, and 100 times the concentration of the Na ion. The experimental parameters for this study are shown in Table 8.

Table 8. Experimental Parameters for the Ionization Effect.

Wavelength (Å):	5980
PAR Sensitivity (μV):	500
Photomultiplier Voltage (volts):	500
Hollow Cathode Current (mA):	10.0
Purge Gas:	Argon
Purge Gas Pressure:	1 atm
Analysis Time (sec):	1.0
Variac Setting for Analysis Time:	20
Dry Time (sec):	15
Variac Setting for Dry Time:	4
Height above Boat (mm):	2.0
Concentration of Analyte (g/μl):	1×10^{-11}

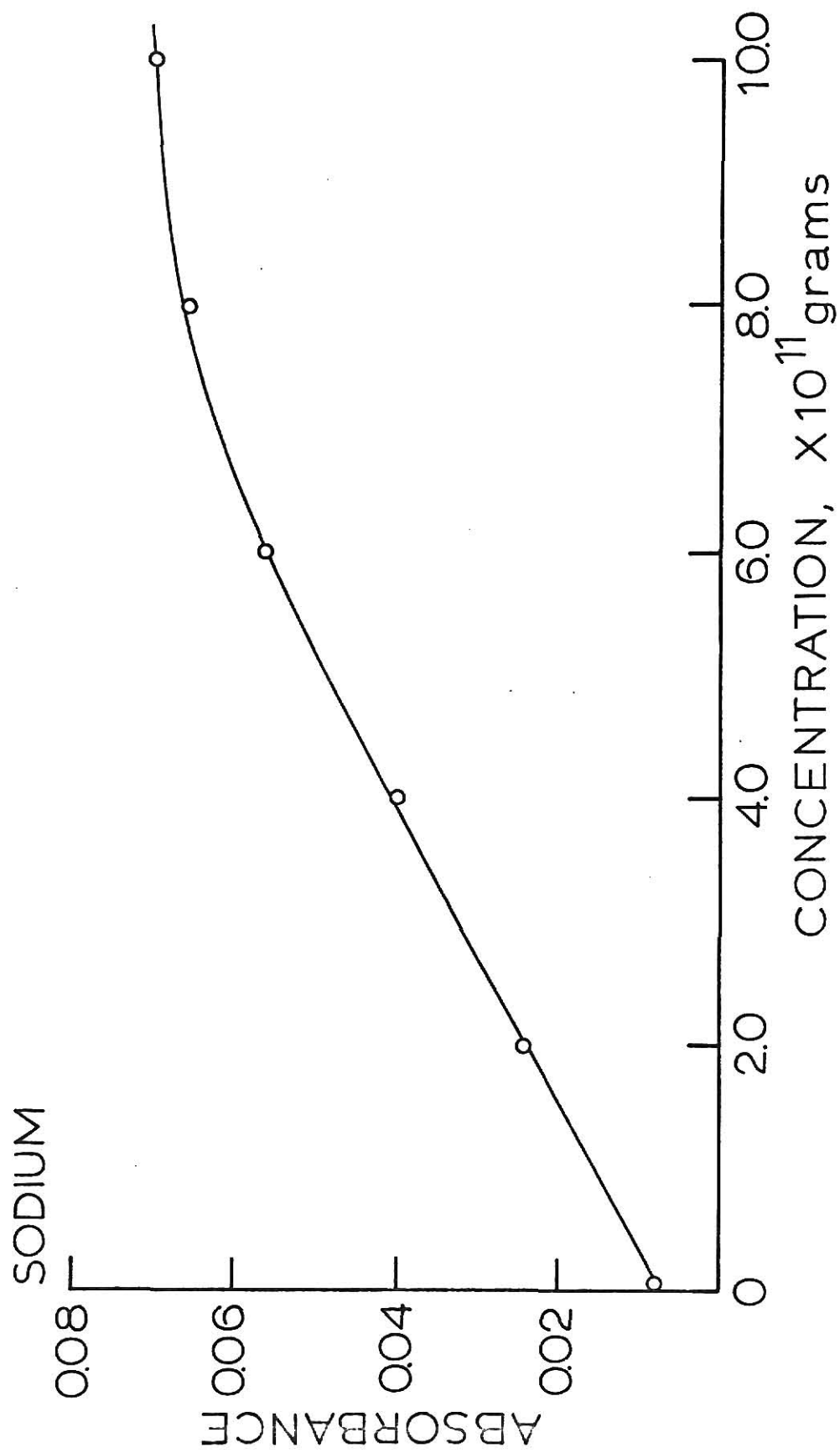
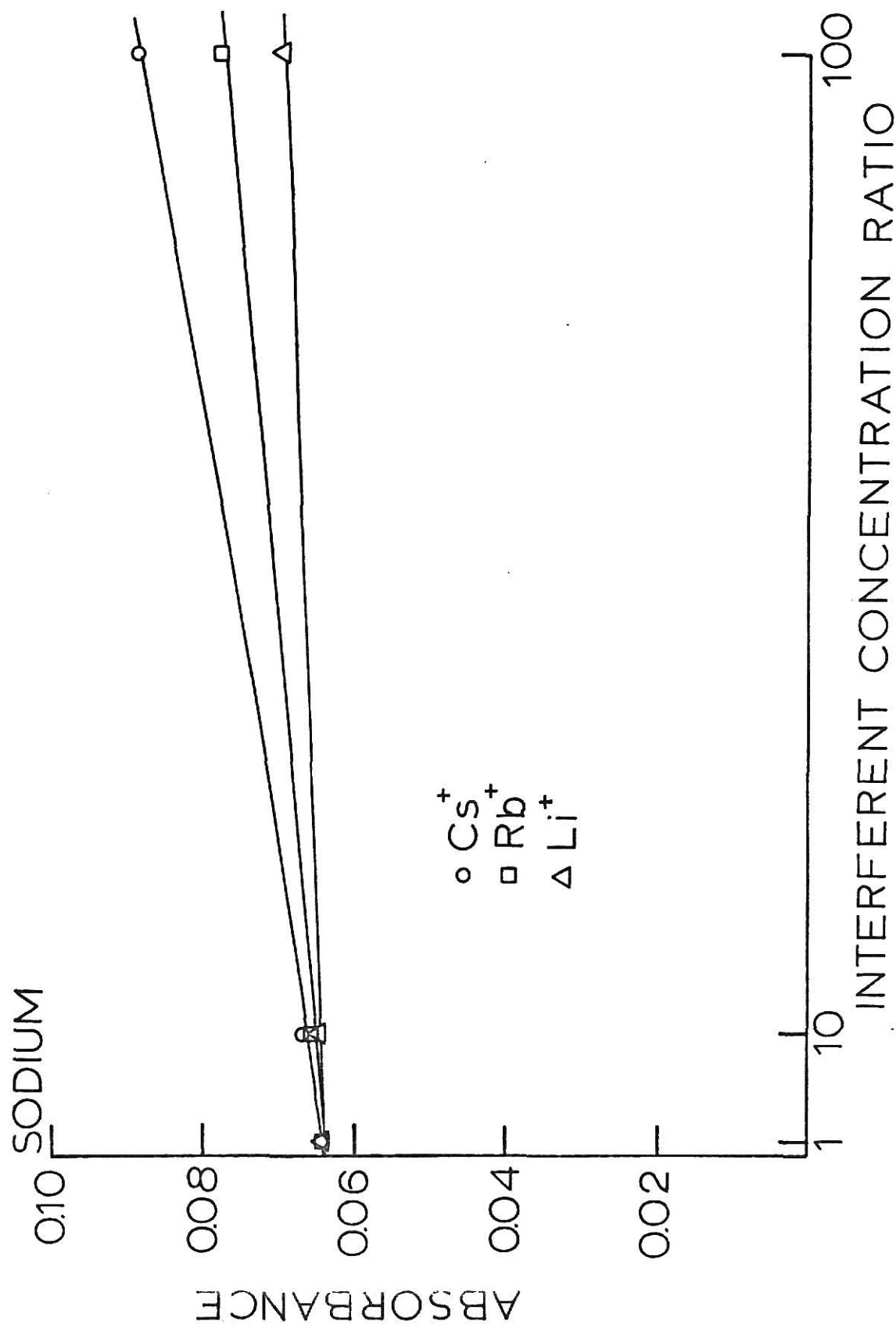


Figure 42. Calibration curve for Sodium.

The results of this investigation are shown in Figure 43. Contrary to the ionization effect exhibited in the flame little ionization interference was observed with the use of the tantalum boat system. In the ionization interference that did occur, Cs produced the most and Li the least. This was to be expected since Cs is the easiest ionized and Li the least. Also the interference increased as a higher concentration of interferent was used. This was probably due to more electrons being present to aid the ionization process.

EXPLANATION: FIG. 43

The Interferent Concentration Ratio is the ratio of the interferent to that of the analyte for the element studied.



Conclusions

The flameless atomic absorption system developed in this study exhibits a number of characteristics which indicate that it can be used to advantage in many trace element analysis problems.

The design of the absorption unit allows an ease in sample introduction and the modified gas and electrical systems provide an overall ease of operation. The operation of the system allows the rapid determination of various samples. The system is very economical to operate requiring only two liters per minute argon as a purge gas and sample boats constructed from commercially available tantalum.

Sensitivity is sufficiently high for the system to be utilized in a wide range of trace analysis using minimum amounts of sample. The high degree of stability permits the use of simple data handling and the good reproducibility allows minimum replication of analyses. The linear analytical response for many elements simplified sample preparation procedures.

The determination of trace elements with differing amounts of interferences present seems to be much less than those associated with the conventional flame process. The main disadvantage of the system is the interference effect associated with the formation of certain oxides, however the high temperature of the tantalum boat reduces most of these interferences to a tolerable level except in the cases of Ca^{++} , $\text{PO}_4^{=}$, and $\text{SO}_4^{=}$. Ionization interferences prove to be almost nonexistent.

Memory effects, different matrix conditions, and other associated interference conditions to a wider range of samples need to be thoroughly investigated before the full utility of the system can be determined. However, at the present time, the system is quite adequate in the determination of many trace elements with a variety of interferents present.

ACKNOWLEDGMENT

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THE DESIGN AND SOME ABSORPTION CHARACTERISTICS
OF A TANTALUM BOAT ATOMIZING SYSTEM FOR
ATOMIC ABSORPTION SPECTROSCOPY

BY

RICHARD TODD EVERSON

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The need for a rapid and simple method of analysis in atomic absorption for the determination of ultra trace elements has lead to the construction of many non-flame absorption systems. One such system, the tantalum boat unit, was developed and constructed to provide an ease of operation and improved sensitivity over the conventional flame.

Modifications in the construction of the system provided many operational improvements over previously constructed units. The final design of the unit and system are presented in detail.

Operating conditions for performing the analysis of different elements were established for the system. The temperature and current flow at different variac settings were determined for the different tantalum boats used.

Optimum tantalum boat temperatures for zinc, copper, manganese, and iron were characterized and a time-related study of the current application to the absorption peak was also investigated. Calibration curves for zinc, copper, manganese, and sodium were determined and showed that the analytical response was quite linear over an order of magnitude. Sensitivities and detection limits were calculated from these curves for the different elements studied.

The absorption response of different compounds of the same element i.e. ZnCl_2 , ZnSO_4 , and $\text{Zn}(\text{NO}_3)_2$, were obtained to determine whether the different compounds of the same element produced the same absorption response. The investigation was conducted for zinc, copper, and magnesium and in

no case was the absorption signal of the different compounds the same. However the biggest deviation was only 11 percent.

Other ions known to affect the response of elements in the flame, including Fe^{++} , Na^+ , Ca^{++} , Mg^{++} , Cl^- , $\text{PO}_4^{=}$, and $\text{SO}_4^{=}$, were added to the analyte in concentration of 1, 10, 100, 1000, 5000, and 10,000 times the concentration of the analyte. The elements, zinc, copper, and manganese, were studied for possible interference effects. $\text{PO}_4^{=}$, and $\text{SO}_4^{=}$, produced small decreases in the elements response when added in concentrations above 1000 times that of the analyte and Ca^{++} produced as much as a 20 percent decrease in the absorption signal when added to the analyte in the highest concentration.

Ionization interferences when Cs^+ , Rb^+ , and Li^+ were added to sodium in concentrations of 1, 10, and 100 times that of sodium were almost non-existent.