Constant temperature electrothermal atomizers as a solution to matrix interferences in atomic absorption spectroscopy
by Lynn Robert Hageman

A thesis submitted in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Chemistry
Montana State University
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Abstract:
The application of electrothermal atomization techniques for atomic absorption spectroscopy has increased many fold in recent years. Along with this widespread application, matrix interferences in pulsed-type electrothermal atomizers have been observed. Until recently, few interference studies have involved constant temperature electrothermal atomizers. In this thesis a comparison is made of interferences in pulsed-type versus constant temperature atomizers for various metals.

During the one to three seconds necessary to heat commercial electrothermal atomizers to the desired atomization temperature, many reactions take place and analyte compounds may be lost from the rapidly heating furnace at varying temperatures with varying matrices—often at sub-optimal temperatures with inadequate atomization, since residence times are short. Thus, matrix interferences are common in these pulsed-type atomizers. However, the same solutions, when atomized in a constant temperature furnace (CTP), show no significant matrix interferences. Lack of ruggedness of analytical procedures using pulsed-type atomizers seems to be an inherent limitation, whereas equipment ruggedness limitations of the GTF are amenable to elimination by appropriate attention to engineering aspects of fabrication. Difficult samples representing common matrices reveal the ease of obtaining interference free results directly with the CTF--and the difficulty, even with pretreatments, of correcting for interferences on a routine basis in pulsed-type atomizers.

CONSTANT TEMPERATURE ELECTROTHERMAL ATOMIZERS AS A SOLUTION TO MATRIX INTERFERENCES IN ATOMIC ABSORPTION SPECTROSCOPY

by

LYNN ROBERT HAGEMAN

A thesis submitted in partial fulfillment
of the requirements for the degree

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Approved:

Ray W. Woodriff
Chairperson, Graduate Committee

Edwin H. Abbott
Head, Major Department

Henry L. Parsons
Graduate Dean

MONTANA STATE UNIVERSITY
Bozeman, Montana

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ABSTRACT

The application of electrothermal atomization techniques for atomic absorption spectroscopy has increased many fold in recent years. Along with this widespread application, matrix interferences in pulsed-type electrothermal atomizers have been observed. Until recently, few interference studies have involved constant temperature electrothermal atomizers. In this thesis a comparison is made of interferences in pulsed-type versus constant temperature atomizers for various metals.

During the one to three seconds necessary to heat commercial electrothermal atomizers to the desired atomization temperature, many reactions take place and analyte compounds may be lost from the rapidly heating furnace at varying temperatures with varying matrices--often at sub-optimal temperatures with inadequate atomization, since residence times are short. Thus, matrix interferences are common in these pulsed-type atomizers. However, the same solutions, when atomized in a constant temperature furnace (CTF), show no significant matrix interferences. Lack of ruggedness of analytical procedures using pulsed-type atomizers seems to be an inherent limitation, whereas equipment ruggedness limitations of the CTF are amenable to elimination by appropriate attention to engineering aspects of fabrication. Difficult samples representing common matrices reveal the ease of obtaining interference free results directly with the CTF--and the difficulty, even with pretreatments, of correcting for interferences on a routine basis in pulsed-type atomizers.

INTRODUCTION

HISTORY

Atomic absorption (AA) has developed into the most widely used technique for analysis of metals and many metalloids [1] since its introduction as an analytical technique about 20 years ago [2]. The widespread use is justified by its versatility, low cost, and high sensitivity. In addition, the high degree of selectivity and relative freedom from interferences are obvious advantages over conventional emission spectrometry. Although considerable research has been aimed at higher sensitivities and lower detection limits, the most ubiquitous and most pressing problem in using the technique is one of matrix interferences - in many cases the response to an analyte in distilled water is simply not the same as the response in a more complex matrix. If all analyte atoms were desolvated, dehydrated, decomposed, and atomized at the same rate regardless of matrix components few interferences would exist [3]. This of course has not been the case for flame [3-5] and most electrothermal atomizers [6-10].

Theoretically, electrothermal (ET) atomization is an absolute method of quantitative analysis by AA spectra involving complete vaporization and atomization of a known amount of substance in a graphite cell. In a 1959 publication by L'vov [11] dealing with ET technique of sample atomization, it is concluded that matrix effects

on the results of the quantitative analysis are eliminated, providing considerable advantage over flame version of atomic absorption as well as over the emission methods of spectral analysis. The conclusion was supported by manganese analyses in the presence of NaCl $Pb(NO_3)_2$, and $Sr(NO_3)_2$. Subsequent publications [12, 13] also indicated absence of matrix effects. But since that early work, numerous publications have appeared in the literature [14-18] dealing with significant and varied interference problems associated with ET atomization for AA spectroscopy. If L'vov's early findings with electrothermal atomizers are correct, interference problems are now present in a technique which theoretically should not have interference problems.

The history of electrothermal atomization use with atomic absorption spectroscopy can be divided into two periods. The boundary between the two periods is sometime in the late 1960's. The first period witnessed the emergence of electrothermal atomization, development, and use by research teams on laboratory designed equipment. The second period, involved the rapid spread of ET atomization methods in analytical laboratories as a promising method of microanalyses due to the advent of commercially available equipment.

Excellent work was done during the first historical period by L'vov in Russia. L'vov developed a graphite atomizer which involves

a graphite tube (40 mm by 2.5 mm) held constantly at a high temperature in the optical path of the AA instrument (see Figure 1,a). The graphite tube is heated to the desired temperature and maintained at this temperature by an electric current and resistance heating. The samples contained in a small carbon cup, are brought to an opening in the side of this tube and heated to attain vaporization and atomization by a separate power supply. The entire atomizer is enclosed in a chamber pressurized with argon. This chamber must be depressurized and the carbon tube must be cooled before the next group of samples can be introduced to the chamber. Extensive work has been done with this type of atomizer attaining very good absolute sensitivities and as has been stated previously with very few matrix effects.

At about the same time that L'vov was developing his graphite atomizer, a similar type was developed by Woodriff and associates at Montana State University [19-21]. It is similar to that of L'vov's in that the graphite tube is maintained at constant temperature in the optical path by resistance heating (Figure 1,b). The sample, introduction, on the other hand, is at atmospheric pressure against a stream of argon. The Woodriff Constant Temperature Furnace (300 mm by 7 mm) is also larger than that developed by L'vov. No auxillary power supply is necessary for the volatilization of

sample. A stream of argon is also used to flush the graphite tube as a means of preventing oxidation.

During this period, Massmann in Germany[22], also developed an electrothermal atomizer. This atomizer consisted of a graphite tube 55 mm long with an inside diameter of 8 mm supported at the ends by water cooled electrodes (Figure 1, e). It employs a different mode of operation than the two ET atomizers discussed previously. The sample is placed in the tube at room temperature. A three step program is then employed - drying the sample near 370 K, ashing the sample from 370 to 1800 K depending on the matrix and finally, atomizing at temperatures as high as 3300 K. A sheath of Ar or N_2 is used to reduce reaction with O_2 in the air.

At the onset of the second historical period, when electrothermal atomizers became readily available through commercial production, the companies involved opted to use the most simple equipment and technique, which is the Massmann design. The Massmann design was adopted essentially without change by Perkin-Elmer Instrument Company, and a mini-Massmann ET atomizer was developed by Amos and Matousek[23] and adopted by Varian Techtron Instrument (Figure 1, d). The mini-Massmann or carbon rod atomizer (CRA) is operated with the same type of three step program as the Massmann, but is much smaller in size (9 mm long with an inside diameter of

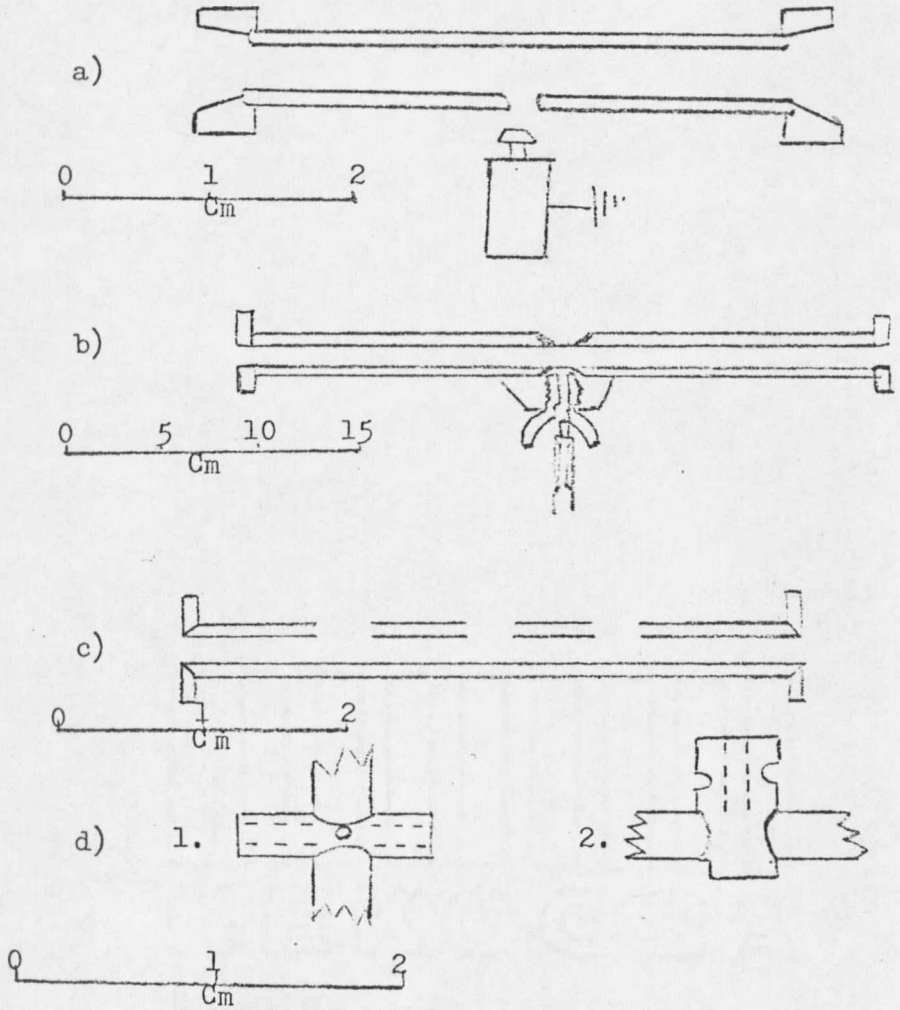


Figure 1. Electrothermal atomizers

a) L'vov Constant Temperature Furnace

b) Woodriff Constant Temperature Furnace

c) Massmann Pulsed-Type Atomizer

d) Varian Mini-Massmann Atomizer
   1. Carbon Rod Atomizer
   2. Carbon Cup Atomizer

3 mm). There have been some other ET atomizers developed since 1970 such as, Instrumental Laboratories graphite furnace, but the present state-of-the art of ET atomizers is still divided into two types. The first being the constant temperature type where the atomizing chamber is held constantly at optimum atomization temperature and the samples are introduced to it. The second type includes the commercially available ET atomizers using a pulsed-type mode of operation; i.e., introduction of sample at room temperature, drying, ashing, and finally volatizing and atomizing under condition of rapidly increasing temperature. Although "electrothermal" is probably the most descriptive nomenclature, during the first period electrothermal atomizers were generally referred to as furnace atomizers and the first commercial electrothermal atomizers were referred to as "flameless" or "nonflame", as opposed to previous "flame" atomizers. Therefore, occasionally in this thesis when referring to previous literature reports, the terms furnace or flameless atomizer are used interchangeably with electrothermal atomizer.

The commercial atomizers were accepted enthusiastically during the early 1970's with expectations of analytical applications to essentially all metals in any type of sample. Many methods were published, especially by instrument companies, with no mention of interferences. However, perusal of the ever-growing number of

recent publications in the field of AA analysis using ET atomization of samples, it could be concluded that, unfortunately, ET atomization has not lived up to this high expectation. Rather, the reverse has taken place, a disappointment exists regarding the possibility of ET atomizers for complete atomization and absolute methods. In fact, the trend in recent literature is toward cataloging the many matrix interferences that are observed and then working out an organic chelation and extraction, matrix modification, coprecipitation, or standard addition to alleviate the problem. All these techniques involve time, possibility for contamination, and often are applicable only to a specific type of sample. Also reported recently is an unpredicatable dependence of sensitivity on the conditions of measurement such as: heating mode, position of the sample in the furnace, gas flow rate, age of tube, etc. This has lead up to statements such as: "...It has become apparent for sometime that the greatest barrier to the acceptance of flameless atomization as a normal tool in atomic absorption spectrometry is its susceptibility to matrix interferences[24]". Such statements resulted in the contention that electrothermal atomizers, in general, are very susceptible to matrix interference, an opinion which is contradictory to theoretical evaluation and optimistic forecast of the early publications.

STATEMENT OF THE PROBLEM

The purpose of this work was to establish a matrix interference comparison of commercially available ET atomizers to the constant temperature ET atomizer developed at Montana State University. The comparison was made on the basis of data accumulated in this laboratory, some of which has already been reported in recent literature, and on data reported in the literature by other investigators. Through this comparison, it was intended that a better understanding of the mechanisms and causes of interferences in the pulsed atomizers would be derived. Several elements, representing a broad spectrum of properties, have been used to accomplish this comparison. The instrumentation and experimental set up allowed for direct comparison on the same solutions with the atomizer being the only significant variable.

INTRODUCTION TO MATRIX EFFECTS

There are several general considerations to take into account when considering possible ways in which matrix materials can affect analyte absorption signals. Chemical matrix interferences can have an effect on the rate of atomization of the analyte. This influences the sensitivity in two ways. First, absorption can be lowered because some of the atoms may have time to leave the light path before the last evaporates. Second, a change in atomization rate can also

change the time at which the maximum analyte atom concentration enters the light path. In pulsed-type atomizers, where the temperature is changing rapidly, this means that the peak reading will be taken at different temperatures depending on the matrix elements. Absolute sensitivity in general varies with temperature, that is if atomization is delayed until the temperature has increased, the diffusion rate will also have increased and less absorption will be observed than at lower temperatures. Chemical interferences may also be attributed to formation of compounds which are volatile at the temperatures attained in ET atomizers, but yet have enough stability to escape without atomization. This could include either a recombination of analyte atoms with interferents, or a lack of dissociation of volatile analyte containing compounds before atomization temperature is achieved. Chemical interferents such as these will receive the most attention in following discussion, but there are other ways in which matrix materials affect analyte absorption of which the investigator need be aware.

For example, as the matrix becomes gaseous it tends to sweep the analyte out of the chamber. A long chamber helps to minimize loss of analyte. Another physical effect which may be an extreme of the first, involves the loss of agglomerates of matrix with analyte trapped in them during the period of rapid volatilization and

expansion. Compound formation with the walls of the atomizer is thought to be responsible for matrix effects when certain elements such as boron or tungsten are involved in the matrix.

Matrix materials can also cause interferences by broad band absorption (background absorption) and scattering of light from condensed particles. Effective methods have been developed for avoiding these two types of nonatomic absorption except for excessive background absorption that occurs with some organic matter[25-27]. Most techniques used to correct for non-atomic absorption involve its measurement by use of a continuum lamp source such as hydrogen or deuterium hollow cathode lamps. This absorption is then subtracted from the total absorption measured when using the elemental hollow cathode lamp of the analyte. The total absorption minus the nonatomic absorption is then equal to the atomic absorption of interest. Most of the early work with electrothermal atomizers therefore, involved introduction of the sample twice to obtain a single atomic absorption. One measurement is made with the elemental lamp in place to measure the total and one with the continuum lamp to measure nonatomic absorption. In this work, total and nonatomic absorption were measured on one sample introduction by a technique of simultaneous background correction. When using this technique, light from both the continuum and elemental lamp are

directed along the optical path by means of beam splitter. The current through the two lamps is adjusted to provide equal intensity. The two lamps are pulsed out of phase so that the lock-in amplifier which is designed to detect only the AC signal will output only the atomic absorption with the nonatomic absorption already subtracted electronically.

EXPERIMENTAL

INSTRUMENTATION

Several instruments were employed in collecting the data presented in this thesis. A Varian AA-5 spectrophotometer equipped with an IM-6 lock-in amplifier conversion module, BC-6 simultaneous background corrector, model 63 carbon rod atomizer, and a Beckman model 1005 strip chart recorder was used for collection of most of the data involving the carbon rod atomizer. A Varian AA 1150, also with simultaneous background correction and a model 63 carbon rod atomizer was used at times for confirmation of the results. This was done to assure that a certain interference was not just a characteristic of the instrument being used, but was indeed a characteristic common to the mini-Massmann model 63 CRA.

Most of the comparison data for the constant temperature electrothermal atomizer that is shown in the charts and figures was been obtained when using a Varian AA-6 spectrophotometer equipped with a BC-6 simultaneous background corrector, a Beckman model 1005 strip chart recorder, and the constant temperature ET atomizer developed at Montana State University. Some minor adaptations were necessary to allow convenient use of the CTA in the Varian AA-6. These modifications involved raising the ends of the spectrophotometer to allow access to the bottom of the constant temperature

atomizer (CTA) for sample introduction, removal of the housing which normally encases the flame area, and removal of the lens which normally focuses light on the entrance slit of the monochromator (Figure 2). A focusing lens is included in the exit end cap of the atomizer to avoid use of the extra lens. This instrument is excellent for the comparison data because the electronics and monochromator are exactly the same as the updated AA-5 used to collect the CRA data. The only difference between the two instruments is the ET atomizer.

Much of the preliminary data using the CTA was obtained on an instrument constructed by combination of available components within the laboratory. These components included a Beckman DU quartz prism - spectrometer equipped with a photomultiplier attachment, a Heathkit D.C. power supply, and a Varian AA-5 lock-in amplifier to provide photomultiplier voltage and output of the absorption signal. The AA-5 amplifier was adapted to enable simultaneous background correction by addition of a logarithmic amplifier for combination of the transmission signals before converting to absorption. A NAND gate was also added to provide a hollow cathode pulse which is 180^{o} out of phase with the normal hollow cathode pulse [28]. Electronic circuitry was constructed to enable the AA-5 amplifier pulses to control the Heathkit D.C. power supply for the hollow

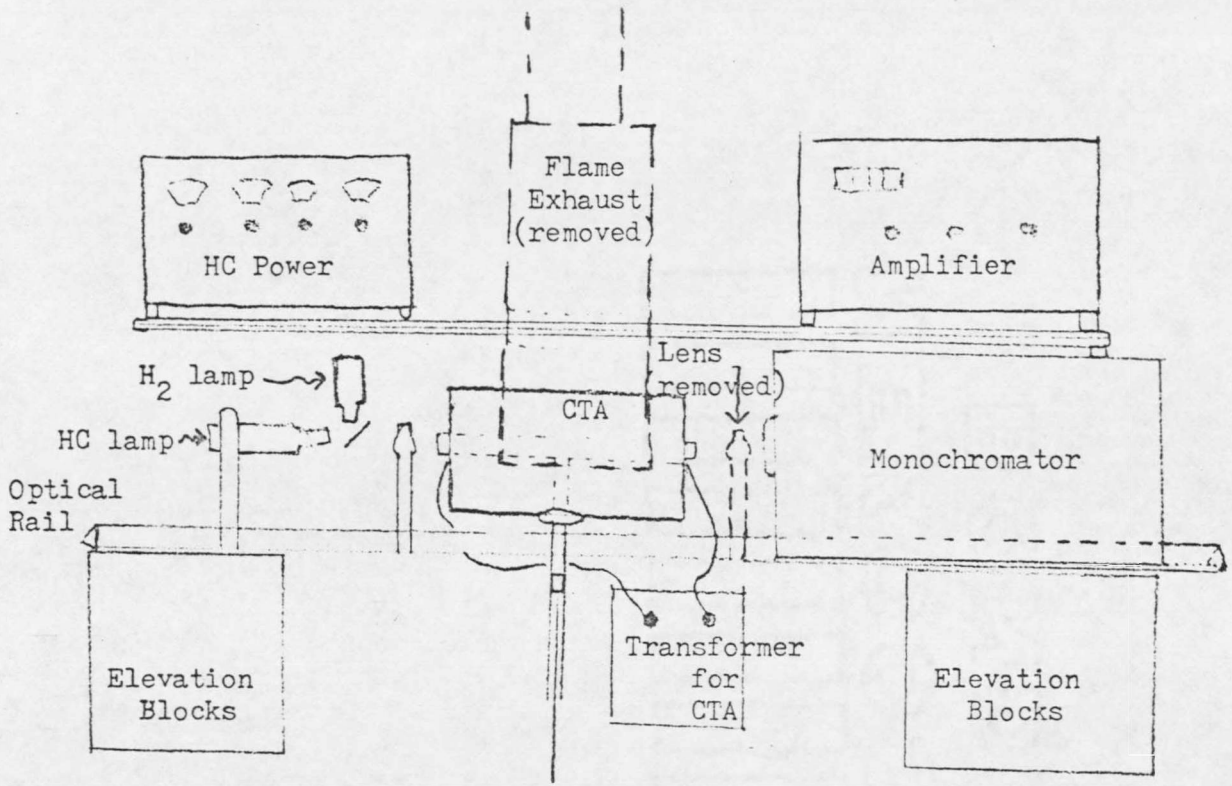


Figure 2. AA-6 Adapted for use with Constant Temperature Furnace.

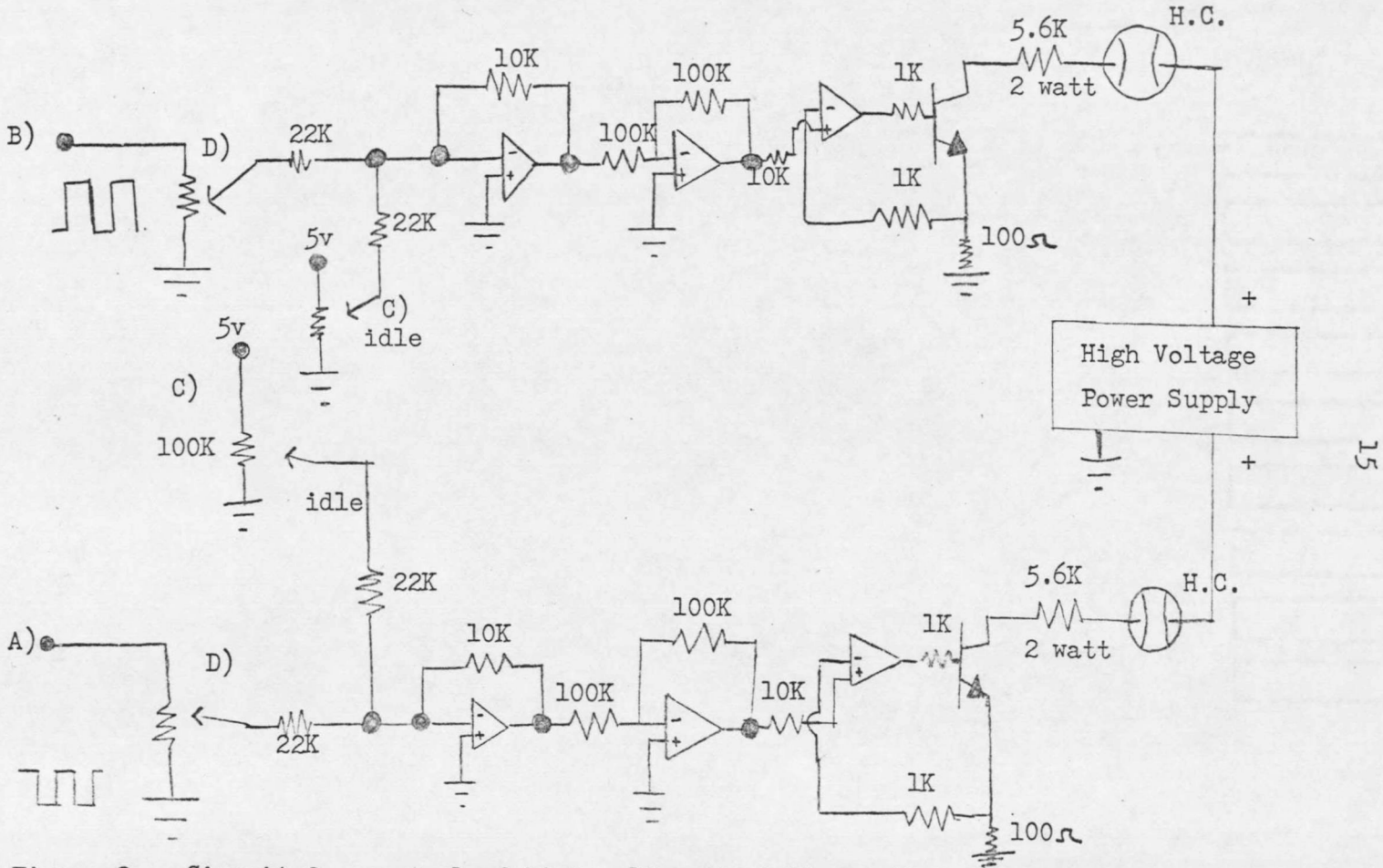


Figure 3. Circuit for control of high voltage to hollow cathode lamps.

cathode lamps. The circuit is shown in Figure 3. This is a two channel circuit to allow for control of two hollow cathode lamps (H_2 lamp and element lamp). The incoming pulses are the normal AA-5 pulse (A) and the out of phase pulse from the NAND gate (B). Therefore, the lamps will be pulsed 180° out of phase by the identical circuits involving several operational amplifiers required for compatibility with the transistor. The TR 60 transistor is necessary for pulsing the high voltage (up to 400 volts) from the Heathkit power supply to the hollow cathode lamps. Two ten-turn pots are used in each channel for controlling the DC idle current (C) and the pulsed current (D).

In addition to the strip chart recorders used, a digital integrator was used for obtaining the area of the absorption signals for both types of ET atomizers. The integrator was constructed with an operational amplifier, voltage-to-frequency converter, and a digital counter. A diagram of the circuit is shown in Figure 4. AA-5 and AA-6 amplifiers both have a 10 mv and 100 mv output. The recorders used in this work have a 10 mv input so that the 100 mv output of the amplifier is available for input to the integrator with no interaction with the recorder. The voltage-to-frequency converter has a linear operation range from 0-10 volts. Therefore, an operational amplifier is used to provide a gain of 100 and a follower amplifier is used to isolate the signal.

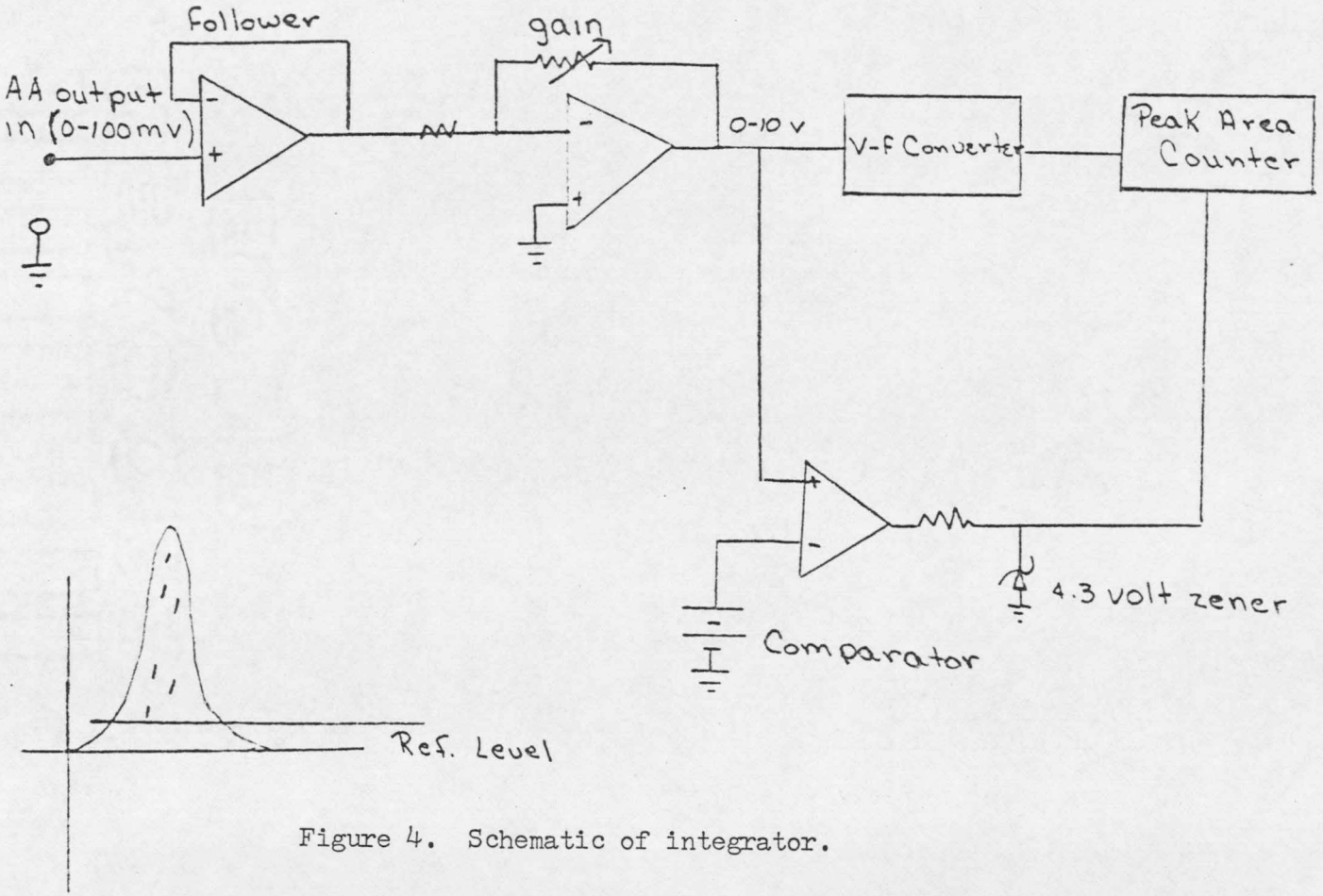


Figure 4. Schematic of integrator.

A reference voltage is established above the noise level at which the comparator starts and stops the digital counter. The number of counts obtained as pulses from the voltage-to-frequency converter is directly proportional to the input voltage, thus directly proportional to peak area. This is illustrated in Figures 5 and 6 by plots of input voltage for a known period of time versus counts, and by a plot of counts versus weight of chart paper for several peaks.

Temperature measurements for the CTA were made with a Pyro-optical pyrometer. Temperature is difficult to measure for the CRA because it can be changing by as much as 800 degrees per second. Therefore, CRA temperature was estimated by combining optical pyrometer readings and plots of temperature versus instrument setting in the Varian manual.

The CRA was operated according to the manufacturer's specifications and directions; ash and atomization temperatures were optimized to minimize interferences. One modification to the manufacturers instructions is that methane was added to the sheath of N_2 during the ashing and atomizing cycles. The purpose of the methane was to assure a reducing atmosphere and to maintain a pyrolytic coating on the carbon atomizer tube. The presence of methane causes only a slight increase in background, which is adequately compensated

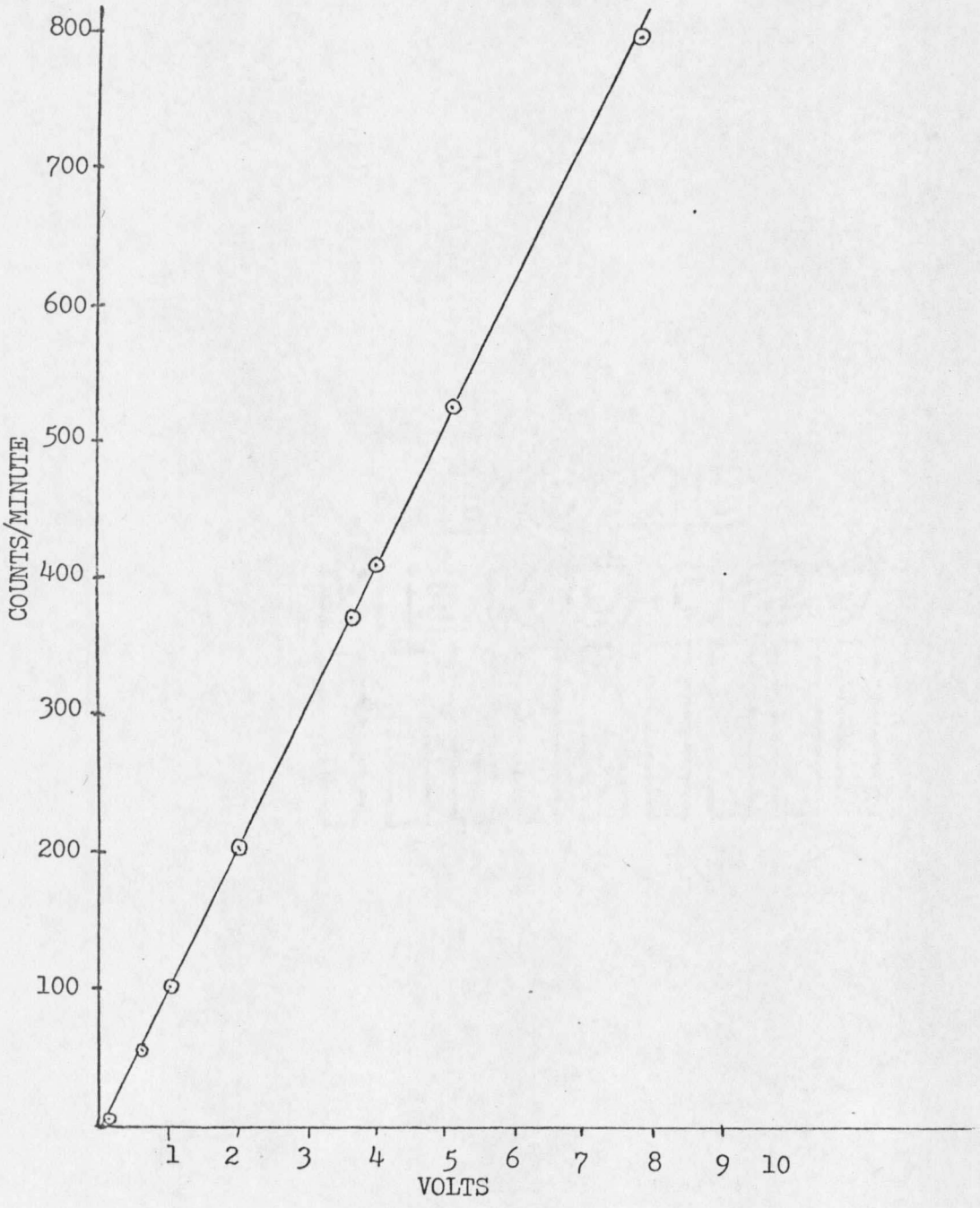


Figure 5. Voltage input versus voltage-to-frequency converter count output.

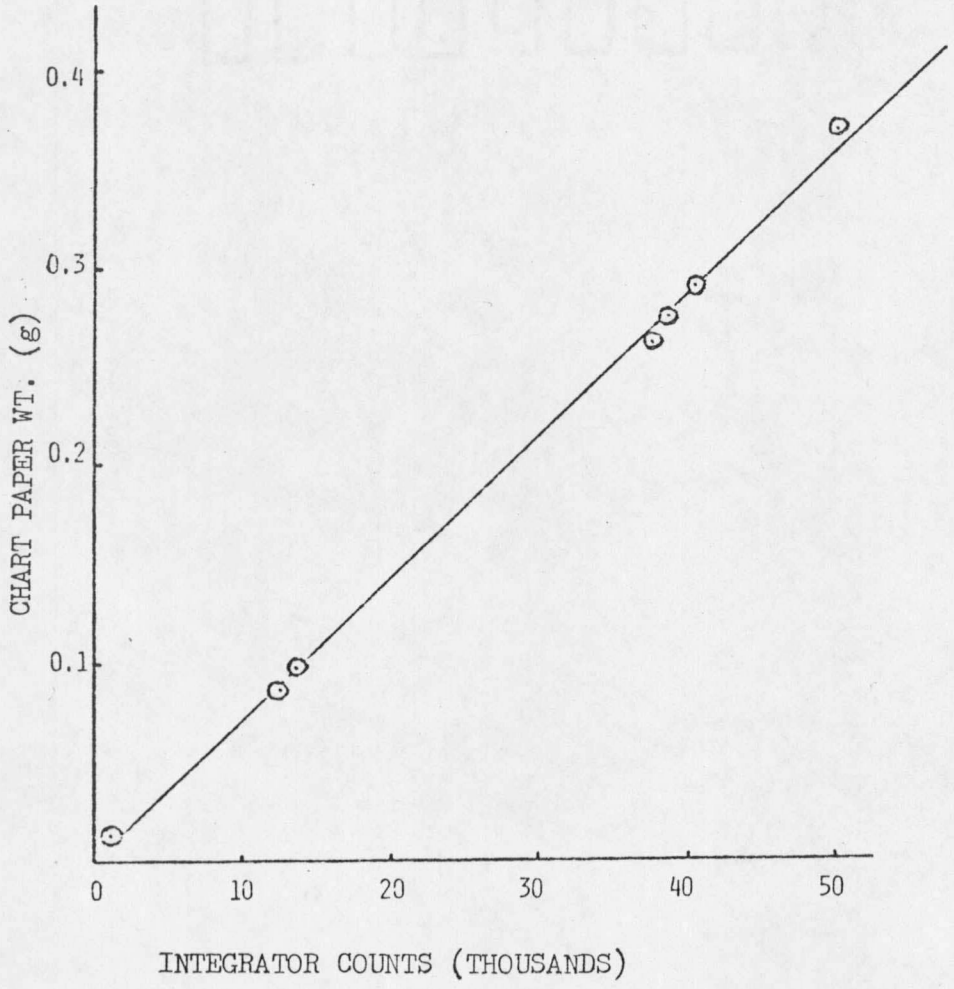


Figure 6. Integrator counts versus weight of chart paper.

for by the simultaneous background correction. Previous reports have shown that methane passing over carbon in a hot environment forms an impermeable pyrolitic coating [29]. In this case it also forms a good electrical connection between the carbon tube and electrodes, which prevents sparking.

The design, construction, and operation of the constant temperature ET atomizer has been adequately discussed in the literature [30-33] so as a matter of convenience only a brief operational description and a schematic drawing of the CTA will be included (Figure 7). The design used in this work is not the most recent or convenient of the CTA, but works efficiently for research applications.

The carbon tube [1] of length 30 cm and diameter one cm in the optical path is maintained at any desired temperature (up to 3000 K) by resistance heating. Samples pipeted into small graphite crucibles [4] and dried subsequently under a heat lamp are introduced into the furnace by means of a pedestal [3] and push rod assembly in the side tube [2], which is at right angles to the optical path. The crucible is flushed with argon as it enters the furnace. Owing to its relatively small mass, the crucible is heated by conduction and radiation rapidly enough that the evaporation time is small in comparison to the residence time. The pedestal makes a seal with the constriction in the side tube and the sample

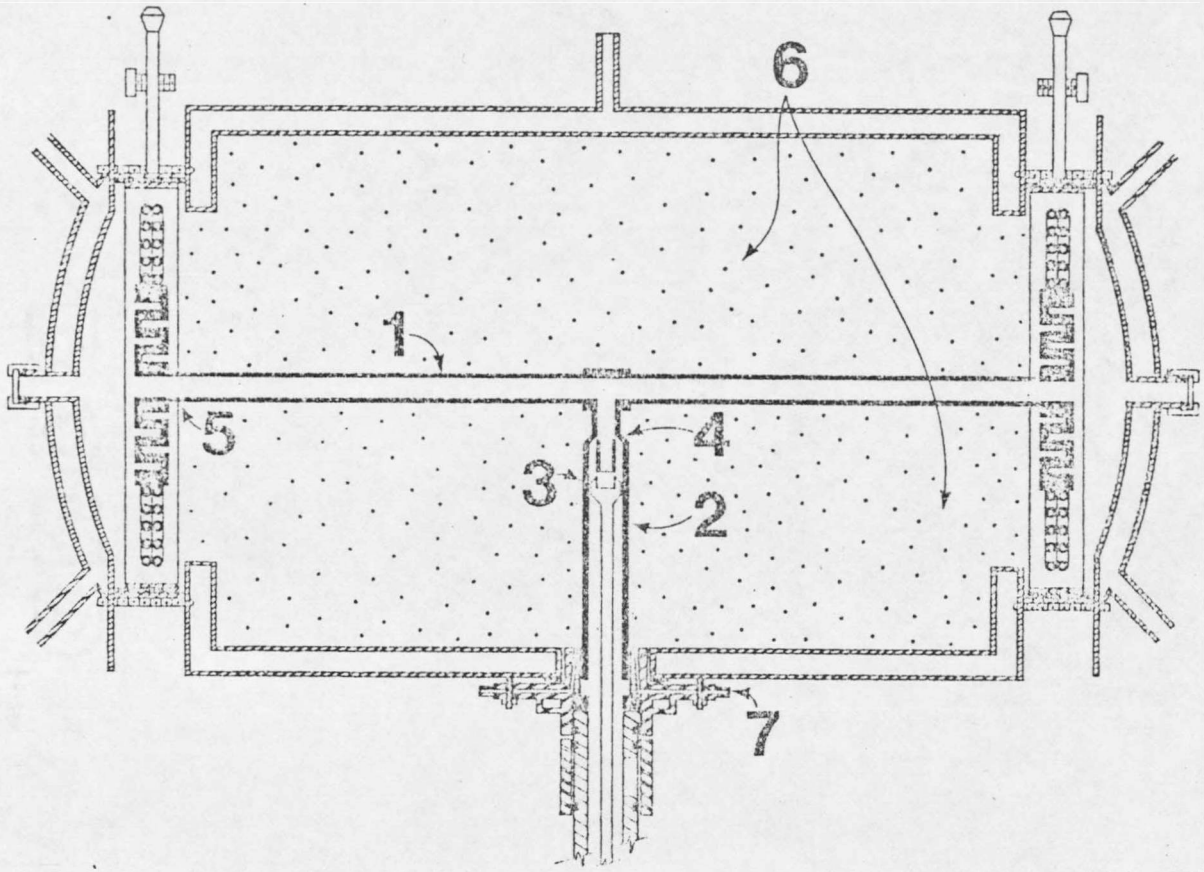


Figure 7. Constant temperature furnace (schmatically). (1) Heater tube, (2) side tube, (3) pedestal, (4) crucible, (5) heater tube holder, (6) thermal insulation, (7) argon inlet.

vapors diffuse out through the heater tube. Graphite felt insulation [6] surrounding the heater tube reduces heat losses, facilitating the use of a small power supply.

Specific instrument settings, pertaining to the elements of interest, are included in each section for both CRA and CTA.

PROCEDURE

Whole fish samples were prepared for analysis using a method of shattering cold, brittle tissue (34). These samples are extremely difficult to homogenize and reduce for representative sampling due to presence of fibrous and bony parts. Therefore, the following procedure was developed and used for sample preparations. Small fish on the order of three grams are handled conveniently in a 100 ml stainless steel blender container. The sample is first chilled with liquid nitrogen (or dry ice), and then placed in the blender with a scoop of dry ice weighing about 10 to 50 grams. Precautions are taken in that the sample is blended immediately. If too much time is allowed the blade/shaft assembly may freeze up within a minute, resulting in "lift-off" of the metal container or other hazards when the power to the blender is turned on. Although the amount of dry ice usually tends toward 10 grams as the sample size decreases, the smallest samples require some extra dry ice just to provide enough bulk for efficient blending.

After the sample has been blended to a powder (usually 10 to 30 seconds suffice) it is poured into a clean container where the dry ice is allowed to sublime. This can take place at a low temperature, if a solid sample is desired or at room temperature if a paste is desired. Samples as small as 5 to 10 mg have been taken routinely for mercury analysis by direct solid sampling [35] and have been found to be homogeneous, that is relative standard deviations of less than 8% in sub samples.

For larger fish (up to 500 g) a pre-shattering with a hammer or mallet is included. The materials used are: liquid nitrogen in a large Dewar flask; plastic bags and canvas for wrapping the sample; and any convenient weight of hammer (e.g. 0.5 kg) or other blunt object. Poly bags (30 by 24 cm, 0.1 mm thick polyethylene, purchased from Fisher) were described in the catalog as flexible when frozen; yet, they became brittle at liquid nitrogen temperatures. Samples are placed on a board with back and side boards to contain any errant sample fragments. Samples are placed in a Baggie or other plastic bag, tied to a long string so that a label can be attached, and immersed in liquid nitrogen until adequately chilled. After freezing, the sample is slipped into a polyethylene bag, which is then folded shut and put into another poly bag; this may be repeated until 3 or 4 poly bags are enclosing the sample. Several bags are needed because the inner bag quickly reaches the

sample temperature and therefore, may shatter; however, the outer bag will stay flexible and should remain (substantially) intact even if 5 or 10 minutes of hammering should be necessary. Finally, the poly-enclosed sample is normally wrapped with a single layer of ordinary, unsized artist's canvas which can be folded shut. The canvas protects the plastic from possible tearing due to impact, as well as providing a margin of safety just in case the plastic bags fail to contain the sample. Using a blunt side of the hammer, vigorous blows are now delivered to the wrapped sample, which shatters by brittle fracture. Large chunks that result are located by feel and successive blows are delivered to break them up until no pieces of excessive size can be found. Then the canvas is removed, the plastic bags are cut or torn open to expose the sample pieces. The sample will most likely be mixed with some broken pieces of plastic, which are visible and easily rejected. If large sample sizes (5 - 10 g) are used for analyses, representative samples may be obtained at this point. The frozen chunks may be placed in an appropriately sized stainless steel blender container and handled as the small fish, to reduce to a fine homogeneous powder, compatible with small sample weight useage.

This shattering of brittle tissue procedure has several advantages aside from convenient handling of bony fibrous samples.

There are obvious advantages of cold temperatures for preservation both of organic matter and metallic species; but less well known are the advantages of handling samples cold and "dry" in minimizing the amount of contamination picked up by the sample [36]. In a frozen sample, all water is present as ice and the surface is devoid of liquid--consequently, adhesion of contaminants is less likely, and there is less contact with container surfaces due to the absence of a flowing medium.

Thus, a modern and versatile sampling method for trace metals was developed to meet four criteria. The method must (1) be able to handle conveniently a wide variety of materials; (2) provide a reasonably representative sample; (3) avoid contamination of the sample by elements of interest (relative to low or high levels present, of course), and include the option of completely omitting any blade from the procedure if larger samples can be used; and (4) allow handling the sample while frozen.

Homogenized fish samples and other biological samples were digested for metals analyses using an acid digestion in a microwave oven [37]. The digestion is accomplished by weighing 3-8 g into a 125 ml Erlenmeyer flask, adding 25 ml of HNO_3 and heating in a microwave oven to achieve lead solubilization and removal of about half of the acid. The digested solution is then transferred

to a 50 ml volumetric flask and made up to volume with deionized water. At this point the solution is ready to be pipetted into the two ET atomizers used in this study.

CHAPTER 1

MANGANESE INTERFERENCES

INTRODUCTION

Significant matrix interferences on manganese absorption have been reported with pulse type flameless atomizers of the Massmann design [38-41]. Massart el at. reported interferences of various salts on manganese and copper atomic absorption using a Perkin-Elmer graphite furnace HGA 72. However, much work still remains to be done to explain the observations that have been made. Previous interference studies have involved very few observations under constant temperature conditions. This study with the Varian mini-Massmann CRA confirms the reported matrix effects in the pulsed-type atomizers. The observations from the pulsed-type atomizers are compared with those made with the same matrices in a constant temperature graphite electrothermal atomizer. Although considerable interferences are observed in the pulsed-type atomizer, similar interferences are not observed in the constant temperature atomizer.

EXPERIMENTAL

INSTRUMENTATION

Three different instruments were employed in collecting the data: The constant temperature furnace (CTF) developed at Montana State University was used in conjunction with a Varian AA-6 spectrometer and a Varian carbon rod atomizer was used in conjunction with either a Varian AA-5 or a Varian 1150. Instrument conditions used are shown in Table I.

REAGENTS

Trace metal standards were prepared by diluting an appropriately certified reference standard solution from Fisher Scientific Company. The concentration of the standard solution is one mg of Mn metal in one ml of dilute nitric acid. The interferent solutions containing 1000 ug/ml salt were prepared by dissolving one gram of analytical reagent grade salt in 1000 ml of deionized water. These solutions were diluted to obtain other concentrations used. The solutions were analyzed within a few hours after their preparation and no preservatives were added.

TABLE I

INSTRUMENTAL CONDITIONS

	CRA	Constant Temp. Furnace
Spectral Line (nm)	279.48	279.48
Spectral Band Pass (nm)	0.2	0.2
Mn Lamp Current (mA)	4	9
H_2 Lamp Current (mA)	8	20
Inert Gas Flow (l/min)	6 N_2	0.3 Ar
CH_4 Flow During Ashing and Atomization (l/min)	0.5	-
Drying	370 K[1] 28 sec	Drying is achieved under a heat lamp before sample enters atomizer 2220 K; no ashing necessary.
Ashing	1100 K[2] 10 sec	
Atomizing	2900 K[2] 3 sec	

[1]Estimated maximum temperature obtained during dry cycle.

[2]Maximum temperatures obtained during ashing and atomization stages as measured by optical pyrometer.

PROCEDURE

In order to obtain the Mn absorbance with no interference present, 2.5 ul of 0.1 ug/ml Mn solution was pipeted into the CRA tube as described by the manufacturer with an adjustable 10 ul Unimetrics teflon tipped syringe. The interference absorption values were obtained by pipeting the same amount of solution containing both the analyte and the specified amount of interfering salt. The same solutions and techniques were used to load the sample crucible of the CTF as were used for the CRA.

RESULTS AND DISCUSSION

The results obtained with the 100- and 1000 ug/ml amounts of all added salts investigated are shown in Table II. It should be noted that these high amounts of interfering salts are realistic. Soil solution obtained from semiarid soils and dissolved biological materials are two examples of low analyte concentration and very high ionic strength. The interferences are expressed as a percent change of the absorption signal caused by added interferents. Since the precision of electrothermal atomization atomic absorption spectroscopy is about 5 to 8% [38], observed interferences of less than 10% have been considered insignificant in Table II.

TABLE II

INTERFERENCES OBSERVED IN ELECTROTHERMAL ATOMIZATION AAS DETERMINATION OF Mn (EXPRESSED IN %)

Salt	Varian Model 63 CRA Effect on 0.1 ppm Mn of		Constant Temp Furnace Effect on 0.1 ppm Mn of	
	100 ug/ml Salt	1000 ug/ml Salt	100 ug/ml Salt	1000 ug/ml Salt
$CaCl_2$	-90	-100	±<10	±<10
$Ca(NO_3)_2$	±<10	±<10	±<10	±<10
$Ca_3(PO_4)_2$	±<10	-10	±<10	±<10
$MgCl_2$	-10	-76	±<10	±<10
$Mg(NO_3)_2$	±<10	±<10	±<10	±<10
$MgSO_4$	±<10	±<10	±<10	±<10
NaCl	-10	-50	±<10	±<10
$NaNO_3$	±<10	+10	±<10	±<10
Na_2SO_4	±<10	±<10	±<10	±<10
Na_2HPO_4	±<10	±<10	±<10	±<10
KCl	±<10	±<10	±<10	±<10
KNO_3	±<10	±<10	±<10	±<10
K_2SO_4	±<10	±<10	±<10	±<10
K_2HPO_4	±<10	±<10	±<10	±<10
$ZnCl_2$	-15	-70	±<10	±<10

A more detailed investigation was carried out with metal chlorides because they caused significant interference. The effects of $CaCl_2$, $MgCl_2$, and NaCl on the manganese atomic absorption signal are illustrated in Figure 8. The interference is plotted as a function of the concentration of matrix elements.

The efforts to decrease interference in the CRA revealed that no significant interference changes were noted with variation in atomization temperature. A temperature of about 1670 K was necessary to completely atomize the Mn solutions (Fig. 9) in the CRA, therefore atomization temperatures studied ranged from about 1700 to 3000 K. Also, in an effort to minimize interference of chlorides on manganese in the CRA it was found that by increasing the ashing temperature the magnitude of the interference was decreased. At a voltage of 4.5 for 10 seconds the magnitude of the observed interferences was about 20% greater than at the optimum 6.5 volts for 10 seconds. At a voltage of 8.5 for 15 seconds the magnitude of the interference was about 20% less than at 6.5 volts for 10 seconds, but at the 8.5 volt ashing there was about a 20% loss of the Mn. In order to achieve the least amount of interference without significant loss of Mn the 6.5 volts for 10 seconds ashing was used to collect the data in Table II and Figure 8. According to the Varian manual, this setting should provide a

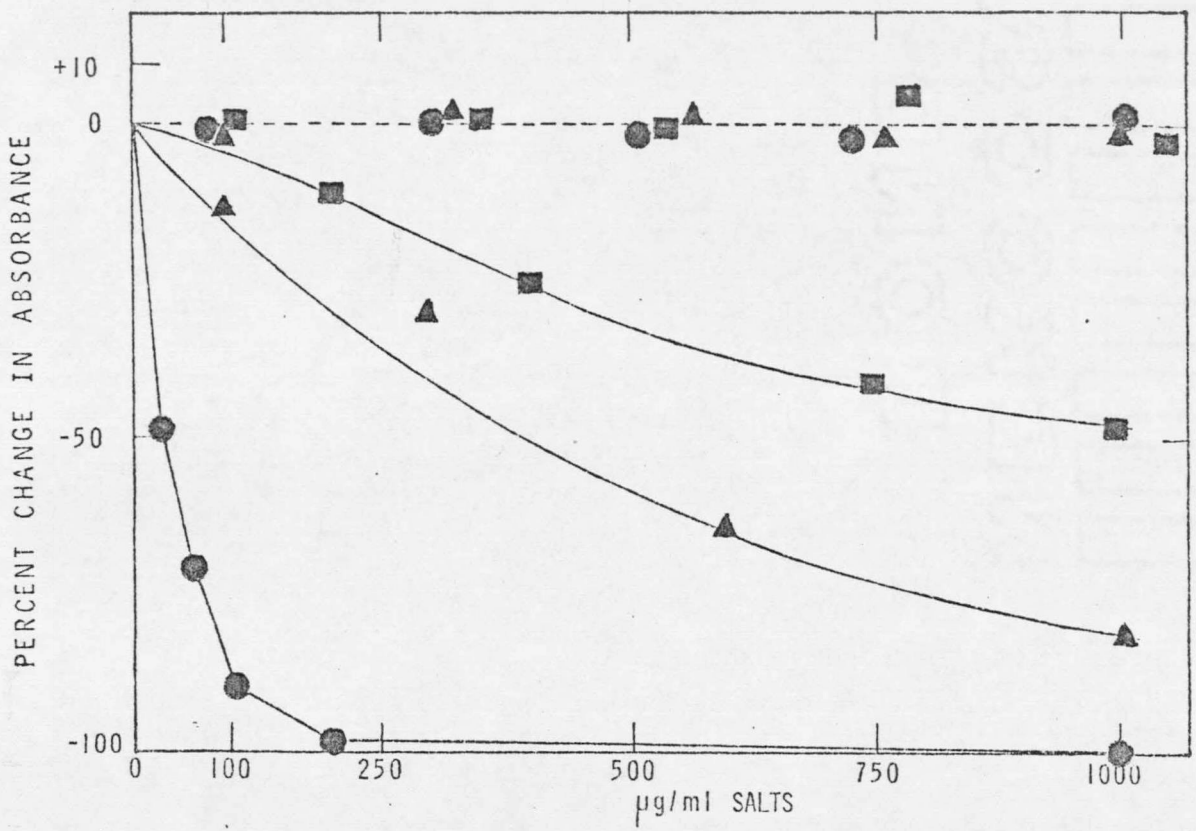


Figure 8. Percent interference of various metal chlorides on the Mn abs. signal as a function of concentration in the model 63 CRA (——) and constant temperature furnace (----). ●, $CaCl_2$; ▲, $MgCl_2$; ■, NaCl.

maximum temperature of about 1000 K, but an optical pyrometer estimate indicated that a maximum temperature of 1100 ± 50 K was obtained. It should be noted that both the ash and atomization temperature discussed here are the maximum attained during that cycle and the carbon rod is at that temperature for only a very small part of the cycle.

The absorption versus temperature curves for Mn in the constant temperature furnace is also shown in Figure 9. All data were obtained near the temperature of maximum sensitivity (above 2220 K). The conditions under which the carbon rod atomizer and constant temperature furnace were operated are shown in Table I. Absorbances of 0.30 and 0.60 were obtained for 2.5 ul of 0.1 ug/ml Mn in the constant temperature furnace and the CRA, respectively. The background correction was found to be satisfactory for both electrothermal atomizers, since no signal was observed for solution of interfering elements without analyte.

The large interferences observed in the case of the pulsed-type carbon rod atomizer for the chlorides agree with those previously reported for the pulsed-type atomizer of the Massmann design [38], but a significant difference is noted in the case of the constant temperature furnace. The most pronounced example is that due to the $CaCl_2$ interference. The Mn atomic absorption

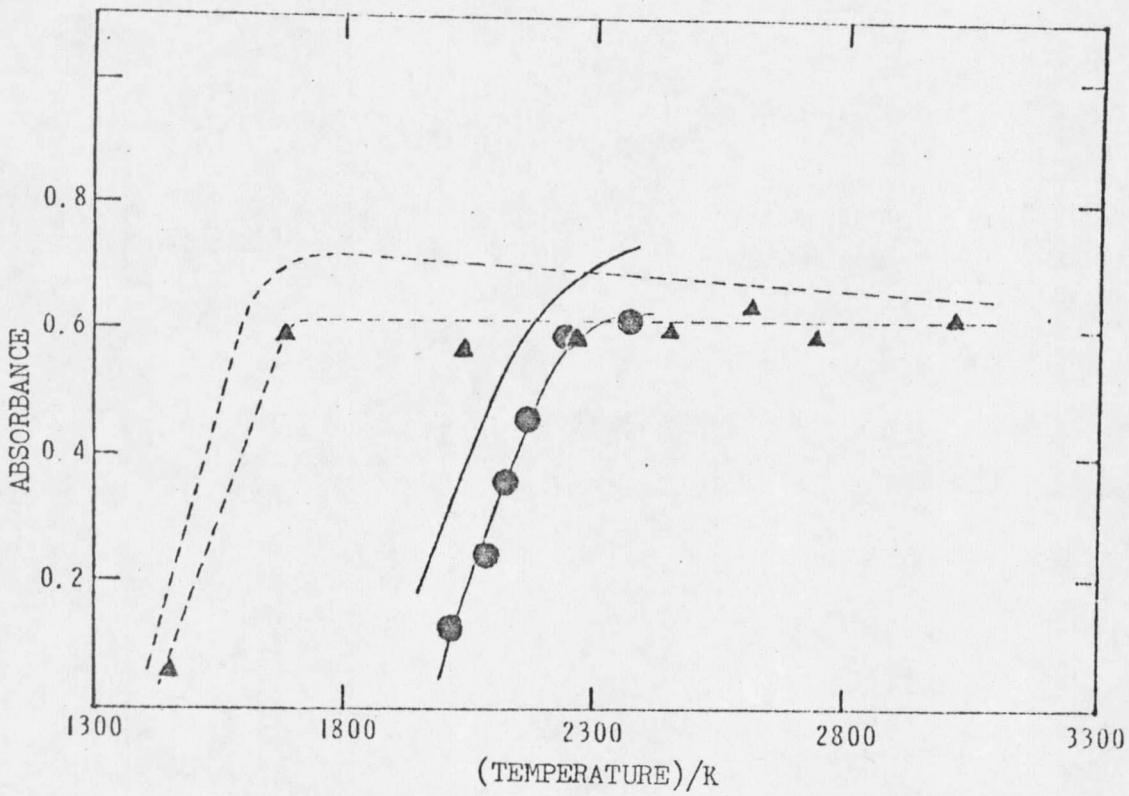


Figure 9. Absorption vs. temperature for 2.5 ng Mn in Varian Carbon Rod Atomizer (- -, peak ht,; ----, peak area) and 5 ng of Mn in the Constant Temperature Furnace (—o—, peak ht,; —— peak area).

signal is virtually eliminated in the pulsed-type atomization, at 100 ug/ml $CaCl_2$ or higher, but in the constant temperature furnace no interference on the Mn absorption signal is noted. The results plotted in Figure 8 are based on peak height absorption values. The recorded peak area results have not been included here because of their similarity to the peak height data.

Many authors have emphasized that interferences in pulsed-type atomizers are often complex [42, 43]. It is, therefore, necessary when studying interferences to consider the effect of the interferent at various concentrations. It is also necessary to consider the effect of both the cation and the anion, as is demonstrated by the effects of various chloride compounds on the Mn atomic absorption signal. Comparison of the percent suppressions for constant chloride level shows that the cation with which the chloride is associated has a significant effect on the extent of interference (Table III). The data suggest that the interference taking place in the pulsed-type atomizers is dependent upon the bond dissociation energy and the boiling point of the interfering chloride. The magnitude of interference correlates with bond dissociation energy for high boiling interferents; the boiling point becomes the important factor with low boiling interferents such as $ZnCl_2$. A lower bond dissociation energy should cause more chloride to be available for interference, except in the case of $ZnCl_2$ where the low boiling point

TABLE III

COMPARISON OF INTERFERENCE MAGNITUDE IN PULSE-TYPE ATOMIZER DUE TO VARIOUS CHLORIDE SALTS WITH PROPERTIES OF THESE SALTS

Chloride	Interference From 750 ng Cl %	M-Cl Bond Dissociation Energy[48] KCal/mole	Boiling Point[48] K
K	0	101.3	1780 (sublimes)
Na	-30	97.5	1686
Mg	-45	89.0	1685
Ca	-100	81.0	>1900
Zn	-50	50.0	1000

would cause much of the chloride to boil off and escape before the Mn vaporizes. Therefore, both the bond dissociation energy and the boiling point appear to be important in interference mechanisms.

There have been many studies on the mechanisms of atomization in carbon furnaces [44-47]. Both the thermodynamic and kinetic approaches have considered the importance of the hot carbon in the atomization process based on Reaction 1.

$$MO(s) + C(s) \longrightarrow CO(g) + M(g) \qquad \text{Reaction 1}$$

Aggett and Sprott [44] concluded that Reaction 1 is not operative for Mn, based upon free energy considerations and comparison of appearance temperatures on carbon and tantalum strips. Since their appearance temperature of about 1470 K agrees well with the appearance temperatures seen in this study (Figure 9), it is believed that the carbon does not enter into the Mn atomization process and the chloride interference is probably involved in the vapor phase. For the pulsed-type atomization it is obvious that some chloride compounds interfere, in such a manner as to reduce the absorption signal. There are several processes by which this type interference could occur as has previously been reported

by Woodriff [6].

It appears that the interferences seen in the pulse furnaces are due to the formation of intermediate chlorides. This conclusion was reached after considering the relationship of bond dissociation energies and boiling points to interference and the fact that no interference is present in the constant temperature furnace. These chlorides escape before they have time to decompose into atoms. In the case of the CRA the small size could easily allow the manganese chloride to escape out of the ends before sufficient temperature has been attained for atomization. Similarily, in the Massmann furnace the chlorides could escape out of the exit hole or condense in the cooler portions of the tube before decomposition. But in the large volume constant temperature furnace two important factors are responsible for the minimization of interference. First, in CTF, as the sample approaches the hot carbon tube and attains vaporization temperature, the vaporized molecules are immediately in a very high temperature environment in the optical path. This is in contrast to the pulsed-type atomizers where a molecule such as manganese chloride could possibly start to volatilize very soon after the ashing stage. During the one to three seconds necessary for the atomizer to reach atomization temperature volatile molecules containing the analyte could have

already been expelled from the atomizer. Second, the residence time is much longer in the constant temperature furnace. In the constant temperature furnace the sample must diffuse along the length or through the walls of a 30 cm carbon tube before leaving the optical path as opposed to the pulsed-type atomizers from which the sample can escape readily after volatilization.

A comparative study such as this not only suggests the probable mechanism of the CRA interference, but the absence of matrix interferences in the constant temperature furnace eliminates certain mechanisms that would be common to both atomizers. Further, work involving other elements and possible interferent mechanisms will be reported in ensuing sections.

It should be also noted that for analytical purposes there are methods of eliminating these interferences observed in the carbon rod atomizer. Removal of the chlorides by precipitation with Ag^+ and filtering the precipitate works quite well. A second method involves incorporation of a strong acid (20%) such as nitric acid into the sample plus metal chloride solution. The effect of the acid is to expel hydrochloric acid during the drying stage. The results using these methods on some known interfering salt concentrations are shown in Table IV.

In conclusion, matrix interference occurs when using the pulsed-type atomizer and does not take place with the constant temperature furnace. In the constant temperature furnace, the sample cannot escape without going through the furnace which is above the dissociation temperature of the chloride. The interference results reported here enable a better understanding of the mechanisms by which matrix interferences occur in pulsed-type atomizers.

TABLE IV

Mn INTERFERENCE CORRECTIONS FOR MODEL 63 CRA

	No Interferent	300 ug/ml $CaCl_2$	600 ug/ml $MgCl_2$	1000 ug/ml NaCl
No Correction	0.75	0.05	0.18	0.40
$AgNO_3$ Correction	0.75	0.78	0.71	0.76
HNO_3 Correction	0.75	0.70	0.72	0.73

All values are peak height absorptions values for 5 ul of 0.1 ug/ml Mn.

LEAD INTERFERENCES

INTRODUCTION

Lead was chosen as the element of interest in this study for several reasons: (1) the importance of lead analyses in many different matrices for environmental and health studies; (2) the availability of extensive literature an lead analysis and interferences in pulsed-type atomizers; and (3) the desire to extend the type of comparative interference study, previously implemented with a constant temperature furnace atomizer for manganese [40, 41], to a more volatile element.

Many simple matrix interferences observed in pulsed-type atomizers have been documented in the literature. Regan and Warren [49, 50] reported about 40% enhancement of lead AAS signals from a 1% ascorbic acid solution, using a Perkin-Elmer HGA 72. Tartaric acid and sucrose also caused enhancement. The same authors also found a suppression of the lead signal due to various salts of calcium, magnesium, strontium, and barium--up to 88% suppression for 100 ug/ml $MgCl_2$; ascorbic acid was used to eliminate suppressions. McLaren and Wheeler [51] observed an interference in the form of double peaks for lead absorption in the presence of ascorbic acid, HF, or digested NBS orchard leaves, using a Perkin Elmer 2000.

Czobik and Matousek [52] observed that the absorption versus time profile is influenced by the presence of phosphate ions when using a Varian carbon rod atomizer (CRA), model 63. Significant suppression of the lead signal due to various salts in urine was noted by Hodges [53] with an Instrumentation Laboratory 445 carbon furnace. However, the interferences were overcome using a furnace precoated with molybdenum in the presence of phosphoric acid. Thompson et al. [54] noted up to a 70% suppression of lead while analyzing natural waters using a Varian CRA-90. A lanthanum precoated carbon tube was employed to overcome the interference and improve precision. Large suppressions of lead signals by sulfate salts have been shown to occur when using the Perkin-Elmer HGA 2100 [55]. The order of decreasing interference of the salts reported is sodium > potassium > calcium > magnesium.

The mechanisms of complex-matrix interferences are generally not known; however, a number of simple matrix interference mechanisms have been described, especially for the common chloride interference. Frech and Cedergren [56] used high temperature equilibrium calculations to show that undissociated volatile PbCl could be lost during the early moments of heating toward atomization temperature. They also showed how hydrogen and a high ash temperature could eliminate the chloride from dissolved steel samples via the following reaction:

$$FeCl_2(g) + H_2(g) \longrightarrow Fe(S) + 2\,HCl(g) \qquad \text{Reaction 2}$$

Czobik and Matousek [57] studied chloride interference effects in pulsed-type atomizers using both conventional and fast oscilloscopic detection. They concluded, from comparisons of analyte atomization times to time-resolved interferent populations, that atom populations are depleted by chloride formation in the vapor phase.

Few publications have dealt with the interferences from sulphate salts in the determination of lead with ET atomization. Johanson, Frech, and Cedergren [55] used high temperature equilibrium calculations with sulphate salts similar to those used for chloride salts. Using experimental data to support equilibrium calculations they conclude that undissociated volatile PbS could be lost during early moments of heating, much as with PbCl.

Another type of interference has been attributed to solid phase interactions prior to volatilization, causing more or less thermally stable analyte species to shift their appearance time. McLaren and Wheeler [51] attributed double peaks for lead to the presence of dimorphic forms of lead (II) oxide; by studying powder patterns, they have shown that under conditions similar to those during ashing in a graphite furnace, lead nitrate decomposes to a less stable form of lead oxide when organic matter is present.

Instead of forming only the more stable red litharge, 10% ascorbic acid in the lead nitrate resulted in the thermally unstable yellow massicot's composing as much as 40% of the lead oxide formed. The differing thermal stability of the yellow massicot caused it to vaporize and atomize at an earlier time. Phosphate interference has also been attributed to a reaction in the solid phase which caused a change in thermal stability [52]. Lead hydrogen phosphate decomposes at 623 K to produce the relatively stable lead pyrophosphate, which is stable to 1200 K. An interference occurs due to the increased stability of the lead compound causing later peak time, relative to standards.

Previous reports [11, 40, 41] show that little or no interferece is observed in the analysis of manganese and several other elements when utilizing the constant temperature Electrothermal Atomizers. Data showing reduction of background and minimal interferences for direct analysis of biological samples have also appeared [58]. Thus, a comparison study of the CTF and CRA, for the volatile element lead, was undertaken. The emphasis in this study will be on difficult sample materials, such as digested whole fish, livestock feeds, and coal slurry waters. Synthetic interferent solutions are also studied.

EXPERIMENTAL

Two different electrothermal atomizers were employed in collecting data: A constant temperature furnace (CTF) developed at Montana State University (MSU) used in conjunction with a Varian AA-6 spectrometer, and a Varian model 63 carbon rod atomizer (CRA) used in conjunction with a Varian AA-5 spectrometer as described in more detail in the general experimental. In addition to the strip chart recorder, a Hewlett Packard model 1220 A oscilloscope was used to observe the absorption signals, especially truncated or double peaks that might otherwise be missed because of slower response of the chart recorder. Similar operating conditions were used for both the instruments. The lead resonance line at 217.0 nm and a spectral band pass of 0.33 nm were employed for all absorption measurements. The Varian Pb lamp was operated at 10 mA current for the CRA-AA-5 and 15 mA for CTF-AA-6. The Varian H_2 lamp for background correction was operated at 2 mA for the CRA-AA-5 and at 5 mA for the CTF-AA-6. Simultaneous background correction was used for all absorption measurements. When using the CRA, nitrogen was used as the inert gas at a flow rate of 5 l/min. Methane was introduced at 0.5 l/min during the ashing and atomization cycles as discussed in a previous section. The thermal program with the carbon rod was comprised

of drying at 3.5 for 28 sec. (380 K), ashing at 4 for 15 sec. (750 K), and atomization at 7 for 2.5 sec. (2100 K). Temperatures cited are maximum temperatures attained during each cycle; 2100 K is attained after about 2 sec. of the atomize cycle has elapses. Argon was flushed through the CTF at a flow rate of 0.3 l/min. The temperature of the CTF was set at 1900 K for maximum sensitivity, with a current through-put of 100 A.

The CRA was operated according to the manufacturer's specifications and directions; ash and atomization temperatures were optimized on real samples to minimize interferences. The description and operation of the CTF has already been discussed in an earlier section.

Simple matrices with one or several possible interferents were prepared from analytical reagent grade interferent salts and deionized water. The 1000 ug/ml lead reference standard was obtained from the Fisher Scientific Company. All the acids used in the study were reagent grade chemicals. Working standards were prepared by appropriate dilution of 1000 ug/ml lead and interfering solutions. Working standards were analyzed within a few hours of preparation and no preservatives were added. In cases of interference in the presence of nitric acid, the acid was included in the standard solution.

Biological materials that were used for analysis and spiking experiments were treated as described in the general procedure. Interference data was obtained by addition of 2.5 ul of standard and 2.5 ul of sample or interferent solution, both pipeted into the CRA or CTF crucible with an adjustable 10 ul Unimetrics teflon tipped syringe. Data for standard curves were obtained in the same manner using 2.5 ul of standard and 2.5 ul of 20 percent HNO_3. Total volume and acid concentration is kept constant because CRA absorptions are somewhat dependent on these factors. Each absorbance value reported is a mean of at least three replicate measurements on each solution.

In order to examine if the suppressions are occurring due to volatilization in the drying and ashing cycles, sample crucible of CTF was placed between the CRA electrodes and was subjected to the drying and ashing cycles in the usual manner. The crucible was then removed and introduced into the CTF and the absorbance was measured.

RESULTS

Data obtained on three typical samples, each representing a common matrix type (plant, animal, or coal material), are represented graphically in Figures 10 and 11. The method of standard additions

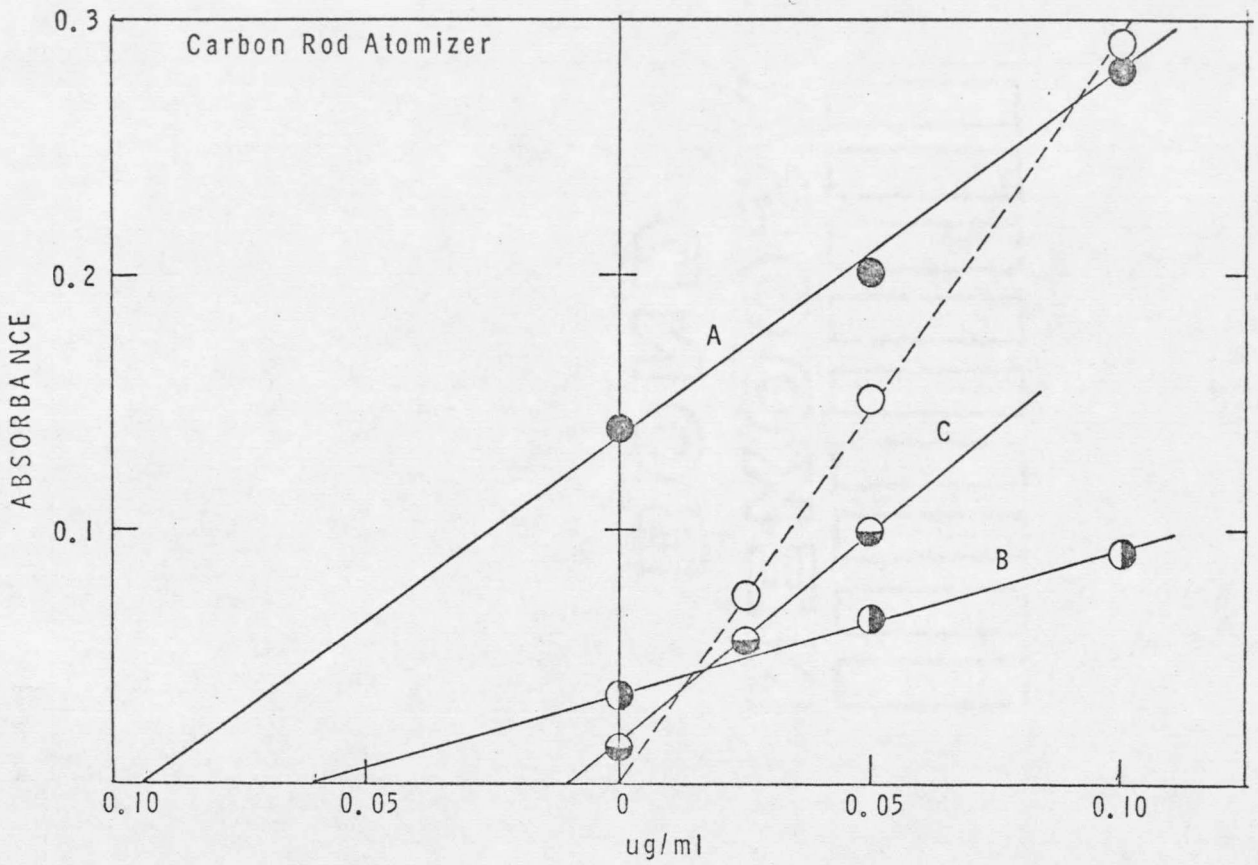


Figure 10. Lead analyses with carbon rod atomizer: Standard curve ---0---, standard addition curves for livestock feed —●—(A), fish —◑—(B) and coal slurry water —⊖—(C).

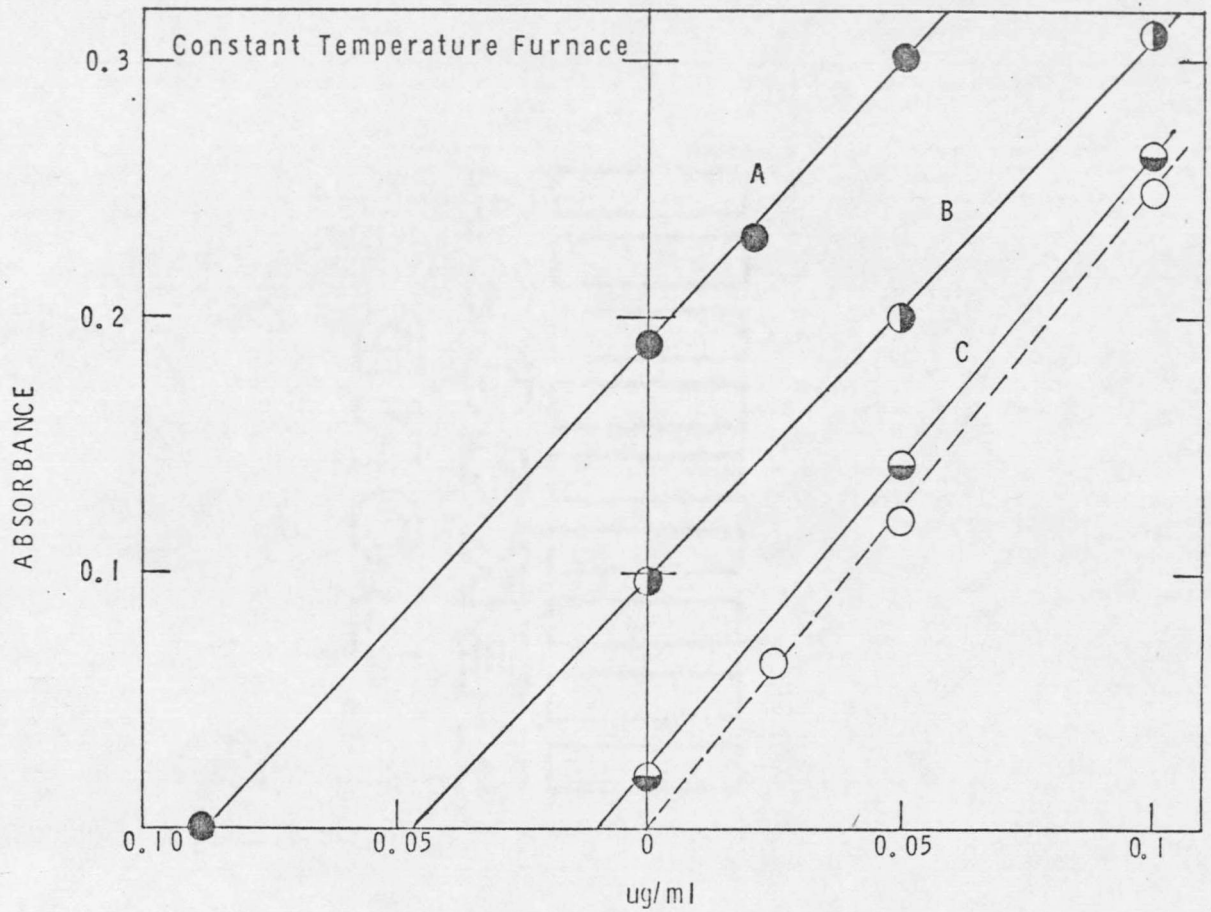


Figure 11. Lead analysis with constant temperature furnace: standard curve -----O-----, standard addition curves for feed ——●——(A), fish ——◐——(B), and coal slurry water ——○——(C).

was used in all cases. Figure 10 depicts standard addition plots for three samples when run on the CRA; the standard curve is also shown as a dashed line, to allow visualization of the extent of suppression for each sample. Slopes ranged from 25 to 83 percent of that of the calibration curve. Figure 11 depicts analogous data for the same three sample solutions atomized in the CTF; the standard addition slopes are parallel to the calibration curve within 5 percent and no suppressions are observed in the CTF. Reading the standard addition plots and comparing the CRA and CTF results shows agreement to within 20 percent as follows:

Atomizer	Feed	Fish	Coal
CRA	.094 ug/g	.060 ug/g	.010 ug/g
CTF	.088 ug/g	.050 ug/g	.010 ug/g

Five fish samples, all northern pike from the Tongue River Reservoir in Montana, were analyzed after microwave digestion with nitric acid. The results of analyses with the CRA and CTF are compared in Table V . The data obtained with the CTF did not require use of the method of standard additions, as is shown for one fish in Figure 11, and hence the direct results from the calibration curve is presented. Data obtained with the CRA, on the other hand, had to be calculated using the method of standard additions; both the result and the percent suppression observed

TABLE V

COMPARISON OF LEAD RESULTS FOR FISH ANALYSIS

WITH CRA AND CONSTANT TEMPERATURE FURNACE

SAMPLE	LIVE WEIGHT OF FISH(g)	CRA		CTF
		STD. ADDN. RESULTS ug/g	% SUPPRESSION FROM STD. CURVE	STD. CURVE CALCULATION ug/g
16	4.8	.007	58	.010
17	16.0	.110	72	.125
18	8.4	.060	83	.050
19	18.0	.050	75	.060
20	12.3	.050	75	.030

(from the relative slopes of the sample plot and the standard curve) are tabulated. It should be noted that these samples contained about 20% HNO_3 which has been demonstrated to be effective for removal of certain simple interferences.

To test whether lead was being lost in the dry or ash cycles in the CRA, samples were subjected to these treatments on the CRA and then introduced into the CTF for atomization. The CTF results showed no suppression and no lead loss due to the CRA dry and ash steps.

Tables VI, VII, VIII, IX, & X summarize the results of interference studies with synthetic samples. Several results from published literature are also included and are identified by the reference number. Peak height measurements were used to construct these tables; analogous tables based on peak area data, collected simultaneously, is very similar.

Varying interferences occur in the pulsed-type atomizers, as seen in the Tables - often 50% or greater for common chlorides and sulfates. The identical solutions showed less than 7% interference when atomized in the CTF. (A typical standard deviation of 5-8% is generally encountered using an electrothermal atomizer [38].)

Data in the Table VI concerning chlorides show a significant suppression, except with KCl and HCl. Most can be eliminated by the

TABLE VI

INTERFERENCES IN ELECTROTHERMAL ATOMIZATION AAS
DURING DETERMINATION OF LEAD (EXPRESSED IN %)

INTERFERING CHLORIDES	CONSTANT TEMP. FURNACE 1000 ug/ml	MINI-MASSMANN ATOMIZER 100 ug/ml	MINI-MASSMANN ATOMIZER 1000 ug/ml	MASSMANN AND IL FURNACE 100 ug/ml
K	-1	+2	+2	
K + HNO_3	+1	-5	-4	
Na	0	-30	-50	
Na + HNO_3	+2	-2	-10	
Zn	-5	-20	-68	
Zn + HNO_3	-3	+3	+4	
Ca	-3	-33	-72	-36 (50), +2 (53)
Ca + HNO_3	0	-21	-60	
Mg	-3	-40	-75	-88 (50), -76 (53)
Mg + HNO_3	-1	-2	+2	
Cu	-2	-50 (52)	-100 (52)	

TABLE VII

INTERFERENCES IN ELECTROTHERMAL ATOMIZATION AAS DURING DETERMINATION OF LEAD (EXPRESSED IN %)

INTERFERING PHOSPHATES	CONSTANT TEMP. FURNACE 1000 ug/ml	MINI-MASSMANN ATOMIZER 100 ug/ml	MINI-MASSMANN ATOMIZER 1000 ug/ml	MASSMANN AND IL FURNACE 100 ug/ml
Ca	+3	-20	-50	
$Ca_3 + HNO_3$	+3	-18	-57	
Na	-1	+15	+19	
$Na_2 + HNO_3$	+2	+5	+5	
K	+1	+22	+28	
$K_2 + HNO_3$	+2	+4	+6	

TABLE VIII

INTERFERENCES IN ELECTROTHERMAL ATOMIZATION AAS DURING DETERMINATION OF LEAD (EXPRESSED IN %)

INTERFERING NITRATES	CONSTANT TEMP. FURNACE 1000 ug/ml	MINI-MASSMANN ATOMIZER 100 ug/ml	MINI-MASSMANN ATOMIZER 1000 ug/ml	MASSMANN AND IL FURNACE 100 ug/ml
Mg	+3	+2	+3	+33 (50)
Mg + HNO_3	0	+4	+7	
Na	+3	+5	+6	
Na + HNO_3	+6	+3	+7	
K	-1	-1	-2	
K + HNO_3	0	0	-4	
Ca	-4	-6	-23	-17 (50)
Ca + HNO_3	-4	-10	-20	

TABLE IX

INTERFERENCES IN ELECTROTHERMAL ATOMIZATION AAS DURING DETERMINATION OF LEAD (EXPRESSED IN %)

INTERFERING SULFATES	CONSTANT TEMP. FURNACE 1000 ug/ml	MINI-MASSMANN ATOMIZER 100 ug/ml	MINI-MASSMANN ATOMIZER 1000 ug/ml	MASSMANN AND IL FURNACE 100 ug/ml
Na	-4	-22	-60	-12 (50)
$Na_2 + HNO_3$	-3	-22	-50	
K			-75	
$K_2 + HNO_3$	0	0	-42	
Mg				
$Mg + HNO_3$	0	-11	-40	

TABLE X

INTERFERENCES IN ELECTROTHERMAL ATOMIZATION AAS
DURING DETERMINATION OF LEAD (EXPRESSED IN %)

INTERFERING ACIDS	CONSTANT TEMP. FURNACE	MINI-MASSMAN ATOMIZER	MASSMANN AND IL FURNACE
1% Ascorbic Acid	+1	+45	+40 (50)
1% HF	0	+33	+30
20% HNO_3	0	+3	
20% HCL	0	-5	
20% H_2SO_4	-2	-4	

addition of nitric acid; however, the interference from $CaCl_2$ cannot be eliminated by addition of HNO_3. Sulfates are also shown to cause suppression of the lead atomic absorption, and addition of HNO_3 does not effectively decrease the amount of interference. Phosphates in general cause an enhancement of lead absorption which can be decreased with nitric acid, except in the case of calcium phosphate which causes a suppression that is not significantly affected by nitric acid addition. The results with nitrates generally show no significant interference except for the calcium salt, which again causes a suppression of the lead signal. The one percent HF or ascorbic acid solutions caused an enhancement in the CRA-63 similar to the enhancement which has been reported using a Perkin-Elmer HGA 72 (57). In the present study, the degree of enhancement relative to standards run before or after ascorbic acid test solutions varied widely, ranging as high as 150% when new furnace tubes were used. The amount of difference between the standard and test solution signals diminished progressively as the tube aged and the pyrolytic coating on the furnace deteriorated, allowing greater penetration of the solutions into the graphite. The 45% enhancement observed for old furnace tubes agrees with the literature value reported for an uncoated tube (50).

Typical traces are shown in Figure 12 for lead and lead-ascorbic acid solutions in the CRA (top) and CTF (bottom). The enhancement

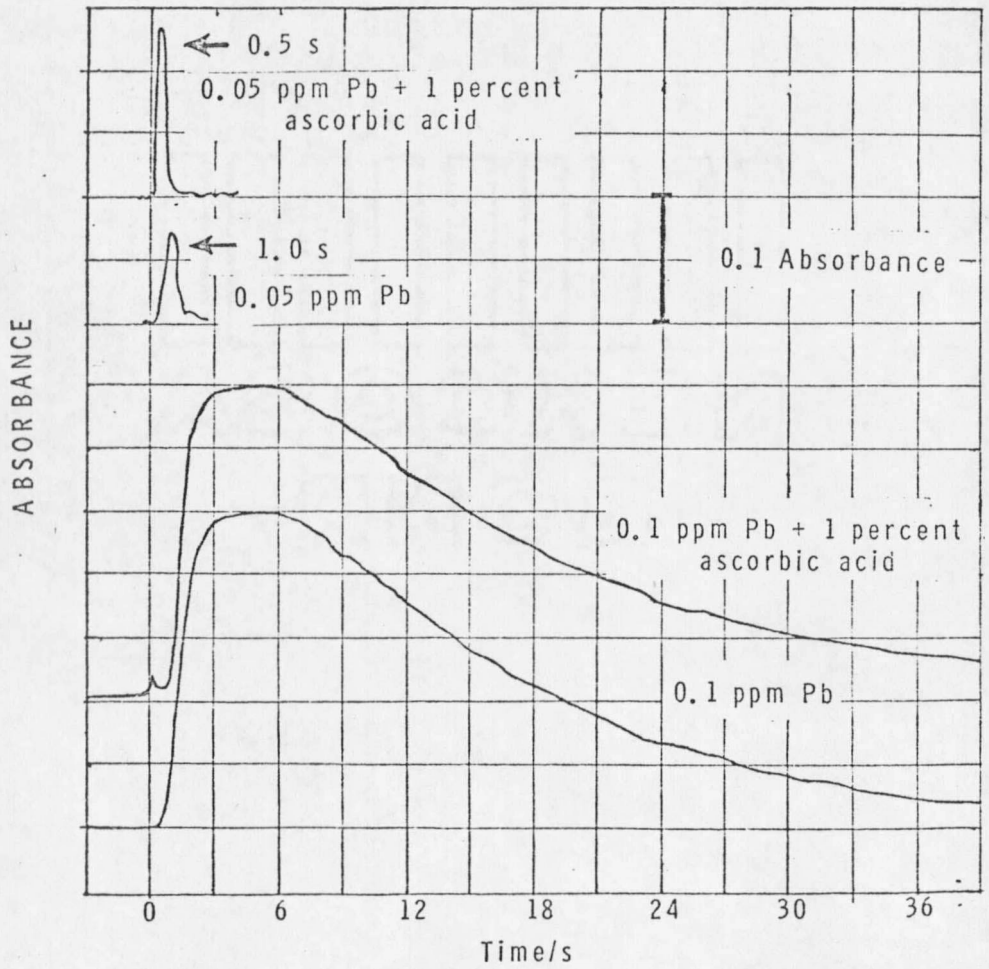


Figure 12. High chart speed (25 cm/min) traces of lead absorption with and without presence of 1% ascorbic acid. Top two curves, carbon rod atomizer; bottom two curves, constant temperature furnace.

and shift to an earlier peak with ascorbic acid in the CRA are clearly discernible on the recorder trace. The recorder traces for the CTF show neither effect. A chart speed of 25 cm/min was used, and the pen's time constant was about 0.2 to 0.3 seconds for 95% of full scale response. Although a fast response detection system is generally unnecessary with the CTF, an oscilloscopic trace of the CTF signal was also observed, and no evidence of a peak shift or peak doubling was discernible -- the traces appeared identical whether ascorbic acid was present or not. All four recorder traces are plotted on the same time axis; thus, the differing residence times in the CRA and the CTF are evident.

DISSCUSSION

ACCURACY AND RUGGEDNESS

Several types of interferences which have been described in the literature have been examined in this comparative study using both simple and complex matrices. The constant temperature atomizer has proven to be resistant to interferences which occur when the same solutions are atomized in pulsed-type atomizers. The pulsed-type atomizer, when used in accepted procedures for the analysis of fish samples, not only showed severe interferences, but also gave variable suppressions on different samples with essentially the

same matrix. Even for simple synthetic solutions, e.g., ascorbic acid, varying degrees of interference could be obtained with slight variations in operating conditions.

A procedure in which the results are sensitive to apparently minor input variables is deemed to be not rugged [59]; it appears that a number of CRA procedures for analyzing real samples fit into this category. In all fairness, it should be pointed out that ruggedness is normally tested by variations in procedural steps applied to replicate aliquots of a single sample. However, it seems highly relevant to analytical needs to extend the concept of ruggedness to cover a nonprocedural input variable when the said variable would not be expected to affect the dependent variable of interest.

For example, in Table V , it would be reasonable to expect that different fish from the same species and environment would exhibit the same percent suppression, just as they should show the same precision (RSD). When the digested solutions were applied to the CTF instead of the CRA, consistently accurate results were obtained. The CTF procedure was, therefore, not sensitive to input variables other than the actual analyte concentration, and thus meets both the normal and the extended criteria for ruggedness of the procedure.

Variability of percent suppression among similar samples on the CRA, such as than seen in Table V , has also been cited by other

authors using the Massmann or mini-Massmann pulsed-type atomizers. Thompson et al. [54] reported from 35 to 81% suppression of lead for four river water samples. Furnace condition was held constant by using only relatively new tubes. Regan and Warren [49] reported 22-84% suppression of lead for nine drinking water samples. In both publications hardness and other constituents were included in their data, but no correlations with percent suppression were evident. Unpublished data [60], using a CRA-63 reveals that from two- to ten-fold suppression of lead has been measured in filtered river water collected at the same location in different months throughout the year. Chloride interference was a significant part of the problem, and use of hydrogen [56] and 800 K ash temperature reduced a typical three-fold suppression. The worst interferences occurred in spring and summer, when snowmelt increased stream flow and diluted the total solids by up to 40%.

In the case of variable suppressions when digested fish samples were run on the CRA, it can be speculated that the lack of ruggedness is due to varying amounts of organic matter remaining after digestion, or that it is due to variations in the minor inorganic constituents of the fish. The first is plausible because some samples may have digested more rapidly or completely than others; a carbonaceous residue may provide enough of an enhancement effect to partially

offset the more severe suppression due to major inorganic salts in the matrix. The second makes sense, at least theoretically, in the light of recent thermodynamic studies [55,56] showing a significant role of various matrix constituents (including Fe and Mg) in determining the volatility of the lead compounds just about normal ash temperatures; such constituents would, therefore, affect the degree of chloride interference on lead during the early stages of atomization. The first could be solved by more exhaustive digestion procedures, but these are more time consuming and may even risk loss of volatile elements. The second type of problem is more fundamental to the atomizer. It could conceivably be dealt with in a manner analogous to the interelement corrections used in x-ray techniques, provided all relevant interferent concentrations were known. Many workers have also tried various reagents to alleviate interferences, but these seem to lack general applicability.

PRETREATMENTS

In order to improve accuracy and ruggedness obtainable with pulsed-type atomizers, many pretreatments including extraction or coprecipitations have been tried [61-63]. These data with simple matrices show that HNO_3 is generally effective in minimizing simple chloride interferences, as are other methods that remove chloride before the atomization cycle begins. However, $CaCl_2$ interference remains, and

other complex matrix interferences probably remain also. Thus, the failure of 20% HNO_3 to eliminate the interferences seen in Table V does not rule out vapor phase interference due to chloride. A related problem is that, if NaCl is a major matrix component, HNO_3 has the disadvantage of producing lead volatility losses at ash temperatures which would otherwise be satisfactory [57]. Generally, a simple HNO_3 pretreatment has not been effective for reducing interferences other than chlorides.

The difficulty of using pretreatments takes on a new dimension once we realize the practical importance of being able to do multi-element analysis. While use of H_3PO_4 is a recommended means [57, 64] to eliminate the interference in the Cu-NaCl system, H_3PO_4 causes enhancement in the Pb-NaCl system [52, 57]. This is but one of the many possible examples indicating why the implementation of practical multielement analysis with electrothermal AAS system is further delayed by the analyte-specific approach to interference reduction. However, this approach seems to be necessary [39] when consideration is limited to pulsed-type atomizers.

MECHANISM OF INTERFERENCE

It is impossible to find one or two well-defined mechanisms that can explain the wide variety of lead interferences observed in pulsed-type atomizers, especially when we go beyond the studies of mechanisms in synthetic solutions to consider complex matrices. Nonetheless,

it may be helpful to classify interference mechanisms into two broad and easily expandable groups which are evident from this and other work.

The first is a vapor phase type of interference, caused by inadequate heat delivery to the analyte as it moves out of the furnace. Here the term "vapor phase interference" is used to include either a recombination of analyte atoms with interferent species, or a lack of dissocation of volatile analyte containing compounds before atomization temperature is achieved. This type of interference is always a suppression, since it involves a depletion of the observable analyte atomic population. It will appear as a major suppression regardless of whether peak height or peak area is measured.

The second type of interference is what we might term a solid phase interference, in which differing volatilities of analyte occur, depending upon the form(s) and thermal stability of the analyte in the furnace before volatilization begins. Less stable forms of the analyte may come off at an earlier time. In the simplest model case, the analyte would presumable be dissociated promptly or at the same rate as the more stable forms. This results in an enhancement effect -- or a double peak, if relatively stable and unstable forms coexisted in the sample before atomization. Prompt dissociation is an unlikely assumption in the most general case; it may be more

likely to be valid for lead, with an appearance temperature of 1040 K [65], than for most elements. This type of interference has been documented [66] and confirmed in this study for ascorbic acid and HF interference on lead. The exact reason(s) why an earlier peak is a larger one have not been fully explored; it may also be difficult to isolate this interference from the vapor phase interference. Rate of atom introduction is one factor, and lower temperature is another with its slower diffusion rate and lesser convective disturbances resulting in a larger number of analyte atoms accumulating in the absorption cell before they move out of the optical path. Thus, although peak area might reduce the extent of interference slightly, peak area and peak height would both suffer interference relative to standards due to longer residence time at lower temperatures --because a single atom absorbs more light during the longer interval.

This work supports the vapor phase mechanisms as a primary mechanism for chloride and probably other interferences in pulsed-type atomizers. The fact that the amount of chloride interference is dependent upon the cation with which the chloride is associated suggests that the chloride formation is occurring in the vapor state; a similar situation has been demonstrated for Cl interference on manganese [40]. In each case, those metal chlorides which vaporize

and dissociate to provide chlorine at the temperature when the analyte normally atomizes show the greatest interferences. Analysis of the varying cation effects in Table VI indicate general agreement with Czobik and Maousek's excellent work using time-resolved studies [57], showing that the degree of suppression depends upon the availability of atomic chlorine for recombination in the vapor phase at the time of Pb atomization. Frech and Cedergren [56] also indicate the thermodynamic stability of gaseous PbCl during early atomization. L'vov [11] has theoretically and experimentally illustrated the effects of Cl as a vapor phase interferent and its suppression by the addition of excess $LiNO_3$, thereby binding excess Cl through formation of thermally stable LiCl. Ohta and Suzuki [67] have devised a simple experimental procedure enabling the analyst to establish the relative importance of vapor phase vs condensed phase interferences in pulsed-type atomizers. By vaporizing the analyte and interferent from separate sites within the atomizer, and also a mixture from a single site, a comparison of the two atomization processes based on the absorbance-time characteristics of the signals may be made.

An important additional clarification of the vapor phase mechanism can be inferred from the absence of chloride interferences in the constant temperature furnace. In the CTF, the same reactions

are most likely occurring, as the sample crucible heats up immediately after insertion into the furnace, but the lead compounds have a much greater chance to decompose before leaving the optical path (or, perhaps, a lesser chance of forming at all due to the close proximity of the heater tube). Because the sample is volatilized into a carbon tube which is already at optimum atomization temperature, there is no pathway available for a molecule to escape from the furnace without attaining atomization temperature.

Thus, an important point of disagreement with Czobik and Matousek [57] is reached concerning the role of residence time. Although this work generally supports their data, their conclusion that increased residence time in a longer furnace causes a greater probability of interference (due to concurrent presence of analyte and interferent in the vapor phase) may be not valid beyond a limited set of apparatus parameters. The lack of interferences cited for both Mn and Pb using a 30 cm CTF, can lay to rest the notion that one must effect a physical separation of analyte from potential interferents -- which is what time-resolution of analyte and chloride peaks in a short residence-time furnace accomplishes.

The data presented in this work also supports a vapor phase mechanism for sulphate interference on lead. As with chloride, the sulfate interference is dependent upon the cation with which the sulfate is associated, suggesting a vapor state PbS formation.

Sulfuric acid causes a neglible interference indicating that a solid phase interference is not a logical explanation. Sulfuric acid vaporizes at a temperature below the appearance temperature for lead, thus effecting a vapor phase time separation of the sulfur and lead. In the presence of hot carbon, sulfate is readily reduced; therefore metallic sulphates volatilize and decompose to produce sulfur at a temperature similar to that of lead. This process provides the sulfur at the proper time to cause a lead interference through formation of PbS. This mechanism is further supported by the absence of sulfate interference at optimum atomization temperature in the CTF. As previously stated there is no pathway of escape for a PbS molecule without attaining atomization temperature. A temperature variation study of this interference indicates that an escape pathway for the PbS can be induced by performing the analyses below the optimum atomization temperature. With the temperature of the CTF decreased to 1500 K (about 200 K above appearance temperature, see Figure 13) the following data were obtained:

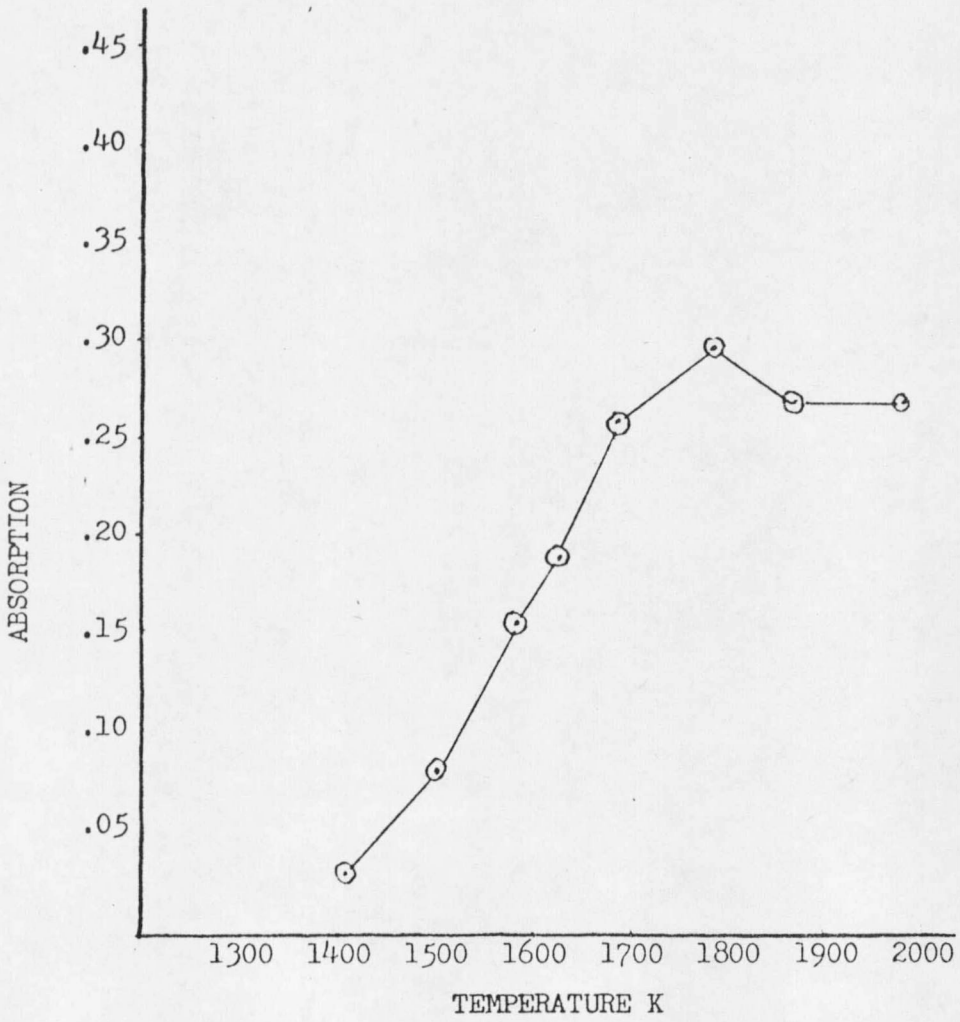


Figure 13. Absorption versus temperature for .25 ng lead in CTF.

Temp of CTF	Interferent	Suppression (Pk ht)	Suppression (Pk area)
1500 K	1000 ug/ml $MgSO_4$	26%	30%
1500 K	1000 ug/ml Na_2SO_4	22%	25%

At this temperature the carbon tube is evidently not hot enough to completely atomize PbS, therefore, it can escape through the walls or out the end of the graphite tube. It is important to note that the peak area suppression is at least as large as the peak height suppression. This is to be expected for a loss of analyte by the vapor phase mechanism. This again eliminates possibility of a solid phase interference where peak area would be expected to show less suppression than peak height.

If long residence time doesn't enhance interference, what does? The data from the CTF reveals that the fundamental variable is temperature -- specifically, the temperature seen by the sample as it vaporizes and before it leaves the furnace; this is generally not even close to the maximum atomization temperature obtained late in the atomization cycle. In either the Massman or mini-Massman furnace, lead has a short residence time compared to the time required to heat the furnace tube; only 1% of the lead remains in the CRA furnace after 0.1 sec. (57). Also, the vapor temperature

has been shown to lag behind the furnace wall temperature by as much as 900 K in some configurations of the Massman furnace [66], but this issue is presently being disputed for pulsed-tupe furnaces that do not allow gas flow through the tube [68]. It has also been suggested that the amount of lag is dependent on matrix present. In the constant temperature furnace, vapor phase interferences do not occur because the samples are heated sufficiently to avoid interferences before leaving the furnace. Thus, the results of this study support those who believe on theoretical grounds that vapor phase interferences should be unlikely, provided that an optimally high atomization temperature is maintained. It has been the failure to realize the need for improved temperature control -- when and where it counts -- that has caused many difficulties for analytical chemists using pulsed-type atomizers. Attempts to reduce interferences in pulsed-type atomizers with rapid heating [69], or with L'vov platform [69-71] to delay atomization of analyte, have tended to confirm that temperature is the key variable - but not the only variable [71]. In a recent publication, H. Koizumi et al. [72] also describe attempts to apply constant temperature atomization to mini-Massman atomizer. Plots are shown in Figure 14 to demonstrate this phenomenon in pulsed-type atomizers. Although these techniques for interference elimination are reportedly successful in some instances long residence time relative to volatilization time also

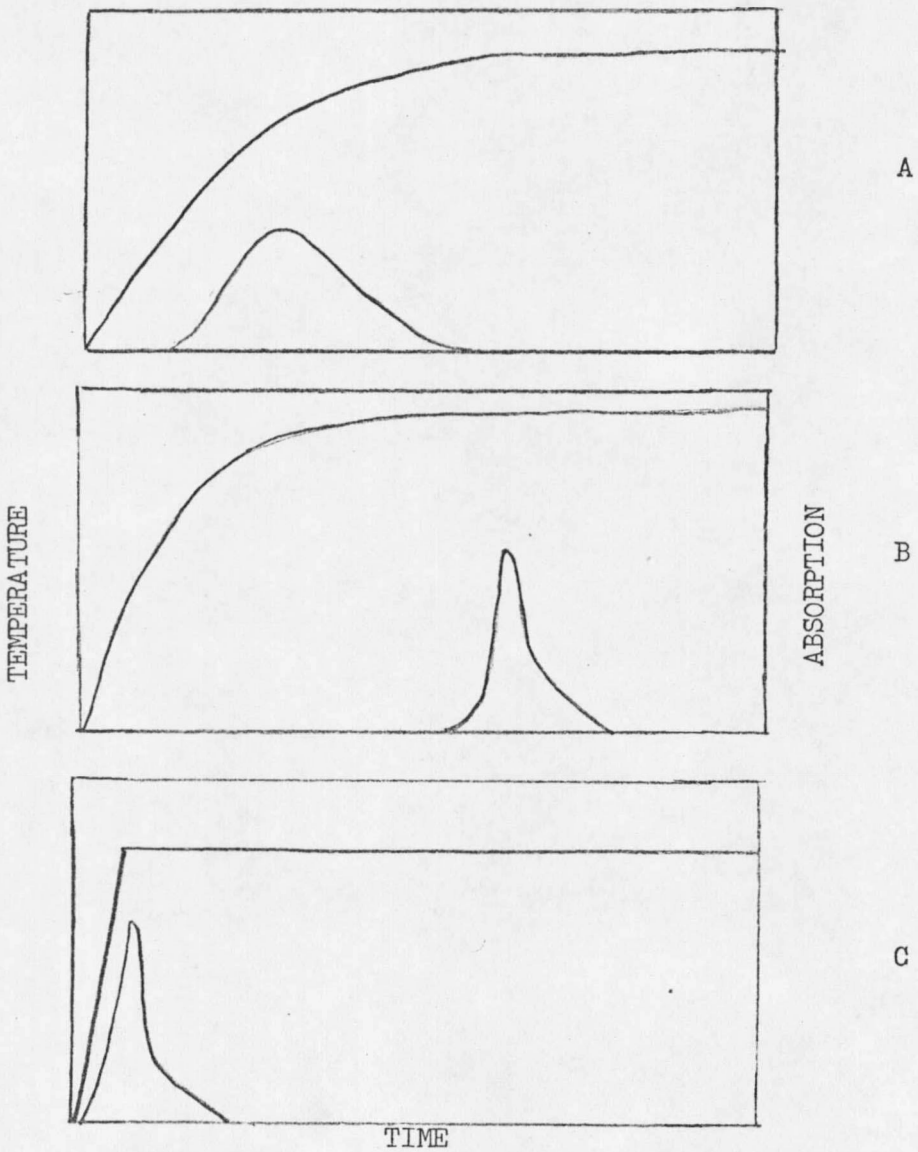


Figure 14. Potentional methods of providing more nearly constant temperature atomization.
A. Normal pulsed-type atomization.
B. Shifting atomization into range of equilibrium temperatures (e.i., L'vov platform)
C. Rapid pulsed heating

appears to be an important factor for minimization of the significance of most variables.

The advantage of a long residence time in minimizing the effect of differing volatilities may be seen by considering Figure 12 in the light of McLaren and Wheeler's proposed mechanism [51] for the formation of a less stable dimorphic form of Pb in the presence of ascorbic acid. No interference is seen in the CTF, where the difference in vaporization times during the rapid heating-up of the crucible becomes negligible compared to the longer residence time at the pre-set heater tube temperature. In the CRA a pronounced interference is observed because the time of volatilization is larger than the residence time.

It has been noted that a solid-phase interference, of the general type described by McLaren and Wheeler [51], can be induced in the CTF when operated at very low furnace temperatures -- roughly as interferences can be exaggerated in the CRA by using lower than optimal atomization voltages. Work on zinc in this laboratory [73], using the three-post CTF described in reference [58] operated at 1180 K, shows a 30% lower peak height when 1 ug of zinc is run as $Zn(NO_3)_2$ rather than as $ZnCl_2$. This is because of differing volatilities and appearance temperatures; ZnO (to which $Zn(NO_3)_2$ decomposes) has an appearance temperature of 1140 K, vs 940 K for

$ZnCl_2$ (65). By increasing the temperature from 1180 to 1350 K (still well below the 1900 K temperature at which optimal sensitivity for zinc is obtained), the peak heights agree within 5%. Peak area is less prone to this induced interference at 1180 K, although 10% less peak area was measured for the nitrate. The diffusion rate and residence time are scarcely affected by the original form of the zinc, therefore, but the rate at which atoms enter the optical path differs. This rate differs greatly when the furnace temperature is only 40 K above the appearance temperature of the less volatile species, but only insignificantly when the furnace temperature is raised slightly.

CONCLUSION

It is shown that use of constant temperature furnace electrothermal atomization is demonstrably less prone to a large number of matrix interferences involved in lead analysis. It is effective in analyzing large numbers of samples in rapid succession because pretreatments and standard addition techniques are not necessary. Considerable insight regarding the causes and mechanisms of interferences has been gained by comparison studies on lead in the presence of various matrices, synthetic, and real-using various types of atomizers. This lead interference work has recently been accepted for publication in Analytical Chemistry.

CHAPTER III

COBALT INTERFERENCES

INTRODUCTION

Cobalt was chosen for this study for several reasons. Cobalt analysis is of primary importance to agricultural researchers, because of livestock health problems associated with cobalt deficiencies [75, 76]. The cobalt contents of the feed grains and forages of interest range from a few thousandths to a few tenths ug/g [77]. At these extremely low levels, normal flame AA methods are not applicable. Some methods have been suggested involving an extraction procedure and flame AA [78, 79], but they have for the most part been applied only to surface water analysis. The offical AOAC methods of cobalt analysis at this level by colorimetric procedures are laborious and tedious [80]. The development of electrothermal atomization techniques opened up new possibilities for this difficult analysis. Aside from the interest in cobalt because of the need for a quick, reliable AA method, there is also interest because preliminary results with pulsed-type atomizers has shown some interesting interference problems [14]. Also, cobalt is of interest for this study because it represents an element of less volatility and different

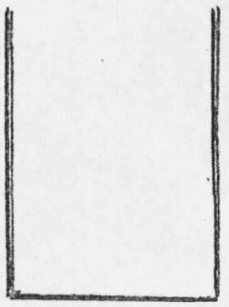
characteristics than either Pb or Mn.

Unlike lead[14], cobalt has not been the object of extensive interference studies. Most publications concerning cobalt analysis have been directed towards practical applications and have involved some type of Co separation from matrix elements. A method of cobalt analysis involving ET atomization and a 1-nitroso-2-naphthal extraction was published in 1975 by Hageman et al. [14]. Data on interference from plant material matrices is also included. At approximately the same time a method involving Co extraction with 2-nitroso-1-naphthal for ET analyses at low concentration in plant material was reported by Simmons [81]. Several other organic extraction techniques have been reported since that time for ET atomizer analysis of Co. A dithiazone extraction was reported in 1977 by Armannson [82] for analysis of sediments and rocks. Young and Baldwin [83] reported an extraction used for complex matrices involved with radioactive materials. Alt and Massmann [84] used an organic chelation and extraction for Co analysis of blood sera. A coprecipitation separation technique was used by Hudnik et al. [85]. Some more direct methods have been used such as a computerized flameless technique for Co, Mn, and Cu which makes no reference to interferences [86] and an analysis of carbonate rocks with an HGA-70 which reports no interference problems for cobalt [87].

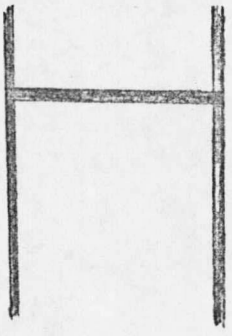
EXPERIMENTAL

INSTRUMENTATION

Varian AA-5 equipped with model 63 carbon rod atomizer was operated as follows: cobalt lamp 10 mA, slit 75 um, wavelength 240.7 nm, Varian R 213 photomultilpier tube, nitrogen gas flow 6.5 l/min, dry stage 3 v for 30 sec, ash stage 6 v for 18 sec, and atomize stage 7.5 v for 2.5 sec. When organic solutions are pipeted into CRA, the dry stage is initiated at very low temperature before addition of the sample and raised to 5 v over a 30 sec period. The Varian AA-6 equipped with a CTF was operated as follows: Cobalt lamp 15 mA, slit 100 um, wavelength 240.7 nm, Varian R 213 photomultiplier tube, argon gas flow for 0.3 l/min, operating temperature of 2600 K. Cups from both porous graphite and vitreous carbon were used for cobalt analysis in the constant temperature ET atomizer. Also a vitreous carbon cup with a raised bottom as illustrated in Figure 15 was used for some analyses.



A



B

Figure 15. Constant temperature furnace cup designs.
A. Normal CTF cup design
B. Raised bottom CTF cup design

PROCEDURES

Several techniques were used in this work in efforts to identify specific interferences and establish a reliable method of cobalt analysis using electrothermal atomization. Early efforts made in this investigation included attempts to use the CRA cup for direct analysis. Plant material was placed directly in the cup or ashed in a muffle furnace and then the ash weighed into the graphite cup. Most samples were dry ashed in a muffle furnace and the ash dissolved in acid. The dissolved samples were analyzed by different methods. Preliminary work involved direct analysis of the sample solution. For some analyses a general metal extraction method was used which has been applied successfully to metal extraction from surface waters [79]. The method uses diethyl ammonium diethyldithiocarbamate as a chleting agent and methyl isobutyl ketone (DADDC-MIBK) as the organic extracting solvent. Synthetic aqueous solutions of elements that appeared to cause the most significant suppressions were also analyzed by both CRA and CTF electrothermal atomizers.

Many samples were extracted with a cobalt specific system [88, 89] using 1-nitroso-2-naphthol as a chelating agent and chloroform for extraction of the chelated Co. This procedure has been adopted for routine trace level cobalt analysis as follows [14]. Two to three grams of plant material are weighed into a Vycor crucible and ashed

6 hours in muffle furnace at 450°C, cooled and dissolved in 40 ml HCl (1 part HCl to 3 parts water) and 3-4 drops of concentrated HNO_3 by simmering at low heat on hot plate 2-3 hours until volume is 5-10 ml. This solution is diluted with ca 50 ml water and adjusted to pH between 3 and 4 with sodium citrate solution. The solution is quantitatively transfered to a separatory funnel and 5 ml 1-nitroso-2-naphthol solution are added with mixing. After at least one hour is allowed for chelation, the solution is extracted twice with 10 ml portions of $CHCl_3$ by shaking 3 min with each portion. Both portions of $CHCl_3$ containing chelated cobalt are collected in a glass vial. The $CHCl_3$ is evaported at 35°C in a drying oven overnight or under a gentle stream of air. The residue is dissolved in $CHCl_3$; this volume is usually 4 ml, but can easily be increased or decreased for samples with unusually high or low Co concentrations. A portion (2-8 ul depending on cobalt concentration) of this solution is pipeted into the carbon rod atomizer tube with Hamilton 10 ul syringe (No. 701N). Various amounts (1-9 ul) of working standard are also pipeted into the CRA. Absorbances are recorded and a standard curve is constructed from these measurements. The amount of Co in the sample is calculated by comparing absorbance of sample solution with the standard curve.

REAGENTS

(a) 1-nitroso-2-naphthol solution. -- 2.5 g 1-nitroso-2-naphthol is dissovled in 125 ml acetic acid and diluted to 250 ml with water.

(b) Sodium citrate solution. -- 500 g dihydrated sodium citrate is dissolved in water and diluted to ca 900 ml. Citric acid is used to adjust to pH 7 before diluting to 1 l with water.

(c) Cobalt stock solution. -- (1000 ug/g). 1.000 g metallic cobalt is dissolved in minimum amount of concentrated HNO_3 and dilute to 1 L. Intermediate solution. -- (0.1 ug/g). Stock solution is diluted 1:10,000 with water. Working solution. -- (0.1 ug/g). 25 ml of cobalt stock solution is carried through the extraction in same manner as samples and diluted to 25 ml with $CHCl_3$. If tightly capped, this is stable 1 month.

(d) Synthetic plant solution. -- A solution was synthesized containing Mn, Cl, S, Ca, P, Fe, Na, K, Cu, and Mg at appropriate levels such that 5 ml of solution contained approximately the same inorganic salts as 1 gram of a Montana hay material. This was used to check recoveries and interferences.

(e) DADDC. -- Diethyl ammonium diethyldithiocarbamate is dissolved in MIBK to provide 1% solution.

RESULTS

Some typical results on forage and grain samples using 1-nitroso-2-naphthal:$CHCl_3$ extraction method are shown in Table XI. Wheat hay, a mixture of brome grass and wheat hay, and barley grain were each analyzed 6 times independently. The means and standard deviations are shown in Table XI. The mean of 5 independent analyses of NBS 1571 Orchard Leaves was 0.142 ug/g with a standard deviation of 0.0070. The cobalt content of NBS 1571 is given as an uncertified 0.2 ug/g by the National Bureau of Standards. NBS 1571 was also analyzed by the Varian Application Laboratory, by an atomic absorption method [90]. The results was 0.13 ug/g. Spiking of synthetic solutions and actual plant samples with known amounts of cobalt prior to ashing and then analyzing by the procedure decribed gave recoveries of greater than 90% in all cases.

A linear standard curve is obtained between 10^{-10} and 10^{-9} g cobalt; therefore, all sample sizes and final volumnes are adjusted so that concentrations fall within this range. Above 10^{-9} g the curve becomes too flat to work with accurately and below 10^{-10} g the sensitivity limit is approached.

Results obtained by direct method utilizing the carbon cup arrangement in the CRA were generally unusable for routine analysis. The results were inconsistent, non-atomic absorption was very large,

TABLE XI

TYPICAL COBALT ANALYSIS USING
1-NITROSO-2-NAPHTHOL EXTRACTION IN
CONNECTION WITH CARBON ROD ANALYZER

	ANALYSIS							
COMPOSITION	1	2	3	4	5	6	MEAN	STD. DEV.
wheat hay	0.056	0.055	0.050	0.050	0.062	0.062	0.056	0.0054
brome and wheat hay	0.064	0.051	0.055	0.062	0.077	0.077	0.064	0.0109
barley grain	1.25	1.25	1.19	1.23	1.27	1.25	1.24	0.0276
orchard leaves	0.150	0.146	0.137	0.145	0.133	--	0.142	0.0070

recovery of added cobalt was low (50-60%) and Co results on known samples were low. Another problem is that, the analyses are being performed very near the detection limit because of the small sample weights that can be accomodated by the carbon cup. Since these attempts at solid sample analyses with the mini-Massmann ET atomizer, successful results have been obtained using the CTF for direct analysis of solid samples for some elements [58]. Results obtained from analysis with the CRA of ashed, dissolved plant materials was similar to that with solid samples in that inconsistant results were obtained (probably due to working near the detection limit) large non-atomic absorption was still present, and most important low recoveries of added cobalt or serious suppression of Co absorption was observed.

Results obtained with CRA utilizing the general metal extraction purposed by Trujillo, Olsen and Skogerboe [79] are shown in Table XII for both spiked samples and synthetic solutions. This extraction completely eliminated problems with non-atomic absorption, but there is still only about 60% apparent recovery of Co added to samples, and there is obvious suppression from simple synthetic solutions. Since there are two possible explanations for these data (suppressions of Co absorption or interference causing incomplete cobalt extraction) an extensive study involving Co interferences in aqueous solution was undertaken. Chloride salts of

TABLE XII

EXTRACTION WITH DADDC-MIBK PRIOR

TO ANALYSIS WITH CRA

	ABS.	% SUPPRESSION
0.8 ng Co	.24	--
" + $CaCl_2$	.24	0
" + $FeCl_3$	.14	42
" + $CuCl_2$	.24	0
" + $MgCl_2$	.13	46
" + K_2HPO_4	.24	0
" + $MnCl_2$	.14	42
" + NaCl	.24	0
" + Syn. P.M.	.12	50
" + Syn. P.M.*	.13	46
0.4 ng Co	.12	--
Digested NBS 1571	.02	--
0.4 ng Co + NBS 1571	.06	67
Digested NBS 1571*	.03	--
0.4 ng Co + NB 1571*	.08	58

* The extracted solution was taken to dryness and redissolved in 50% HNO_3

eight elements abundant in plant material were added to aqueous Co solutions in varying amounts, which cover the range normally encountered in plant material. The CRA data obtained for Ca, Mn, Mg and Fe salts at the various levels and two concentrations of cobalt are shown in Table XIII. These four elements are all shown to cause significant suppression of Co absorption therefore, the results are also plotted in Figure 15, for easy visualization of interference severity. It is seen that a Mg concentration of only 100 ppm, essentially eliminates the Co absorption. Similar studies with K, Na, Zn, and Cu salts resulted in neglible effect from these elements when using the CRA. All these elements tested were added as chloride salts or made up by dissolving pure metal in HCl.

Table XIV contains data from a Co interference study in aqueous solutions with the constant temperature ET atomizer. Unlike previous findings involving Pb and Mn, some interferences are observed when using the constant temperature at optimum temperature. Most of the chloride salts demonstrate a significant enhancement of cobalt absorption when a normal porous graphite cup is used. When vitreous carbon cups, which have been demonstrated to have a high level of impremeability [91, 92] are used, the interference is eliminated. That is the apparent enhancement with chlorides is present as increased sensitivity with all cobalt solutions. A greater increased

TABLE XIII

EFFECT OF VARIOUS QUANTITIES OF CALCIUM, MAGNESIUM, MANGANESE, AND IRON ON COBALT ATOMIC ABSORPTION IN AQUEOUS SOLUTIONS, USING A CARBON ROD ATOMIZER

Co concn ug/ml	Cation added	Concn cation added ug/ml	Approx. molar ratio cation: Co	Observed signal of 5 ul soln	Observed interference in abs.
0.1	none	----	---	0.18	---
0.1	Ca	50	740	0.15	-0.03
		200	2,950	0.15	-0.03
		500	7,370	0.12	none
		1000	14,750	0.12	+0.06
0.1	Mn	10	107	0.17	-0.01
		50	540	0.08	-0.10
		100	1,070	0.08	-0.10
		200	2,140	0.05	-0.13
0.1	Mg	10	250	0.17	-0.01
		50	1,230	0.03	-0.15
		100	2,460	0.01	-0.17
		200	4,920	0.01	-0.17
0.1	Fe	10	105	0.18	none
		50	520	0.16	-0.02
		100	1,050	0.14	-0.04
		200	2,100	0.11	-0.07
0.05	none	---	---	0.09	---
0.05	Ca	50	1,480	0.07	-0.02
		200	3,800	0.08	-0.01
		500	14,740	0.16	+0.07
		1000	15,500	0.20	+0.11
0.05	Mn	10	214	0.08	-0.01
		50	1,080	0.05	-0.04
		100	2,160	0.03	-0.06
		200	4,280	0.03	-0.06
0.05	Mg	10	500	0.08	-0.01
		50	2,460	0.01	-0.08
		100	4,920	0.01	-0.08
		200	9,840	0.01	-0.08
0.05	Fe	10	210	0.10	-0.01
		50	1,060	0.08	-0.01
		100	2,100	0.07	-0.02
		200	4,200	0.05	-0.04

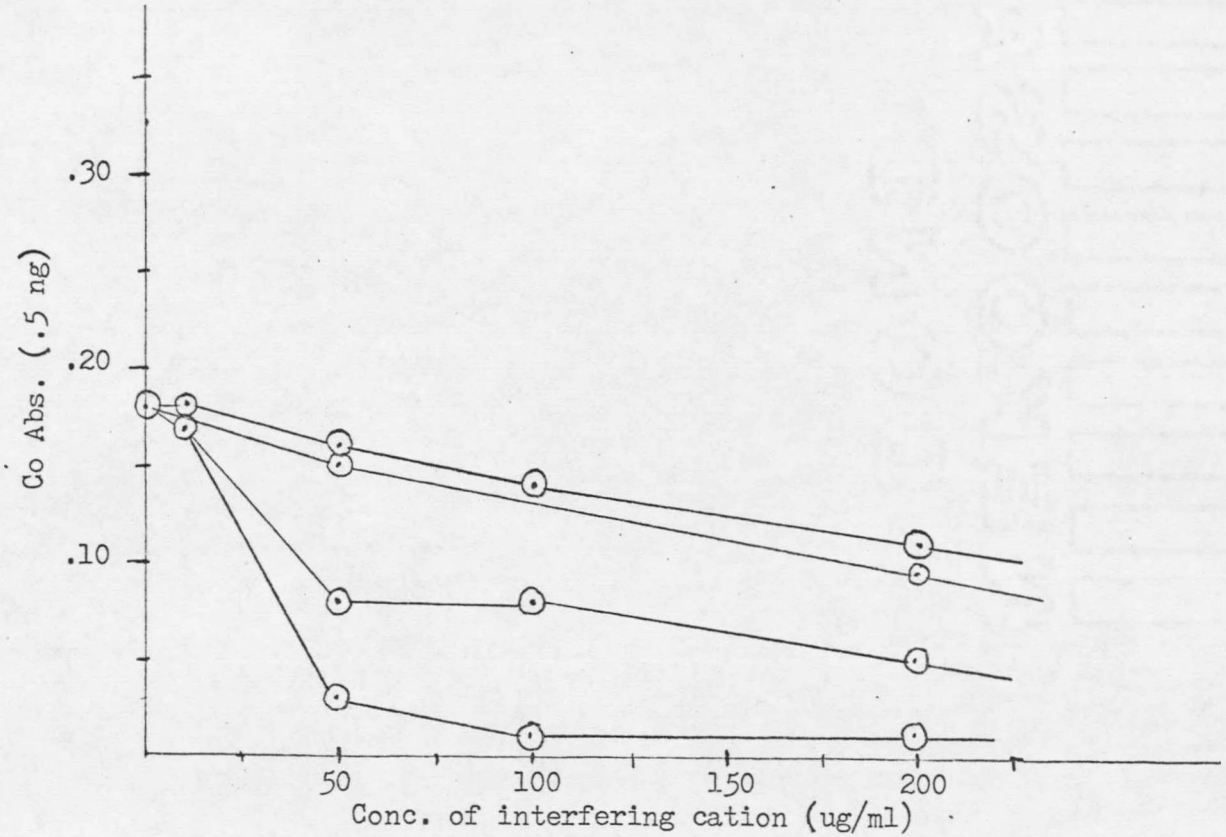


Figure 16. Plots of concentration of interfering cobalt absorbance.

TABLE XIV

COBALT INTERFERENCE STUDY USING
CONSTANT TEMPERATURE ET ATOMIZER

Interfering Salt (1000 ppm)	Porous Cup		Vitreous Carbon Cups	
	Abs.	% Interf.	Normal Abs.	Raised Abs.
.25 ng Co	.20	--	.26	.35
$CaCl_2$	.21	+5	.26	.34
$MgCl_2$	.27	+36	.27	.37
$ZnCl_2$	.25	+26	.25	.35
KCl	.24	+20	.24	.35
$FeCl_3$	.25	+25	.26	.36
$ZnCl_2 + HNO_3$	.20	0	--	--
$FeCl_3 + HNO_3$	.21	+5	--	--
$Mg(NO_3)_2$		+6		
$NaNO_3$		0		
$Ca(NO_3)_2$		+6		
$Ca_3(PO_4)_2$		+5		
Na_2HPO_4		-5		
Na_2SO_4		+10		
K_2SO_4		+13		

sensitivity is noted when using a vitreous carbon cup with a raised bottom.

DISCUSSION

For routine analysis the described interferences are avoided by a cobalt specific extraction procedure, which serves two purposes. First, a separation of cobalt from iron, magnesium, manganese, calcium, and other elements which are abundant in plant material is accomplished. Second, a concentration of all the cobalt in the sample into a small volume of $CHCl_3$ is accomplished. When considering the molar ratio of other elements to cobalt, it becomes evident that some type of cleanup and concentration is necessary. In plant material, the ratio of elements such as calcium and sodium to cobalt is often as high as 15,000:1. These inorganic salts cause a large non-atomic absorption at the 240.7 nm wavelength used for Co analysis.

Many of the observed interferences in analyses of aqueous solutions with the pulsed-type atomizer are probably a vapor phase interference similar to those described previously for Mn and Pb. Since chloride is present in many of the aqueous solutions, it is probable that metal chlorides are decomposing at an appropriate time for formation of a CoCl molecule. The relatively volatile

but yet stable CoCl will deplete the Co concentration in the vapor state by escaping without atomization. The solid samples used and the plant materials that were dissolved in acid contain chloride far in excess of the cobalt, therefore at least part of the interference in these complex matrices can be attributed to a loss of Co as CoCl.

In samples and standards to which the DADDC-MIBK extraction has been applied the amount of chloride present should be small. In fact, in an earilier publication, it was assumed no anions were present and the interferences were attributed entirely to some type of metal-metal interaction, but this is most likely not the case. Although the amount of chloride complexed in the chelate is small, it is feasible that there is enough present to cause interference. It is demonstrated in Table XII that a relatively small amount of metal chloride can cause significant interference. Therefore, to further eliminate the presence of chloride, the extracts were dried to drive off the organic solvent and then redissolved in HNO_3. Chloride will be lost as HCl during drying of the 50% HNO_3 solutions in the CRA, but the results in Table XI show presistance of significant interference. When considering the chelating agent used there is still possibility of anion interference due to the sulfur content of diethyl ammonium diethyldithiocarbamate.

Sulfur in combination with the extracted metal is probably causing a vapor phase interference in much the same manner as occurs with lead as discussed in Chapter II. DADDC by itself causes no interference because with an absence of the appropriate metal atoms, the sulfur is vaporized before Co vaporization thus accomplishing a separation of Co and S. The sulfur interference is not eliminated by 50% HNO_3, but it has been found that the chloride suppressions shown in Table XIII can be reduced to less than 10% by making the solution 20% HNO_3.

The results shown in Table XIV for Co analysis with the CTF are indeed unusual. First, essentially no interferences have been seen in the CTF at optimum temperatures in previous studies. Second, an enhancement in the presence of chloride is rare, since most chloride interferences seen up to this point have been suppressions. Third, why should a change of cup porousity result in elimination of the interference? It is felt that the key to answering these questions lies in the fact that the process of interference elimination involves increasing the standard absorption to the level of the absorption with chloride. That is, it is not a case of removing the chloride suppression, but a case of enhancing standard absorption to the same level. It has been observed (6) that it is possible to lose analyte through the walls of a porous

graphite cup. Analysis has even been accomplished by atomizing samples through porous lids placed on graphite cups [58]. Therefore, a possible explanation follows which is supported by the experimental data in Table XIV.

An assumption must be made that normally a portion of the analyte is lost to the graphite insulation through the cup walls. The amount lost is dependent upon the volatility and size of the species being lost. CoCl has a lower volatility than Co and also a larger size, therfore, CoCl diffusion through the cup walls will be less than Co atoms. The CoCl diffusion through the opening into the optical path with subsequent atomization will be greater, resulting in an enhancement of signal over the same amount of Co in the absence of Cl, where a larger portion escapes through the cup walls. The use of cups with impermeable walls will result in an increased sensitivity by preventing loss of Co atoms. The increase equals the increase observed in the presence of chlorides. This effect will be more obvious for elements of high volatility such as Co which form stable chloride complexes.

CONCLUSION

Indications are that with use of vitreous carbon cups, the constant temperature ET atomizer can be used for interference free cobalt analysis. Work is presently in progress on the use of vitreous carbon for the entire tube atomizer. This may provide an increase residence time by avoiding losses through walls. Although interferences do not appear to be a problem with the CTF an organic extraction may still be necessary to concentrate the cobalt. The vapor phase interferences that have been seen with Pb and Mn in pulsed-type atomizers also appear to be present for Co analysis, but an effective method of analysis has been developed to eliminate the interfering elements and proven to be accurate. By a simple separation of the cobalt either pulsed-type or constant temperature electrothermal atomizers can be used effectively, but a less specific extraction can be used with the CTF.

CHAPTER IV

CADMIUM AND NICKEL INTERFERENCES

INTRODUCTION

Electrothermal atomizer interferences were studied for cadmium and nickel. This study was not as extensive as previous studies and is included mostly for the purpose of comparison of interference severity of pulsed-type and constant temperature ET atomizers. Detailed explanations of interferences observed are not provided. Chloride has received the greatest emphasis since it has been shown to cause significant interferences for several elements.

EXPERIMENTAL

Instrument setting for the CRA and CTF are shown in Table XV and XVI respectively. Reagents used for preparing trace metal standards were Fisher Scientific Company Certified Reference Standards. Reagent grade chemicals were used for preparation of interference solutions.

RESULTS AND DISCUSSION

The results obtained from cadmium analysis are shown in Table XVII. The data indicates that Mg ion, irrespective of the

TABLE XV

CRA INSTRUMENT CONDITIONS (Ni & Cd)

	Ni	Cd
Spectral line (nm)	232.0	228.8
Spectral band pass (nm)	0.2	0.5
Element lamp current (mA)	10.0	4.5
H_2 lamp current (mA)	1.5	2.0
N_2 flow (l/min)	6.0	6.0
CH_4 flow (l/min)	0.5	0.5
Drying stage	3 v (28 sec)	3 v (28 sec)
Ashing stage	4.5 v (10 sec)	4.5 v (10 sec)
Atomizing stage	8 v (3 sec)	7.5 v (25 sec)

TABLE XVI

CTF INSTRUMENT CONDITIONS (Ni & Cd)

	Ni	Cd
Spectral line (nm)	232.0	228.8
Spectral band pass (nm)	0.5	0.5
Elemental lamp current (mA)	15	7
H_2 lamp current (mA)	4	5
Argon flow (l/min)	0.3	0.3
Temperature	2600 K	2000 K

of the associated anion causes a suppression of cadmium absorption. This is confirmed further by the fact that precipitation of chloride with $AgNO_3$ does not eliminate the interference. Other chloride salts appear to lack a similar interference. CTF furnace results shows no significant interference for the interferents tested.

The results obtained for Ni analysis are shown in Table XVIII. Certain chloride salts such as $CaCl_2$ again cause significant suppression, probably via the vapor phase mechanism discussed previously.

CONCLUSION

The constant temperature furnace appears promising for interference free analysis of cadmium and nickel from the data collected on these simple matrices. The pulsed-type atomizer again, shows significant suppression of absorption signals in the presence of certain interfering salts for both Cd and Ni.

TABLE XVII

CADMIUM INTERFERENCES (.02 ppm Cd)

Interferent	% Interference	
	CRA	CTF
400 ppm $MgCl_2$	-4	
1200 ppm $MgCl_2$	-13	0
2000 ppm $MgCl_2$	-22	
4000 ppm $MgCl_2$	-36	+5
4000 ppm $MgCl_2$ + $AgNO_3$	-27	
4000 ppm $MgSO_4$	-25	
4000 ppm $Mg(NO_3)_2$	-20	+2
200 ppm $CaCl_2$	-4	
2000 ppm $CaCl_2$	0	+5
2000 ppm NaCl	-9	-2
1000 ppm K_2SO_4		-6
1000 ppm $MgSO_4$		0
1000 ppm Na_2HPO_4		-4
1000 ppm Na_2SO_4		-1
1000 ppm $NaNO_3$		+1

TABLE XVIII

NICKEL INTERFERENCES (.2 ppm Ni)

Interferent	% Interference	
	CRA	CTF
100 ppm $MgCl_2$	-11	+1
1000 ppm $MgCl_2$	-25	+5
1000 ppm $MgSO_4$	0	0
1000 ppm $MgCl_2$ + $AgNO_3$	-11	
1000 ppm $MgCl_2$ + HNO_3	-4	
1000 ppm $MgNO_3$	-4	
100 ppm $CaCl_2$	-4	+2
1000 ppm $CaCl_2$	-21	+8
1000 ppm $CaCl_2$ + $AgNO_3$	-4	
1000 ppm $CaCl_2$ + HNO_3	-20	
1000 ppm NaCl	-3	+3

FINAL CONCLUSION

CONSIDERATIONS FOR PRACTICAL ANALYSES Now that the several interrelationships of temperature and residence time have been explored, it is appropriate to summarize several practical advantages of the relatively interference-free atomizer over the currently available, interference-prone atomizers. (1) It facilitates determination of many elements simultaneously in the same sample solution[74]; in other words accurate elemental analysis is not highly sensitive to matrix composition (direct or pretreated) or operating conditions such as temperature. (2) Pretreatments of a sample solution are generally unnecessary, and consequently reagent contamination, time-consuming extraction or other separation procedures, etc., are not a factor. (3) Simple nitric acid digestion is sufficient for solubilizing (large) samples. (4) Direct solid sampling of complex matrices is feasible[58]. (5) Relatively large sample sizes, on the order of 50 mg of solids, can be accommodated and thus sampling errors are less. (6) Most importantly, one can realize great time savings: standard additions are generally unnecessary; batch processing avoids tying up the atomizer during the dry and ash cycles; and, finally, less uncertainty and fewer reruns are associated with data interpretation.

These advantages must be weighed against several disadvantages. which have been cited for the current CTF's. (1) Sample introduction has been cumbersome in pressurized systems such as L'vov's [25]; however, well over a hundred samples per hour can be run easily when sample crucibles are introduced against a flushing stream of argon from atmospheric pressure [19]. (2) Long CTF's do not fit most atomic absorption spectrometers. However, a shorter constant temperature furnace has been built which possesses essentially the same resistance to interferences as the larger ones [93]. (3) Heater tubes tend to burn out every few months or so, and a replacement tube may require careful realignment for the best results. (4) General maintenance, such as prevention of electrical shorts, occasionally takes up an operator's time. (5) The high temperature limit of the CTF has been somewhat lower than pulsed-type atomizers, but with proper design the sublimation temperature of graphite will be the limiting factor for both atomizers. (6) With some instruments light attenuation due to long tube length may cause poorer signal to noise ratio than with the smaller pulsed-type atomizers. But, it is possible to design optics which efficiently direct light through a long tube.

Thus, it is fair to say that the current home-made models of the CTF do not yet have "ruggedness" built into the equipment. Such problems are normally worked out of equipment during the

commercialization process. On the other hand, with the pulsed-type atomizers, the lack of ruggedness and general applicablity of analytical procedures may now appear to be a more fundamental difficulty from the standpoint of the analytical chemist. As Massart et. al. [39] have cogently expressed, pulsed-type atomizers' interferences for each kind of matrix on each atomized species should probably be regarded as a separate phenomenon. The constant temperature furnace, engineered for routine use, would provide a viable alternative to the extensive cataloging of analtye- and matrix-specific pretreatments now coming into vogue for pulsed-type atomizers.

REFERENCES CITED

1. Walsh, A. Spectrochim. Acta. 7:108 (1955).
2. Walsh, A. Anal. Chem. 46:698A (1974).
3. Bastiaans, G.J. and G.M. Hieftje. Anal. Chem. 46:901 (1974).
4. Clampitt, N.C. Jr. and G.M. Hieftje. Anal. Chem. 46:382 (1974).
5. Bradfield, E.G. Analyst. 99:403 (1974).
6. Woodriff, R. Appl. Spectrosc. 28:413 (1974).
7. Amos, M.D. Amer. Lab. Aug:57 (1972).
8. Kirkbright, G.F. Analyst. 96:609 (1971).
9. West, A.C. V.A. Fussel and R.N. Kniseley. Anal. Chem. 45:1586 (1973).
10. Marks, J.Y. and G.C. Welcher. Anal. Chem. 42:1033 (1970).
11. L'vov, B.V. Inzh. Fiz. Zh. 2:56 (1959).
12. L'vov, B.V. Spectrochim. Acta. 17:761 (1961).
13. L'vov, B.V. Zavodsk. Lab. 28:931 (1962).
14. Hageman, L., L. Torma and B. Ginther. JAOAC. 58:990 (1975).
15. Fernandez, F.J. and D.C. Manning. At. Absorpt. Newslett. 10:3 (1971).
16. Segar, D.A. and J.G. Gonzalez. Anal. Chim. Acta. 58:7 (1972).
17. Barnard, W.M. and M.J. Fishman. At. Absorpt. Newslett. 12:118 (1973).
18. Person F., W. Frech and A. Cedergren. Anal. Chim. Acta. 82:85 (1977).

19. Woodriff, R. and G. Ramelow. Spectrochim. Act. 233:665 (1968).

20. Woodriff, R., R.W. Stone and A.M. Held. Appl. Spect. 22:408 (1968).

21. Woodriff, R. and R.W. Stone. Appl. Opt. 7:1337 (1968).

22. Massmann, H. Spectrochim. Acta. 238:215 (1968).

23. Amos, M.D. and J.P. Matousek. "Some Advantageous Applications of Nonflame Atomization in Atomic Absorption." Paper 42 at the Pittsburg Conference. (1972).

24. Aggett, J. 5th Internat. Conf. Atomic Spectrosc. Melborne. Book of Abstracts, A2. (August 1975).

25. L'vov, B.V. Atomic Absorption Spectrochemical Analysis. American Elsevier Publishing Co. New York. (1970).

26. Koirtyohan, S.R. and E.E. Picket. Anal. Chem. 37:601 (1965).

27. Woodriff, R., B.A. Culver and K.W. Olsen. Appli. Spectrosc. 24:530 (1970).

28. Dick, D.L., S.J. Urtamo, F.E. Lickte and R.K. Skogerboe. Appl. Spect. 27:467 (1973).

29. Siemer, D.D. Ph.D. Thesis. Montana State University. (1974).

30. Woodriff, R. Appl. Spectrosc. 22:207 (1968).

31. Woodriff, R. and J. Lech. Anal. Chem. 44:1323 (1972).

32. Marinkovic, M. and R. Woodriff. Appl. Spectrosc. 30:458 (1976).

33. Woodriff, R., M. Marinkovic, R. Howald and I. Eliezer. Anal. Chem. 49:2008 (1977).

34. Nichols, J.A. and L. Hageman. submitted to Anal. Chem. (1979).

35. Siemer, D. and R. Woodriff. Anal. Chem. 46:597 (1974).

36. Ferguson, W.S. and R. Burns. personal communication. (1973).

37. Abu-Samra, J. Morris and S. Koirtyohann. Anal. Chem. 47:1475 (1975).

38. Smeyers-Verbeke, J., Y. Michotte, P. Vanden Winkel and D.L. Massart. Anal. Chem. 48:125 (1976).

39. Smeyers-Verbeke, J., Y. Michotte and D.L. Massart. Anal. Chem. 50:10 (1978).

40. Hageman, L., A. Mubarak and R. Woodriff. Appl. Spetroc. in print. (1979).

41. Mubarak, A., L. Hageman, R.A. Howald and R. Woodriff. Soil Sci. Soc. Am. J. 42:889 (1978).

42. Czobik, E. and J. Matousek. Anal. Chem. 50:2 (1978).

43. Matousek, J.P. Am. Lab. 3:(6) 45 (1971).

44. Aggett, J. and A.J. Sprott. Anal. Chim. Acta. 72:49 (1974).

45. Campbell, W.C. and J.M. Ottaway. Talanta. 21:837 (1974).

46. Frech, W. and A Cedergren. Anal. Chim. Acta. 82:83 (1976).

47. Fuller, C.W. Analyst. 99:739 (1974).

48. "Handbook of Chemistry and Physics." 55th ed. R.C. Weast, Ed. Chemical Rubber Co. Cleveland, OH. (1975).

49. Regan, J. and J. Warren. Analyst. 103:447 (1978).

50. Regan, J. and J. Warren. Analyst. 101:220 (1976).

51. McLaren, J. and R. Wheeler. Analyst. 102:542 (1977).

52. Czokik, E. and J. Matousek. Talanta. 24:573 (1977).

53. Hodges, D.J. Analyst. 102:66 (1977).

54. Thompson, K., K. Wagstaff and K. Wheatstone. Analyst. 102:310 (1977).

55. Johanson, K., W. Frech and A. Cedergren. Anal. Chim. Acta. 94:245 (1977).

56. Frech, W. and A. Cedergren. Anal. Chim. Acta. 82:83 (1976).

57. Czobik, E. and J. Matousek. Anal. Chem. 50:2 (1978).

58. Nichols, J.A., R.D. Jones and R. Woodriff. Anal. Chem. 50:2071 (1978).

59. Youden, W.J. JAOAC. 46:55 (1963).

60. Nichols, J.A. and W.S. Ferguson. unpublished data. Colorado State University. (1973-74).

61. Okuno, I., J. Whitehead and R. White. JAOAC. 61:664 (1978).

62. Boyle, E.A. and J.M. Edmond. "Determination of Trace Metals in Aqueous Solution by APCD Chelate Coprecipitation". Analytical Methods in Oceanography. ACS Advances in Chemistry Series #147. Washington D.C. (1975).

63. Nichols, J.A. Trace Analysis Research Centre International Conference III. Dalhousie University, Halifax, N.S. Canada. Paper No. 11. (August 4, 1976).

64. Churella, D.J. and T.C. Copeland. Anal. Chem. 50:309 (1978).

65. Sturgeon, R.E., C.L. Chakrabarti and C.H. Langford. Anal. Chem. 48:1792 (1976).

66. Adams, M.J. and G.F. Kirkbright. Anal. Chim. Acta. 84:79 (1976).

67. Ohta and Suziki. Talanta. 23:560 (1976).

68. Van Den Brook, DeGalan, Matousek and Czobik. Anal. Chim. Acta. 100:121 (1978).

69. L'vov, B.V. Spectrochim. Acta. Part B. 33:153 (1978).

70. Gregoire, D.C. and C.L. Chakrabarti. Anal. Chem. 49:2018 (1977).

71. Slavin, W. and D.C. Manning. Anal. Chem. 51:261 (1979).

72. Kolzumi, H., R. McLauglin and R. Hadeishi. Anal. Chem. 51:387 (1979).

73. Nichols, J.A., F.G. Dewalt and R. Woodriff. ACS/CSJ Chemical Congress. Honolulu, Hawaii. Anal. Chem. Session Paper No. 27. (April 2, 1979).

74. Woodriff, R. and D. Shrader. Appl. Spectrosc. (27:181 (1973).

75. Underwood, E.J. Trace Elements in Human and Animal Nutrition. Third Edition. Academic Press. New York and London. (1971).

76. Marston, H.R., J.H. Lee and I.W. McDonald. J. Agr. Sci. 38:216 (1948).

77. Miller, D.J. Composition of Cereal Grains and Forages. Publ. No. 585. pp. 369-403. National Academy of Sciences-National Research Council. Washington, D.C. (1958).

78. Nix, H. and T. Goodwin. At. Absorption Newslett. 9:119 (1970).

79. Trujillo, J., K. Olsen and R. Skogerboe. personal communication. Colorado State University, Fort Collins, CO. (1971).

80. Official Methods of Analysis. 11th Edition. AOAC. Washington, D.C. secs. 3.025-3.037. (1970).

81. Simmons, W.J. Anal. Chem. 47:2015 (1975).

82. Armannson. Anal. Chim. Acta. 88:89 (1977).

83. Young, C.M., and J.M. Baldwin. Microchem. J. 22:489 (1977).

84. Alt, F. and H. Massman. Z. Anal. Chem. 279:100 (1976).

85. Hudnik, V., S. Gomisck and B. Gorenc. Anal. Chim. Acta. 98:39 (1978).

86. Lungberg, E. and G. Johanson. Anal. Chem. 48:1922 (1976).

87. Schweizer, V.B. At. Absorption Newslett. 14:137 (1975).

88. Saltzman, B.E. Anal. Chem. 27:284 (1955).

89. Sandell, E.B. Colorimetric Determination of Traces of Metals. Vol. 3. pp. 409-436. Interscience Publishers Inc. New York. (1959).

90. Lech, J. and B. Culver. Palo Alto, CA. personal communication. (1974).

91. Cowlard, F.C. and JCA Lewis. Encyclopaedic Dictionary of Physics. Supplementary Vol. 4. Pergamon Press, Oxford and New York. (1971).

92. Kawamura, K. and T. Tsuzuku. Carbon. 12:352 (1974).

93. Howell, H. Masters Thesis, Montana State University. (1978).

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