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Determination of Trace Elements in Water Utilizaing Atomic Absorption Spectroscopy Measurement

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DETERMINATION OF TRACE ELEMENTS IN WATER
UTILIZING ATOMIC ABSORPTION SPECTROSCOPY
MEASUREMENT

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ABSTRACT

A variety of flameless atomic absorption methods have been investigated for the possible determination of trace elements in water. The general applicability of each technique was determined and where applicable, procedures have been developed for the determination of trace elements in natural waters.

Metals were preconcentrated by electrodeposition on a wire. The metals were then atomized for atomic absorption measurement by resistive heating of the wire. As little as 0.01 part per million (ppm) of mercury could be determined in this way.

A mercury cold vapor cell was constructed in which the sample is treated with a reducing agent to reduce mercury to the elemental state and then argon gas is bubbled through the sample to carry mercury vapor into a quartz-ended tube where its atomic absorption is measured. Water vapor condensation and consequent light scattering in the absorption tube was minimized by heating the tube. As little as 5×10^{-8} g or 0.5 part per billion (ppb) of mercury was determined in natural waters.

A heated tube atomizer was designed for the determination of relatively volatile elements such as arsenic.

The sample is placed in a vertical tube that is connected to a horizontal absorption tube. The system is evacuated and heated to 660°C with nichrome wire. Arsenic sublimes at 613°C and results in a significant absorbance at 1937⁰Å, probably as As₄. Ten micrograms of arsenic could be detected.

A simple and inexpensive tantalum ribbon flameless atomizer cell was constructed in which a few microliters of sample were dried and atomized on a tantalum ribbon heated resistively. This is applicable to a large number of elements, giving detection limits down to 10⁻¹³ gram in favorable cases. Interference effects were studied. This system has been applied to the determination of traces of silver, zinc, cadmium, manganese, and lead in natural waters with no sample preparation required. A standard additions calibration is most satisfactory.

KEYWORDS: atomic absorption spectroscopy*, flameless atomizers*, trace elements, water.

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CHAPTER I

INTRODUCTION

The finding of mercury in fish from the Lake Erie-St. Clair River water system has emphasized the significance and the danger of heavy metals occurring in water and the importance of being able to detect and measure these elements. The widespread occurrence of mercury in waters is now well documented; and evidence has been reported that mercury is released into water by complexation with organic molecules from sewage or dead organisms² and that it accumulates in fish as methyl mercury.^{3,4,5} However, little is known concerning the occurrence and the fate of other metals nor of their cumulative effects. There is evidence that similar complexation may solubilize other metals.² The Food and Drug Administration admits that "scientific data on heavy metal toxicity are scarce" and to "knowing little about toxicity levels of metals in foods."² The Federal Water Quality Control Administration has been directed "to identify and prepare a list of all toxic substances now being discharged in waters throughout the U.S."² Currently, FWQA is investigating bottom sediments for magnesium, cadmium, chromium, manganese, nickel, iron, copper, and zinc, as well as mercury. The study of the

effects of these elements on fish is also underway. How, or if, these metals affect humans is still a very open question. FWQA says that "heavy metals, when present in sufficient concentrations, are toxic to aquatic bottom organisms and fish."² Christian and Feldman⁶ have described the distribution of trace metals in biological systems and have summarized results of studies dealing with their function in biological systems.

It is apparent from the above statements that reliable methods must be available for the analysis of a large number of heavy and trace metals in water; in order to determine their fate and distribution, the same is true for the analysis of biological systems. Although considerable work has been done on the determination of many elements, three principal problems remain for several of them. First, a number of elements occur at such small concentrations that their analysis is difficult at best. Second, while methods of sufficient sensitivity may be available, precision and/or accuracy may be poor. Third, many of the routinely used methods are time-consuming and preclude large scale screening of many water samples, which it appears must soon be done. Coupled with the solution of these problems is the requirement to maintain selective procedures.

The Analytical Reference Service (ARS)* is a voluntary association of 302 laboratories responsible for the detection, identification, and measurement of contaminants in the environment; participants include Federal, state, municipal, and foreign agencies, and industries and universities. The primary purpose of ARS is to evaluate analytical methods by submitting samples of known composition to member laboratories for analysis. Statistical parameters of precision and accuracy are calculated from the results obtained and used as measures of the acceptability or non-acceptability of various methods. ARS has performed three recent studies involving the analysis of inorganics in water, including 15 trace or heavy elements. Based on these studies, it was concluded that no satisfactory procedure exists for a number of the elements or that several of the commonly used procedures result in only fair to poor accuracy or precision.⁷ The best procedures for a majority of the elements, including copper, iron, manganese, cadmium, selenium, beryllium, boron, arsenic, and vanadium were colorimetric procedures. Most of these are quite time-consuming and require that the element be in a non-complexed form. In view of the evidence that has been obtained that metals may frequently be solubilized by

*National Center for Urban and Industrial Health,
Public Health Service, Cincinnati, Ohio.

complexation,² these procedures could lead to inaccurate results.

One of the most successful tools developed in recent years for the determination of trace elements is atomic absorption spectroscopy.⁶ It is sensitive, specific, and rapid, allowing the measurement of many samples. This technique is being used more and more for the determination of elements in water. Boethner and Grunder⁸ have investigated the precision for the determination of several elements in water by atomic absorption spectroscopy and flame emission spectroscopy, using conventional commercially available instruments. They found that the precision can vary considerably from one instrument to another and that a major source of fluctuation occurred in the burner-aspirator system. For example, with a Beckman three-burner (total consumption) set, percent standard deviation ranged from 10.8% to 53.0% for sodium, potassium, magnesium, calcium, zinc, lead, manganese, and copper! The precision for the last three elements was poorest, all 40% or above. These precisions could be improved considerably by employing different aspirator-burner systems, but these still remain a major source of fluctuation.

When the detection limit of a particular element falls below its concentration in water samples, then a pre-concentration technique is required. The technique that

has been used most frequently is that of solvent extraction. The metal can be concentrated into a small volume of organic solvent and the sensitivity of atomic absorption is enhanced by organic solvents due to more favorable atomization properties.⁶ Fishman and Midgett⁹ for example, have extracted cobalt, nickel, and lead from fresh water with ammonium 1-pyrrolidinecarbodithioate (APCD) into methylisobutyl ketone (MIBK), while Platte¹⁰ has concentrated iron, copper, zinc, cadmium, and lead from industrial waters by extracting with sodium diethyldithiocarbamate into MIBK. An obvious danger exists in this practice in that any complexed metals in the water may not be extracted, and so direct aspiration of the water sample is preferred whenever possible.

From the above discussion, it is apparent that there is considerable room for improvement in the analysis of many trace elements in water with regard to precision, sensitivity, or speed. Atomic absorption spectroscopy should offer considerable advantage over conventional colorimetric procedures, particularly with respect to speed. However, we see that there is a need for improvement in precision and that a definite danger may exist in the common procedure (solvent extraction) used for preconcentration. Because atomic absorption spectroscopy without a doubt is rapidly becoming one of the most popular tools

for performing trace and heavy element analysis in water, it is highly desirable that methods be developed to improve the precision. It is also desirable that alternative preconcentration procedures be investigated.

In the present proposal, techniques are offered to attack both of these problems. The use of internal standards is proposed to improve the precision of atomic absorption measurements. Internal standards should improve the precision, particularly when the source of fluctuation is the burner-aspirator system. Metal complexes are frequently electroreducible and a preconcentration technique is proposed in which the element of interest is electroplated onto an appropriate electrode from which it can be atomized in a non-flame cell; the non-flame cell should at the same time improve the sensitivity. Other non-flame atomizers are investigated for the sensitive determination of a large number of elements.

CHAPTER II

PRECONCENTRATION BY ELECTROLYSIS

A. Experimental. An electrical heating circuit for the vaporization of metals from a wire was constructed. This consisted of a variable transformer (Variac) with a step-down transformer of 12V output at 10 amps. A number 10 copper wire was used to connect the output of the stepdown transformer to the electrolysis wire. Initial studies were performed with a 0.1 mm diameter platinum wire. The wire was coiled into a 5 mm diameter spiral 1 inch long, and the ends were connected to the power source by means of alligator clips. The light path of the hollow cathode lamp was passed through the center of the spiral.

The system was tested by electroplating mercury onto the wire using a 3.0V battery source. The coiled platinum wire was the cathode and an auxiliary platinum wire anode was used. The solution (5 ml volume) was stirred with a magnetic stirrer during electrolysis. Following the electrolysis step, the wire was washed with deionized water, 95% ethanol, and acetone, and then was air dried for 4 minutes. Then the wire was mounted in the heating circuit and positioned in the light path. The platinum wire was heated to red heat, using a Variac setting of 80, just below

the melting point of platinum, and the peak absorbance was recorded.

B. Results and Discussion. Results are shown in Table 1. Both mercuric chloride (in 0.1M nitric acid) and phenylmercuric acetate were used as the source of mercury. Both inorganic and organo mercury were deposited and good reproducibility was obtained, even at the very low concentrations. Significant self-absorption occurred at the high concentrations resulting in non-linearity; this is not surprising for this volatile element.

Studies were performed with lead in a similar manner. Solutions contained 0.1M potassium nitrate as supporting electrolyte and hydrazine sulfate was added as an anodic depolarizer to prevent the deposition of lead as the oxide on the anode. At relatively high concentrations of lead (50-100 ppm) and short electrolysis times of 2-5 minutes, atomic absorption was obtained, but reproducibility was poor. Absorbance was recorded for solutions down to 10 ppm lead, but at 5 ppm no apparent electrodeposition took place.

A small constant amount of mercury (0.05 ppm) was added to lead solutions to allow mercury to plate out with the lead and reduce the hydrogen overvoltage on the platinum wire and thereby minimize hydrogen gas evaluation. Although lead could be visually detected to plate onto the wire, only small absorbance was obtained. The same was

TABLE 1
 ATOMIC ABSORPTION DETERMINATION OF MERCURY
 BY ELECTROLYSIS PRECONCENTRATION
 ON A PLATINUM WIRE

<u>Solution</u>	<u>Concentration of Hg, ppm</u>	<u>Electrolysis time, min</u>	<u>Peak Absorbance</u>
HgCl ₂	0.01	5	0.045;0.038;0.037
	0.1	5	0.170;0.190;0.185
	1.	5	0.450;0.480;0.475
Phenyl- mercuric Acetate	0.025	8	0.059;0.059;0.070
	0.05	8	0.099;0.099;0.103
	0.1	8	0.185;0.185;0.185

true when solutions were deaerated with nitrogen. It appears that, due to the low melting point of platinum, sufficiently high temperatures cannot be achieved to atomize any but the most volatile elements.

Tantalum wire was substituted for the platinum wire in order to achieve high temperatures. This was enclosed in a Plexiglass cell containing quartz windows to allow operation in an inert atmosphere of argon. This was necessary in order to prevent oxidation and burning of the tantalum wire at high temperatures. A 1 ppm mercury solution, electrolyzed for 20 minutes, resulted in an absorbance that went off scale (>2.5 absorbance). However, 0.1 and 0.01 ppm solutions, using the same wire, resulted in no absorbance. The wire becomes partially oxidized and brittle after heating, even in the argon atmosphere, and this appears to affect the efficiency of tantalum for electrodeposition. A tungsten wire was even more rapidly oxidized.

C. Conclusions. It appears that an electrode material with a low hydrogen overvoltage that is stable to high temperatures will be required to achieve versatility with this technique for a number of elements. A graphite electrode for example, may be applicable for the efficient electrodeposition of several elements.

While the technique of preconcentration by electrolysis may be useful for the determination of a number of elements, we have decided to investigate other non-flame atomizing systems that show promise and to compare the relative effectiveness of the different methods. Three other systems investigated include the mercury cold vapor technique, a heated tube atomizer for arsenic and mercury, and a tantalum ribbon flameless atomizer for general application. The last system shows considerable promise of being a very sensitive and versatile tool for trace metal analysis.

CHAPTER III

MERCURY COLD VAPOR CELL

A. Introduction. The technique is based on the principle of reducing mercury compounds to elemental mercury in the sample solution. Elemental mercury has appreciable vapor pressure at room temperature, and when argon is bubbled through the solution, it carries mercury vapor into the cell where the atomic vapor absorbs radiation from the mercury hollow cathode source.

B. Experimental. A cell was designed and constructed which consists of a flask containing the sample through which argon is bubbled. Tygon tubing connects the flask to the "cold" cell which contains quartz end windows. The cell is heated with nichrome wire wrapped around it and covered asbestos insulation. The sample, usually 100 ml volume, is treated with 1 drop of 10% (w/v) potassium permanganate solution and 5 ml each of 5.6N nitric acid. This dissolves and oxidizes any inorganic or organic mercury. Then 5 ml of 18N sulfuric acid and 5 ml of 1.5M hydroxylamine hydrochloride is added to reduce the excess permanganate, followed by 5 ml of 10% (w/v) stannous chloride to reduce the mercury to the elemental state. The argon is immediately bubbled through the sample.

C. Results and Discussion. A major difficulty with this method is that appreciable water vapor is carried into the cell, and this scatters the ultraviolet radiation from the source, giving a high and variable blank reading. Most investigators have eliminated this by placing a drying agent, either calcium chloride or magnesium perchlorate, between the flask and the cell. However, we have found that frequently significant quantities of mercury are lost in the drying tube. A more satisfactory solution to the problem is to heat the cell to at least 70°C (Variac setting 15) and prevent water vapor from condensing.

Using the described procedure, we have obtained a detection limit of 5×10^{-8} g of mercury in the 100 ml sample, or 0.5 part per billion (ppb). Linearity is achieved up to at least 50 ppb, a 100-fold range. Tap water was analyzed and found to contain 0.7 ppb mercury. A number of water effluent samples from across the state were obtained from OWRR and their mercury contents determined. The sample sources were unknown. Results (ppb) were as follows: 2, 0.8, 1.3, 0.8, and five at <0.5. Four samples analyzed when the procedure was first set up showed <3 ppb, the detection limit before the procedure was refined.

D. Conclusions. This technique is extremely sensitive for mercury. However, it is rather cumbersome to initially set

up and calibrate and hence somewhat inconvenient for single samples. The flameless tantalum ribbon cell described below is more convenient for non-routine analysis. For routine analysis, the cold cell technique is certainly the method of choice.

CHAPTER IV

HEATED TUBE ATOMIZER

Arsenic sublimes at 613°C and should exhibit appreciable vapor pressure at relatively low temperatures. A cell was designed similar in principle to the one described above for mercury, except that volatilization is based on heating. The sample is placed in a vertical tube and dried. The tube is connected to a horizontal absorption cell via a vacuum joint. The system is evacuated and the tube and cell are heated to 660°C with nichrome wire to vaporize the arsenic or mercury into the cell where its absorption is measured.

One nanogram of mercury could be detected using this cell. A methanol solution of mercuric chloride was placed in the cell in order to facilitate drying. Traces of the solvent caused a relatively high blank and aqueous solutions are preferred.

A solid solution of small concentrations of elemental arsenic was prepared by grinding arsenic with potassium sulfate. A concentration of 0.03g As/30g K₂SO₄ was prepared and 0.02-0.1g of this was taken for analysis. This corresponded to 20-100µg arsenic. An absorbance reading of 0.160 at the 1937 Å resonance line was obtained

for the lowest quantity of arsenic. Background absorbance at a non-absorbing line of 2180 Å was 0.020. The arsenic vapor probably exists as As_4 at 660° and temperatures of about 1500°C would be required to obtain atomic arsenic vapor. Although a detection limit of less than 10µg can be obtained by this method, some selectivity is lost due to the molecular band absorption.

CHAPTER V

TANTALUM RIBBON FLAMELESS ATOMIZER

A. Experimental. A cell was designed similar to the one described in Chapter II. The heart of the system is a tantalum ribbon that is heated resistively. The ribbon is enclosed in a cell with quartz windows to allow flushing with argon. This prevents oxidation of the ribbon when it is heated to high temperatures. A few microliters of sample are placed on the ribbon and the solvent is evaporated at about 100°C (setting of 10 on the Variac). The Variac is then set at maximum voltage and the current is turned on to heat the ribbon to 2000-2800°C. This will atomize most elements. The absorbance is measured just above the tantalum ribbon and recorded on a fast response recorder. The result is a peak of absorbance vs. time, the height of which is proportional to the quantity of element placed on the ribbon. The efficiency of atomization is near 100%, approximately one thousand times greater than that using the ordinary flame. Consequently, detection limits are vastly improved.

B. Results and Discussion. Preliminary experiments and detection limits have been determined for the elements for which we have hollow cathode lamps available. The results

are summarized in Table 2. The detection limit is defined as the quantity of element, in grams, that gives a deflection equal to twice the baseline noise.

These results look very promising for a number of the elements. Several of the detection limits should be improved with slight modifications. Nickel could not be determined because the terminals used to clamp the ends of the tantalum ribbon were nickel plated and resulted in large blank readings. The arsenic hollow cathode lamp was very unstable and a new lamp should result in improved sensitivity. The refractory elements should give good sensitivities in a reducing atmosphere. These include molybdenum, vanadium, and chromium. It appears that significant mercury is lost in the drying step and lower drying temperatures should improve its sensitivity. The zinc detection limit was limited only by the presence of minute traces of zinc impurities in the water to prepare solutions. For one microliter samples of 1 ppm lead, manganese, silver, cadmium, or zinc the coefficient of variation was 1.37, 2.40, 3.34, 1.52, and 0.73%, respectively, for 10 measurements. The absorbance was linear over the concentration ranges 0.10-1.0, 0.02-0.20, 0.04-0.50, 0.02-0.30, and 0.02-0.20 ppm for these respective elements (1 μ l samples).

Interference studies were performed and results are summarized in Table 3. The results are the average of five

TABLE 2
 DETECTION LIMITS USING THE TANTALUM RIBBON
 FLAMELESS ATOMIZER

<u>Element</u>	<u>Detection Limit, g</u>
Ag	6×10^{-12}
As	1×10^{-7}
Ca	6×10^{-11}
Cd	1×10^{-12}
Co	3×10^{-10}
Cr	1×10^{-8}
Cu	6×10^{-10}
Hg	2×10^{-8}
Mn	4×10^{-12}
Mo	Not detected
Ni	Not detected
Pb	2×10^{-11}
Pt	1×10^{-6}
V	1×10^{-7}
Zn	5×10^{-13}

TABLE 3

INTERFERENCE STUDIES USING THE TANTALUM
RIBBON FLAMELESS ATOMIZER.
EACH ELEMENT AT 1 PPM CONCENTRATION.

Added	Percent Error				
	Ag	Cd	Pb	Zn	Mn
45 ppm NO ₃ ⁻	-20%	0%	-15%	0%	0%
250 ppm SO ₄ ⁼	-10	+ 5	-25	0	0
250 ppm Cl ⁻	+20	0	- 5	0	-10
100 ppm Cu	-10	0	+15	+15	-55
100 ppm Cd	+35	-	-15	-10	+10
100 ppm Mn	+10	- 5	- 5	- 5	-
100 ppm Cr	+20	0	-65	0	-30
100 ppm Fe	+40	- 5	+15	- 5	+15
0.1M HNO ₃	-10	0	-10	- 5	- 5
0.1M H ₂ SO ₄	-20	+10	+20	0	- 5
0.1M HCl	0	+10	+10	+ 5	- 5
0.1M HClO ₄	+20	+10	-25	+ 5	-25
A solution of 100 ppm each of					
Fe, Cr, Cu, Mn, Cd	0	- 5 (no added Cd)	- 5	0	-40 (no added Mn)

compounds used: (next page)

TABLE 3 (continued)

Compounds Used:

NO_3^-	NaNO_3
$\text{SO}_4^{=}$	Na_2SO_4
Cl^-	NaCl
Cu	CuSO_4
Zn	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
Mn	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$
Cr	$\text{K}_2\text{Cr}_2\text{O}_7$
Fe	FeCl_3 in 0.1N HCl
Cd	$\text{CdCl}_2 \cdot 2\frac{1}{2} \text{H}_2\text{O}$

determinations. Procedures were investigated for the determination of several of the elements in water.

1. Determination of zinc in water. Water samples were taken directly from the tap and stored in polyethylene bottles. Two types of samples were run: a) water with no treatment and b) samples in which 1 ml of concentrated HCl was added per 100ml of H₂O and the sample boiled for 10 minutes, followed by addition of deionized water to bring the volume back to 100ml after evaporation. Two microliter aliquots were taken for the determination. Optimized conditions of argon flow and variac settings were used. The light beam was positioned directly over the strip which contained an indentation for sample placement. Standardization was accomplished by either: a) direct comparison with a calibration curve (0.01-0.20 ppm) prepared with deionized water or with 1ml HCl added per 100 ml, or b) by standard additions. In the standard additions methods, concentrations of zinc added bracketed the sample concentration. Results are summarized in Table 4 and are compared with results obtained using an air-acetylene flame. Blanks and background correction (using a non-absorbing line) were made in each case.

Results were low in untreated samples when a calibration curve was used for standardization but were closer to the flame results when standard additions were used. If samples were boiled with HCl, direct calibration was satisfactory.

TABLE 4

DETERMINATION OF ZINC IN TAP WATER

<u>Sample</u>	<u>Treatment</u>	<u>Results, ppm</u>		
		<u>Calibration Curve</u>	<u>Standard Additions</u>	<u>Air-C₂H₂ flame²</u>
#1	untreated	0.038	0.064	0.070
#2	untreated	0.048	0.072	0.060
#1	HCl added and boiled	0.078	0.085	0.067
#2	HCl added and boiled	0.068	0.077	0.069

2. Determination of cadmium in water. Water samples taken directly from the tap were concentrated 10 fold by evaporation. No net cadmium absorbance was observed, indicating no appreciable cadmium was present in the sample. Thus, cadmium was added to the samples for recovery studies. A blank value was recorded and subtracted using the water sample without any cadmium added. As with zinc, both direct calibration (0.002-0.06 ppm standards) and standard additions were used for standardization. A ten microliter aliquot was taken for analysis. Results are summarized in Table 5.

Recovery was generally satisfactory in both untreated and evaporated samples provided standard additions was used for standardization.

3. Determination of manganese in water. One microliter aliquots were analyzed as previously. When 0.01 or 0.02 ppm manganese was added to tap water with 0.1 ml HCl/100 ml, and then concentrated 10 fold by evaporation, no signal could be detected above the background. Hence, only recovery studies in which samples were analyzed directly were made. Results are shown in Table 6. Results were comparable by either direct calibration or standard additions.

4. Determination of lead in water. Ten microliter aliquots were analyzed and results are shown in Table 7.

TABLE 5

DETERMINATION OF CADMIUM IN TAP WATER

A. 10 microliter aliquot analyzed

<u>Treatment</u>	<u>ppm Cd added</u>	<u>ppm Cd found, calibration curve</u>	<u>ppm Cd found, standard additions</u>
untreated	0.0050	0.0052	0.0041
Concd. 10x by evapn., then Cd added to 0.005 ppm	0.0050	0.0026	0.0043

B. 1 microliter aliquot analyzed

Cd added to 0.005 ppm, 0.1 ml HCl/ 100 ml added, and then concd. 10x by evapn.	0.050	0.071	0.058
Same, but 0.008 ppm Cd	0.080	0.087	0.087

TABLE 6.

DETERMINATION OF MANGANESE IN TAP WATER

<u>ppm Mn added</u>	<u>ppm Mn found, calibration curve</u>	<u>ppm Mn found, standard additions</u>
0.120	0.135	0.123
0.200	0.215	0.235

TABLE 7

DETERMINATION OF LEAD IN TAP WATER

<u>ppm Pb added</u>	<u>ppm Pb found, calibration curve</u>	<u>ppm Pb found, standard additions</u>
0.050	0.040	0.046
0.080	0.074	0.076

Either direct calibration or standard additions could be used, but recoveries were somewhat improved using the latter technique.

5. Determination of silver in water. Distilled water was delivered through plastic-lined silver pipes and so this was analyzed for silver content using procedures as before. Ten microliters were analyzed with the following results: 0.0212 ppm (calibration curve), 0.0320 ppm (standard additions), 0.030 ppm (Air-C₂H₂ flame). It appears that standard additions is required for standardization, as supported by the data in Table 3 on interferences.

C. Conclusions. The tantalum ribbon flameless atomizer is useful for determining trace elements in water at parts per billion concentrations using microliter samples. The most generally satisfactory method in calibration is standard additions in order to compensate for matrix interferences.

CHAPTER VI

USE OF INTERNAL STANDARDS

This study to improve precision of measurements was not undertaken due to early termination of the project upon the resignation of the principal investigator from the University of Kentucky.

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