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THE INVESTIGATION OF NICKEL AS A
MATRIX MODIFIER IN THE ATOMIC
ABSORPTION ANALYSIS OF TIN

by

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B.S. May 1981, Christopher Newport College

A Thesis Submitted to the Faculty of
Old Dominion University in Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE
(CHEMISTRY)

OLD DOMINION UNIVERSITY

Approved by:

Dr. Patricia Pleban
Director

Dr. John Van Norman

Dr. Frank Scully

Dr. Kenneth Brown

ABSTRACT

INVESTIGATION OF NICKEL AS A MATRIX MODIFIER IN THE ATOMIC ABSORPTION ANALYSIS OF TIN

Charles Wm. Saunders
Old Dominion University, 1986
Director: Dr. Patricia A. Pleban

Nickel has been widely used as a matrix modifier in the flameless atomic absorption analysis of arsenic and selenium. Its utility as a modifier for tin has been investigated using Polarized Zeeman effect Graphite Furnace Atomic Absorption Spectroscopy. Peak area, peak shape, and appearance times were compared in modified and nonmodified standards using the system computer's internal integration and a detector/readout system with 18 msec resolution.

The addition of nickel at 600 mg/L increased the tin absorbance signal five-fold. The improved signal to noise ratio resulted in a two-fold increase in the sensitivity and a lower limit of detection. The appearance time of the signal, defined as generation of ten percent of the peak height, was delayed by 30 percent, and the peaks were more symmetric. The appearance temperature of the nickel modified signal was 700 K higher than when no nickel was present. The precision of the analysis, both within a run and between runs, is improved by the addition of nickel. A mechanism to account for the altered atomization profile is proposed using the aid of Arrhenius plots.

The effect of the modifier in the presence of interfering salts was examined. Sodium and potassium sulfates exhibited severe depression of the tin signal when present at low ppm concentrations, an effect which was eliminated by the addition of nickel at 600 mg/L. Ferric chloride exhibited a progressive enhancement of the signal, an effect also eliminated by the addition of nickel. Aluminum nitrate and aluminum chloride each exhibited a more erratic and less reproducible enhancement which was reduced but not eliminated by the addition of nickel. Sulfuric acid had a mild depressive effect on the signal which was unaffected by the presence of nickel. The relative standard deviations of the measurements in these matrices was improved at virtually every level tested.

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Steve Cioccio and the staff of the Applied Marine Research Laboratory are gratefully acknowledged for obtaining the Hampton Roads Harbour water.

George Wood and NASA-Langley are gratefully acknowledged for the loan of the optical pyrometer used in the mechanism study.

I would lastly like to thank my friend and former employer, Dr. James R. Reed for his interest and support in my academic career.

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INTRODUCTION

Tin compounds are widely used in industry as algicides, fungicides, disinfectants, and stabilizers (1,2). Recent data (1) has emphasized the sensitivity of the environment to certain of these, particularly the trialkyl organotins, which have been shown to be neurotoxic (3,4). Trimethyltin affects the limbic system, cerebral cortex, and brainstem of mammals, while triethyltin exposure results in myelinic edema.

While tributyltins exhibit much lower toxicity in mammals than triethyl or trimethyl tins, they are quite toxic to fish, molluscs, and fungi (2). It is for this activity that they find use as wood preservatives and marine antifouling paints. There is increasing concern, however, with the effects these compounds may have on non-target species in the open environment. In recent aquatic toxicity studies, 96 hour LC_{50} 's of as low as 6 ppb were determined for a species of fish (Bleak) and as low as 1 ppb for the Harpacticoid (1).

Low levels of tin compounds pose serious problems when analyzing complex matrices such as tissue or seawater due to interference effects from other matrix components. While speciation of the organotin compounds is sometimes desirable, total tin content is often a suitable parameter and is a simpler measurement (5). Atomic absorption has been the most common method used for this purpose,

however, matrix effects often necessitate separation of the analyte from the matrix (5). This is usually accomplished by converting the tin to the iodide, extracting with a solvent such as toluene, and repartitioning back into laboratory pure water for analysis.

The use of flameless techniques greatly enhances the sensitivity of atomic absorption measurements. Detection levels are 100 to 1000 times lower for most metals (6). The graphite tube atomizer is the most popular of these, but along with the increased sensitivity it provides there are increased interference effects from the sample matrix. These effects may be either spectral or chemical in nature. Of the spectral effects, broadband absorption by the sample matrix can be corrected by any of several background correction techniques. Polarized Zeeman effect offers many advantages, however, over the more conventional Deuterium Continuum Source method (7). The Zeeman correction effect arises from the differential absorption of the parallel and perpendicular components of the source lamp radiation by the analyte and matrix in the presence of a magnetic field applied normal to the direction of radiation. Since the same source lamp is utilized for analyte absorption and background correction, precise optical alignment is not of critical concern, and correction is performed at the analyte wavelength (8). The technique can correct up to 1.7 absorbance units compared to 1.0 units by the continuum method. Zeeman effect correction is not a fault-free

technique, however, since pyrolysis products of some common matrix components have been shown to exhibit a Zeeman effect (9).

Chemical interferences have no equivalent correction system. They are many and vary from element to element, and must often be identified and corrected for independently. Lundberg and Frech demonstrated that such interferences can alter vaporization characteristics of the analyte by either changing the atomization interval and/or the rate of atom formation (10). Altering the atomization interval will change the peak area, while altering the rate of atom formation will change the peak height. For example, Sturgeon, et al (11), used higher atomization temperatures, which results in more rapid furnace heating by increasing the applied voltage, leading to enhanced peak heights from faster atomization of the analyte species. They also showed that interrupting the carrier gas flow will increase the atom residence time, resulting in enhanced peak areas. Lundberg and Frech also demonstrated that in order to evaluate peak characteristics it is necessary to have a detector/readout system with a time constant of one tenth of the temporal half-width of the peak. They determined a time constant of 10 to 12 msec to be adequate for most applications.

The processes by which the matrix may alter peak characteristics have been investigated by several authors. Van den Brock and de Galan (12) described atom formation

processes as a combined function of two mechanisms: [1] Release of the gaseous atom from the surface of the cuvette and [2] removal of the atom by diffusion or convection out of the cuvette. The release of gaseous atoms is controlled by the heating rate of the furnace and the activation energy of the analyte release process. The removal process is controlled by either convection in flow-through systems or diffusion in static systems.

Chakrabarti, et al (13), using the same line of thinking, postulated five pathways by which atomic species may be formed in electrothermal atomizers:

- [1] The dissociation of the metal oxide
- [2] The dissociation of the metal halide
- [3] Vaporization of the solid or liquid metal
- [4] Metal-metal bond dissociation
- [5] Metal-carbon bond dissociation

In their thermodynamic/kinetic treatment of the data, they derived an Arrhenius type equation which related the activation energy of the rate limiting step to the signal absorbance through a logarithmic equation:

$$\log \text{Abs} = - (E_a + \Delta H)/2.3 RT + A_0 \quad [1]$$

where the constant A_0 contains the diffusion terms which are negligible at the first appearance of the peak, R is the gas constant, T the absolute temperature, E_a is the activation energy of the intermediate species, and H is the contribution to the absorbance by the liquid to gas phase equilibrium constant. The sum $(E_a + \Delta H)$ to a first

approximation can be equated to the activation energy of the reaction forming the atomic species (13). Utilizing absorbance versus temperature data from the early rising portion of the peak, where diffusion of the analyte out of the cell is negligible, they were able to postulate reasonable formation mechanisms for several elements in the graphite furnace. For tin, they proposed reduction of the metal oxide at the surface by carbon followed by vaporization of the liquid metal. This suggests that the introduction of carbide forming elements such as nickel into the system may alter the atomization mechanism by competing for reaction with carbon at the surface or by coating the the surface of the graphite.

HISTORICAL

Efforts to improve the analysis of tin in electrothermal atomizers has led to investigations of several matrix modifiers. Tominaga and Umezaki have described the utility of various organic reagents as modifiers (14). Of those tested, they determined that ascorbic acid was the most useful when the interfering compound was present at 1000 times the analyte concentration. They described the interference caused by 16 compounds. The most notable of these was sodium and potassium sulfates, which yielded 31 and 38 percent recovery of the signal of the matrix free sample respectively. Ferric chloride, and zinc nitrate and zinc chloride also resulted in low recoveries (52, 34, and 48 %). Aluminum chloride and aluminum nitrate each yielded high recoveries (158 and 175 %). Ascorbic acid added at 10 percent (wt/vol) was found to improve the analysis in all of these systems, but deviations as high as 16 percent from matrix free samples still existed.

Pruszkowska, et al (15), also examined ascorbic acid as a modifier, and in addition looked at magnesium nitrate, and ammonium phosphate plus sodium chloride. They obtained some preliminary data on the use of nickel as a potential modifier; looking at useful charring and atomization temperatures. Their ascorbic acid data was similar to Tominaga and Umezaki's. They also found that ammonium

phosphate in conjunction with magnesium nitrate was a useful modification system. They did not test the effectiveness of magnesium nitrate alone or nickel in removing interferences.

Pleban used nickel nitrate as a modifier in the analysis of tin in biological specimens (16). She reported improved sensitivity by a factor of 2.5, delayed appearance by a factor of 2, and improved analytical precision at low levels by a factor of 4. Pruszkowska's group also reported delayed appearance when nickel was added, though they did not state by how much the signal was delayed (15).

Thompson, et al, found that the addition of calcium nitrate enhanced the tin signal by about a factor of 2, and improved the sensitivity by a factor of 5. (17). They theorized that the calcium formed a preferential carbide and reduced the partial pressure of oxygen in the region above the analyte. In addition, they studied the formation of pyrolytic graphite by bleeding mixtures of hydrocarbons into the carrier gas. They found 90 % argon/10 % methane easiest to use and improved the sensitivity ten-fold.

Fritzsche, et al, examined the use of other carbide forming elements to compete with tin in reactions at the carbon surface (18). These elements formed a carbide when present in large concentration, though like tin they generally exist as the oxide when present in trace amounts. They coated the cuvettes by soaking them in solutions of the competing elements overnight and drying. They found

improvement in the tin analysis with tungsten, molybdenum, zirconium, and tantalum coatings.

Vickrey, et al, also examined the use of a zirconium coated graphite cuvette in the analysis of tin (19). Using scanning electron microscopy, they found that the zirconium coating was more uniform than that of tungsten or molybdenum, which they believe accounts for zirconium's better performance as a modifier in their study.

Aggett and Sprott studied the influence of carbon from the graphite surface on the atomization of carbide-forming elements (20). Comparing atomization temperatures of the elements from tantalum and graphite atomizers, they looked for evidence of carbon reduction of metal oxides, indicated by a significantly lower temperature when atomized from a graphite surface. They found this to be the case with cobalt, iron, nickel, and tin.

Wendl and Muller-Vogt looked at reactions of some carbide and oxide forming elements in the graphite tube, using x-ray diffraction to determine the element form on the surface (21). For tin, they found that when temperatures of 450 K or greater and an oxidant such as nitric acid were used, tin(IV) oxide was formed regardless of the form originally introduced. If the oxidant were absent, the monoxide formed initially and was further oxidized to the dioxide at 700 K by oxygen present as a contaminant in the carrier gas. These findings support the atomization mechanism proposed by Chakrabarti, et al (13).

They theorized that the oxide was reduced at the surface of the cuvette to the liquid metal, which was subsequently atomized in the gaseous state.

Statement of Problem

Matrix modifiers have been evaluated previously for the graphite furnace analysis of tin (13,14,15,16). Of these, ascorbic acid added at 10 % (wt/vol) and addition of 200 ug of ammonium phosphate have been the most successful (13,14). Neither has been shown effective with all interfering compounds (13,14), and ascorbic acid has been found to leave a large carbon residue on the surface of the cuvette (14). Preliminary data on nickel indicate it has potential as a matrix modifier for the tin furnace analysis (14,15). This has been reported in the form of enhanced peak areas, and the ability to use higher ashing temperatures.

The objective of this study was to evaluate the effectiveness of nickel as a matrix modifier for the tin graphite furnace analysis. The characteristics of a useful matrix modifier, and the parameters to be evaluated for nickel, are:

- [1] Improved sensitivity
- [2] Lower levels of detection
- [3] Reduction of matrix interferences

In addition, some information as to the nature of the nickel modification will be examined using the method of Chakrabarti, et al (13).

EXPERIMENTAL

Apparatus

All analyses were performed with a Polarized Zeeman Effect Flameless Atomic Absorption Spectrophotometer, Hitachi model 180-70, equipped with a dual pen fast response recorder, model 056. The instrument's computer resolved the furnace signal in 18 msec readings and stored them for later recall to the recorder so that the true signal could be observed. A diagram of the instrument can be found in Figure 1. The more sensitive 224.6 nm wavelength was used for these analyses. The instrument was operated in the Zeeman mode, which can correct up to 1.7 absorbance units of background absorption. Pyrolytic graphite cuvettes were used throughout.

Reagents

A commercially prepared 1000 ppm tin stock solution was used (# S7385-50 American Scientific Products, McGaw Park, Illinois 60085). Working standards were prepared daily in acid washed polystyrene autosampler cups (# 127-1212-010 Evergreen Scientific, 2300 E. 49th St., Los Angeles, Ca. 90058). Eppendorf micropipets (Brinkmann Instruments, Westbury, N.Y. 11590) were used for all pipetting purposes. Disposable pipet tips used were rinsed with deionized water four times prior to use to remove contamination.

The nickel modifier was prepared from the nitrate

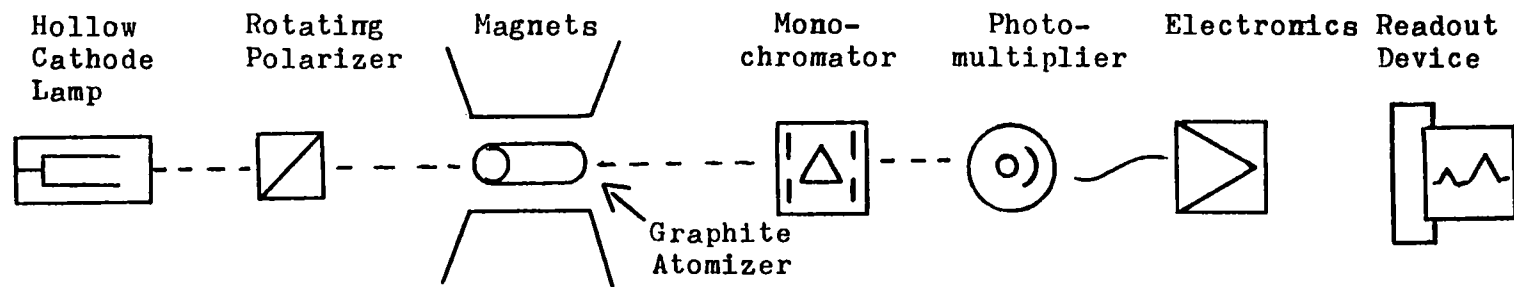


Figure 1. Block Diagram of the Polarized Zeeman Effect Atomic Absorption Spectrophotometer

hexahydrate (# 2789 J.T. Baker Chem. Co., Phillipsburg, N.J.) by dissolving 4.953 grams of the salt and diluting with deionized water to 200 mL to yield a 5000 ppm nickel solution.

Stock interferent solutions were prepared by dissolving and diluting to 100 mL with deionized water the following reagents:

(1) Sodium sulfate (J.T. Baker residue grade) : 1.4827 grams of the salt. The resulting solution contained 10,028 mg Sulfate/L.

(2) Sulfuric acid (Reagent grade, Mallinckrodt Inc., Paris, Ky.40361) : 1.2803 grams. The solution contained 12,064 mg Sulfate/L.

(3) Ferric chloride (Mallinckrodt AR grade) : 2.5458 grams of the hexahydrate. The solution contained 5259 mg Iron/L.

(4) Potassium sulfate (Mallinckrodt AR grade) : 0.1818 grams of the salt. The solution contained 1002 mg Sulfate/L.

(5) Aluminum nitrate (reagent grade) : 0.2208 grams of the nonahydrate. The solution contained 159 mg Aluminum/L.

(6) Aluminum chloride (reagent grade) : 0.1324 grams of the anhydrous salt. The solution contained 268 mg Aluminum/L.

The National Bureau of Standards control samples, # 10576 Dibutyltin Bis(2-ethyl hexanoate) and #1572 Citrus Leaves, were obtained directly from the U.S. Dept. of Commerce, NBS, Wash. D.C. 20234. They were digested using

high purity reagents: Ultrex Nitric acid, # 4801-1, Instra-Analyzed Sulfuric acid for trace metals analysis, # 9673-1, and Ultrex Hydrochloric acid, # 4800-1, all from J.T. Baker Chem. Co., Phillipsburg, N.J. Suprapur Ammonium Hydroxide, # AX1302-90 from MCB Manuf., Cincinnati, Ohio.

Hampton Roads Harbor water of 28 parts per thousand salinity for the salt water matrix study was obtained for us by the Applied Marine Research Laboratory, 45th St., Norfolk, Va.

Procedure

Tin working standards were prepared daily. The salt concentrations listed in Table 1 were prepared daily from their respective stock solutions. The levels were chosen from trials which indicated interference effects were first detected at these levels. Possible tin contamination was checked by analyzing concentrations greater than those of Table 1 for tin content. These results are in Table 2.

Instrumental operating conditions are listed in Table 3. Argon carrier gas was used at 50 mL/min flow rate and interrupted during atomization. Injections of 10 ul were made in triplicate using the instrument autosampler.

All solutions were analyzed by Polarized Zeeman Effect Atomic Absorption Spectrophotometry using constant optical emission temperature control. The effects of the interfering salts on the analysis were determined by comparing the peak areas of the matrix-containing and matrix-free samples. Peak areas were calculated by the

TABLE 1

SALT CONCENTRATIONS USED IN INTERFERENCE STUDIES

<u>Compound</u>	<u>Concentration Range, mg/L</u>
Na_2SO_4 (as SO_4)	0 - 5
K_2SO_4 (as SO_4)	0 - 5
H_2SO_4 (as SO_4)	0 - 4000
FeCl_3 (as Fe)	0 - 26
AlCl_3 (as Al)	0 - 13
$\text{Al}(\text{NO}_3)_3$ (as Al)	0 - 7

TABLE 2

Results of Contamination Check of Salt Solutions

<u>Salt</u>	<u>Conc, mg/L</u>	<u>Conc Tin Found</u>
$\text{Al}(\text{NO}_3)_3$ (as Al)	15	BDL*
AlCl_3 (as Al)	25	BDL
FeCl_3 (as Fe)	50	BDL
H_2SO_4 (as SO_4)	6000	BDL
Na_2SO_4 (as SO_4)	100	BDL
K_2SO_4 (as SO_4)	100	BDL
$\text{Ni}(\text{NO}_3)_2$ (as Ni)	600	BDL

* BDL= Below Detectable Levels

TABLE 3

Instrumental Operating Conditions

Lamp Current (mA)	12.5
Wavelength (nm)	224.6
Bandwidth (nm)	0.4

Heating Program (initial-final temp., °C/time, sec)

Dry	45 - 85/10
	85 - 120/20
Ash	1050 - 1050/20
Atomize	2500 - 2500/7
Clean	2800 - 2800/3

instruments' electronic integrator.

Appearance times were measured as the time from the start of the atomization cycle, played back by the instrument's computer in expanded form, to the time of generation of one tenth of the signal peak height. Knowledge of the chart speed and atomization interval permitted conversion from centimeters to seconds. Changes in peak shapes were determined by visual inspection of the signal tracing.

For the Arrhenius plots, tracings of absorbances and temperatures were collected simultaneously. The temperature deflections throughout the range in the atomization cycle were calibrated using an optical pyrometer loaned by NASA-Langley, Hampton, Va. (Micro Optical Pyrometer model # 95, Pyrometer Inst. Co., Bergenfield, N.J.). For these data the atomization stage was ramped under current control so that more accurate readings could be obtained. For the unmodified data, the atomization was ramped from 1500 °C to 2900 °C over 20 sec. When nickel was added the range was set to 1900 °C to 2900 °C for 20 sec. The stripchart recordings read absorbance versus time and temperature versus time, from which the necessary data were calculated by hand.

Ten mL of the Hampton Roads Harbor water was lyophilized to remove the water, and the remaining residue diluted to 2.0 mL with deionized water. An aliquot of this was mixed one to one with the nickel nitrate solution and

spiked with tin standard to a concentration of 76 ppb immediately prior to analysis. This resulted in a concentration factor of 2.5 of the sample matrix.

The NBS dibutyltin compound was dried over phosphorus pentoxide for two hours. The citrus leaves were dried for two hours at 85 °C. Exactly 0.2200 grams of the dibutyltin and 0.3057 grams of the citrus leaves were acid digested according to the Association of Official Analytical Chemists method 25.137 scaled down ten-fold for use in a micro Kjeldahl unit. The dibutyltin digest was diluted to 100 mL final volume with deionized water; the citrus leaves digest was diluted to 10 mL final volume with deionized water.

RESULTS AND DISCUSSION

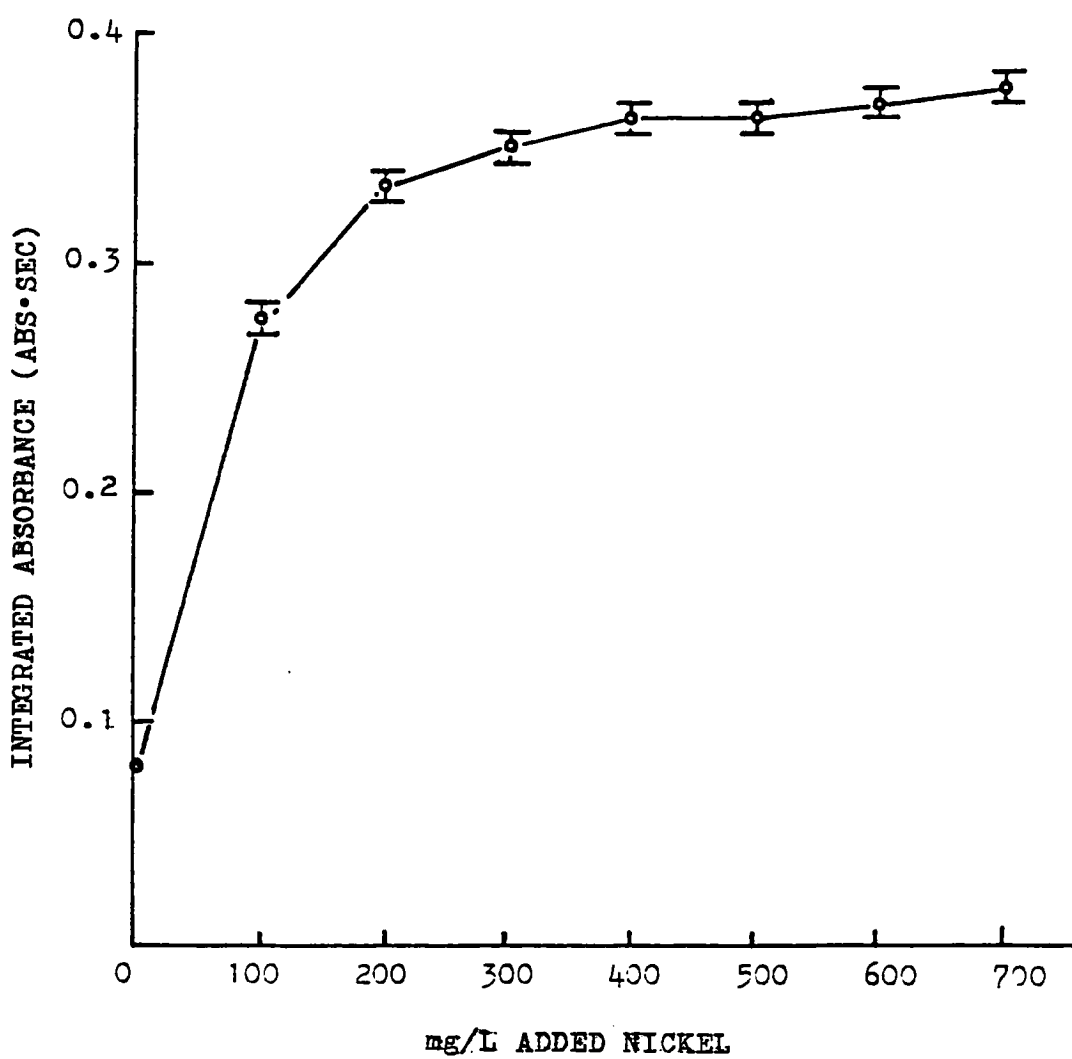
GENERAL

The effect of adding increasing amounts of nickel to a 200 ppb tin standard is shown in Figure 2. The integrated absorbance is seen to increase initially, and above 500 mg/L added nickel no additional increase occurs in the absorbance. At this level, the integrated absorbance is five times that of the nickel free sample. Since there is no tin contamination at this level (Table 2), and maximization of sensitivity is one of the prime objectives, 600 mg Ni²⁺/L was chosen for the modification studies which followed. In every case except that of sulfuric acid, this level was sufficient to maintain enhancement and/or reduce interference effects.

The calibration curve for tin was linear below 200 ppb, as shown in Figure 3. Above 200 ppb the nickel added curve began to bend back toward the concentration axis. The sensitivity of the analysis, defined as the quantity yielding one percent absorption, was improved from 56 pg to 22 pg. The lower limit of detection, defined as the concentration giving a signal of twice the standard deviation of the lowest standard, was lowered from 16 ppb to 2 ppb. These results are summarized in Table 4.

The precision of the data within runs and between runs is also improved when nickel is added as a modifier, as shown in Tables 5 and 6.

The appearance of the peak is dramatically altered. In



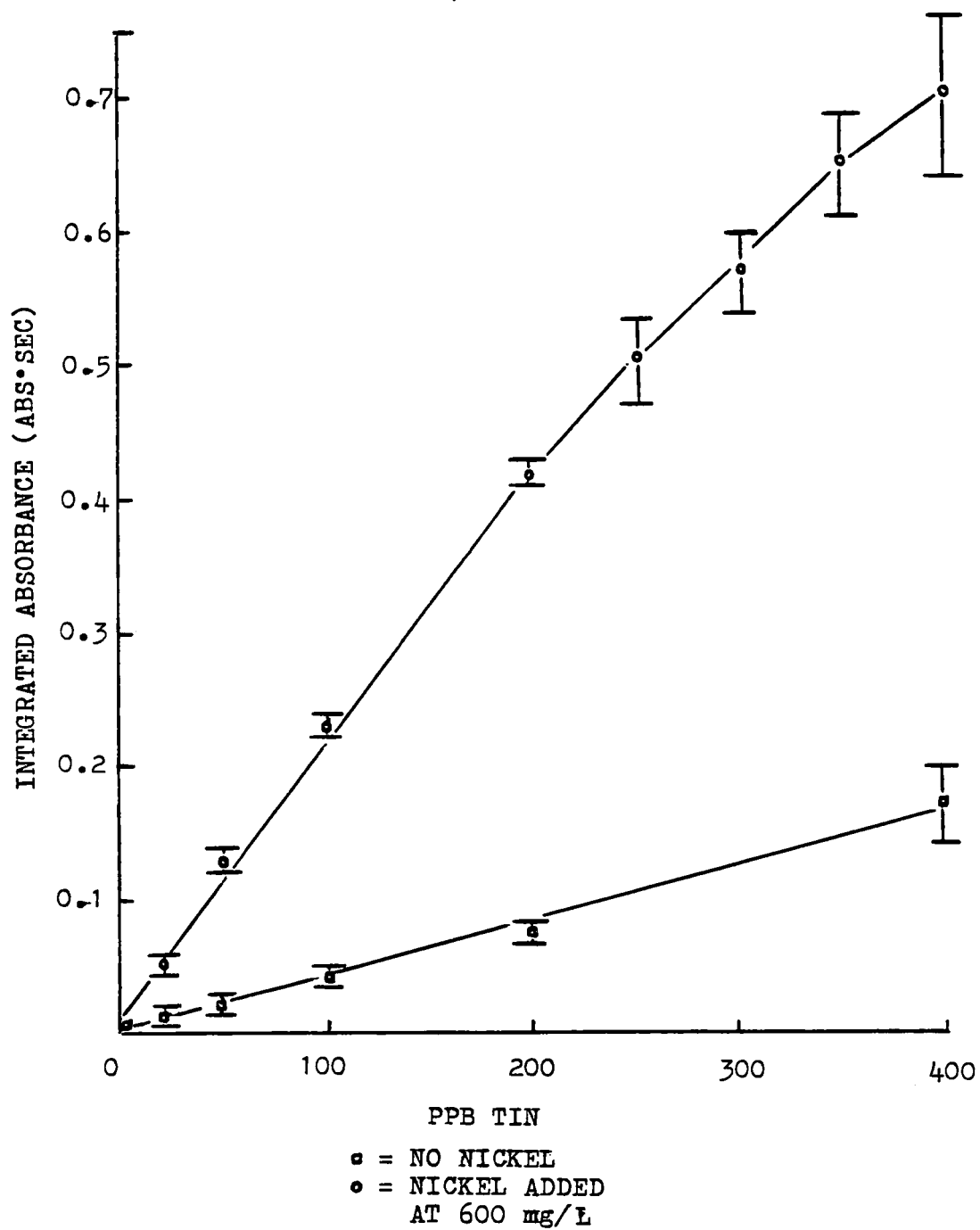


Table 4

Comparison of Sensitivity and
Lower Limit of Detection

	<u>Sensitivity, pg</u>	<u>LOD, ug/L</u>
No Additive	56	16
Ni ²⁺ , 600 mg/L	22	2

Sensitivity = mass in picograms
giving 0.0044 signal area

LOD = concentration in ug/L of a signal
= to 2 times the standard deviation of the blank

Table 5

Comparison of Within Run Precision

<u>Conc, ug/L</u>	<u>N</u>	<u>No Additive</u>	<u>600 mg Ni /L</u>
		<u>mean (SD) % RSD</u>	<u>mean (SD) % RSD</u>
20	6	21.9 (1.4) 6.4	20.0 (1.7) 8.5
100	6	99.8 (6.7) 6.7	98.2 (2.0) 2.0

Table 6

Comparison of Between Run Precision

<u>Conc, ug/L</u>	<u>N</u>	<u>No Additive</u>	<u>600 mg Ni /L</u>
		<u>mean (SD) % RSD</u>	<u>mean (SD) % RSD</u>
20	4	22.4 (5.2) 23.2	19.5 (0.6) 3.1
100	4	98.3 (9.3) 9.5	99.5 (1.5) 1.5

the tracings reproduced in Figure 4, the enhanced response of a 50 ppb tin standard in the presence of nickel is evident. The peak height and area are five-fold greater than the no nickel additive peaks'. The overall shape is also more symmetric. The signal to background noise ratio is improved as well.

The appearance time of the signal, defined as the time at which ten percent of the signal peak height maximum is generated, is also altered by the addition of nickel. The signal was delayed by 30 percent, from 0.75 sec to 0.98 sec. The appearance temperature was raised from 1519 K in the no nickel added sample to 2285 K in the nickel added sample. These results are summarized in Table 7.

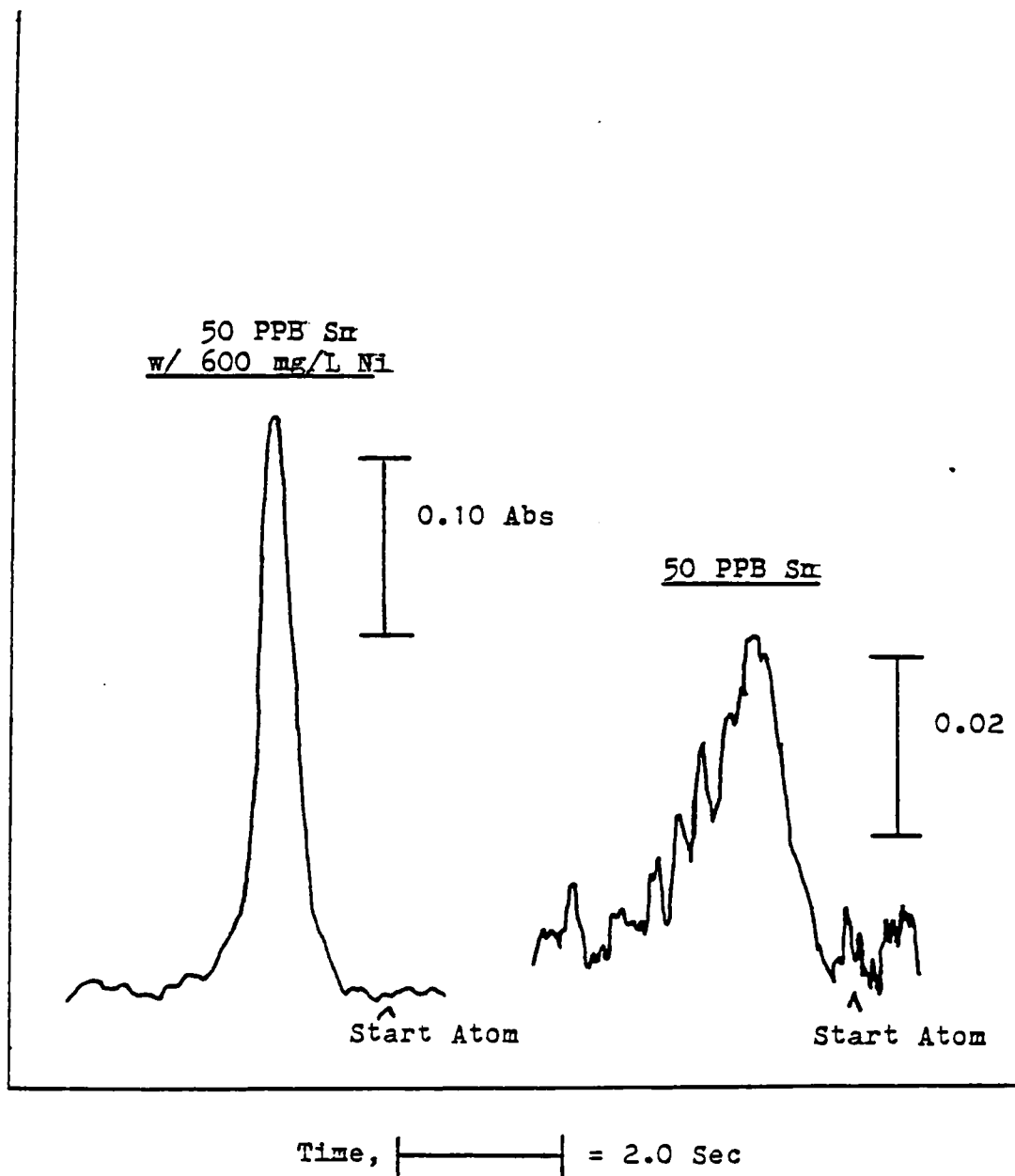


TABLE 7

Comparison of Appearance Times and Temperatures
for Unmodified and Nickel Modified Tin

	<u>N</u>	<u>No Modifier</u>	<u>Nickel added</u> <u>at 600 mg/L</u>
App. Time, sec	6	0.75 +/- 0.04	0.98 +/- 0.09
App. Temp., K	2	1519 +/- 85	2285 +/- 50

MECHANISM

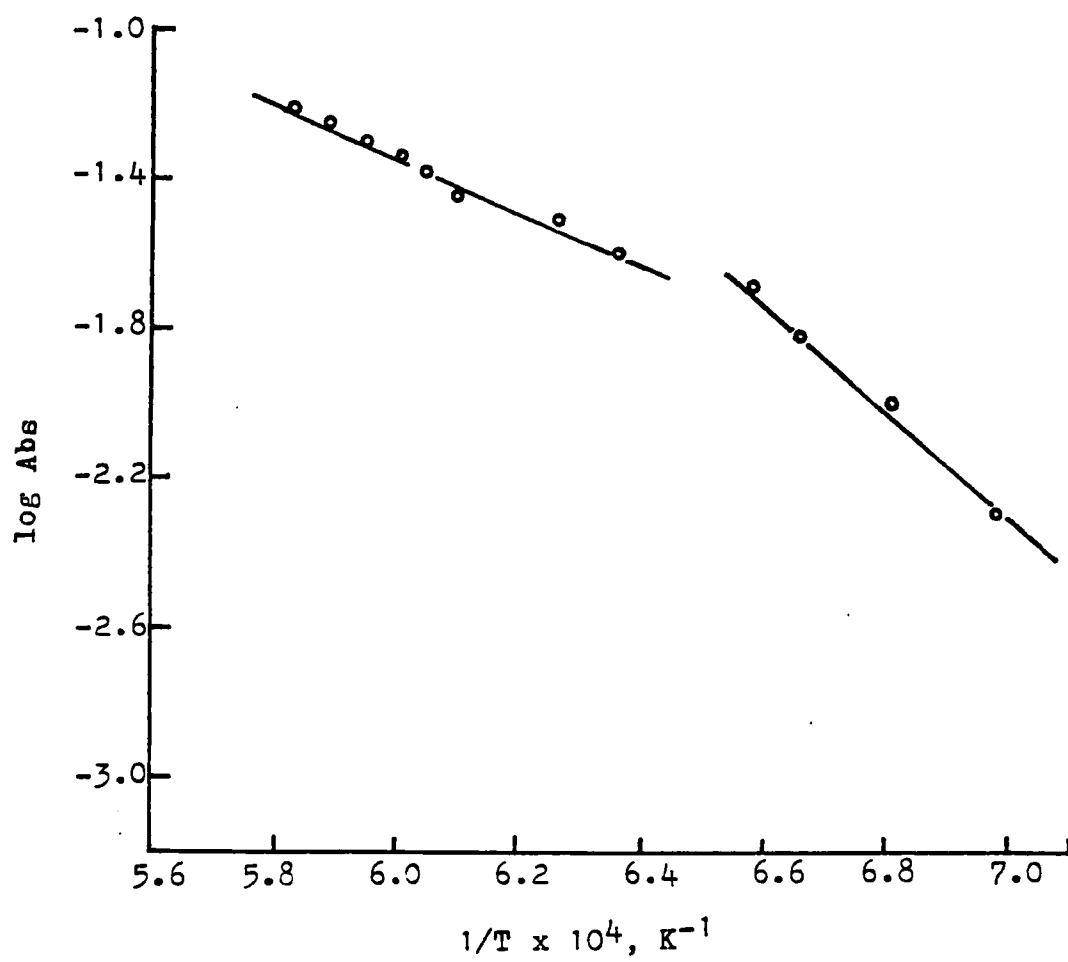
The delayed appearance, higher atomization temperature, and altered peak shape are all indicators of an altered atomization mechanism. The change in peak height indicates a change in the rate of atom formation, while the delayed appearance and narrower peak width indicate a different atomization interval and hence, a different atom residence time (10). The latter factor is also the source of the enhanced peak area, since the integrated absorbance is dependant on the atom residence time in the absorption pathlength.

In order to study the atomization mechanism of the nickel modified analysis more fully, the thermodynamic/kinetic approach of Chakrabarti, et al (13), for determining reaction intermediates was used. From equation 1, a graph of the log Absorbance versus inverse absolute temperature should yield a straight line whose slope equals $-(E_a + H)/2.3R$. Performing a least squares analysis on the data and multiplying the slope by $2.3R$ gives an energy value which can be related to the intermediate form of the element generating the atomic species in the gas phase. In order to verify methodology, data was collected for the no nickel added case first and the results compared with those obtained by Chakrabarti's group. These data are shown in Table 8 and a representative graph shown in Figure 5. For the no added modifier analysis, a two-stage process with two energies close to

Table 8

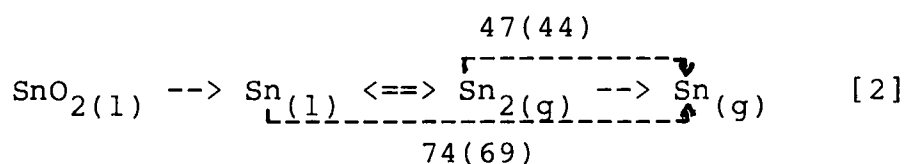
Data For Arrhenius Graph - No Modifier

<u>Run #</u>	<u>Abs</u>	<u>log Abs</u>	<u>T, K</u>	<u>1/T x 10⁴, K</u>
1	0.005	-2.303	1434	6.974
	0.010	-2.000	1469	6.807
	0.015	-1.825	1505	6.645
	0.020	-1.695	1519	6.583
	0.025	-1.600	1572	6.361
	0.030	-1.525	1604	6.234
	0.035	-1.455	1638	6.105
	0.040	-1.395	1656	6.039
	0.045	-1.350	1666	6.002
	0.050	-1.305	1681	5.949
	0.055	-1.255	1699	5.886
	0.060	-1.221	1717	5.824
2	0.010	-2.000	1605	6.231
	0.015	-1.825	1640	6.098
	0.020	-1.695	1656	6.039
	0.025	-1.600	1680	5.952
	0.035	-1.455	1698	5.889
	0.045	-1.350	1723	5.804
	0.055	-1.255	1758	5.688
	0.065	-1.161	1783	5.609



the previously reported values was obtained (Table 9). This indicated our instrumental method was producing acceptable results, and was then applied to the added nickel case. The data for those runs is shown in Table 10 and a representative graph shown in Figure 6. The results are summarized in Table 11.

The mechanism proposed by Chakrabarti's group for the no modifier present process is carbon reduction of the oxide at the surface of the cuvette followed by vaporization of the liquid metal:



where the numbers indicate the activation energies obtained in their research and (in this study) in Kcal/mole. In the vaporization process, tin forms a metal dimer in the gaseous state as well as the atomic species. Thus, two energies are seen, the first from the vaporization of tin liquid to gaseous tin when the concentration of the dimer is relatively small; and the second from the dissociation of the dimer after all the tin has vaporized from the surface. Wendl and Muller-Vogt established that upon drying, the tin monoxide is formed, and at an ashing temperature of 450 °C, this is oxidized to the dioxide (21). Above 850 °C the dioxide is reduced thermally back to

Table 9

Results From Arrhenius Graphs - No Modifier

	<u>(Ea + ΔH), Kcal/mole</u>	
	<u>First Stage</u>	<u>Second Stage</u>
This Study	69 +/- 10	44 +/- 10
Previously Reported (13)	74 +/- 7	47 +/- 5
Literature Values *	72.2 (Δ H _f , Sn)	46.7 (Sn-Sn)

* Handbook of Chemistry and Physics,
64th Ed. 1983/4; R.C. Weast, Ed.;
The Chemical Rubber Co., Cleveland, Ohio

Table 10

Data For Arrhenius Graph - Nickel Added

<u>Run #</u>	<u>Abs</u>	<u>log Abs</u>	<u>T, K</u>	<u>1/T x 10⁴, K</u>
1	0.005	-2.301	2268	4.409
	0.007	-2.155	2285	4.376
	0.009	-2.046	2294	4.359
	0.010	-2.000	2319	4.312
	0.014	-1.854	2353	4.250
	0.019	-1.721	2370	4.219
	0.024	-1.620	2387	4.189
	0.031	-1.509	2404	4.160
	0.039	-1.409	2430	4.115
2	0.003	-2.523	2302	4.344
	0.005	-2.301	2328	4.296
	0.007	-2.155	2353	4.250
	0.009	-2.046	2370	4.219
	0.010	-2.000	2387	4.189
	0.012	-1.921	2413	4.144
	0.014	-1.854	2430	4.115
	0.020	-1.699	2447	4.087
	0.029	-1.538	2464	4.058
	0.043	-1.367	2472	4.045

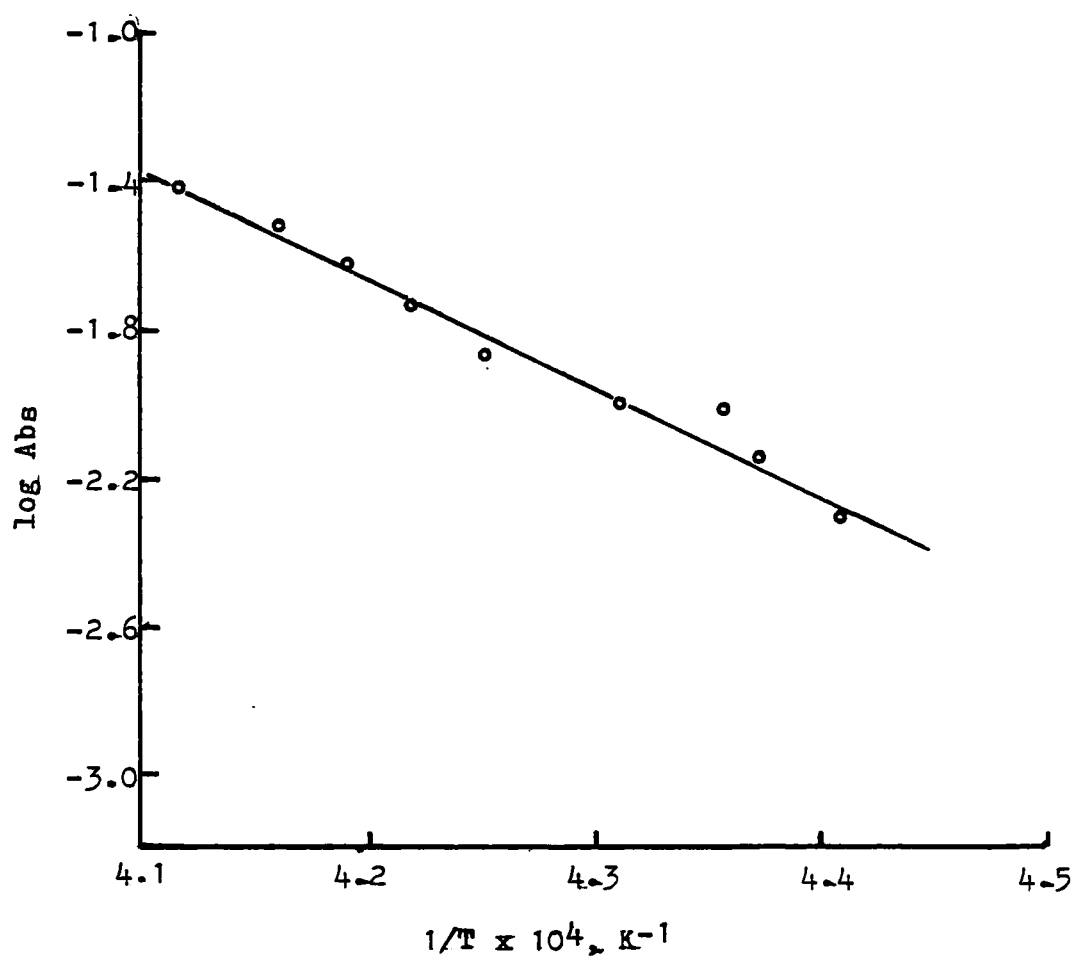


Table 11

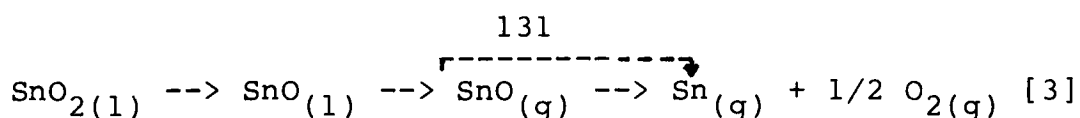
Results From Arrhenius Graphs - Nickel Added

	<u>(Ea + ΔH), Kcal/mole</u>
This Study	145 +/- 10
Literature	131 +/- 5
Value *	(Sn-O)

- * Handbook of Chemistry and Physics,
64th Ed. 1983/4; R.C. Weast, Ed.;
The Chemical Rubber Co., Cleveland, Ohio

the monoxide. Above 1000 °C losses of the volatile monoxide begin to occur. No losses of tin were detected in this study using an ashing temperature of 1050 °C. Aggett and Sprott calculated the temperature at which carbon reduction of tin oxide to metallic tin occurs to be 1140 °C (20). Thus, carbon reduction would be expected to occur at the start of the atomization cycle. L'vov and Ryabchuk (22) also concluded that reduction was favored for tin based on measurements of the partial pressure of oxygen in the furnace compared with calculated equilibrium values. Chakrabarti, et al, calculated species equilibrium temperatures for several metal oxides, incorporating carbon as a reactive intermediate (23). Their calculated and observed temperatures for tin, 1600 K and 1560 K respectively, are very close to other values obtained (1560 K, Ref. 13) and this study (1519 K). They concluded that carbon reduction was indeed thermodynamically favorable. Since a lower atomization temperature accompanies carbon reduction, a higher atomization temperature should occur if the reduction process were inhibited. Blocking the reduction process would also suggest that thermal dissociation of the oxide would be the process by which the atomic species is then formed.

This is a likely scenario for the altered atomization of tin in the presence of nickel. The reaction sequence proposed for this process is:



where the gas phase dissociation of the monoxide takes 131 +/- 5 Kcal/mole. The mean energy obtained in this study was a bit higher, 145 +/- 10 Kcal/mole, but within range to suggest the reasonableness of the proposed mechanism. A more sophisticated instrumental setup for collecting the absorbance versus temperature data might yield more accurate results. The altered appearance time and temperature are more clearly evident in the smoothed tracings of the unmodified and modified peak regions utilized, depicted in Figure 7.

An alternate mechanism for the tin atomization in the presence of nickel might be the formation of a tin-nickel diatomic moiety. This is less likely to occur, however, based on the observations by Thompson, et al (17) and Vickrey, et al (19), mentioned earlier. Vickrey's surface analysis and Thompson's calcium addition indicate that where carbide forming elements exist together in a matrix on the surface of a graphite cuvette, competition for reaction at the surface occurs. Modification of atomization then, is performed most effectively by uniform coating of the graphite surface, thereby blocking the carbon reduction process.

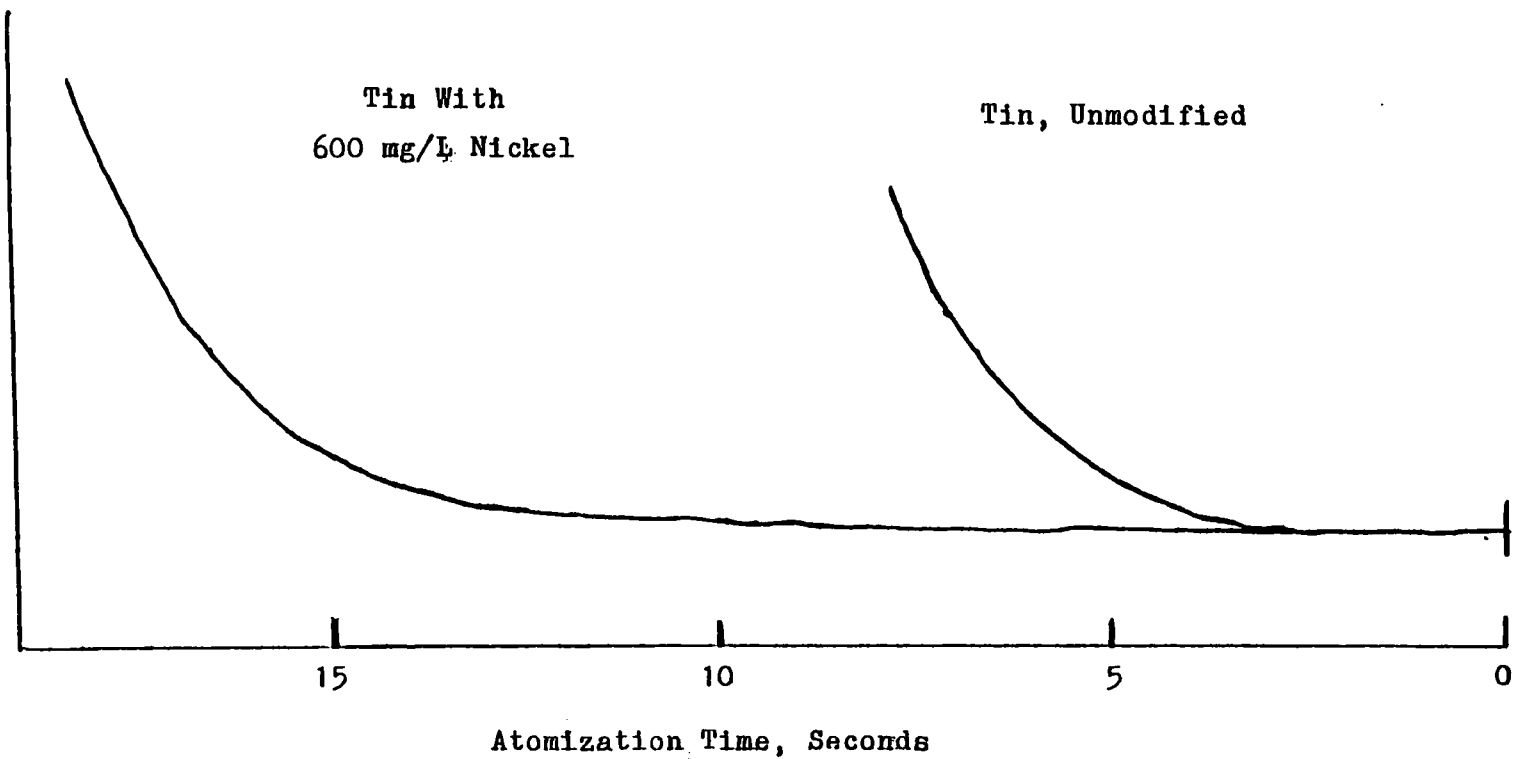


Figure 7. Early Rising Portion of Peaks from Absorbance versus Time Data

INTERFERENCES

For most of the compounds studied, nickel either eliminated or greatly reduced their effect upon the tin signal. The exception was sulfuric acid, which at high concentrations gave low and inconsistent results. The data are shown in Figure 8. The figure shows the percent integrated absorbance obtained relative to the matrix free sample as a function of added sulfate; eg $(\text{Abs}_{\text{matrix}} / \text{Abs}_{\text{free}}) \times 100$. The data with and without nickel were tabulated separately, thus nickel plus matrix compared to nickel without matrix, not to the no nickel added sample. Table 12 lists the nickel nitrate concentrations used in the added nickel runs. The reasons for the inconsistencies are not known with certainty at this time, but the effect has been observed previously (24). Spectral interferences from sulfuric acid in the analysis of selenium by graphite furnace A. A. has been reported by Martinsen and Langmyhr (25). The pyrolysis products CS, COS, S₂, and SO₂ absorb near the selenium line. SO₂ also has a strong absorption line near the tin 224.6 nm line (26), and has been shown to exhibit a Zeeman effect (9).

Sodium and potassium sulfates depressed the tin signal considerably at low ppm concentrations. Figures 9 and 10 show the percent absorbances obtained for these compounds. Figure 9-B shows the absolute absorbances for the sodium sulfate data for comparison with the percent relative absorbance graph. The percent relative absorbance was

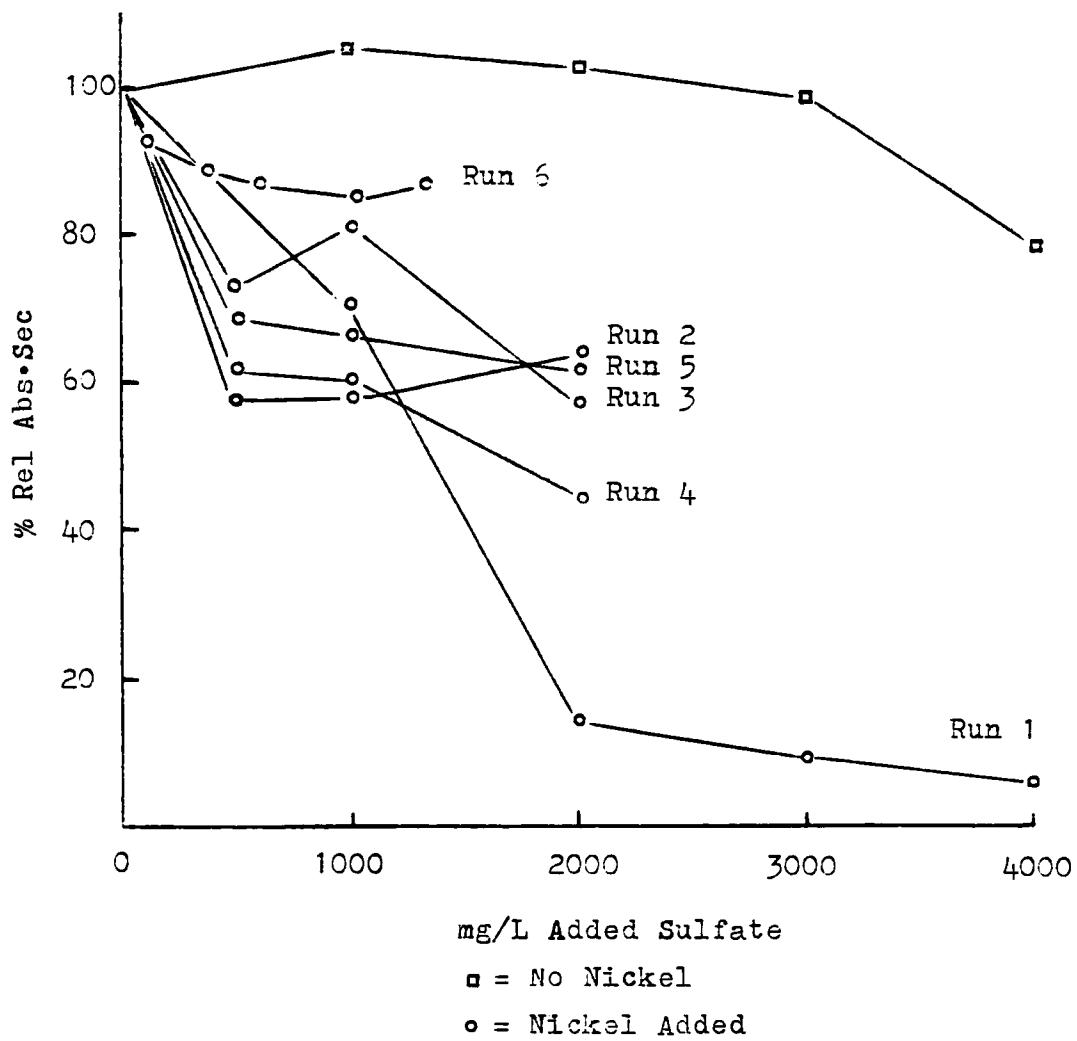
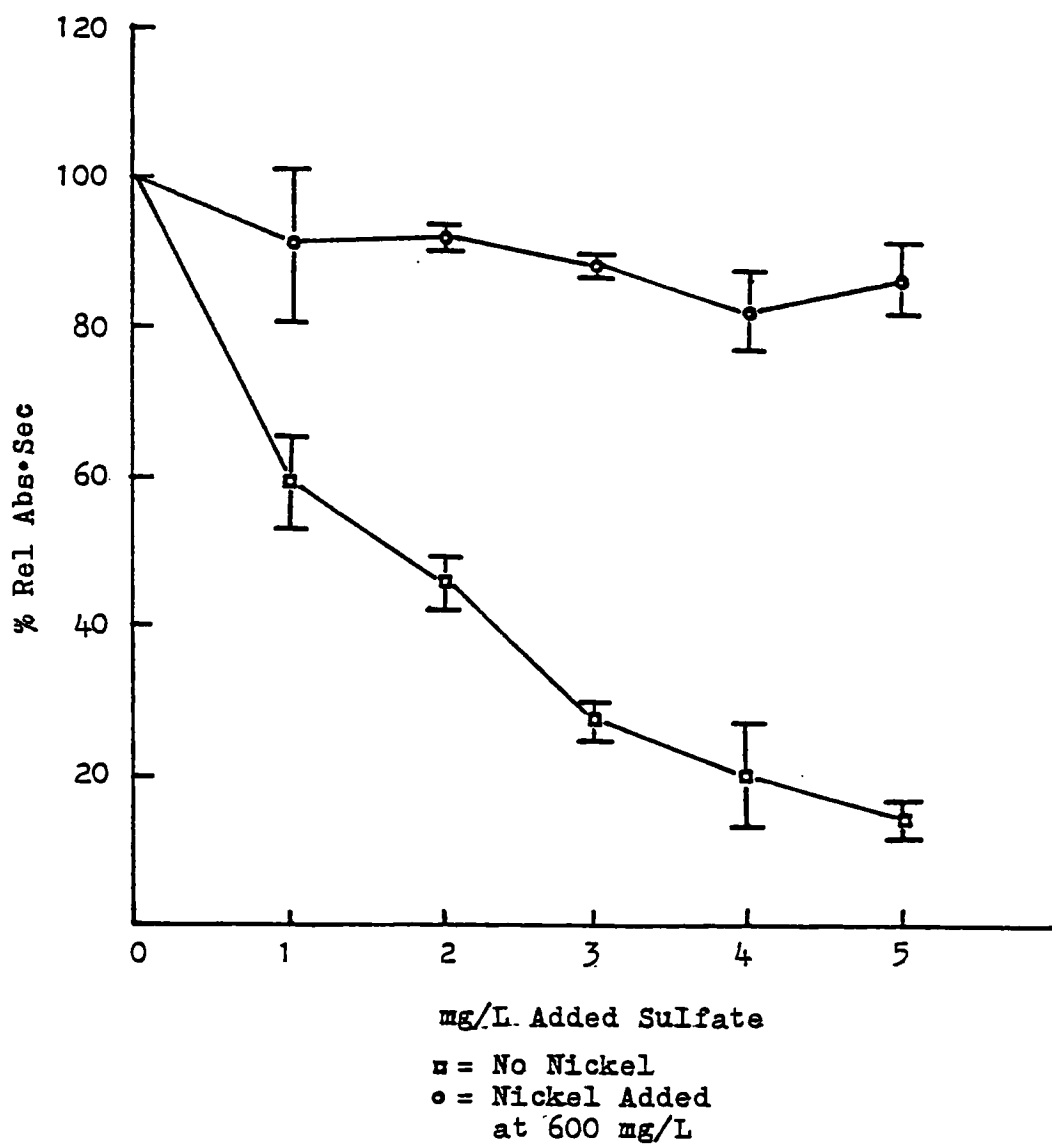
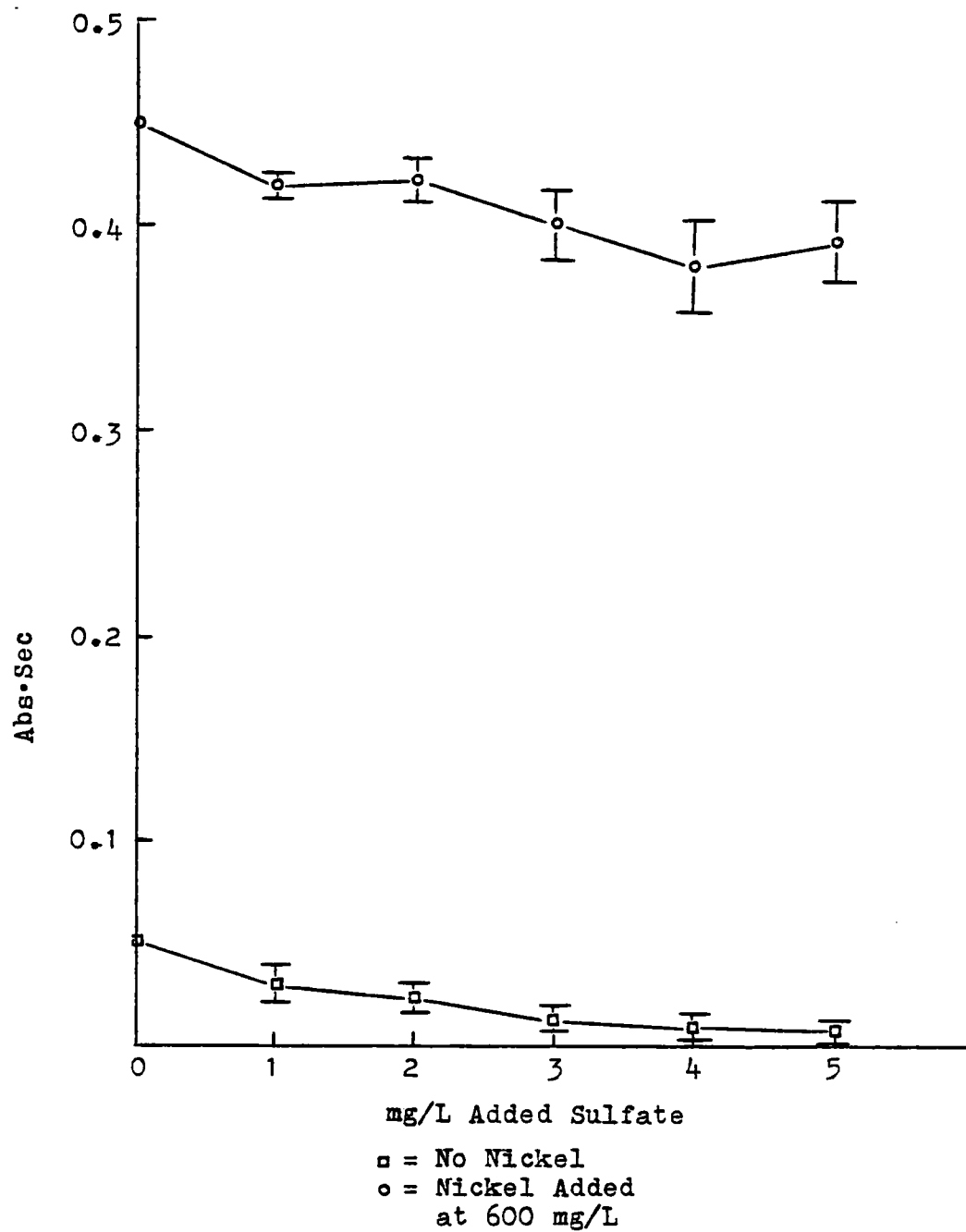


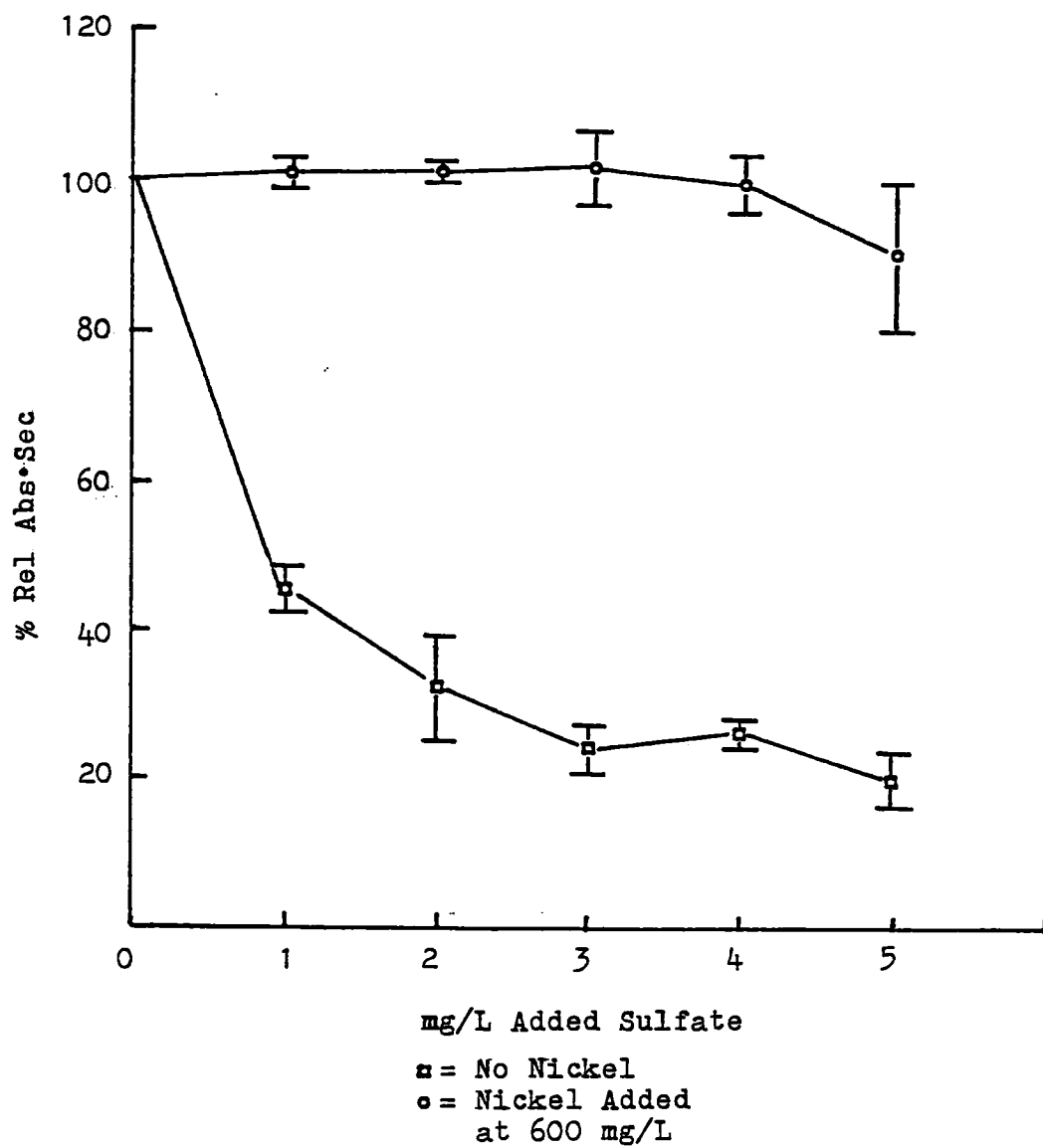
Table 12

Nickel Nitrate Concentrations Used in
Sulfuric Acid Data of Figure 8

<u>Run #</u>	<u>conc H₂SO₄, mg/L</u>	<u>conc Ni²⁺, mg/L</u>
1	0	600
	1000	600
	2000	600
	3000	600
	4000	600
2, 3	0	600
	500	600
	1000	600
	2000	600
4, 5	0	600
	500	1100
	1000	1600
	2000	2600
6	0	600
	120	800
	360	1000
	600	1200
	1100	1100
	1320	1300

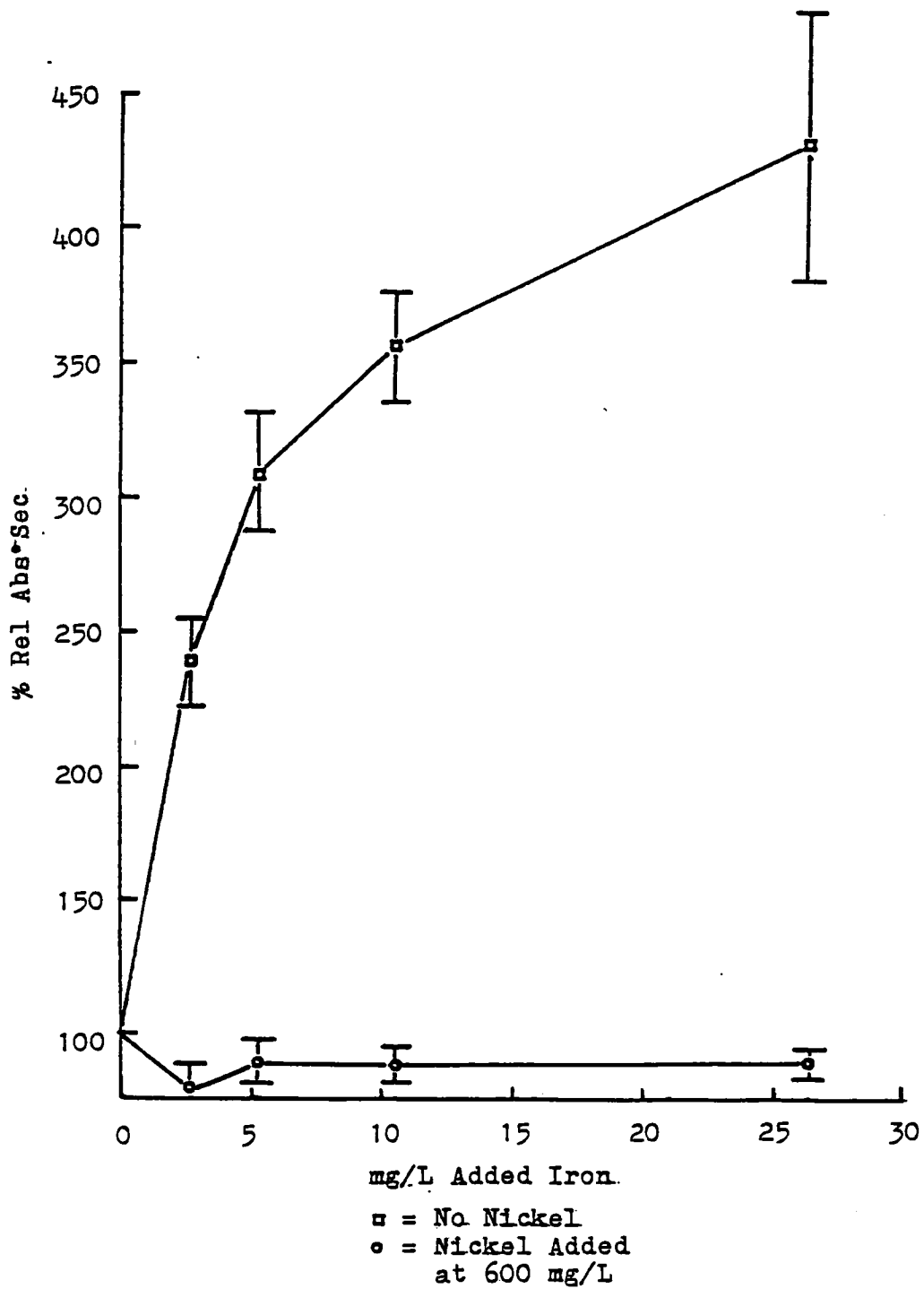






utilized to maximize the trends observed in each series of data, and shall be relied upon for the remaining interference data. Thus in the presence of as little as 5 mg/L sulfate from the sodium salt the signal is reduced by more than 80 percent. The addition of nickel is seen to limit the interference to about ten percent reduction throughout the concentration range studied for each salt. Since the nickel modified signal absorbance was initially five-fold greater, this significantly improves the sensitivity of the tin analysis in a sodium or potassium sulfate matrix.

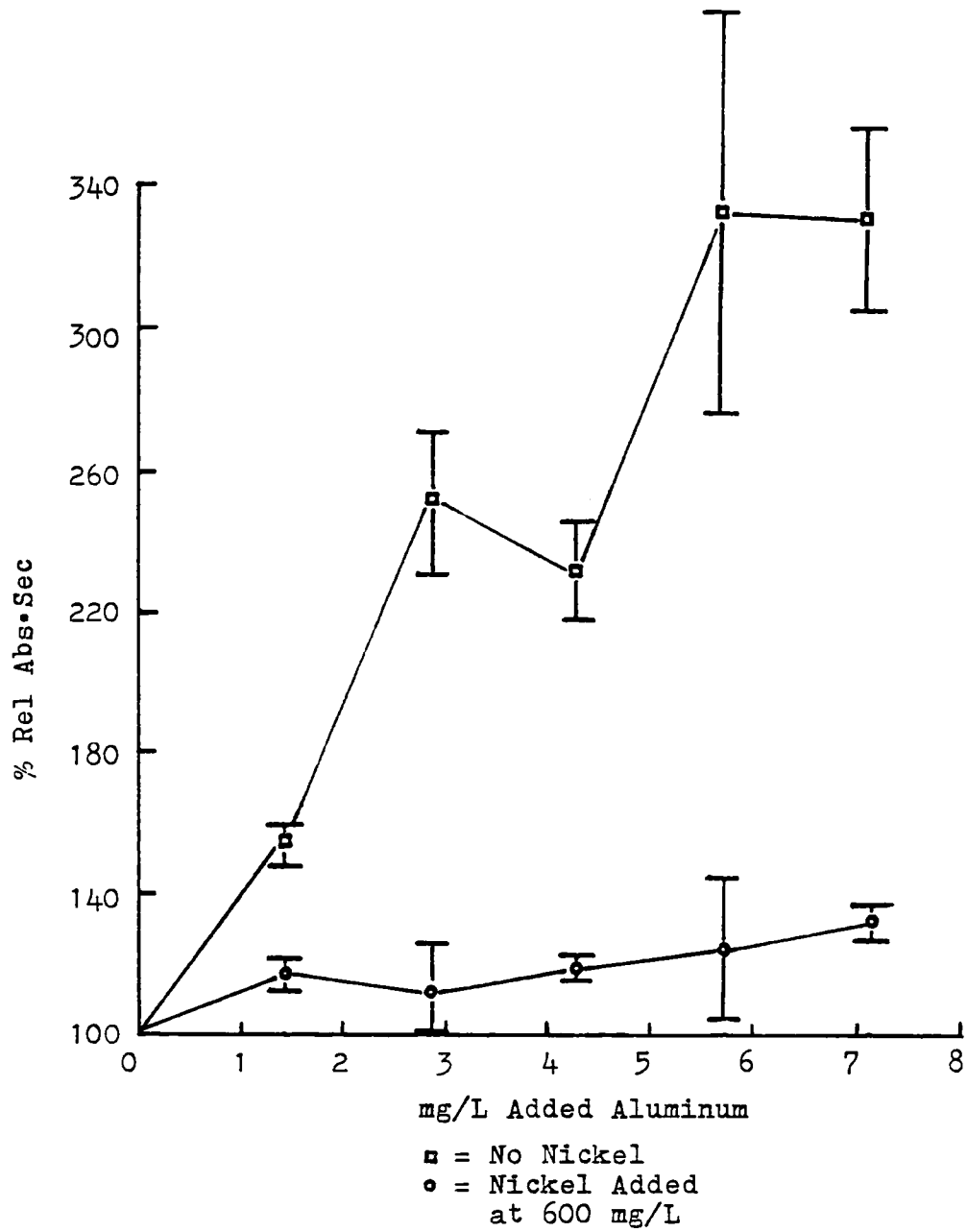
When ferric chloride was the matrix, a progressive enhancement of the signal was observed. As shown in Figure 11, at 26 mg/L added iron, the absorbance was over 400 percent of the that of the matrix free sample. This is the opposite of what was reported by Tominaga and Umezaki in 1979 (14). The differences in their instrumental setup were the ashing temperature (700 °C versus 1050 °C in this study) and the use of deuterium background correction versus Zeeman effect. They did not indicate the use of nitric acid or other oxidizing agent, which Pruszkowska's group (14) and we found necessary when chloride was present. It is possible the signal loss they observed was due to loss of volatile tin(IV) chloride rather than suppression by the matrix. In addition, iron was one of the elements, along with tin and nickel, whose atomization temperature Aggett and Sprott found was significantly



influenced by the use of a graphite cuvette versus a tantalum one (20).

Aluminum nitrate and aluminum chloride also exhibited an enhanced absorbance in the tin analysis. Figures 12 and 13 show the percent relative absorbances obtained for the nitrate and chloride respectively. The effect is not as large as that exhibited by ferric chloride, and is more erratic. The reproducibility, especially the aluminum chloride, was quite poor. While the addition of nickel improved the analysis in both situations, the nickel modified aluminum chloride matrix is especially interesting. Comparing the shape of the curve, rising at a steadily decreasing slope to a plateau, with the effect of added nickel on 200 ppb tin shown in Figure 2, suggests the possibility of a nickel nitrate/aluminum chloride combination modifier. Aluminum also forms a carbide, and combines with nickel in a diatomic and polyatomic molecules (27). The difference between the chloride and nitrate of aluminum in interacting with nickel nitrate as a modifier may be the efficiency in coating the graphite surface, as was found to be the case with zirconium, tantalum, and molybdenum salts by Vickrey and Harrison (19).

Table 13 summarizes the performance of nickel in reducing interferences in the tin furnace analysis. The effect in each case is improved over the no modifier added analysis, as indicated by the reduced percent change in the absorbance when nickel is added. The reproducibility of the



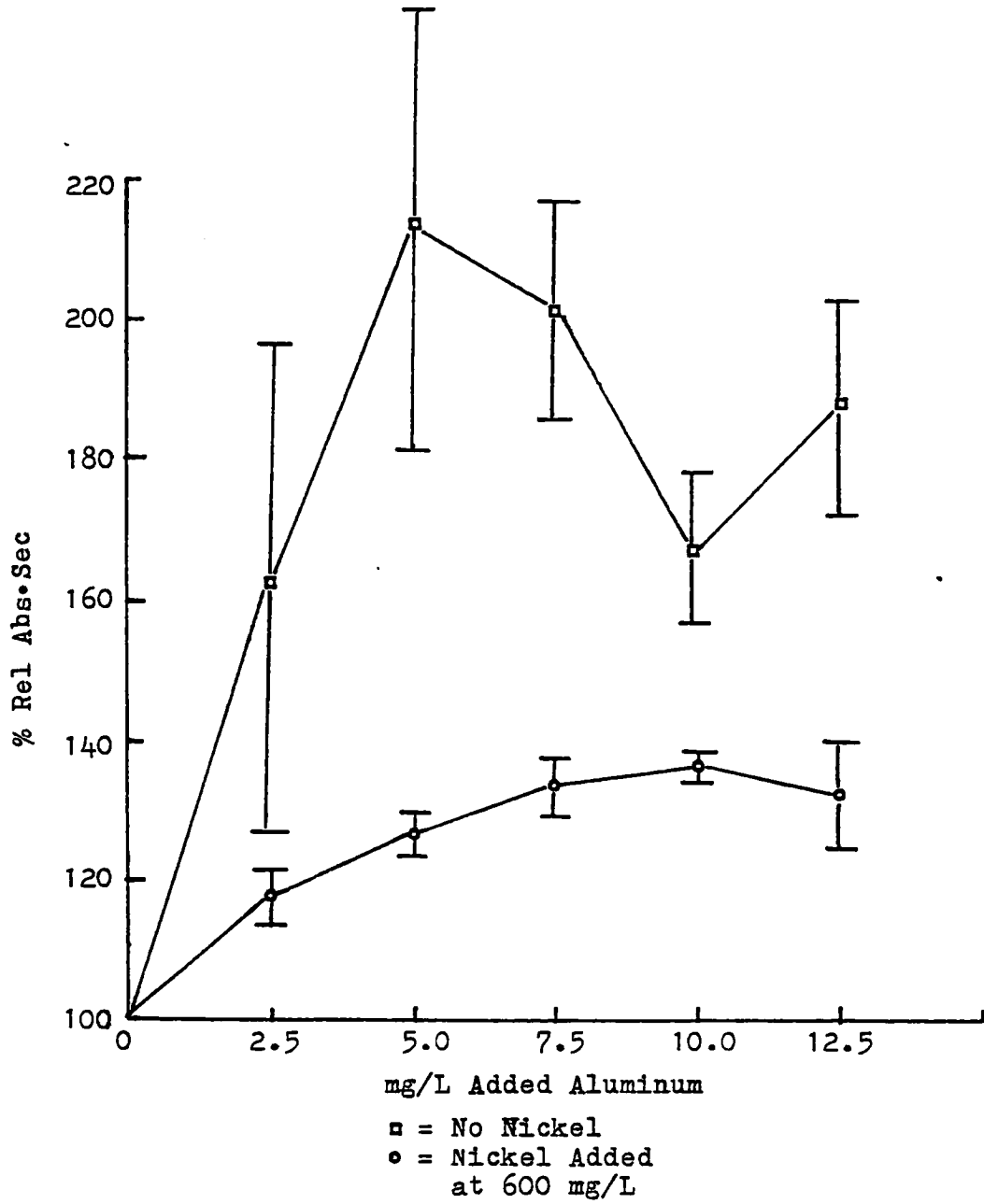


Table 13

Summary of Nickel Performance in Reducing Interferences

<u>Compound</u>	<u>Level</u>	<u>% Change</u>	<u>(% RSD)</u>	<u>% Change</u>	<u>(% RSD)</u>
	<u>mg/L</u>	<u>No Modifier</u>		<u>Nickel Added</u>	
Na ₂ SO ₄	1	-40.9	(10.7)	-8.7	(10.9)
	5	-84.2	(15.8)	-14.1	(5.0)
K ₂ SO ₄	1	-54.6	(7.5)	+1.3	(2.2)
	5	-80.0	(17.0)	-9.1	(11.6)
Al(NO ₃) ₃	1.5	+55.1	(3.6)	+18.2	(13.1)
	7.3	+230	(7.7)	+33.5	(4.2)
AlCl ₃	2.5	+62.7	(21.2)	+18.3	(3.6)
	12.5	+88.3	(8.2)	+32.8	(6.0)
FeCl ₃	5.2	+138	(6.9)	-21.1	(11.9)
	26.3	+332	(11.8)	-12.4	(6.2)

measurements is improved for most levels as well, indicated by the improved percent relative standard deviation.

Having examined some of the major interferences individually, a spiked natural sample was run to observe combined interference effects. Sea water was chosen because it is one of the most difficult matrices in graphite furnace analysis, and because of the interest expressed by the Applied Marine Research Laboratory, Norfolk, Va. in developing a method for analyzing tin in the furnace at low levels in this matrix. The results of the Hampton Roads Harbor spikes were somewhat disappointing. It had been hoped that the nickel modifier would enable us to concentrate the seawater and still get a reading at low levels. However, when the water was concentrated to 40 % of its original volume, the tin absorbance was only 15 percent of the expected value. Diluting the sample to 80 % of its original volume improved recovery to 30 percent. To achieve these results it was necessary to modify the furnace temperature program to remove most of the matrix. The program utilized, listed in Table 14, extended the drying cycle to three steps totalling 60 secs, and the ashing temperature and time to 1100 °C and 30 secs, respectively. At the higher ashing temperature, it is possible that some losses of tin monoxide could occur (21), accounting for some of the effect observed. Since the sample was spiked with tin just prior to analysis, suppression by the matrix is likely responsible for most of the effect. This could

TABLE 14

Heating Program Utilized for Salt
Water and High Acid Content Matrices

<u>Stage</u>	<u>Temp, °C</u>	<u>Time, sec</u>
Dry	25 - 55	30
	55 - 85	30
	85 - 120	20
Ash	1100	50
Atomize	2500	7
Clean	2800	3

arise from trapping of the analyte at the surface or production of a more volatile species, such as the chloride (BP 652 °C).

National Bureau of Standards samples were used to check the accuracy of the analyses. The results are reported in Table 15. A low level aqueous standard would have been more appropriate for this study, however none was available. The dibutyltin hexanoate digest had to be serially diluted to be read in the linear range of this method. The temperature program in the furnace was the same as that for the salt water matrix outlined in Table 14. This was necessary due to the high acid content of the digest. The value for the citrus leaves is not certified, but provided for information purposes. The values obtained in both cases are low, but by less than five percent. The percent relative standard deviations are high for both assays. In the case of the dibutyltin hexanoate, this is probably due to the dilutions which were necessary to bring the sample within the linear range of the method. These dilution factors were incorporated into the final results. The citrus leaves digest had an acid concentration of 80 percent, which made pipetting of the solution more difficult due to increased viscosity, and affected the reproducibility of the measurements.

TABLE 15

Results of National Bureau of Standards Assay

<u>Sample</u>	<u>N</u>	<u>Value Obtained</u>		<u>Reference Value</u>
		<u>mean(SD)</u>	<u>(% RSD)</u>	
Dibutyltin				
Bis(2-Ethyl Hexanoate)	4	22.5(3.1) %	(13.8)	22.95 +/- .07 %
# 1057b				
Citrus Leaves	4	0.23(0.08) ug/g	(34.8)	0.24 ug/g*
# 1572				

* This value is not certified

CONCLUSIONS

This study has shown that nickel is indeed a suitable matrix modifier for tin in graphite furnace atomic absorption analyses. The signal response is increased five-fold, the standard curve is linear below 200 ppb tin and the sensitivity is improved two-fold, from 56 pg tin to 22 pg. The minimum detectable level is reduced from 16 ppb tin to 2 ppb. It is as effective as ascorbic acid and ammonium phosphate in removing interference effects, but does not leave a residue on the surface.

The mechanism of this modification is thought to arise from preferential carbide formation at the surface by nickel, effectively blocking carbon reduction of tin(IV) oxide to metallic tin. The dissociation of the oxide in the gas phase takes place at a higher temperature, allowing for higher ashing temperatures and improved matrix removal in the furnace.

Interference effects for sodium and potassium sulfates, and ferric chloride are reduced to ten percent loss of signal absorbance when nickel is added. Aluminum nitrate and aluminum chloride still show positive interference in the presence of nickel, but only 30 percent compared to 200-300 percent when no modifier is used. Aluminum chloride could be a possible additive modifier with nickel, based on results seen here. Further work could verify this.

Salt water matrices are still a problem for the

graphite furnace analysis of tin. Presently, a 30 percent recovery of spiked samples has been the best achieved, but even this is an improvement over the analysis with no modification. Such samples will still require acid digestion with nitric acid, concentration, and a large quantity of modifier to obtain any usable results.

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