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**STUDIES ON ELECTROTHERMAL ATOMIZATION IN
GRAPHITE FURNACE ATOMIC ABSORPTION
SPECTROMETRY AND ELECTROTHERMAL
VAPORIZATION INDUCTIVELY COUPLED PLASMA
MASS SPECTROMETRY**

by

Sabah Al-Maawali, B. Sc.

A thesis submitted to
the Faculty of graduate research
in partial fulfilment of
the requirements for the degree of

Master of Science

Department of Chemistry

Ottawa, Ontario

September, 1991

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ABSTRACT

In order to determine the cause for low analytical sensitivity of tin in graphite furnace atomic absorption spectrometry (GFAAS), mechanisms for atomization of tin in GFAAS were studied using isothermal atomization from a graphite probe furnace. The absorbance signal profiles were used to determine rate constants for atom formation and atom loss and the energy of activation for atom formation. Also, the gas combination factor, n , for diffusion of tin in argon purge gas was evaluated from diffusion coefficients obtained at different temperatures. Experimental evidence shows that tin is lost, probably as $\text{SnO}_{(g)}$ at low temperatures (≥ 950 K). At high temperatures (≥ 2050 K), $\text{SnO}_{(g)}$ is thermally dissociated to $\text{Sn}_{(g)}$ and O_2 . The low analytical sensitivity of tin in GFAAS is due to the pre-atomization loss of the $\text{SnO}_{(g)}$ from the graphite furnace at temperatures (< 2050 K). Since this loss of tin as $\text{SnO}_{(g)}$ in GFAAS is due to the employment of one single heated medium (graphite furnace) for two different functions, vaporization and atomization, which are separate processes for tin (both spatially and temporally), the way to prevent such loss is to employ an analytical technique for tin which allows two heated media—one for vaporization and the other for atomization or ionization. Electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) which was such an analytical technique was therefore employed together with chemical modifiers. The analytical sensitivity of ETV-ICP-MS for Sn, Ag and Pb were enhanced five-fold by the use of mixed, chemical modifiers: $\text{Mg}(\text{NO}_3)_2 + \text{Pd}(\text{NO}_3)_2$, or $\text{Mg}(\text{NO}_3)_2 + \text{PdCl}_2$.

The undersigned hereby recommend to
The Faculty of graduate studies and Research
acceptance of the thesis,

Studies on Electrothermal atomization in Graphite Furnace
Atomic Absorption Spectrometry and Electrothermal vaporization
Inductively Coupled Plasma Mass Spectrometry

submitted by

Sabah M.A. Al-Maawali

in partial fulfillment of the requirements
for the degree of Master of Science

Thesis Supervisor

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Chairman, Department of Chemistry

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OBJECTIVES

The objectives of this research were as follows:

- 1 To investigate the cause for low analytical sensitivity of tin in graphite furnace atomic absorption spectrometry (GFAAS).
- 2 To investigate mechanisms of tin atom formation and loss in GFAAS.
- 3 To investigate the effects of the mixed chemical modifiers, $\text{Mg}(\text{NO}_3)_2$ + $\text{Pd}(\text{NO}_3)_2$, or $\text{Mg}(\text{NO}_3)_2$ + PdCl_2 on the determination of tin, lead and silver by electrothermal vaporization inductively coupled plasma spectrometry (ETV-ICP-MS).

The objectives 1 and 2 were fulfilled by studying mechanisms for formation and loss of tin atoms in GFAAS using isothermal atomization by the graphite probe technique. The objective 3 was fulfilled by studying the quantitative determination of tin, lead and silver by ETV-ICP-MS using the mixed, chemical modifiers named above.

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Chapter 1

MECHANISMS OF FORMATION AND LOSS OF TIN ATOMS IN GRAPHITE

PROBE FURNACE ATOMIC ABSORPTION SPECTROMETRY

INTRODUCTION

Tin has been found to be one of the most difficult elements to be determined by graphite furnace atomic absorption spectrometry (GFAAS) [1,2,3]. Tin has also been observed to have a tendency to form volatile compounds [1,4]: gaseous oxides, halides and sulphides, which are stable up to relatively high temperatures. If tin is determined by GFAAS in non-isothermal conditions, the sensitivity is found to be poor [1] because tin is lost from the furnace as gaseous, molecular species before the high atomization temperature is attained. However, the sensitivity is improved if tin is determined in an isothermal environment [1]. In spite of this, tin is still a very difficult element to be determined by GFAAS [1,4]. Mechanism of atomization of tin may hold the key to understanding the unusually low analytical sensitivity for tin by GFAAS, and should therefore be studied.

The state of our knowledge of the mechanisms of atomization in GFAAS has been summarized by Chang and Chakrabarti [5]. Several workers [6-12] have studied mechanisms of gaseous atom formation in graphite furnace atomizers using the following

approaches: thermodynamic [2,8], kinetic [6,9] and empirical approach based on atomization/decomposition curves [13]. Smets [14] and L'vov [15] have discussed atomization processes in graphite atomic absorption spectrometry. Sturgeon et al. [10,11] proposed a model in which the logarithm of the absorbance value from the initial, leading edge of the atomic absorption signal profile was plotted against the reciprocal of the absolute temperature to yield an "activation energy" for the rate determining step in the sequence of reactions leading to atomization of the analyte. Vaporization or sublimation of the analyte from its elemental form has been reported to be one of the mechanisms of the atom formation in GFAAS [10,11]. This mechanism has also been supported by independent data from x-ray diffraction analysis of the products left on the surface of the graphite atomizer after the analyte has been atomized at a high temperature. The results from x-ray structure analysis indicate that the free metal is formed in the case of Cu, Fe, Co, Pb and Ni [16].

In pulse-heated graphite furnace atomic absorption spectrometry, the metal, usually as the nitrate or sulphate in aqueous solutions, is injected into the furnace. The metal oxide usually results when the analyte is heated even when the analyte is taken as the halide, since hydrolysis to oxygen containing species frequently occurs. Recently, the experimental results of a multiple-probe, combining atomic absorption spectrometry and mass spectrometry show that the atomization of vanadium [17] and lead [18] in an ultra-high vacuum of a mass spectrometer produces VO_2^+ and VO^+ at a temperature of about 1500 K, and PbO^+ at a temperature of about 700 K, respectively. The majority

of precursors to gas phase atoms are either free metal, metal oxides (usually monoxides [19, p.129]), halides or carbides.

When a metal oxide is a precursor, conversion to the metal in the condensed phase at low temperatures (even below the appearance temperature of the analyte element) may occur by thermal decomposition or dissociation of the metal oxide. Sturgeon et al. [20] have defined the appearance temperature as the lowest temperature at which the atomic absorption signal of the analyte element is just detectable above the baseline signal.

Campbell and Ottaway [2] have assumed that reduction of metal oxides by carbon is rapid, and have correlated the appearance temperature of the atomic absorption signal with the temperature at which reduction of the metal oxides by solid carbon at the surface of the graphite atomizer becomes thermodynamically favourable, using the temperature at which $\Delta G^0 < 0$ as the appearance temperature. The work of Campbell and Ottaway [2] suggests that a large number of analyte species produce gaseous analyte atoms by carbon reduction. Sturgeon et al. [20] have calculated the standard free energy change for the conversion of the metal oxide into metal in the condensed phase at the temperature nearest to the experimentally determined appearance temperature and have concluded that for some elements, gaseous atoms are formed by carbon reduction of the metal oxide to the metal in the condensed phase, followed by vaporization or sublimation of the metal into the gas phase. However, in spite of the above advances made in mechanisms of atomization, mechanisms for atom formation and loss for many

elements including tin in GFAAS are still far from resolved.

THEORY

A kinetic model for atom formation and loss

A model for the atomization reaction is proposed by considering that the reactions that occur in GFAAS are consecutive first order reactions which can be described as follows:

where

[A] represents the concentration of the pre-atomization analyte species,

[X] the concentration of the analyte atomic vapour,

and [Z] the concentration of the analyte atomic vapour that is lost from the analysis volume,

k_1 and k_2 are first order rate constants for atom formation and atom loss, respectively.

At all times

$$[A]_t + [X]_t + [Z]_t = [A]_0 \quad (2)$$

where subscripts refer to time.

If the initial concentration of A is $[A]_0$ and its concentration at any time is [A], then the first order rate law for the consumption of A is,

$$-\frac{d[A]}{dt} = k_1 [A] \quad (3)$$

It rearranges to

$$\frac{d[A]}{[A]} = -k_1 dt \quad (4)$$

Integrating the above equation

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -k_1 \int_0^t dt \quad (5)$$

one obtains

$$[A] = [A]_0 \exp (-k_1 t) \quad (6)$$

The intermediate X is formed from A (at a rate $k_1 [A]$) but decays to Z (at a rate $k_2 [X]$). Its net rate of formation is therefore

$$\frac{d[X]}{dt} = k_1 [A] - k_2 [X] \quad (7)$$

$$\frac{d[X]}{dt} = k_1 [A]_0 \exp (-k_1 t) - k_2 [X] \quad (8)$$

In the limit, $[A]$ tends to zero, which is identified with the exhaustion of the supply of

A. At this point equation (8) simplifies to

$$\frac{d[X]}{dt} = -k_2 [X] \quad (9)$$

By rearranging and integrating equation (9) one gets

$$\ln \frac{[X]}{[X]_0} = -k_2 t \quad (10)$$

Since absorbance is proportional to the concentration of the absorbing species, X, the rate constant for atom loss, k_2 , can be determined from the trailing edge of the absorbance signal profile by using equation (10). Using absorbance values from the trailing edge of the absorbance signal profile and plotting log absorbance vs time one should get a straight line from equation (10); the slope of the straight line plot should yield the rate constant, k_2 .

If the kinetic parameters are evaluated, the shape of the absorbance signal profile may then be determined by solving equation (7). The use of the solution of equation (3) with the initial concentration of A as $[A]_0$ and with no X present initially, gives the following solution of equation (7):

$$[X]_t = \frac{[A]_0 k_1}{k_1 - k_2} (\exp (-k_2 t) - \exp (-k_1 t)) \quad (11)$$

where $[X]_t$ represents $[X]$ at time t .

$[X]_t$ can be related to the measured absorbance by using a factor p :

$$\text{Absorbance} = \frac{p [A]_0 k_1}{k_1 - k_2} (\exp (-k_2 t) - \exp (-k_1 t)) \quad (12)$$

where p is a function of oscillator strength of the atomic line (a constant) and the efficiency with which the analyte atoms are produced (a variable). The efficiency with

which the analyte atoms are produced is dependant upon the nature of the analyte species, and the atomization temperature. The efficiency of atomization can be increased by using an analyte species that is readily vaporized and atomized, and by use of high atomization temperature since the atomization reactions are highly endothermic.

The concentration of the pre-atomization species [A] decreases exponentially from the start of the atomization. The concentration of [X], which is the absorbing species and which is initially zero, at first increases, goes through a maximum when $d[X]/dt$ is zero, and thereafter decreases exponentially with respect to time. When $d[X]/dt$ is zero, the system is said to have attained a stationary state. At that instant and thereafter one sees from equations (6) and (7) that

$$[X] = \frac{k_1}{k_2} [A] = [A]_0 \frac{k_1}{k_2} \exp (-k_1 t) \quad (13)$$

and

$$\frac{[X]}{[A]} = \frac{k_1}{k_2} \quad (14)$$

At a given temperature, the concentrations of both A and X diminish exponentially while maintaining a constant ratio. On differentiating equation (11) one obtains the following expression for the time, $t_{\max}$, required for the attainment of the stationery state:

$$k_1 \exp (-k_1 t_{\max}) = k_2 \exp (-k_2 t_{\max}) \quad (15)$$

$$t_{\max} = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2} \quad (16)$$

where $t_{\max}$ is identified as the time required to attain the absorbance maximum. The values of the $t_{\max}$, and k_2 , rate constant for atom loss, can be obtained experimentally; hence, k_1 , the rate constant for atom formation can be calculated from equation (16). The rate constant for atom formation, k_1 , can be expressed by the Arrhenius equation given below:

$$k_1 = F \exp \left(\frac{-E_a}{RT} \right) \quad (17)$$

E_a is the energy of activation for the rate-determining step

R is the gas constant

T is the absolute temperature

F is the pre-exponential factor

k_1 is the rate constant for atom formation.

A plot of $\log k_1$ as a function of the inverse of the absolute temperature should yield a straight line, from which activation energy, E_a , can be obtained from the slope and the value of the pre-exponential factor, F , from the intercept.

Mechanisms for atom formation

The mechanisms by which atoms are formed in a commercial, semi-enclosed, tube-type graphite furnace have been described by Sturgeon et al. [10,11],

and are summarized below,

- 1 Reduction of solid oxide by carbon of the graphite furnace at elevated temperatures.

- 2 Thermal decomposition of the solid oxide,

- 3 Sublimation of the solid oxide and dissociation of the oxide vapour,

- 4 Dissociation of the halide vapour,

where M represents a metal, MO a metal oxide, MX a metal halide and X, a halogen atom, and s, l, and g stand for solid, liquid, and gas, respectively. Since atomization reactions in GFAAS are highly endothermic, the E_a values are usually

correlated with the reaction enthalpies.

EXPERIMENTAL

The experiments were done using the Perkin-Elmer atomic absorption spectrometer, Model 603, equipped with the Perkin-Elmer Heated Graphite Atomizer (HGA), Model 400, which was converted into a graphite probe furnace as described in an earlier publication [21] from this laboratory. A probe insertion device was used to allow precise timing of the probe insertion into the graphite furnace. The probes were fabricated from anisotropic pyrolytic graphite. The dimensions of probes were: 25mm long, 4mm wide at the head, 2mm wide at the base and 0.35mm thick.

Figure 1 shows a schematic diagram of the graphite probe furnace. The probe was mounted on a ceramic holder, which was fixed on the shaft of a 2-way gas cylinder with a maximum 3-inch moving distance. The probe insertion device consisted of a microprocessor-controlled timer which was activated by a trigger pulse from the programmable power supply. The automatic insertion of the probe into the heated graphite tube was controlled by a solenoid-operated power supply controller.

Signals were recorded using a Nicolet Model 4094, 4-channel programmable digital oscilloscope, (Nicolet Instrument Corporation, Madison, Wisconsin, U.S.A) fitted with an XF 44 disk recorder. The integrated absorbance was measured with the programmable digital oscilloscope using a software program supplied by Nicolet Instrument Corporation. Table 1 shows the experimental and instrumental conditions.

Figure 1: Schematic diagram of the probe apparatus.

- 1 Graphite probe
- 2 Probe holder
- 3 Cylinder shaft
- 4 Stop
- 5 Slide guide (fixed to the cylinder shaft)
- 6 Adjustable support rods
- 7 Air flow control valve

Table 1. Experimental and instrumental conditions used for GFAAS.

Mass of Sn atomized (ng)	20
Analytical wavelength (nm)	283.8
Lamp current (mA)	9
Spectral bandwidth (nm)	0.4
Purge gas	Argon
Graphite tube	Pyrolytically-coated graphite tube (Perkin-Elmer part No.091504)

Reagents.

A stock solution of tin was prepared by dissolving 0.2500 g of tin powder (99.98 % pure) in 50 % (v/v) hydrochloric acid (ULTREX, Baker Chemical Co.) by gentle heating; the solution was then transferred to a 250 mL volumetric flask and made up to the mark with ultrapure water. The stock solution was made to contain 10 % (v/v) hydrochloric acid. Test solutions contained 5 % (v/v) hydrochloric acid and were prepared by serial dilution of the stock solution using ultrapure water of resistivity 18.3 megohm-cm, obtained direct from a Milli Q2 water purification system (Millipore corporation).

Procedure

Test solution of 1 μ L volume was pipetted on the tip of the probe head using an Eppendorf microsyringe, fitted with polyethylene disposable pipettes. The test solutions were dried outside the furnace under an infrared lamp. In the operation of the probe furnace the usual drying and charring cycles used for atomization from the tube-wall were omitted and only the atomization cycle was used as follows. The atomization cycle (on the power supply) was switched on for 20 s. The tube-wall temperature attained a steady-state value within a few seconds depending on the atomization temperature set, and the furnace from that time onwards was equivalent to a constant-temperature furnace required for the study of kinetics of atom formation and loss undertaken in this work. The probe was automatically inserted into the constant-temperature furnace after a lapse of 11 seconds from the time of switching on the atomization cycle.

RESULTS AND DISCUSSION

Despite the fact that the most sensitive analytical wavelength reported frequently for tin was 224-nm line, for the graphite probe furnace work it was found not very suitable because it produced low peak areas as shown in Figure 2 and gave poor reproducibility of absorbance signal profiles. Figure 2 shows that the analytical wavelength of 283.8 nm gave the highest peak areas and peak heights for tin; in addition, the absorbance signal profiles were much more reproducible. Several other authors [3,21] also used the 283.8 nm wavelength for tin in graphite furnace atomic absorption spectrometry because it gave reduced noise level.

Figure 3 shows that the absorbance signal profile of tin has a shoulder, which may suggest that probably two mechanisms of tin atom formation are operating simultaneously: one may be that the metal oxide is reduced on the graphite surface, and the other be that the metal oxide is dissociated in the gas phase.

Figure 4 shows the charring and the atomization curve for tin obtained by using the graphite probe furnace. The charring curve has been drawn by plotting peak area absorbance obtained by using the optimum (pre-determined) atomization temperature (2400 K) as a function of the charring temperature. The atomization curve has been drawn by plotting peak area absorbance obtained by using the optimum (pre-determined) charring temperature (900 K) as a function of the atomization temperature. Figure 4 provides a significant experimental evidence, which is that the charring curve starts descending at a temperature ≥ 950 K, i.e. tin begins to be lost as the charring

Figure 2: Peak areas and peak heights of tin for various wavelengths.

Figure 3: Atomic absorbance profile for tin. The arrow points to a shoulder.

Figure 4: Charring and atomization curves for tin obtained with the graphite probe furnace.

temperature ≥ 950 K is attained, and yet, no atomic absorption signal for tin is observed, (i.e., there are no tin atoms present) till a temperature ≥ 2050 K is attained. This observation can be explained if one assumes that tin is lost as a molecular species at a temperature ≥ 950 K, and the processes responsible for formation of tin atoms do not occur till a temperature ≥ 2050 K is attained. Any mechanism for tin atomization in GFAAS must explain or at least be consistent with the above observation in order to be acceptable.

As shown in the THEORY section, the kinetic model employed to calculate the rate constants, k_1 , for formation of tin atoms, k_2 , for loss of tin atoms, and the energy of activation, E_a , from the Arrhenius equation (equation 17) was based on the kinetic model reported by Fuller [6], and C.L. Chakrabarti et al [9]. The above mentioned model uses the absorbance signal profile, which indicates the variation in the concentration of atoms at a constant temperature, and calculates the rate constants of atom formation and loss, and the energy of activation. The atomic absorbance is proportional to the concentration of the absorbing atomic species, $[X]$. Using equation (10) rate constant for atom loss, k_2 , can be determined from the trailing edge of the absorbance signal profile. As shown by Figure 5, a plot of logarithm of absorbance versus time was drawn, and the slope of the straight line plot gave the rate constant for atom loss, k_2 . The above procedure was employed to obtain the rate constants for atom loss, k_2 , at other temperatures, as shown in Table 2. The rate constant for atom formation, k_1 , on the other hand was calculated using equation (16), where the value of $t_{\max}$ (defined as the time required to reach the absorbance maximum) was obtained

Figure 5: Plot of logarithm of absorbance, A , versus time for tin at a temperature of 2260 K.

Table 2. The values of $t_{\max}$ and rate constants for tin.

Temperature (K)	$t_{\max}/s$ (experimental)	k_2/s (experimental)	k_1/s (calculated)
2260	0.36	2.70	2.8
2340	0.31	2.92	3.6
2430	0.26	3.05	4.9
2480	0.23	3.16	6.0

from the absorbance signal profiles. Table 2 shows the value of $t_{\max}$, k_1 and k_2 for tin. Since atomization reactions are highly endothermic, their rates should increase with increasing temperature. Hence, for a given concentration, the rate constant for atom formation, k_1 , should show similar trends, as was observed. The rate constant for loss of tin atoms, k_2 , also increased with temperature, as would be expected from purely diffusional loss.

Figure 6 shows a plot of $\ln k_1$ as a function of absolute temperature; the slope of the straight-line plot gave the activation energy E_a , 45 kcal mol⁻¹. The E_a value, 45 kcal mol⁻¹, does not show correlation with any of the bulk properties of the Sn_(s) or SnO(s) and is probably related to the energy of desorption of SnO_(s) molecules from the graphite probe surface.

To test the kinetic model for atom formation formulated in the THEORY, the rate constants for atom formation and loss obtained at a temperature of 2260 K were used to plot the atomic absorbance profile of tin (Figure 7) using equation (12) of the THEORY. It can be seen that the theoretically calculated absorbance profile shows close agreement with the experimentally-determined absorbance profile after the initial few data points. The deviation at earlier times is most likely due to the fact that the temperature of the graphite probe is still increasing and has not yet attained a constant value. The increasing temperature of the graphite probe would lead to an increase in k_1 until the final, constant temperature is attained. After the initial heating period the probe furnace would be isothermal and only then would the theoretically-predicted absorbance profile be expected to match exactly the experimentally-determined absorbance profile.

Figure 6: Plot of $\ln k$ versus $1/T$

Figure 7: Absorbance signal profiles of tin. (■) - Experimentally-determined absorbance profile for tin. (-) - Theoretically-calculated absorbance profile for tin using equation (12).

If it is assumed that the loss of atoms from the analysis volume is due to diffusion alone (first-order kinetics), then the rate constants for atom loss, k_2 , obtained at a given temperature can be related to the diffusion coefficient, D , as follows: (see Appendix 1 for derivation of the equation).

$$D = \frac{l^2}{8} k_2 \quad (23)$$

where l is the length of the graphite tube,

k_2 is the rate constant for diffusional loss for first-order kinetics,

D is the diffusion coefficient of atoms (cm^2/s).

Diffusion coefficient in the GFAAS has been reported to vary with absolute temperature, T , as follows [19, p.287]:

$$D = D_0 \left(\frac{T}{T_0} \right)^n \quad (24)$$

where D_0 is the diffusion coefficient at temperature T_0 , and n has a value close to 2 .

A plot of logarithm of D versus logarithm of T was drawn after converting k_2 values into D , using equation (13) of the Appendix. As shown in Figure 8, a plot of logarithm of D versus logarithm of T , gives a straight line, the slope of which gives the value of n as 1.6. This value is comparable to the value 1.9 reported by L'vov [22] for tin. Figure 8 confirm that the loss of tin atoms from the graphite probe furnace is of diffusional nature and follows first-order kinetics.

Figure 8: Plot of logarithm of diffusion coefficient, D , versus logarithm of absolute temperature.

MECHANISM FOR TIN ATOM FORMATION

Figure 4 shows that tin begins to be lost at charring temperature ≥ 950 K, whereas the atomic absorption signal of tin is not observed till an atomization temperature of ≥ 2050 K is attained, indicating that tin atoms are not formed till the atomization temperature is ≥ 2050 K. This means that tin is lost as a molecular species at a charring temperature ≥ 950 K. It is necessary to determine experimentally whether the molecular tin species is lost as a condensed-phase or vapour-phase species. This was determined by the exposure-time experiment, as described below, using the tin chloride solution.

Exposure-time experiment.

For this experiment, the test solution of tin chloride was deposited on the graphite probe and dried outside the graphite furnace using an infrared lamp. The graphite furnace was then heated to a temperature 970 K and the probe was then inserted into the furnace and held inside the furnace for a set time (10 s) so that the loss of tin would be readily measurable. After the lapse of the set time (10 s), the power to the graphite furnace was cut off; the furnace and the probe (held inside the furnace) were rapidly cooled in a forced, convective flow of Ar gas. The probe was then removed from the furnace and the furnace was re-heated to a constant temperature of 2420 K. The probe was then re-inserted into the constant-temperature (2420 K) furnace after a lapse of 11 seconds from the start of the heating of the furnace and was held inside the furnace for a further 10 s till the atomization of tin was complete and the atomic absorption signal profile was recorded. Figure 9 shows the results of the

Figure 9: Atomic absorbance profile for tin observed when the probe was inserted into the graphite furnace at 970 K for 10 s; the probe was then withdrawn and was again inserted into the graphite furnace at 2420 K.

exposure-time experiment--both peaks A and B were observed during the (second) heating of the graphite furnace from the room temperature to the temperature of 2420 K. Since the probe was inserted into the furnace during the heating of the furnace only at the time indicated by the second arrow (i.e. 11 s after the initiation of the heating of the furnace), the atomic absorbance peak A must have originated from the molecular tin species desorbed from the tube wall. This means that the molecular tin species lost during the charring cycle in Figure 4 was a vapour-phase species. This species was adsorbed on the tube wall during the first heating of the furnace to 970 K and was desorbed from the tube-wall during the second heating of the furnace to a temperature of 2420 K. According to the literature [1], the most likely molecular tin species that can be formed under the above experimental conditions is SnO. The following mechanism for the loss of tin in the charring cycle in Figure 4 is therefore proposed.

where k_f and k_r are rate constants for the forward and the reverse reaction, respectively.

At equilibrium,

$$K = \frac{[\text{SnO}]_{(g)}}{[\text{SnO}]_{(s)}} \quad (26)$$

$$\text{with } K = \frac{k_f}{k_r} \quad (27)$$

where K is the equilibrium constant, and the subscripts g and s stand for gas and solid, respectively. In equation (25), if the rates of formation of $\text{SnO}_{(g)}$ and its decay back into $\text{SnO}_{(s)}$ are much faster than the rate of loss of $\text{SnO}_{(g)}$, the above equilibrium will exist as long as $\text{SnO}_{(s)}$ exists. If and when the above equilibrium exists, one would expect from equation (25) that under the flow of the argon purge gas more $\text{SnO}_{(g)}$ would be lost than in the absence of such a flow.

It is now necessary to prove experimentally the existence of the pre-equilibrium postulated above in equation (25). This will be done by the experiment of the purge gas flow on and flow off mode of furnace operation, as described below.

In the forced, convective flow of an argon purge gas flow on and flow off mode of furnace operation, the effect of a forced, convective flow of an argon purge gas on tin signals was measured and the result was interpreted in terms of the hypothesis of existence or non-existence of the pre-equilibrium shown in equation (25). Figure 10 and Table 3 show that the absence of the convective flow of argon purge gas (Curve A) gives more than a four-fold increase in the peak area compared to the peak area in the presence of the convective flow of the argon purge gas (Curve B). The peak heights also show similar trends. These results can be interpreted as confirming the above hypothesis that the molecular tin species that is lost in the charring cycle in Figure 4 is $\text{SnO}_{(g)}$. Figure 10 and Table 3 also confirm the pre-equilibrium step and the mechanism for tin loss presented above as equation (25). The results presented above are consistent with the proposed atomization mechanism (equation (28)) for tin, in which $\text{SnO}_{(g)}$ is formed by desorption of SnO from the tube-wall surface and is then dissociated in the gas phase

Figure 10: Absorbance profiles for tin with or without a convective flow of Ar purge gas. Curve A: Ar gas flow-off mode. Curve B: Ar flow-on mode. Flow rate of Ar 325 mL/min.

Table 3. Peak areas and peak heights of tin determined with the Ar purge gas flow-on and the Ar purge gas flow-off mode of the furnace operation.

	Gas flow off	Gas flow-on
Peak area/s	0.395 ± 0.004	0.088 ± 0.002
Peak height absorbance	0.379 ± 0.003	0.117 ± 0.003
Mass of Sn 20ng		
Atomization temperature		
2420 K		

The numbers after $\pm$ represent one standard deviation of replicate measurements.

as shown below. The $\text{SnO}_{(s)}$ in equation (28) is the product of hydrolysis of the analyte, tin chloride, when it is heated in a graphite furnace [10, 11].

The above reaction sequence explains all the experimental observations, including the loss of tin at temperatures ≥ 950 K (Figure 4). Figure 4 also shows that tin atoms are not formed till a temperature ≥ 2050 K is attained. This difference (in the two temperatures) = 1100 K reflects the stability of $\text{SnO}_{(g)}$ molecule, as shown by its dissociation energy, $548 \pm 21 \text{ kJ mol}^{-1}$, since $\text{Sn}_{(g)}$ is formed by dissociation of $\text{SnO}_{(g)}$. The above mechanism, by its ability to explain all the experimental observations, is a satisfactory atomization mechanism for formation and loss of tin atoms in graphite probe furnace atomic absorption spectrometry.

LOW SENSITIVITY OF TIN IN GFAAS

The reason for low sensitivity of tin in GFAAS can be now explored in the light of the above atomization mechanism for tin in GFAAS. Figure 4 shows that tin is lost from the furnace as $\text{SnO}_{(g)}$, starting from a temperature of ~ 950 K up to a temperature of ~ 2400 K. In GFAAS, with a heating rate of 2 K ms^{-1} (which is near the maximum heating rate attainable with the graphite furnace used) it takes 725 ms for the furnace to span this temperature range of 1450 K; this is also true for graphite probe furnace. A large fraction of a tin sample is lost from the furnace as $\text{SnO}_{(g)}$ during this period of 725 ms. This loss is unavoidable in any analytical techniques such as GFAAS which employ a single heated medium (a single furnace) to do different functions which are both

spatially and temporally separate: vaporization and atomization. Any furnace that employs a single heating medium to do both vaporization and atomization will suffer from loss of analytes as gaseous molecular species (such as $\text{SnO}_{(g)}$) if gaseous or volatile analyte species are formed that are not dissociated at the temperature used; this will reduce the analytical sensitivity for the analyte, as was experimentally observed for tin. The only way to prevent such analyte loss and thereby prevent loss in analytical sensitivity is to employ two physically separate (i.e. located in separate places) heated media—one for vaporization and the other for atomization (if neutral, gaseous atoms, in ground state or excited state, are used for generating analytical signals) or for ionization (if gaseous ions are used for generating analytical signals). The recently-devised technique of electrothermal vaporization (ETV) when coupled to inductively coupled plasma mass spectrometry (ICP-MS) provides a convenient analytical technique which combines two physically separate heated media: one for vaporization (ETV) and the other for ionization (ICP), combined with mass spectrometry (MS) as a detection technique par excellence because of its extremely high sensitivity. The ETV-ICP-MS technique was therefore used for further investigation of tin (see Chapter 2).

An alternative analytical technique would have been the use of the following laboratory-made, graphite furnace developed and used by C.L. Chakrabarti [23]. This furnace consists of a detachable graphite tube and cup furnace which employs two separate power supplies, one for heating the graphite cup (for vaporization) and the other for heating the graphite tube (for atomization). Such a furnace would permit spatial and temporal separation of two separate processes: vaporization and atomization.

However, such a furnace was not available for this work.

Walter Slavin in a recent review paper [24] has compared the atomic spectroscopic analytical techniques as follows. The limits of detection for ETV-ICP-MS and GFAAS are generally in the range of femtogram (10^{-15} g) and picogram (10^{-12} g), respectively. However, The ICP-MS requires mL of sample to achieve these limits while GFAAS requires only 20 μ L. Additionally, these ICP-MS detection limits will not be found if the total matrix concentration is greater than about 0.1 %, whereas GFAAS detection limits are hardly degraded at matrix concentrations of several percent. Thus for many real samples, the GFAAS provides better real detection limits than the other techniques.

Chapter 2

ELECTROTHERMAL VAPORIZATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ETV-ICP-MS)

INTRODUCTION

The electrothermal vaporization technique (ETV) is used to introduce samples into an inductively coupled plasma-mass spectrometry (ICP-MS). This technique is reported to have the following advantages over the solution nebulization technique for sample introduction for ICP-MS [25,26].

1. Ability to analyze small sample volumes (e.g. $< 5 \mu\text{L}$) of liquid samples.
2. Avoidance of solvent loading effects on plasmas.
3. Reduced formation of oxides.
4. Higher sensitivity.

The electrothermal vaporizer is so designed as to allow for conversion of the analyte into microparticles, which are then transported quantitatively to the argon plasma. Complete vaporization and mass transport of the sample from the vaporizing

surface to the ICP-MS is of paramount importance and is most effectively achieved by the electrothermal vaporization technique.

CHEMICAL MODIFICATION AND CHEMICAL MODIFIERS

Chemical modifiers are chemical compounds that are added to samples to change their chemical and/or physical properties and/or the vaporizer/atomizer surface in such a way as to make samples more readily amenable to analysis. The analytical performance of the ETV-ICP-MS can be greatly improved by use of chemical modifiers. D.C. Gregoire [26] reported a 10-fold enhancement in the sensitivity for determination of platinum group metals using $\text{Ni}(\text{NO}_3)_2$ as a chemical modifier. He also reported [27] a 20-fold enhancement in the Os ion count rate (peak-height sensitivity) using Te as a chemical modifier. The concept of chemical modification is not new; it was introduced first by Ediger [28] in 1975 for GFAAS. He added $\text{Ni}(\text{NO}_3)_2$ to As and Se to reduce their volatility in graphite atomic absorption spectrometry (GFAAS). Ever since that time there has been a large number of papers in the literature on this subject. A comprehensive list of chemical modification has been compiled and reviewed by Tsalev et al. [29]. The objective of chemical modification is to improve chemical properties of the vaporization surface, of the analyte or the matrix or a combination of these. There is an on-going search for chemical modifiers that are universally applicable, the so-called universal chemical modifier. Welz et al. [30] proposed a mixed, chemical modifier made of Mg and Pd nitrates for GFAAS, which comes close to the universal

chemical modifier. They [30] succeeded in improving thermal stabilities of analytes: As, Bi, In, Pb, Sn, Te and Tl. Weibust et al. [31] reported a thermal stabilizing effect of 15 metals on Te; among these metals Pd had the greatest effect. Slavin et al. [32] used $\text{Mg}(\text{NO}_3)_2$ in the determination of Mn and Al so as to enable use of higher charring temperatures for GFAAS [29]; however, only some preliminary results have been reported for the relatively new ETV-ICP-MS technique. For this work, the mixed, chemical modifiers, $\text{Mg}(\text{NO}_3)_2 + \text{Pd}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2 + \text{PdCl}_2$ were selected from the literature [29-34] and applied because of their wide applicability in GFAAS to improve analytical features, such as extremely low or high volatilities of the analytes. These mixed, chemical modifiers have been reported to improve thermal stabilities of about 18 analytes in GFAAS [29,30,31]. Despite the fact that chemical modification has been widely used in GFAAS [29] and infrequently in ETV-ICP-MS, not much is known about their mechanisms of operation. Further research is necessary in order to elucidate their mechanisms of operation.

D.L. Styrís [34] studied the mechanisms of atomization of Al and its modification by Mg in GFAAS using molecular beam sampling mass spectrometry. Volynsky et al. [35] proposed the mechanism of chemical modification done by palladium and nickel in GFAAS. They reported that nickel and palladium salts promoted reduction of compounds in GFAAS, resulting in formation of free elements, which could form intermetallic compounds or solid solutions with metallic Pd and Ni; these reactions in turn could reduce the analyte loss caused by sublimation of its halides, oxides, dimers

and other compounds in GFAAS. They also suggested that the usefulness of palladium was due to its ease of formation of chemical compounds and its unique catalytic properties.

The mechanisms by which signal enhancement occurs in ETV-ICP-MS are presently unknown. However, the mechanisms may involve the following:

1. A physical phenomenon
2. A chemical phenomenon
3. Or, a combination of both 1 and 2.

A physical phenomenon refers, for example, to the mass transport of the analyte from the vaporizing surface of the ETV to the ICP-MS and any alteration caused by the chemical modifier. Chemical phenomenon, refers, for example to the change in the chemistry of the analyte and/or the matrix caused by the chemical modifier. However both phenomena could be occurring at the same time. Currently, the cause for the effectiveness of the mixed, chemical modifiers of Mg and Pd is little known and even less understood. Hence, there is a need for research in chemical modification in ETV-ICP-MS.

OBJECTIVES

The objectives of this research were to investigate the various parameters that determine the analysis signal in ETV-ICP-MS, and the effectiveness of the above chemical modifiers and the mechanisms of their chemical modification in ETV-ICP-MS.

Apparatus

The inductively coupled plasma mass spectrometer (ICP-MS) used for this work was a Perkin-Elmer/ SCIEX Elan Model 250. The extended quartz torch was used throughout this work. The electrothermal vaporizer (ETV) consisted of a resistively heated strip of pyrolytically-coated electrographite, measuring 11 mm long, 4 mm wide and 1 mm thick. Samples of 5 μ L volume were deposited on the graphite strip using an Eppendorf syringe fitted with disposable plastic tips. The sample was vaporized from the graphite strip and transported into the plasma by a stream of 99.9% pure argon gas. The flow of argon was directed tangentially to the metal supports on which the graphite supports were mounted. Figures 11 and 12 show schematic diagrams of the ETV and the ETV-ICP-MS, respectively. The quartz cover of Figure 11 was designed to reduce the condensation of the sample material on the surface of the cover and to optimize sample transport to the plasma. Sample vapour leaving the ETV unit was transported into the plasma through a tygon tubing of 0.5 m in length and 0.5 cm in internal diameter. A quadrupole mass spectrometer detector was used for the mass analysis. The temperature of the ETV unit was measured using an automatic optical pyrometer, Ircon 300 series, Model 1100 (Ircon Ltd.).

Gas

Argon gas, 99.9% pure, obtained commercially, was used both as the plasma gas and the auxilliary gas for the ICP, and as the carrier gas for the ETV.

Figure 11: Schematic diagram of the ETV.

Figure 12: Schematic diagram of the ETV-ICP-MS.

EXPERIMENTAL

Standard solutions and Reagents

Stock solutions of standards and reagents for ETV-ICP-MS were supplied by SPEX Industries, Inc., Edison, NJ. Test solutions were prepared from the stock solutions by diluting them with ultrapure water obtained direct from a Milli Q2 water purification system (Millipore Corporation, Mississauga, ON, Canada). Since acidic solutions rapidly spreaded to the end of the graphite contact parts giving non-reproducible results, neutral solutions were used. The following solutions were prepared on the day they were used. 0.1 $\mu\text{g/mL}$ of Ag solution was prepared from the stock solution of 1000 $\mu\text{g/mL}$ of Ag in 2 % (v/v) HNO_3 . 0.1 $\mu\text{g/mL}$ of Sn solution was prepared from the stock solution of 1000 $\mu\text{g/mL}$ of Sn in 10 % (v/v) HCl . 0.1 $\mu\text{g/mL}$ of Pb solution was prepared from the stock solution of 1000 $\mu\text{g/mL}$ Pb in 2 % (v/v) HNO_3 . The two mixed Mg + Pd chemical modifiers were prepared : one by mixing 1 $\mu\text{g/mL}$ solutions of $\text{Pd}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$ and the other by mixing 1 $\mu\text{g/mL}$ solutions of PdCl_2 and $\text{Mg}(\text{NO}_3)_2$. The 1 $\mu\text{g/mL}$ solutions of $\text{Pd}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$ and PdCl_2 were obtained by serial dilution of the 1000 $\mu\text{g/mL}$ stock solutions of these reagents prepared by dissolving the pure reagents in ultrapure water.

Procedure

5 μL of the analyte solution was deposited together with 5 μL of the mixed chemical modifier solution on the graphite strip of the ETV using an Eppendorf pipette. At each vaporization cycle, the ion intensities of three elements, Mg, Pd and the

analyte, were monitored. Ion count rates (peak heights) were measured sequentially at each m/z (mass/charge) ratio and the data printed out every 5 ms for 50 ms. The data were then transferred to the computer and graphs plotted. Integrated ion counts (peak areas) were calculated using the Trapezoidal Rule for numerical integration. Net ion counts for each run were obtained by averaging five to ten of the above runs and subtracting blank values from the averages.

Instrumental Parameters and Operating Conditions

Table 4 shows the instrumental parameters and operating conditions used for ETV-ICP-MS.

Table 4. Instrumental parameters and operating conditions used for ETV-ICP-MS.

Sampler	Nickel
Skimmer	Nickel
Inductively Coupled Plasma	
Conditions	
R.F. Power	1.0 kW
Reflected Power	5.8 W
Auxilliary Ar gas flow rate	2.0 L/min
Plasma Ar gas flow rate	13.0 L/min
Sampling Depth	10 mm
Electrothermal Vaporizer Conditions	
Carrier gas (Ar) flow rate	1 L/min
Heating Cycle:	
Dry	100°C
Char	N/A
Atomization	2100°C

The ETV technique for introducing samples into the inductively coupled plasma mass spectrometer has been reported [25,26,27] to be an important analytical advance in ultratrace analysis. The ETV technique has been applied to the analysis of relatively small samples (1 to 10 μL) [25,26,36], which are vaporized from the ETV and transported into the inductively coupled plasma (ICP) source using an argon carrier gas flow rate of 1 L/min. Several instrumental operating parameters, however, have to be carefully controlled since they are known to have significant effects on the analysis signals [37,38].

Tables 5, 6, 7 and Figure 13 show the effects of variation of sampling depth on the analysis signals. The sampling depth is defined as the distance in millimetres from the tip of the mass spectrometer sampling cone to the downstream turn of the load coil of the ICP. Change in the sampling depth was achieved by pushing the torch box, step by step, 2.5 mm at a time, towards the sampling cone. Tables 5, 6, 7 and Figure 13 show that a change in the sampling depth has great effects on peak areas and peak heights of 0.5 ng of Ag, Sn and Pb; peak areas and peak heights increase continuously with decrease in sampling depth, indicating greater precision resulting probably from greater stability of the plasma at shorter sampling depths; this is probably also an indication that the plasma is inhomogeneous in terms of stability. D.C. Gregoire [37] has reported that the position of the torch (sampling depth) has an effect on the analyte ion count because the distribution of analyte varies within the argon plasma. For better reproducibility one should carefully select the position of the torch (sampling depth) and

Table 5. Effect of variation of sampling depth* on peak areas and peak heights for 0.5 ng Sn.

Sampling depth* (mm)	Peak areas (Ion counts)	%Relative standard deviation of peak areas	Peak heights (Ion count s ⁻¹)	% Relative standard deviation of peak heights
40.5	-	-	-	-
38.0	2264	18.9	3208	17.0
35.5	3208	19.2	6605	21.0
33.0	8564	8.6	13558	12.3
30.5	16446	4.7	26536	4.5
28.0	26090	9.2	39998	2.9
25.5	34260	8.3	53394	4.1
23.0	42263	6.9	58158	4.4
18.0	60708	4.8	85190	2.3

* Distance in millimetres from the tip of the mass spectrometer sampling cone to the downstream turn of the load coil.

Table 6. Effect of variation of sampling depth* on peak areas and peak heights for 0.5 ng Ag.

Sampling depth* (mm)	Peak areas (Ion counts)	%Relative standard deviation of peak areas	Peak heights (Ion count s ⁻¹)	%Relative standard deviation of peak heights
40.5	-	-	-	-
38.0	969	24.0	1496	19.8
35.5	1826	8.9	2802	17.5
33.0	3144	6.9	5068	8.4
30.5	5369	6.6	8806	6.8
28.0	8338	8.3	13792	5.5
25.5	10646	6.2	18010	4.9
23.0	13168	10.0	20938	8.6
18.0	17176	9.2	24458	5.8

* Distance in millimetres from the tip of the mass spectrometer sampling cone to the downstream turn of the load coil.

Table 7. Effect of variation of sampling depth* on peak areas and peak heights for 0.5 ng Pb.

Sampling depth* (mm)	Peak areas (Ion counts)	%Relative standard deviation of peak areas	Peak heights (Ion count s ⁻¹)	%Relative standard deviation of peak heights
40.5	-	-	-	-
38.5	6531	19.0	9078	17.0
35.5	12023	14.9	15380	14.2
33.0	18080	4.9	21925	6.5
30.5	39155	3.2	52205	4.0
28.0	54522	3.2	79824	7.1
25.5	82810	5.0	104928	5.6
23.0	91760	3.4	132350	6.5
18.0	101527	1.9	125767	2.3

* Distance in millimetres from the tip of the mass spectrometer sampling cone to the downstream turn of the load coil.

Figure 13: Plot of peak areas (ion counts) of Ag, Sn and Pb versus sampling depth.

Error bars represent $\pm$ one standard deviation.

work within a stable region of the argon plasma torch.

The effect of Ar carrier gas flow rates on ion count of 0.5 ng Ag, Sn and Pb are presented in Figure 14, and in Tables 8 and 9. The effect of these flow rates was studied in order to determine the optimum Ar carrier gas flow rate for use in subsequent experiments. It is worth noting that in varying the carrier gas (Ar) flow rates two parameters are varied simultaneously: one is the mass transport of the material from the ETV into the ICP-MS and the other is the sampling depth, as explained below. Park and co-workers [39,40] have reported that the efficiency of mass transport of the analytes is dependant upon the conversion efficiency of analytes into microparticles. Since conversion efficiency of analytes into microparticles is dependent on the carrier gas (Ar) flow rates, mass transport efficiency of analytes is also dependent on the carrier gas (Ar) flow rates [39,40]. Wei-Lung et al. [25] have reported the effects of carrier gas (Ar) flow rates in their ETV device on Pb signals at m/z (mass/charge) ratio 208. The importance of carrier gas flow rate has also been emphasized by Horlick et al. [41], who have reported the dependence of the analysis signal on the injector gas flow rate. However, it seems from the above that further research on the effect of change in the carrier gas (Ar) flow rate on mass transport efficiency of various analytes to the ICP torch is necessary in order to characterize the plasma more definitively and to optimize it for determination of various elements. Figure 14 and Tables 8 and 9 show that an increase in the carrier gas (Ar) flow rate increase the ion count exponentially. The Ar gas flow rate of 1 L/min was considered to be the optimum flow rate for this work.

Figure 14: Plot of peak areas (ion counts) of Ag, Sn and Pb versus carrier gas (Ar) flow rates. Error bars represent $\pm$ one standard deviation.

Table 8. Effect of Ar carrier gas flow rates on peak areas (ion counts) and on % RSD of peak areas of Ag, Sn and Pb.

Element	Argon flow rate (L min ⁻¹)	Peak area (Ion counts)	% RSD
Ag	0	0	-
	0.500	1807	9.8
	0.750	6673	6.7
	1.000	24639	4.0
Sn	0	0	-
	0.500	2181	6.5
	0.750	11508	4.0
	1.000	60708	4.8
Pb	0	0	-
	0.500	2577	6.1
	0.750	17116	5.2
	1.000	113673	4.1

RSD is relative standard deviation

Table 9. Effect of carrier Ar gas flow rates on peak heights (ion count s^{-1}) and on % RSD of peak heights of Ag, Sn and Pb.

Element	Argon flow rate ($L\ min^{-1}$)	Peak heights (Ion counts s^{-1})	% RSD
Ag	0	0	-
	0.500	1557	
	0.750	7973	6.4
	1.000	40820	4.2
Sn	0	0	-
	0.500	2010	
	0.750	13087	5.0
	1.000	85190	2.3
Pb	0	0	-
	0.500	2197	
	0.750	16953	8.4
	1.000	130800	4.1

RSD is relative standard deviation.

Optimization of the ion-lens set, B, E1, P, S2, and the RF power were done using a small Hg droplet (μL) placed on the vial cap in the ETV while argon carrier gas flowed through to the ICP continuously. Mercury being an element with adequate vapour pressure at the room temperature entered the plasma, giving a steady signal, thereby allowing selection of the optimum instrumental parameters mentioned above. D.C. Gregoire [27] has studied the effect of ion lens voltage and plasma conditions on non-spectroscopic interferences with several elements and has shown the importance of optimizing these instrumental parameters.

Effects of the Pd + Mg mixed, chemical modifiers.

The effects of the mixed, chemical modifiers, $\text{Mg}(\text{NO}_3)_2 + \text{Pd}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2 + \text{PdCl}_2$ on peak area and peak height of Pb, Sn and Ag were investigated as follows. The sample was deposited on the ETV together with the mixed, chemical modifier and this mixture was then dried and vaporized into the plasma. Table 4 shows the ETV heating cycle used. The dry cycle was set to allow the sample droplet to dry without spattering so as to avoid loss of the sample. The charring (or ashing stage) was omitted. Fast ramping of the graphite strip was done to speed up the vaporization of the sample so as to obtain a maximum analysis signal. The data obtained were plotted using a computer. The results are presented in Figures 15, 16 and 17, and show that the mixed, chemical modifiers, enhanced the analysis signals significantly. It can also be seen from Figures 15-17 that the analysis signal due to the mixed, chemical modifier, $\text{Mg}(\text{NO}_3)_2 + \text{Pd}(\text{NO}_3)_2$, was much higher than that due to the mixed, chemical

Figure 15: Plot of Ag ion count rate versus time for 0.5 ng Ag. (▲) - with the mixed, chemical modifier, $\text{Mg}(\text{NO}_3)_2 + \text{Pd}(\text{NO}_3)_2$. (■) - with the mixed, chemical modifier, $\text{Mg}(\text{NO}_3)_2 + \text{PdCl}_2$. (◆) - without any chemical modifier.

Figure 16: Plot of Pb ion count rate versus time for 0.5 ng Pb. (▲) - with the mixed, chemical modifier, $\text{Mg}(\text{NO}_3)_2 + \text{Pd}(\text{NO}_3)_2$. (■) - with the mixed, chemical modifier, $\text{Mg}(\text{NO}_3)_2 + \text{PdCl}_2$. (◆) - without any chemical modifier.

Figure 17: Plot of Sn ion count rate versus time for 0.5 ng Sn. (▲) - with the mixed, chemical modifier, $\text{Mg}(\text{NO}_3)_2 + \text{Pd}(\text{NO}_3)_2$. (■) - with the mixed, chemical modifier, $\text{Mg}(\text{NO}_3)_2 + \text{PdCl}_2$. (◆) - without any chemical modifier.

modifier, $\text{Mg}(\text{NO}_3)_2 + \text{PdCl}_2$, particularly for Ag and Pb. Tables 10 and 11 show the same trends - the enhancement factors for Pb, Sn and Ag with the mixed, chemical modifier $\text{Mg}(\text{NO}_3)_2 + \text{PdCl}_2$ were 2.8, 2.9 and 3.3, respectively, whereas those with the mixed, chemical modifier $\text{Mg}(\text{NO}_3)_2 + \text{Pd}(\text{NO}_3)_2$ were, 4.4, 5.7 and 5.2, respectively. The effect of palladium in the nitrate form was about twice that of the palladium in the chloride form.

As mentioned earlier in the procedure section, the mass of the mixed, chemical modifier Mg + Pd used was ten times the mass of the analyte (Sn, Pb or Ag). Figure 18 shows that a maximum in response was observed using 0.3 nanomoles of $\text{Mg}(\text{NO}_3)_2$ for Ag, while keeping the number of nanomoles of PdCl_2 constant (0.047). The optimum mass ratio corresponded to 7.5 ng $\text{Mg}(\text{NO}_3)_2$ and 5 ng PdCl_2 . Welz et al. [30] used masses of 15 μg of Pd and 10 μg of $\text{Mg}(\text{NO}_3)_2$ for 9 elements in GFAAS, but did not indicate how they determined the optimum ratios of $\text{Mg}(\text{NO}_3)_2$ to $\text{Pd}(\text{NO}_3)_2$. As reported in a review by Tsalev et al. [29], the effectiveness of chemical modifiers is not only dependent on the mass of their active constituents but also on their relative proportions. This was confirmed by Figure 18.

An important observation of this work is that the use of any of single chemical modifier of the following mixed, chemical modifiers, $\text{Pd}(\text{NO}_3)_2$, PdCl_2 or $\text{Mg}(\text{NO}_3)_2$, singly, did not have an effect on Ag, Pb and Sn signals. However, as mixed, chemical modifiers, they are effective as shown in Table 10 and 11 and in Figure 18. Palladium among the platinum group metals has been reported to be the most catalytically active, and is also the most effective as a chemical modifier in its chemically reduced

Table 10. Effect of the mixed, chemical modifiers, $\text{Mg}(\text{NO}_3)_2 + \text{Pd}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2 + \text{PdCl}_2$, on peak areas (ion counts) of Pb, Sn and Ag.

	With no chemical modifier	$\text{Mg}(\text{NO}_3)_2$ + PdCl_2	$\text{Mg}(\text{NO}_3)_2$ + $\text{Pd}(\text{NO}_3)_2$
Analyte Pb	12468	35360	54691
%RSD	5.5	5.8	3.3
Enhancement factor	1.0	2.8	4.4
Analyte Sn	10934	31714	62233
%RSD	5.3	5.7	1.9
Enhancement factor	1.0	2.9	5.7
Analyte Ag	9220	30505	47523
%RSD	8.7	1.2	2.5
Enhancement factor	1.0	3.3	5.2

%RSD is per cent relative standard deviation.

Table 11. Effect of the mixed, chemical modifiers, $\text{Mg}(\text{NO}_3)_2 + \text{Pd}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2 + \text{PdCl}_2$, on peak heights (ion count s^{-1}) of Pb, Sn and Ag.

	With no chemical modifier	$\text{Mg}(\text{NO}_3)_2$ + PdCl_2	$\text{Mg}(\text{NO}_3)_2$ + $\text{Pd}(\text{NO}_3)_2$
Analyte Pb	13380	56053	72590
%RSD	2.2	2.6	3.3
Enhancement factor	1.0	4.2	5.4
Analyte Sn	26930	37843	67160
%RSD	5.4	8.0	3.2
Enhancement factor	1.0	1.4	2.5
Analyte Ag	18343	51610	63213
%RSD	6.1	4.8	0.9
Enhancement factor	1.0	2.8	3.4

%RSD is per cent relative standard deviation.

Figure 18: Effect of variation in the composition of the mixed, chemical modifier, $\text{Mg}(\text{NO}_3)_2 + \text{PdCl}_2$ on peak areas (curve A) and peak heights (curve B) of 0.5 ng of Ag. Number of nanomoles of $\text{Mg}(\text{NO}_3)_2$ is varied while keeping the number of nanomoles of PdCl_2 constant at 0.047.

form [26,27,30,31].

Mechanisms of chemical modification

The mechanism of reaction of mixed, chemical modifiers, $\text{Mg}(\text{NO}_3)_2 + \text{Pd}(\text{NO}_3)_2$, and $\text{Mg}(\text{NO}_3)_2 + \text{PdCl}_2$ in ETV-ICP-MS is not known. In spite of the fact that these chemical modifiers are widely used [29], only a few workers [34,35] have attempted to study the mechanisms of these chemical modifiers. One can only conjecture that the effectiveness of these chemical modifiers in ETV-ICP-MS to be either due to a chemical phenomenon, or a physical phenomenon, or both. Chemical modifiers may change the chemical form of the sample, the reactivity of the atomizer surface, and may form solid solutions with the analyte, and may change the kinetics of vaporization, atomization or ionization. Currently, there is insufficient evidence to deduce the mechanisms by which these mixed, chemical modifiers enhance the analysis signals. However, it has been suggested by Tsalev et al. [29] that an understanding of the effectiveness of chemical modifiers could be obtained by studying the following:

- a) The physico-chemical-chemical transformation of the modifier and the analyte in graphite strip atomizer.
- b) Identification of the relevant intermediate and final species, their binding states, chemical and crystalline form.
- c) Distribution of the analyte and modifier in the atomizer surface layer and in the gas phase.
- d) Analysis of fundamental characteristics of the analyte elements such as their ionic radii, ionization potential, and other chemical properties.

- e) Isomorphism between pairs of elements, analyte modifier, analyte-analyte, modifier-modifier.

However, time limitations did not allow any of the above studies to be made.

Appendix

If it is assumed that the loss of atoms is due to diffusion alone, and if $k_2 > k_1$ then,

$$M_{(l)} \xrightarrow{k_1} M_{(g)} \xrightarrow{k_2} M_{(out)} \quad (1)$$

$$- \frac{dM_{(g)}}{dt} = k_2 t \quad (2)$$

Integration of the above equation from $t = 0$ to t , gives,

$$- \ln \left(\frac{M_t}{M_0} \right) = k_2 t \quad (3)$$

For a first-order loss process (such as loss by diffusion alone),

$$t_{\left(\frac{1}{e}\right)} = \tau_2 \quad (4)$$

i.e. τ_2 is the time for the signal to fall $1/e$ of its value, ($1/e = 1/2.718, \dots$)

$$- \ln \left(\frac{1}{e} \right) = k_2 \tau_2 \quad (5)$$

$$1 = k_2 \tau_2 \quad (6)$$

$$k_2 = \frac{1}{\tau_2} \quad (7)$$

According to L'vov [19]

$$\tau_2 = \frac{l^2}{8D} \quad (8)$$

Rearranging the above equation, one gets equation (9),

$$D = \frac{l^2}{8\tau_2} \quad (9)$$

$$= \frac{l^2}{8} \cdot \frac{1}{\tau_2} \quad (10)$$

$$k_2 = \frac{1}{\tau_2} \quad (11)$$

$$D = \frac{l^2}{8} k_2 \quad (12)$$

The dimensions of the furnace are: l is 2.8 cm and k_2 is in s^{-1} . D can be evaluated from equation (12) by substituting in it the values of l and k_2 .

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