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**STUDIES ON ATOM FORMATION AND LOSS
PROCESSES OF SOME ELEMENTS IN GRAPHITE
FURNACE ATOMIC ABSORPTION SPECTROMETRY**

by

Glen Fraser Richard Gilchrist

**A thesis submitted to the Faculty of Graduate Studies
and Research in partial fulfillment of the requirements of
the degree of**

Doctor of Philosophy

**Department of Chemistry
Carleton University
Ottawa, Canada**

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in Graphite Furnace Atomic Absorption Spectrometry

submitted by

Glen Fraser Richard Gilchrist

in partial fulfillment of the requirements
for the degree of Doctor of Philosophy

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ABSTRACT

A gas-phase thermodynamic equilibrium model has been used to explain the shift of the appearance temperature of the lead atomic absorption signal to lower values when ascorbic acid and oxalic acid are used as chemical modifiers. The gas phase composition was measured during the atomization of samples having ascorbic acid and oxalic acid added as chemical modifiers. Hydrogen, carbon monoxide and carbon dioxide were identified as the major products of the pyrolysis of ascorbic acid and oxalic acid. Experimental results of the effect of the gas phase composition on the appearance temperature of the lead atomic absorption pulse are presented. Hydrogen and carbon monoxide added to argon purge gas or ascorbic acid added to aqueous solutions of the analytes, was found to shift the absorbance pulses of zinc, lead, selenium, arsenic and chromium to lower temperatures, and carbon dioxide added to argon purge gas was found to shift the absorbance pulses of lead, selenium and chromium to higher temperatures. It is proposed that gas-phase dissociation equilibrium of the analyte oxides is disturbed by the addition of hydrogen, carbon monoxide or carbon dioxide to the gas phase, resulting in hydrogen or carbon monoxide shifting the absorbance pulses to lower appearance temperatures and carbon dioxide shifting the absorbance pulses to higher appearance temperatures. Also, hydrogen or carbon monoxide was found to eliminate the matrix interference caused by hydrochloric acid in the determination of lead, selenium and arsenic, which were the only elements studied for matrix interferences. When carbon monoxide was used as purge gas, large enhancements of selenium and arsenic signals were observed.

A novel technique has been used to measure the rate of vaporization of the molecular species of lead, tin, selenium and arsenic in the graphite probe furnace. From this new technique rate constants and activation energies for the vaporization of PbO , SnO , SeO_2 and As_2 have been determined. Experimental results have been compared to an existing model based on homogeneous gas-phase thermodynamic equilibrium. Kinetic measurements of the atomization of Ag, Cu and Mn made using the new technique have been compared with those made using the kinetic approach published by other authors. The effect of the gas-phase chemical modifiers H_2 and O_2 on the atomic absorption pulses of Pb, Sn, Se, As, Ag, Cu and Mn are discussed. Atomization mechanisms have been proposed for Pb, Sn, Se, As, Ag, Cu and Mn, these mechanisms have been compared to those proposed by other workers.

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INTRODUCTION

The technique of electrothermal atomization (ETA) in atomic absorption spectrometry was introduced by B.V. L'vov in 1959¹. Commercial atomizers became available in 1970. Atomizer design has gone through a number of changes in the past twenty years. Currently, the most common type of commercial atomizer is the Massman-type, semi-enclosed, pulse-heated graphite tube furnace. For this type of atomizer, test solutions are deposited inside a graphite tube which is aligned so that the incident radiation beam from the spectrophotometer passes through the atomizer tube. Resistive heating causes the test solution to be dried, thermally decomposed and atomized at temperatures up to 3400 K. Recent improvements in background correction, stabilized temperature and isothermal atomization, and matrix modification have ensured that Graphite Furnace Atomic Absorption Spectroscopy (GFAAS) will remain the technique of choice for many difficult problems in analytical atomic spectroscopy.

Further improvement of detection limits, sensitivity, selectivity and freedom from interferences may result if the chemical and physical processes that lead to the formation of atoms are better understood. Currently, there is little consensus as to the processes that control atom formation for a number of elements. One possible process is thermal or carbon reduction of analyte species to the elemental form on the graphite surface, followed by direct vaporization of atoms from the graphite surface. Another possible process is the vaporization of analyte-containing molecules, followed by their dissociation in the gas phase. Some points of contention are: the partial pressure of oxygen in the furnace, the existence of diatomic or triatomic analyte-containing molecules in the gas phase and the role of carbon in the atom forming processes.

The purpose of this work is to gain some insight into the processes that control atom formation and loss in the graphite furnace. Chapter One examines homogeneous thermodynamic equilibrium in the gas phase and chemical modification by gases. From the material presented in Chapter One it will be seen that a number of elements are vaporized initially as molecules, particularly oxides and halides, and are then dissociated in the gas phase. Chapter Two deals with vaporization and atomization as separate phenomena, the vaporization of molecules from a graphite probe and their dissociation in the gas phase is examined. A novel technique for measurement of the rate of vaporization, and the activation energy for vaporization of molecules, is also introduced in Chapter Two.

CHAPTER ONE

GAS PHASE THERMODYNAMIC EQUILIBRIUM MODEL AND CHEMICAL MODIFICATION BY GASES IN GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY

INTRODUCTION

The chemical modification effect of ascorbic acid on the lead atomic absorption signal is well documented²⁻⁷. Ascorbic acid causes a shift to a lower appearance temperature, T_{app} (the temperature of the graphite tube wall at the moment that the atomic absorption signal may be measured over the background noise), of the lead atomic absorption signal^{2,4-7} and eliminates chloride chemical interferences⁴⁻⁷. Using an indirect method, Volynskii and Sedykh² have shown that the addition of ascorbic acid or some other organic substances to the analyte solution results in a decrease in the partial pressure of oxygen in the graphite furnace during the atomization cycle. It has been suggested⁶ that CO and CO₂, produced by pyrolysis of ascorbic acid during the atomization of samples containing ascorbic acid reduces or eliminates interferences. Other organic substances have been observed to produce a chemical modification effect similar to that of ascorbic acid^{5,6}. Hydes⁵ has shown that oxalic acid, which has physical properties similar to those of ascorbic acid, removes chloride matrix interferences with cobalt, copper and manganese. Oxalic acid is of particular interest because it is expected that oxalic acid, on pyrolysis, does not leave a residual carbon char in the graphite furnace⁵. Lack of a residual carbon char would lead one to expect that the chemical modification effect of oxalic acid arises from reactions in the gas phase. Hydes⁵, Matousek⁸, Frech and Cedergren⁹, and Chakrabarti et al.¹⁰ have proposed that chloride matrix interferences in the determination of metals are due to the formation and loss of volatile metal chlorides.

Gaseous chemical modifiers have been used by several workers^{7,9,11-21} for the following effects: to enhance sensitivity, to combat matrix interferences, and to assist in studies of chemical modification. Steiner and Kramer¹¹ have used O₂ during the ashing step to assist in the destruction of liver extracts; also, they have used

combinations of several other gases including H_2 , CH_4 and O_2 during the atomization step to increase sensitivity and remove matrix interferences. Ottaway and Hutton¹² have shown that the addition of H_2 to the purge gas reduces the partial pressures of SrO and CaO in the graphite furnace. Frech and Cedergrén⁹ have shown by thermodynamic equilibrium calculations and by experimental evidence¹³ that H_2 is an effective chemical modifier in removal of the chloride matrix interference for the determination of lead in steel. Torsi and Tessari¹⁵ have observed a 500 K decrease in the appearance temperature of lead when switching from either an Ar or a He purge gas to a H_2 purge gas. L'vov et al.¹⁶ have reported that when 10% (v/v) H_2 in Ar is used as the purge gas there is a buffering effect on the atomic absorption signal of certain analytes in the graphite furnace. They have also reported that the presence of H_2 in the gas phase diminishes the pre-atomization loss of volatile metal chlorides. Cedergrén et al.¹⁷ have reported that when CO, instead of Ar, is used as the purge gas, the signal for lead is shifted to a lower temperature and the shoulder of the signal is resolved into a second peak. They have also observed that the signal for tin is shifted to a lower temperature when CO is used and that the atomic absorption signals of silicon and boron are almost completely eliminated. Sturgeon and Berman⁷, and Salmon et al.^{18,19} have reported a shift in the lead signal to higher temperatures when O_2 is added to the Ar purge gas. Byrne et al.²⁰ have reported a shift to higher appearance temperatures for the atomic absorption signal of lead, tin, silicon, aluminum and barium with the addition of O_2 to the Ar purge gas. Salmon et al.^{18,19} were the first to report a shift in the lead signal in an oxygen-containing sheath gas, and also in an inert gas immediately following the heating and cooling of the graphite tube with O_2 present in the sheath gas. They had earlier attributed this "first shot back effect"¹⁸ to a delay in the reduction of $PbO_{(s/l)}$ to $Pb_{(s/l)}$ by graphite. Bass and Holcombe²¹, however, subsequently suggested that the absence of a shift in the lead signal for vaporization from an oxygenated surface under vacuum conditions indicates that the pulse shift

mechanism is not strictly a surface process but may be due to gas phase species that are generated from an oxygenated surface but not from an unoxygenated surface.

PROPOSED MECHANISM FOR PULSE SHIFTS

The gas-phase thermodynamic equilibrium model²⁰ is applicable to only those elements that are initially vaporized as molecular species. Oxides and halides have been identified in the furnace²²⁻²⁶. Also, under certain conditions, hydride, hydroxide, carbide and dimer molecules may be formed in the gas phase in the graphite furnace²⁷. For elements that form gaseous oxides, carbides, halides or hydrides prior to atomization the pulse shifts observed on the addition of a chemical modifier may be explained in terms of disturbances to the following linked equilibria in the gas phase:

where M and X are metal atoms and halogen atoms, respectively. According to the Le Chatelier principle, the degree of shift will increase with the amount of chemical modifier added. This relationship has been quantified by Byrne et. al.²⁰. Equations 4 and 10 arise from the presence of water in a graphite furnace, and do not require the addition of H_2 to the purge gas. It is known that water is tenaciously held by graphite: even at 1200 °C, the fraction of water retained by the graphite after 15 minutes in a vacuum was reported to be 0.005³⁴.

The above gas-phase equilibria can be established only for elements where (i) metal-oxide molecules exist along with metal atoms in the gas phase in the graphite furnace, and (ii) the rate of the reactions is sufficiently rapid to establish thermodynamic equilibrium within the residence time of the metal atoms in the furnace. The loss of lead observed by Byrne et al.²⁰ in their "cut-off temperature" experiments has been accounted for in terms of loss of $\text{PbO}_{(g)}$ at the "cut-off temperatures", which include the appearance temperatures of lead, with and without the chemical modifier. Sedykh et al.²³ have observed PbO molecules in the gas phase by molecular absorption spectrometry. Frech et al.^{9,13,27} have reported the existence of both PbO and Pb in the gas phase at temperatures around 900 K (the lowest cut-off temperature used by Byrne et al.²⁰ for lead). Mass spectrometric studies^{21,25,26} have shown that PbO molecules are vaporized from an electrically-heated graphite surface below the appearance temperature of lead. It has been suggested²⁸ that at atmospheric pressure these PbO molecules will have multiple collisions with the graphite wall and will thus be reduced on the graphite surface to lead. At atmospheric pressure multiple collisions in the gas phase will lead to a greater residence time for the PbO molecules than that experienced under high vacuum conditions. Increased residence time for the

PbO molecules may allow the gas-phase dissociation of PbO.

Based on their thermodynamic equilibrium model, Frech et al.²⁷ have predicted the existence of gas-phase SeO_2 , SeO and Se_2 molecules near the appearance temperature of selenium. Using mass spectrometric analysis, Styris²⁹ and Droessler and Holcombe³⁰ have reported that SeO_2 molecules are formed prior to the atomization of selenium during the electrothermal atomization of aqueous solutions of selenium. Droessler³¹ has also reported the results of selenium atomization under a variety of conditions using time- and spatially-resolved absorbance data, and has postulated that selenium atom formation by gas-phase dissociation of SeO_2 or SeO is supported by the observed uniform spatial distribution of selenium atoms in the furnace. Selenium is known to undergo large losses, during the preatomization charring step, as molecular species such as SeO_2 , SeO and Se_2 ³².

Molecular arsenic species have not yet been observed in the graphite furnace. Akman et al.³³ have proposed that the gas-phase dissociation of AsO is the predominant process for arsenic atom formation. They have shown that there is an excellent agreement between their experimentally-determined activation energy of $(479.3 \pm 10.1) \text{ kJ mol}^{-1}$ for arsenic atomization and the dissociation energy of the As-O bond, $(480 \pm 10) \text{ kJ mol}^{-1}$. They have also stated that carbon reduction of the condensed-phase arsenic oxides provides an alternative mechanism for arsenic atom formation; however, in their opinion, this reduction reaction is likely to be too slow to be predominant³³. Frech et al.²⁷ have calculated that $\text{As}_{2(g)}$ is the predominant arsenic species prior to arsenic atom formation. Thermodynamic data is not available for gas-phase arsenic oxides so Frech et al.²⁷ have not included AsO molecules in their equilibrium calculations.

Molecular chromium species have not yet been observed in the gas phase in the graphite furnace. Using thermodynamic equilibrium calculations Frech et al.³⁴ have predicted that condensed-phase Cr_2O_3 will decompose to give chromium atoms when Ar purge gas is used and that condensed-phase Cr_3C_2 will decompose to give chromium atoms when CO purge gas is used. The oxide and the carbide of chromium will decompose at the same temperature so CO should not affect the chromium atomic absorption signal. Frech et al.³⁴ have shown that CO purge gas does not alter the chromium atomic absorption signal.

Holcombe et al.²² have reported that the presence of O_2 in the Ar purge gas causes the lead atomic absorption pulse to be shifted to higher temperature. They²² have proposed that the pulse shifts are due to an oxygenated graphite surface and that the adsorption and desorption of oxygen gas to and from the graphite surface control the pulse shifts. This mechanism is satisfactory for interpreting the pulse shifts for those elements whose appearance temperatures lie within the range of oxygen adsorption to and desorption from the graphite surface (850 K – 1200 K). However, this mechanism cannot account for the observed pulse shifts of those elements such as Sn and As, the appearance temperatures of which are above the upper limit of oxygen desorption from the graphite surface, and of those elements having appearance temperatures below the lower limit for oxygen adsorption to the graphite surface. Their mechanism²² also cannot account for the absence of a pulse shift for lead from an oxygenated surface under vacuum conditions²¹. The gas phase thermodynamic equilibrium model²⁰ can account for the pulse shifts for the elements including tin and arsenic for which pulse shifts are reported in this work and can also account for the lack of a pulse shift for lead atomized under vacuum conditions.

PROPOSED MECHANISM FOR INTERFERENCE REDUCTION

Reduction of matrix interferences by the use of chemical modifiers may be explained in terms of the gas-phase thermodynamic equilibrium model. In general terms a chemical modifier reacts with an analyte-containing molecule to produce free metal atoms in the gas phase. In the case of chloride interference this equation may be written:

where MX is a metal halide, A is a chemical modifier molecule, M is the free metal atom and AX is molecule containing the halogen atom and an atom of the chemical modifier. The equilibrium constant for equation 11 determines how effective a given chemical modifier is in removing the matrix interference. At equilibrium, the equilibrium constant K is given by:

$$K = \exp(-\Delta G^0/RT) \quad 12$$

At equilibrium, K can be expressed in terms of partial pressures of the reactants and products of equation 11 as follows:

$$K = \frac{P_M}{P_{MX}} \frac{P_{AX}}{P_A} \quad 13$$

where $P_{\text{subscript}}$ is the partial pressure of the subscripted species and M, AX, MX_2 and A_2 are defined as in equation 11.

The partial pressure of the metal atoms may be written as:

$$P_M = \frac{K P_{MX} P_A}{P_{AX}} \quad 14$$

Equation 14 shows that an increase in the partial pressure of the modifier will increase the partial pressure of the metal.

EXPERIMENTAL

Apparatus

A Heated Graphite Atomizer (HGA), model HGA-76B (The Perkin-Elmer Co., Norwalk, CT, USA), was used. Pyrolytically-coated graphite tubes (Perkin-Elmer part No. 091504) and glassy carbon tubes (manufactured by Ringsdorff) were used. The atomic absorption measurements were made with a Varian Techtron spectrophotometer, model AA6, fitted with a Hamamatsu R213 photomultiplier tube. Hollow cathode lamps were modulated at 843 Hz and a laboratory-made, synchronous detection system (a lock-in amplifier) with a time constant of 8 ms was used.

Analysis of the furnace gases was performed with a gas chromatograph (GC), Model Sigma-300 (Perkin Elmer, Norwalk, CT, USA). The GC was fitted with a 72-inch long 0.125-inch outside diameter stainless-steel column packed with 100-120 mesh Carbosieve S-II (Supelco, Bellefonte, PA, USA) and a thermal conductivity detector. Hydrogen, carbon monoxide, methane and carbon dioxide were separated under isothermal conditions at 100 °C. Argon carrier gas was used for the determination of hydrogen and helium carrier gas was used for the determination of all other gases.

Gas samples were collected using a laboratory-made, computerized sampling system. For the collection of gas samples the right-side quartz window was removed from the atomizer and replaced with a high-temperature silicon rubber septum through which samples were injected. The left-side window mount was removed and replaced with a stainless-steel, water-cooled gas extraction head which tapered from 0.6 cm (the inside diameter of the furnace) down to 0.09 cm (the inside diameter of the gas transfer line). The injection hole of the graphite furnace was sealed with a plug made

of solid pyrolytic graphite. Prior to the start of the atomization cycle a trigger pulse would activate a timing program on an Apple IIe computer (Apple Computer, Cupertino, CA, USA). After a user-selected interval, the computer would send one or more trigger pulse(s) to two optically isolated relays (5 mV dc – 120V ac), which would in turn activate two solenoids located at the input terminals of an air-actuated sampling valve (Valco Instruments, Huston, TX, USA). By changing the timer interval the user was able to obtain time-resolved samples of the furnace gas. Figure 1 shows a schematic diagram of this apparatus.

Reagents and Sampling Procedure

Stock solutions were prepared by weighing appropriate masses of pure elements or their salts. Pb, taken as $\text{Pb}(\text{NO}_3)_2$, was dissolved in ultrapure water. Zn metal was dissolved in (1:1) HNO_3 (ULTREX). Se powder was dissolved in (1:1) HNO_3 (ULTREX). Sn metal was dissolved in 50% (v/v) HCl (ULTREX). Cr, taken as $\text{K}_2\text{Cr}_2\text{O}_7$, was dissolved in 1% (v/v) HNO_3 (ULTREX). Test solutions were made up daily by serial dilution of stock solutions with ultrapure water obtained direct from a Millipore water purification system, model Milli-Q2. All test solutions were made to contain 1% (v/v) HNO_3 (ULTREX). Test solutions for study of matrix interferences contained an additional 1% (v/v) HCl (ULTREX). A 10 μL aliquot of the test solution was deposited with an Eppendorf pipet fitted with disposable plastic tips. Aqueous solutions of ascorbic acid, 1% (m/v), and oxalic acid, 1% (m/v) were used.

Figure 1. Schematic diagram for the gas sampling system

Gases and Flow Control

Ar gas of 99.9998% purity was used as internal purge gas and as sheath gas. A Matheson gas proportioner, model 7351, fitted with two model 610 rotameters, was used to set manually the purge gas flow to 50 mL min^{-1} , which was maintained throughout all heating cycles. H_2 , CO, or CO_2 gas in Ar gas was taken from commercially available certified standards. For the chemical modification and matrix interference studies gas mixtures of: 5.00 % H_2 in Ar – denoted H_2/Ar ; 2.10 % CO in Ar – denoted CO/Ar; 2.00 % CO_2 in Ar – denoted CO_2/Ar ; and 100 % CO were used as both purge gas and sheath gas.

Drying and Atomization Procedure

All test solutions were dried in the furnace at 380 K for 30 sec, charred at the appropriate temperatures for 30 sec and atomized using maximum power heating. The heating rate at the appearance temperature of each element is given in Table 1.

Measurement of Temperature

The temperature of the inside surface of the graphite tube opposite the sample injection hole was measured with an Ircon model 300 automatic optical pyrometer. The voltage of the pyrometer was recorded with a Nicolet model 4096 digital oscilloscope. The output voltage of the pyrometer was converted into temperature using the calibration table provided by the manufacturer.

Table 1. Experimental and instrumental parameters.

Element	Mass	Wave— length /nm	Spectral Band Pass /nm	Heating Rate at	
	Atomized /ng			T_{app}^1 (K ms ⁻¹) P.C.T. ²	G.C.T. ³
Zn	50	307.4	0.1	1.5	not used
Pb	1	283.3	0.1	1.5	1.5
Se	100	196.0	0.1	1.5	1.5
Sn	10 ⁴	224.6	0.1	1.5	not used
As	10	193.6	0.1	1.5	1.2
Cr	0.2	357.7	0.1	1.5	not used

¹ T_{app} = Appearance temperature as defined earlier.

²P.C.T. = Pyrolytically coated graphite tube (Perkin–Elmer).

³G.C.T. = Glassy carbon tube (Ringsdorff)

RESULTS AND DISCUSSION

SAMPLING SYSTEM

In order to provide accurate time-resolved samples of the furnace gas, laminar flow of the purge gas must be maintained in the transfer lines between the furnace and the gas sampling valve. Rohsenow and Choi³⁵ have shown that laminar flow through a tube exists when the Reynolds Number, N_{Re} , is less than 2000. The Reynolds number is given by:

$$N_{Re} = \frac{\rho V D}{\mu} \quad 13$$

where ρ is the density of the gas, V is the velocity of the gas, D is the inner diameter of the tube and μ is the viscosity of the gas. For the gas transfer line used in this work N_{Re} has been found to be 79 at 20 °C.

Accurate sampling of the purge gas composition at the furnace temperature can be obtained only if back reactions in the gas phase do not occur as the temperature of the gas drops in the sampling system, and if heterogeneous reactions between the gas phase and the walls of the sampling system do not occur. Quenching of the gas mixture is considered to have occurred for three reasons. (i) The thermal gradient between the end of the tube and the head of the gas extractor is very high because the head of the extractor is water cooled and positioned 0.7 cm from the end of the tube. Under the experimental conditions used in this work the gas will travel from the tube to the extractor head in just 230 ms, giving a thermal gradient of between 2000 K s^{-1} and 8700 K s^{-1} . (ii) Considering the amount of carbon monoxide that was detected one would have found greater amounts of carbon dioxide if in fact back reactions did occur

in the gas phase. (iii) Results given in the following chapter are consistent with quenching of the high-temperature mixtures under the experimental conditions used in this work. Heterogeneous reactions involving the gas phase and the walls of the sample head are not considered to have occurred because the sample head was water cooled and thus remained at a low temperature.

Certified standards (commercially available) of various gases were diluted with Ar using a rotameter/mixer. The following detection limits were obtained using the gas chromatograph described earlier: hydrogen – 20 ppm; carbon monoxide – 100 ppm; methane – 100 ppm; carbon dioxide – 500 ppm.

PYROLYSIS OF ASCORBIC ACID AND OXALIC ACID

Figures 2 and 3 show the partial pressures of hydrogen and carbon monoxide, respectively, during the atomization cycle for test solutions of ascorbic acid, oxalic acid and blanks (whose concentrations are listed in Table 2) when a used pyrolytically coated graphite tube is used and the charring temperature is 680 K. The temperature of the graphite tube wall at the start of the atomization cycle is equal to the charring temperature and the heating rate is 1.5 K ms^{-1} for Figures 2–18. Methane and carbon dioxide were not detected; hence, the partial pressures of these gases were below 0.0001 and 0.0005 atms, respectively. Figures 4, 5 and 6 show the partial pressures of hydrogen, carbon monoxide and carbon dioxide, respectively, for the test solutions deposited in an unused graphite tube and for the charring temperature of 540 K. Table 2 lists the partial pressures of hydrogen, carbon monoxide and carbon dioxide, for the test solutions deposited in an unused graphite tube and for the charring temperature of 680 K. Table 3 shows the partial pressures of the gases at the appearance temperature of lead under the above experimental conditions. Figures 2–6 and Table 3 show that

Figure 2. The partial pressure of hydrogen (P_{H_2}) as a function of time for the test solutions charred at 680 K in a used graphite tube.

Figure 3. The partial pressure of carbon monoxide (P_{CO}) as a function of time for the test solutions charred at 680 K in a used graphite tube.

Figure 4. The partial pressure of hydrogen (P_{H_2}) as a function of time for the test solutions charred at 540 K in an unused graphite tube.

Figure 5. The partial pressure of carbon monoxide (P_{CO}) as a function of time for the test solutions charred at 540 K in an unused tube.

Figure 6. The partial pressure of carbon dioxide (P_{CO_2}) as a function of time for the test solutions charred at 540 K in an unused tube.

Table 2. Partial pressure of the gases for an unused graphite tube and a charring temperature of 680 K.

Temperature, K	Test Solution	Partial pressure x 10 ⁶ , atm		
		H ₂	CO	CO ₂
680	Ascorbic	<20	<100	<500
	Oxalic	<20	<100	<500
	Nitric	<20	<100	<500
1530	Ascorbic	560	200	800
	Oxalic	510	160	<500
	Nitric	200	140	<500
1900	Ascorbic	2200	1900	2100
	Oxalic	1800	1900	5000
	Nitric	2000	1400	2800

Notes: Ascorbic – denotes a test solution containing 1% (w/v) ascorbic acid and 1% (v/v) nitric acid; Oxalic – denotes a test solution containing 1% (w/v) oxalic acid and 1% (v/v) nitric acid; Nitric – denotes a test solution containing 1% nitric acid. All test solution samples deposited in the graphite tube were of 10 µL volume, the balance being ultra-pure water.

Table 3. Partial pressure of the gases at the appearance temperature of lead for the three test solutions.

Tube Type	Charring Temp., K	Test Solution	Partial pressure x 10 ⁶ , atm		
			H ₂	CO	CO ₂
Used	680	Ascorbic	6000	2700	<500
		Oxalic	3400	2700	<500
		Nitric	20	<100	<500
Unused	540	Ascorbic	150	<100	650
		Oxalic	80	<100	2200
		Nitric	<20	<100	940
Unused	680	Ascorbic	≈100	<100	<100
		Oxalic	≈100	<100	<100
		Nitric	≈100	<100	<100

Notes: Ascorbic – denotes a test solution containing 1% (w/v) ascorbic acid and 1% (v/v) nitric acid; Oxalic – denotes a test solution containing 1% (w/v) oxalic acid and 1% (v/v) nitric acid; Nitric – denotes a test solution containing 1% nitric acid. All test solution samples deposited in the graphite tube were of 10 μ L volume, the balance being ultra-pure water.

aqueous solutions containing ascorbic acid and oxalic acid (both containing nitric acid) produce high levels of hydrogen and carbon monoxide during the atomization cycle, compared to test solutions containing only nitric acid. It is also shown that a used, pyrolytically-coated graphite tube produces higher levels of these gases than does an unused, pyrolytically-coated graphite tube. A used tube has a surface that is scored and pitted due to degradation of the pyrolytic coating by acid and oxygen. Such a scored and pitted surface will absorb and retain the test solutions to a greater extent than the smooth regular surface of an unused pyrolytically-coated graphite tube. Considering only the unused tubes one finds that samples charred at 540 K produce equal or higher levels of hydrogen, carbon monoxide and carbon dioxide than those charred at 680 K. This effect is probably due to pyrolysis of the sample and removal of reactive materials at the higher charring temperature. One should note that the gas phase composition varies less between the three test solutions when a higher charring temperature is used. The test solution containing oxalic acid produces high levels of carbon dioxide. It has been shown³⁶ that at high temperatures oxalic acid is decomposed to formic acid and carbon dioxide:

Figures 7–10 show atomic absorption pulses of lead under various conditions of tube age and charring temperature. Table 4 lists the atomic absorption pulse characteristics: peak height, peak area and appearance temperature, for the atomic absorption pulses shown in Figures 7–10. Comparison of Table 3 with Figures 7–10 and Table 4 shows that the pulse shift for Pb is greatest when large amounts of hydrogen and carbon monoxide are present at the appearance temperature. Note that when an unused graphite tube is used and the charring temperature is 680 K there is little change in either the gas-phase composition or the appearance temperature of the

Figure 7. Atomic absorbance pulses for lead with various chemical modifiers. Test solutions were charred at 540 K in a used graphite tube

Figure 8. Atomic absorbance pulses for lead with various chemical modifiers. Test solutions were charred at 680 K in a used graphite tube.

Figure 9. Atomic absorbance pulses for lead with various chemical modifiers. Test solutions were charred at 540 K in an unused graphite tube.

Figure 10. Atomic absorbance pulses for lead with various chemical modifiers Test solutions were charred at 680 K in an unused graphite tube

Table 4. Characteristics of the lead atomic absorption pulses.

Tube Type	Charring Temp., K	Test Solution	Peak Height A	Peak Area A · s	Appearance Temperature K
Used	540	Ascorbic	0.460	0.076	740
		Oxalic	0.280	0.052	900
		Nitric	0.360	0.052	1050
Used	680	Ascorbic	0.440	0.052	920
		Oxalic	0.350	0.051	1000
		Nitric	0.360	0.050	1120
Unused	540	Ascorbic	0.340	0.053	780
		Oxalic	0.280	0.056	870
		Nitric	0.340	0.059	950
Unused	680	Ascorbic	0.400	0.047	960
		Oxalic	0.370	0.058	960
		Nitric	0.370	0.060	980

Notes: Ascorbic — denotes a test solution containing 1% (w/v) ascorbic acid and 1% (v/v) nitric acid; Oxalic — denotes a test solution containing 1% (w/v) oxalic acid and 1% (v/v) nitric acid; Nitric — denotes a test solution containing 1% nitric acid. Tabulated values have uncertainty $\leq 10\%$ relative standard deviation.

atomic absorption pulses, regardless of whether the analyte solution or the modifier solution is initially deposited in the graphite tube.

The amount of hydrogen and carbon monoxide produced by ascorbic acid and oxalic acid during the atomization cycle is reduced when the test solutions are charred at 680 K instead of 540 K. It is not unreasonable to suspect that further reductions in hydrogen and carbon monoxide levels will occur as still higher charring temperatures are used. Figure 11 shows that at higher charring temperatures samples containing ascorbic acid exhibit smaller shifts in appearance temperature; for charring at 1000 K there is no shift in appearance temperature. Figures 12 and 13 show that as the charring temperature is increased, the thermal stability curves for analytes with and without ascorbic acid converge. Figure 14 shows the atomic absorption pulses of samples with and without ascorbic acid charred at 980 K. Note that the appearance temperature and the rising portions of the atomic absorption pulses are the same for both pulses. The preatomization loss of lead evident in Figure 14 is not expected because in this case the ascorbic acid was deposited in the furnace and charred at 980 K before the lead was deposited in the furnace. The preatomization loss of lead evident from the reduced peak area with ascorbic acid may be due to the evolution of gases from the ascorbic acid char but insufficient gases are evolved to cause a pulse shift.

If the chemical modification effect of ascorbic acid is due to the evolution of hydrogen and carbon monoxide then this effect will be reproduced by the addition of hydrogen and carbon monoxide to the purge gas. Figure 15 shows that the chemical modification effect of ascorbic acid can be reproduced by adding hydrogen and carbon monoxide to the gas phase in the same amounts produced by the pyrolysis of ascorbic acid at the appearance temperature of lead. In Figure 15 the lead atomic absorption

Figure 11. Shift in the appearance temperature of lead on the addition of ascorbic acid to the sample.

Figure 12. Peak-height absorbance of 1.00 ng of lead as a function of charring temperature for test solutions with ascorbic acid and without ascorbic acid.

Figure 13. Peak-area absorbance of 1.00 ng of lead as a function of charring temperature for test solutions with ascorbic acid and without ascorbic acid.

Figure 14. Atomic absorption pulses of lead. A, sample in a graphite tube which had just been used to pyrolyse ascorbic acid at 960 K; B lead without the ascorbic acid step charred at 960 K.

Figure 15. Atomic absorbance pulses of lead in test solutions containing: A, ascorbic acid; B, without ascorbic acid but having 0.006 atm hydrogen and 0.003 atm carbon monoxide added to the argon purge gas; C, without ascorbic acid, hydrogen or carbon monoxide.

pulses for ascorbic acid added in solution and for nitric acid but with hydrogen and carbon monoxide added to the gas phase overlap each other and have (within experimental uncertainty) the same appearance temperature, peak height and peak area.

Figure 16 is a scanning electron microscopy (SEM) image of a pyrolytic graphite surface; Figure 16 (a) shows the char left by ascorbic acid (top third of image) when it is charred at 540 K; and Figure 16 (b) shows that no char is left when oxalic acid is charred at 540 K. Figure 16 (b) is identical to that of a bare pyrolytically coated graphite surface. The absence of a char in the case of oxalic acid is consistent with the hypothesis of Tominaga et al.⁶ that chemical modification with ascorbic acid and oxalic acid involves the pyrolysis gases and not the surface char.

a

b

Figure 16. A scanning electron microscopy (SEM) image of a pyrolytically coated graphite surface charred at 540 K after having (a) ascorbic acid deposited and (b) oxalic acid deposited on it. The bare surface appears identical to (b).

Figure 17. Loss of lead analyte as a function of cutoff temperature in a used graphite tube for test solutions containing ascorbic acid, oxalic acid and no chemical modifier (nitric).

Figure 18. Loss of lead analyte as a function of cutoff temperature in an unused graphite tube for test solutions containing ascorbic acid, oxalic acid and no chemical modifier (nitric).

EQUILIBRIUM CALCULATIONS

Calculations were carried out using the computer program SOLGASMIX for free energy minimization as described by Frech et al.²⁷. For given input conditions the output is the composition of the gas phase having minimum Gibbs free energy. Input consists of atomic and molecular species considered to be present in the furnace, the standard free energy of these species, the temperature of the system and the total amount of each element present. An initial guess at the equilibrium concentrations of these species is required to speed up convergence and to increase accuracy. Multiple runs are necessary to increase accuracy and to eliminate species with extremely low partial pressures. The initial input gaseous species were Pb, PbO, PbH, PbOH, PbH₂, Pb₂, H₂, H, OH, HO₂, H₂O, O₂, O, C, C₂, CO, CO₂, CH₄ and Ar. Thermodynamic calculations predict that PbO is the major species of lead in the gas phase prior to atom formation and that H₂, H₂O, CO and CO₂ are the predominant species of hydrogen, carbon and oxygen under the experimental conditions used in this work.

Results of the equilibrium calculations are given in Figure 19, which shows the predicted partial pressure of lead as a function of temperature using the experimentally-determined values for hydrogen and carbon monoxide as input for the test solutions in unused and used tubes for charring temperatures of 540 K and 680 K. The partial pressure which corresponds to the appearance of lead (0.013 absorbance) is shown as a near-horizontal line. The line intersections correspond to the predicted appearance temperature of lead for the test solutions. The calculations for a new tube and charring temperature of 680 K are not presented because under these conditions the composition of the gas phase is the same for all three test solutions at the appearance temperature of lead.

Figure 19. Predicted partial pressure of lead as a function of temperature in a used tube for a test solutions: ▼, containing 1% (m/v) ascorbic acid; ▲, containing 1% (m/v) oxalic acid; □, containing only 1% (v/v) nitric acid; and in an unused tube: ◆, 1% ascorbic acid; ●, 1% oxalic acid; +, 1% nitric. Intersection of the horizontal line with the lead curves gives the appearance temperature for lead for that test solution.

Table 5. Experimental and modelled atomic absorption pulse shifts for lead in the three test solutions.

Tube Type	Charring, Temp., K	Test Solution	Pulse shift, K	
			Experimental	Modelled
Used	540	Ascorbic	−320	not done
		Oxalic	−150	not done
Used	680	Ascorbic	−200	−230
		Oxalic	−150	−170
Unused	540	Ascorbic	−170	−190
		Oxalic	−80	−120
Unused	680	Ascorbic	−20	0
		Oxalic	−20	0

Notes: Ascorbic – denotes a test solution containing 1% (w/v) ascorbic acid and 1% (v/v) nitric acid; Oxalic – denotes a test solution containing 1% (w/v) oxalic acid and 1% (v/v) nitric acid; Nitric – denotes a test solution containing 1% nitric acid. All test solution samples deposited in the graphite tube were of 10 μL volume, the balance being ultra-pure water.

CHEMICAL MODIFICATION OF Zn, Pb, Sn, Se, As and Cr

In order to further test the thermodynamic equilibrium model²⁰ five elements, in addition to lead, were chosen to test the model under a variety of conditions. Zinc was chosen because it has an appearance temperature close to that of lead and it may form atoms by gas-phase dissociation of ZnO. Tin was chosen because the appearance temperature of tin is well above the temperature at which oxygen is completely desorbed from the graphite surface^{18,19}. Selenium and arsenic were chosen for their high appearance temperatures and tendency to form gas-phase molecular species²⁷. Chromium was chosen for its high appearance temperature and tendency to form condensed-phase molecules prior to atomization.

It was mentioned earlier that ascorbic acid causes a shift in the appearance temperature of several elements and eliminates or reduces their matrix interferences. If H₂ and CO gas, produced by the pyrolysis of ascorbic acid, are the agents responsible for the shift in the appearance temperature and the removal or reduction of the above interferences, then one would expect ascorbic acid to be effective only in the temperature range where ascorbic acid produces these gases in abundance. At temperatures below 850 K or above 1500 K ascorbic acid produces only small amounts of H₂ and CO. Therefore, elements having appearance temperatures outside the range 850 K – 1500 K should not be affected by the gaseous products of pyrolysis of ascorbic acid; this has been demonstrated in this work. Ascorbic acid is a reducing agent, and when present in acidic aqueous solutions reacts with selenium or arsenic in higher oxidation states to form a coral-pink suspension, probably containing selenium or arsenic as elements in colloidal state. Ascorbic acid reacts similarly with tellurium in acidic aqueous solutions³⁷. Aliquots taken from such a solution gave no atomic absorption signal for selenium or arsenic. So, ascorbic acid is of limited use as a

chemical modifier for selenium or arsenic in aqueous solutions.

Table 6 shows the appearance temperatures of the six elements with and without the chemical modifiers: ascorbic acid, hydrogen, carbon monoxide and carbon dioxide. It should be noted that the amount of hydrogen or carbon monoxide added was not equivalent to that produced by the pyrolysis of ascorbic acid. Table 6 shows that, generally, the appearance temperatures of lead, zinc, selenium, arsenic, tin and chromium are affected by ascorbic acid or H_2 , CO, and CO_2 gases. Exceptions to this statement exist and warrant further investigation. As predicted from the model, H_2 shifts the appearance temperatures of all elements studied to lower values; CO shifts the appearance temperatures of five of the six elements to lower values, whereas CO_2 shifts only three of the six appearance temperatures to higher values. Also, as expected from the model, zinc and lead, which have appearance temperatures in the range where pyrolysis of ascorbic acid produces the maximum amounts of H_2 and CO gases, have the largest shifts in their appearance temperatures. Ascorbic acid has no effect on the appearance temperature of chromium which is at the higher end of the temperature range where the production of H_2 and CO gases, by pyrolysis of ascorbic acid, has decreased to a small value. The signals of selenium and arsenic with ascorbic acid were obtained by depositing into the graphite tube the selenium or arsenic solution first, and after drying the solution adding the ascorbic acid solution on the dried residue, and then atomizing. This procedure prevents the reduction and formation of colloidal suspensions of selenium and arsenic by ascorbic acid.

Table 7 shows the effect of the chemical modifiers, H_2 or CO gas, on the peak areas of the elements. As explained in an earlier section, the predicted effect of these chemical modifiers is to shift the appearance of atomic absorption signals downscale in temperature, thus reducing the pre-atomization loss of the gaseous oxides and

Table 6. Effect of the chemical modifiers, ascorbic acid, $H_{2(g)}$, $CO_{(g)}$, and $CO_{2(g)}$, on the appearance temperatures¹ (K) of the elements.

Element	Chemical Modifier Used				
	None	Ascorbic Acid	$H_{2(g)}$ 5.0% v/v	$CO_{(g)}$ 2.1% v/v	$CO_{2(g)}$ 2.0% v/v
Zn	1160	830	840	1050	1160
Pb	1110	920	1010	860	1200
Se	1320	1200	1160	1330	1800
Sn	1460	1440	1220	1250	1440
As	1600	1470	1520	1550	1580
Cr	1780	1730	1580	1740	1930

¹The tabulated values are the arithmetic mean of at least 8 replicate determinations; the relative standard deviation is $\leq 5\%$.

Table 7. Effect of the chemical modifiers, H_2 and CO gases, on the peak areas¹ (A · s) of the elements.

Element	Chemical Modifier Used			
	None	Ascorbic Acid	$H_{2(g)}$ 5% v / v	$CO_{(g)}$ 2.1% v/v
Zn	0.020	0.030	0.027	0.028
Pb	0.048	0.056	0.048	0.058
Se	0.190	0.200	0.105	0.300
Sn	0.053	0.077	0.073	0.072
As	0.053	0.061	0.060	0.250
Cr	0.095	0.120	0.128	0.095

¹The tabulated values are the arithmetic mean of at least 8 replicate determinations; the relative standard deviation is $\leq 5\%$.

increasing the peak area. The amount of the gaseous oxide thus saved from loss will depend on the mass of the element, the heating rate, the shift in the appearance temperature (ΔT), the time lag corresponding to ΔT , and the flow rate of the purge gas in the furnace. Table 7 shows the predicted trend; however, there are some exceptions which warrant comment. Lead with H_2 shows no change probably because lead forms volatile PbH_2 , the loss of which exactly cancels the opposing effect of the pulse shift downscale, reducing the loss of PbO molecules. Selenium shows a decrease in the peak area with added H_2 , and an unexpectedly large increase in peak area with CO . The decrease in peak area with H_2 can be explained by the formation and loss of volatile SeH_2 ³² during atomization. The increase in peak area with CO is accounted for below.

If an element forms molecules in the gas phase such that they are only partially dissociated during the residence time of the molecules within the furnace then the chemical modifiers may have an additional effect. In this case, the chemical modifiers may react with analyte-containing molecules to form free atoms such that the extent of free atom formation is greater than in the case where the modifier is absent. Frech et al.²⁷ have shown that selenium forms various molecular species in the gas phase prior to atom formation; at 1600 K only 50 % of the selenium exists as atoms and complete dissociation does not occur until the furnace has reached 1800 K. It will be shown in Chapter Two later that selenium species desorb from graphite at low temperatures, and others have shown that preatomization loss of selenium species occurs³². The presence of CO during this preatomization period will affect the gas phase equilibrium involving SeO_2 , SeO and Se_2 in such a way that ashing and preatomization losses are reduced. It will be shown later (Figure 33) that CO purge gas suppresses the formation of gas phase SeO_2 , SeO and Se_2 molecules during the atomization of selenium. It is also possible that CO gas alters the graphite surface such that volatile molecular species are

more strongly bound to the graphite surface, and thus the loss of selenium during ashing is reduced. This point needs further investigation. A result similar to that for selenium has also been obtained for arsenic with CO.

Frech et al.³⁴ have predicted that chromium atoms are formed by the thermal decomposition of condensed-phase Cr_2O_3 for Ar purge gas and by the thermal decomposition of condensed-phase Cr_3C_2 for CO purge gas. For chromium with added carbon monoxide there is no change in the appearance temperature and no increase in the peak area. This result is expected because decomposition of Cr_2O_3 and Cr_3C_2 occur at the same temperature hence; carbon monoxide will not affect on the partial pressure of the chromium atoms at the appearance temperature of chromium.

ELIMINATION OR REDUCTION OF MATRIX INTERFERENCES

It has been found that for pyrolytically-coated graphite tubes the atomic absorbance signals of lead, selenium and arsenic are strongly affected by aging of the graphite tube due to prolonged use. Matousek⁸ has reported that the sensitivity of selenium and arsenic is lower with pyrolytically-coated graphite tubes than with uncoated tubes and that there is an aging effect (the result of prolonged use) with the pyrolytically-coated tubes. This aging effect is probably due to changes in the graphite surface as it is degraded by chemical reagents and oxygen, especially during the heating cycles. Used graphite surfaces have greater porosity, permeability and density of active sites of carbon. Glassy carbon tubes were found to be free of the above aging effect in this work. Figures 20 and 21 show the effect of hydrochloric acid matrix interference with the lead signal and the effect of the chemical modifier, CO/Ar purge gas as a function of charring temperature. The figures show that CO/Ar purge gas removes the hydrochloric acid matrix interference if a charring temperature of about 980 K is used. Figures 22 and 23 show the effect of hydrochloric acid matrix interference with the lead signal and the effect of the chemical modifier H₂/Ar purge gas as a function of charring temperature. These figures show that H₂/Ar purge gas is an effective chemical modifier at any charring temperature in the range of 730 K – 1200 K. Figures 24 and 25 show the effect of hydrochloric acid matrix with the selenium atomic absorbance signal with and without the chemical modifier, CO purge gas, as a function of charring temperature. The figures show that CO purge gas removes the hydrochloric acid matrix interference if a charring temperature of 1550 K is used. It was found that H₂/Ar purge gas caused a suppression of the selenium signal probably because of the formation and loss of volatile SeH₂. Hence, H₂/Ar cannot be used as a chemical modifier in the determination of selenium. Figures 26 and 27 show the effect of hydrochloric acid matrix interference with the arsenic atomic absorbance

Figure 20. The peak-height absorbance of 1 ng of Pb as a function of charring temperature: A, Pb in 1% HNO_3 with 2.1% CO in Ar purge gas; B, Pb in 1% HNO_3 plus 1% HCl with 2.1% CO in Ar purge gas; C, Pb in 1% HNO_3 with Ar purge gas; D, Pb in 1% HNO_3 plus 1% HCl with Ar purge gas. The error bars represent two standard deviations of at least four replicate measurements.

Figure 21. The peak-area absorbance of 1 ng of Pb as a function of charring temperature: A, Pb in 1% HNO_3 with 2.1% CO in Ar purge gas; B, Pb in 1% HNO_3 plus 1% HCl with 2.1% CO in Ar purge gas; C, Pb in 1% HNO_3 with Ar purge gas; D, Pb in 1% HNO_3 plus 1% HCl with Ar purge gas.

Figure 22. The peak-height absorbance of 1 ng of Pb as a function of charring temperature: A, Pb in 1% HNO_3 with 5.0% H_2 in Ar purge gas; B, Pb in 1% HNO_3 plus 1% HCl with 5.0% H_2 in Ar purge gas; C, Pb in 1% HNO_3 with Ar purge gas; D, Pb in 1% HNO_3 plus 1% HCl with Ar purge gas.

Figure 23. The peak-area absorbance of 1 ng Pb as a function of charring temperature: A, Pb in 1% HNO_3 with 5.0% H_2 in Ar purge gas; B, Pb in 1% HNO_3 plus 1% HCl with 5.0% H_2 in Ar purge gas; C, Pb in 1% HNO_3 with Ar purge gas; D, Pb in 1% HNO_3 plus 1% HCl with Ar purge gas.

Figure 24. The peak-height absorbance of 100 ng of Se as a function of charring temperature. A, Se in 1% HNO_3 with CO purge gas; B, Se in 1% HNO_3 plus 1% HCl with CO purge gas; C, Se in 1% HNO_3 with Ar purge gas; D, As in 1% HNO_3 plus 1% HCl with Ar purge gas.

Figure 25. The peak-area absorbance of 100 ng Se as a function of charring temperature. A, Se in 1% HNO_3 with CO purge gas; B, Se in 1% HNO_3 plus 1% HCl with CO purge gas; C, Se in 1% HNO_3 with Ar purge gas; D, As in 1% HNO_3 plus 1% HCl with Ar purge gas.

Figure 26. The peak-height absorbance of 10 ng As as a function of charring temperature. A, As in 1% HNO_3 with CO purge gas; B, As in 1% HNO_3 plus 1% HCl with CO purge gas; C, As in 1% HNO_3 with Ar purge gas; D, As in 1% HNO_3 plus 1% HCl with Ar purge gas.

Figure 27. The peak-area absorbance of 10 ng As as a function of charring temperature. A, As in 1% HNO₃ with CO purge gas; B, As in 1% HNO₃ plus 1% HCl with CO purge gas; C, As in 1% HNO₃ with Ar purge gas; D, As in 1% HNO₃ plus 1% HCl with Ar purge gas.

signal with and without CO purge gas as a function of charring temperature. These figures show that CO purge gas removes the hydrochloric acid matrix interference if a charring temperature of 1200 K is used.

On the basis of thermodynamic equilibrium calculations Frech et al.^{9,13} have concluded that the chloride matrix interference in the determination of lead in steel is due to the gaseous lead atoms combining with gaseous chlorine molecules during atomization to form gaseous lead chloride molecules that are lost, and that the chloride matrix interference is eliminated if hydrogen is added to the system to form HCl molecules – the larger the P_{H_2} the more efficient is the removal of chlorine from the system.

The hydrochloric acid matrix interferences with lead, selenium and arsenic and their elimination by carbon monoxide or hydrogen as chemical modifiers are similar to those reported by L'vov³⁸, who removed the chloride matrix interferences by adding an excess of a lithium salt (e.g. $LiNO_3$) to the analyte solution or hydrogen to the purge gas. This method involves binding free chlorine in a molecule ($LiCl$ or HCl) which is much more stable than the monochloride of the analyte. Consider, for example, a case when an excess quantity of hydrogen or carbon monoxide is present in the argon purge gas. For an aqueous solution containing lead and hydrochloric acid, after drying and charring the sample, rapid heating results in the formation of gaseous $PbCl_2$. In thermodynamic equilibrium in the gas phase, the partial pressure of lead is related through linked chemical equilibria to the partial pressures of other species in the graphite furnace. Lowering or raising partial pressures of any one of the species participating in the linked equilibria will shift the other chemical equilibria, resulting in an increase or decrease in the partial pressure of lead.

A shift in the equilibrium distribution of species (including lead atoms) will occur when one or more species involved in the linked equilibrium is added or removed. The degree of shift in species concentration depends on the amount of material added to or removed from the system and the relative standard free energies of the various species in the system. A simplified view of the system may be obtained by consideration of the difference in the dissociation energy³⁹ (D_{298}^0) of HCl (431.62 kJ mol⁻¹) with that of PbCl (301 ± 29 kJ mol⁻¹) shows that the addition of an excess of hydrogen or carbon monoxide to the equilibrium mixture of gases will shift the equilibrium shown by equations 6 and 7 to the right, thereby eliminating hydrochloric acid matrix interferences. The equilibria concerning selenium and arsenic which form higher chlorides can be treated in a manner similar to those of PbCl₂.

Figure 28 shows the calculated (using the computer program described earlier) effect of P_{Cl_2} on the distribution of the major gaseous lead species for a furnace temperature of 1400 K, which is the temperature of the wall of the graphite furnace at the peak of the lead atomic absorption signal under the conditions used for the work shown in Figures 20–23. The amount of $Cl_{2(g)}$ input to the calculations is equal to the amount of lead atoms present in the gas phase; in other words all the gaseous chlorine is considered to be derived from the vaporization of PbCl₂. Figure 28 shows that for $P_{Cl_2} \geq 10^{-7}$ atm the lead atomic absorbance pulse will be suppressed by the formation and loss of lead as gaseous PbCl and PbCl₂. Figures 29 and 30 show the calculated distribution of the lead species as a function of temperature when hydrochloric acid is added to the test solution. Figure 29 shows the calculated distribution of the lead species when no chemical modifier is used. Figure 30 shows the calculated distribution when H₂/Ar purge gas is used. Figures 29 and 30 show that in the absence of the chemical modifier, H₂/Ar purge gas, the lead atomic absorbance signal will be suppressed due to the formation and loss of gaseous PbCl and PbCl₂.

Figure 28. The modelled distribution of the lead species at 1400 K as a function of P_{Cl_2} .

Figure 29. The modelled distribution of the lead species as a function of the temperature when hydrochloric acid is the matrix of the test solution and argon is the purge gas.

Figure 30. The modelled distribution of the lead species as a function of the temperature when hydrochloric acid is the matrix of the test solution and H_2/Ar is the purge gas.

Figure 31 shows the calculated effect of P_{Cl_2} on the distribution of the major selenium species for a furnace temperature of 1600 K, which is the temperature of the wall of the graphite furnace at the peak of the selenium atomic absorption signal under the conditions used for the work shown in Figures 24 and 25. Figure 31 shows that for $P_{\text{Cl}_2} \geq 10^{-4}$ atm the selenium atomic absorbance pulse will be suppressed by the formation and loss of selenium as gaseous SeCl_2 . Figure 31 also shows that selenium forms numerous other volatile molecular species. Figures 32 and 33 show the calculated distribution of the selenium species as a function of temperature when hydrochloric acid is added to the test solution. Figure 32 shows the calculated distribution of the selenium species when no chemical modifier is used. Figure 33 shows the calculated distribution when CO purge gas is used. Figure 32 shows that in the absence of the chemical modifier, CO purge gas, the selenium atomic absorbance signal will be suppressed due to the formation and loss of gaseous SeCl_2 , SeO , SeO_2 and Se_2 . Figure 33 shows that when CO is used as purge gas the formation of chlorides and oxides of selenium is suppressed and virtually all the selenium will be in atomic form. Figure 33 is consistent with the experimentally measured, five-fold increase in sensitivity when CO is used as purge gas (see Figure 25).

Figure 34 shows the calculated effect of P_{Cl_2} on the distribution of the major arsenic species for a furnace temperature of 1800 K, which is the temperature of the wall of the graphite furnace at the peak of the arsenic atomic absorption signal under the conditions used for the work shown in Figures 26 and 27. Figure 34 shows that for $P_{\text{Cl}_2} \geq 10^{-5}$ atm the arsenic atomic absorbance pulse will be suppressed by the formation and loss of arsenic as gaseous AsCl_3 . Figures 35 and 36 show the calculated distribution of the arsenic species as a function of temperature when hydrochloric acid is added to the test solution. Figure 35 shows the calculated distribution of the arsenic species when no chemical modifier is used. Figure 36 shows the calculated distribution

when CO purge gas is used. Figure 35 shows that in the absence of the chemical modifier, CO purge gas, the arsenic atomic absorbance signal will be suppressed due to the formation and loss of gaseous AsCl_3 and As_2 . Figure 36 shows that when CO is used as purge gas the formation of AsCl_3 is suppressed but the formation of As_2 is not suppressed and virtually all the arsenic will be in the dimer form. Figures 33–36 were drawn without consideration for the existence of gaseous arsenic oxides, for which no thermodynamic data was found. If a gaseous arsenic oxide did exist then the experimentally measured, five-fold increase in sensitivity with CO purge gas could be explained in a manner similar to that of selenium (see Figure 27).

Figure 31. The modelled distribution of the selenium species at 1600 K as a function of P_{Cl_2} .

Figure 32. The modelled distribution of the selenium species as a function of the temperature when hydrochloric acid is the matrix of the test solution and argon is the purge gas.

Figure 33. The modelled distribution of the selenium species as a function of the temperature whe hydrochloric acid is the matrix of the test solution and CO/Ar is the purge gas.

Figure 34. The modelled distribution of the arsenic species at 1900 K as a function of P_{Cl_2} .

Figure 35. The modelled distribution of the arsenic species as a function of the temperature when hydrochloric acid is the matrix of the test solution and argon is the purge gas.

Figure 36. The modelled distribution of the arsenic species as a function of the temperature when hydrochloric acid is the matrix of the test solution and CO/Ar is the purge gas.

CONCLUSIONS

In light of the evidence presented it is not unreasonable to conclude that the chemical modification effects of ascorbic acid and oxalic acid with lead are due primarily to reactions that occur between gaseous Pb-containing molecules and the gases released by the pyrolysis of ascorbic acid and oxalic acid during the atomization cycle. Furthermore, these reactions may be explained in terms of homogeneous thermodynamic equilibrium in the gas phase. H_2 or CO gas are effective in eliminating hydrochloric acid matrix interferences with Pb. CO is effective in eliminating the hydrochloric acid matrix interferences with Se and As, but H_2 reacts with Se to form volatile SeH_2 , which is lost. In the determination of Se or As in aqueous solutions of HNO_3 or HCl, the use of 100% CO as the purge gas gives a greatly enhanced signal. Since metal-free H_2 and CO are readily available and metal-free ascorbic acid is not, it is more practical to use H_2 or CO gas than to use ascorbic acid as a chemical modifier to eliminate hydrochloric acid matrix interferences. Also, ascorbic acid should not be used with aqueous solutions of Se and As in their higher oxidation states, because of reaction with the analyte in solution prior to analysis.

CHAPTER TWO

VAPORIZATION AND ATOMIZATION OF SOME ELEMENTS IN GRAPHITE PROBE FURNACE ATOMIC ABSORPTION SPECTROMETRY

INTRODUCTION

Several workers⁴⁰⁻⁴⁶ have studied mechanisms of atomization of elements and atom loss in GFAAS. Early workers considered supply of atoms to be by desorption from the surface and diffusion through a Langmuir film. L'vov⁴⁰ has proposed that desorption proceeds as it does in a vacuum except that the diffusion of atoms through a Langmuir film, formed on the atomizer surface, reduces the rate of atomization. Fuller^{41,42} has introduced the kinetic approach to predict the shape of copper atomic absorption pulses. The kinetic approach is based on the supply and removal of atoms by consecutive first-order reactions. Thus, the rate of change in the number of gas-phase atoms is equal to the difference between the supply function and the removal function. Using the kinetic approach Fuller^{41,42} has reported excellent agreement between the predicted and experimental results for copper. Sturgeon et al.⁴³ have used the leading edge of the atomic absorbance pulse to determine the activation energy of the rate limiting step for atom formation. To elucidate reaction mechanisms Sturgeon et al.⁴³ have compared experimental activation energies with the enthalpy of reaction for some appropriate reactions. Smets⁴⁴ has applied a kinetic approach which has allowed use of the whole atomic absorbance pulse to determine the activation energy of the atom formation process. Smets⁴⁴ has found activation energies for atomization which agree with bond dissociation energies for FeO and AlO, whereas activation energies for copper, manganese and gold agree with the enthalpy of vaporization of the condensed-phase metals. Using the kinetic approach Akman and co-workers^{45,46} have proposed that NiO is reduced by carbon in a fast step prior to vaporization of the nickel atoms direct from the graphite surface. Akman et al.⁴⁶ have also concluded that the condensed-phase lead monoxide and manganese monoxide are vaporized direct from the graphite surface and are dissociated in the gas phase and that thermal decomposition of $\text{Cr}_2\text{O}_3(\text{s/l})$ to chromium metal and oxygen gas occurs on the

graphite surface. Holcombe and co-workers^{18,19,21,22,26} have introduced the concept that carbon active sites and chemisorbed species may affect the rate of atomization of certain analyte elements. Holcombe and co-workers^{18,19,21,22,26} have attributed the shifts of atomic absorption pulses of lead to the action of chemisorbed oxygen on the graphite surface and the products of oxygen desorption from the graphite surface: carbon monoxide and carbon dioxide. The kinetic approach has proved to be effective in predicting the behavior of the atomic absorption pulses of many elements under a variety of conditions. Using the kinetic approach various authors have reached a consensus on the atomization mechanism for several elements. However, the kinetic approach in its current form⁴⁰⁻⁴⁶ has three limitations: (1) measurement of the rate of atomization is done by an indirect method involving convolution of the supply function and the removal function to yield the atomic absorption pulse; (2) the rate of vaporization and the partial pressure of analyte molecular species cannot be measured, and (3) reactions between vaporized analyte species and gas-phase species are not considered.

The commercial, pulse-heated graphite furnace (which is almost universally used in analysis) presents a formidable experimental problem to the study of kinetics in GFAAS. The temperature of a pulse-heated graphite furnace increases throughout most of the duration of the atomic absorption pulse, and the rate of atomization is a sensitive function of temperature. To get around this problem, in this study, the graphite furnace has been converted into a constant-temperature furnace, into which a graphite probe containing dried residues of solutions are inserted at preset times⁴⁷, after the graphite furnace has attained a preselected, constant temperature. This technique will henceforth be called the graphite probe technique.

The objective of this study is to differentiate, experimentally, the processes of vaporization and atomization; to make direct measurement of the rate of vaporization of analyte atoms and molecules from the surface of the graphite probe in GFAAS and to investigate formation and dissociation of molecules in the gas phase.

THEORY

One important step in atom formation in GFAAS is vaporization of analyte-containing species, be they atoms or molecules, from the surface of a graphite atomizer. Condensed-phase analytes may be vaporized direct from the graphite surface as atoms, or be vaporized as molecules, which are then dissociated in the gas phase, or be vaporized from the surface with concurrent dissociation, or be reduced by carbon at elevated temperatures to form gaseous analyte atoms:

where M is an analyte atom, MX is an analyte-containing molecule (X may be an oxygen atom), MO is an analyte-containing oxide molecule, k_{15-17b} are rate constants and K is an equilibrium constant. The subscript c will be used to denote a species that exists in a solid, liquid, chemisorbed or physisorbed state.

The condensed-phase metal atoms in equation 15 have been reduced from a higher oxidation state (as a molecule or a compound) prior to vaporization. In the usual analytical situation involving nanograms or less of the analyte, the condensed-phase analyte species may be present on the surface of the graphite

atomizer in extremely small quantities, often in monolayers. For this reason one may expect that the analyte on the atomizer surface may have properties different from those of the bulk material. In such a case, Holcombe et al.¹⁹ have proposed that vaporization may occur as a desorption process:

$$\frac{-d \sigma_M}{dt} = \sigma_M^n v \exp(-E_a/RT) \quad 18$$

where: σ_M is the surface coverage of M at any time; n is the desorption order; v is the frequency factor; E_a is the activation energy barrier to desorption; R is the gas constant and T is the absolute temperature. If the analyte species are distributed on the atomizer surface as a monolayer or sub-monolayer then the order of desorption will be one⁴⁴ and the surface coverage term may be replaced with the number of analyte atoms present on the atomizer surface, $[M_{(c)}]$. Equation 18 may be then rewritten as :

$$\frac{-d[M_{(c)}]}{dt} = k [M_{(c)}] \quad 19$$

where k is the rate constant. Re-writing and integrating equation 19 one gets:

$$-\ln \left[\frac{[M_{(c)}]_t}{[M_{(c)}]_0} \right] = k t \quad 20$$

where $[M_{(c)}]_t$ and $[M_{(c)}]_0$ are the number of atoms on the atomizer surface at time t and the number of atoms initially (at time zero) present on the surface, respectively. The rate constant is related to the activation energy for the reaction by the Arrhenius equation:

$$k = v \exp(-E_a/RT) \quad 21$$

For first-order desorption, a plot of $-\ln([M_{(c)}]_t / [M_{(c)}]_0)$ vs t should be a straight line with slope equal to the rate constant, k . Since $k = \nu \exp(-E_a/RT)$, a plot of $\ln(k)$ vs $1/T$ has a slope of $-E_a/R$ and an intercept of $\ln(\nu)$.

Equation 16 represents the case where molecular species are vaporized direct from the surface, and are then dissociated. If one considers the case where the analyte is desorbed in a molecular form, $MX_{(c)}$ or $MO_{(c)}$ can be substituted for $M_{(c)}$ in equations 18–20. The atomization step in a pulse-heated, semi-enclosed graphite furnace is characterized by high thermal gradients, rapid supply and removal of atomic and molecular species, ingress of ambient atmosphere into the graphite furnace and reactions between gas-phase oxygen and condensed-phase graphite. Under such conditions one may question whether thermodynamic equilibrium can exist in the graphite furnace. However, a large body of experimental data and observations support existence of gas-phase homogeneous equilibrium for many elements in GFAAS^{9–13,20,23,27,31,32}. The high temperatures and pressures that exist in the graphite furnace yield high collision frequencies, high rate constants and high rates of reaction. Gas-phase reactions between atoms or radicals and diatomic molecules typically have high frequency factors, which are due primarily to their high translational partition functions. On the basis of experimental evidence in the literature it is not unreasonable to assume that in the graphite furnace a number of elements can and do exist in homogeneous equilibrium or pseudo-equilibrium with vapour-phase species.

Equation 17 represents the case where the condensed-phase molecular species are thermally decomposed or reduced by carbon and vaporized in a single step. Equation 17a shows the case for thermal decomposition and equation 17b shows the case for carbon reduction of the analyte oxide. The rate constant for atomization in

reactions 17a and 17b may be calculated using equation 20 and substituting $\text{MX}_{(c)}$ or $\text{MO}_{(c)}$ for $\text{M}_{(c)}$.

EXPERIMENTAL

Apparatus

A Model 603 atomic absorption spectrophotometer with a deuterium-arc background correction system, a model 2100 programmable power supply and a model 400 Heated Graphite Atomizer (all from The Perkin-Elmer Co., Norwalk, CT, USA), was converted into a graphite probe furnace⁴⁷. The furnace was modified by adding an automated probe injection device which allowed precise timing of the probe insertion. The injection ports of pyrolytically coated graphite tubes (Perkin-Elmer part No. 091504) were enlarged to make a rectangular slot of height 2 mm, and width 4.5 mm. Pyrolytic graphite probes were fabricated from a block of anisotropic pyrolytic graphite (Airco Speer Carbon Graphite, Pennsylvania, PA, U.S.A.). The graphite probes were 25 mm long, 4 mm wide at the head, and 2 mm wide at the base with thickness ranging from 0.18 to 0.48 mm. Probes were mounted on a ceramic holder, which was fixed on the shaft of a 2-way, gas-operated cylinder.

The probe injection device consists of a microprocessor-controlled timer, which may be activated by a trigger pulse from the programmable power supply. Once activated the time counts down the preset time then sends a pulse to a relay circuit. The relay circuit converts the timer pulse into a 120 V AC pulse which opens a solenoid switch to admit high pressure (45 psi) argon into the probe-insertion cylinder. Figure 37 is a schematic diagram of the apparatus.

Signals were recorded using a Model 4094, 2-channel, programmable digital oscilloscope, fitted with an XF-44 disk recorder (Nicolet Instrument Corporation, Madison, Wisconsin, U.S.A.). The absorbance versus time profiles were plotted with a

Figure 37. Schematic diagram of the graphite probe insertion system.

Hewlett-Packard Model 7470A Graphics Plotter (Hewlett-Packard Company, San Diego, California, U.S.A.). The integrated absorbance was measured with the above-mentioned programmable oscilloscope using a software package supplied by Nicolet Instrument Corporation. In all cases, commercial hollow cathode lamps were used and operated at lamp currents (Table 8) below the maximum lamp currents recommended by the manufacturers.

Aqueous test solutions (1 μL) were deposited on the head of the graphite probe using a Hamilton microsyringe, fitted with a Chaney adapter and then dried using an infrared lamp. The temperature of the inside of the graphite tube wall was measured with an automatic optical pyrometer, Ircon series 300 (Ircon Inc., Skokie, Illinois USA). The pyrometer was focused on the inside surface of the graphite tube wall at the middle point of its longitudinal axis, the pyrometer signal was recorded using the above-mentioned Nicolet oscilloscope and the temperature was read off the calibration curve supplied by the manufacturer. The heating rate of the tube was 450 K s^{-1} so in all cases the tube had attained a steady state temperature before the probe was inserted.

Reagents and Standards

Stock solutions containing 1000 mg/L of the analytes were individually prepared using chemically pure metals or their salts, as follows. For Ag, Mn, and Cu, each metal was separately dissolved in 50% (v/v) nitric acid (ULTREX) with heating and the solution diluted with ultrapure water. For Au, the stock solution, supplied by Harleco (Philadelphia, Pennsylvania, USA), was prepared by dissolving pure Au in aqua regia and diluting the solution with pure water. For As, As_2O_3 was dissolved in nitric acid (ULTREX) and the solution diluted with ultrapure water. For Se, the metal powder was dissolved in nitric acid (ULTREX) and the solution diluted with ultrapure water.

For Pb, $\text{Pb}(\text{NO}_3)_2$ was dissolved in 2% (v/v) nitric acid (ULTREX) and the solution diluted with ultrapure water. For Sn, the metal was dissolved in 50% hydrochloric acid (ULTREX) and the solution diluted with ultrapure water. All stock solutions were made to contain 1% (v/v) of the acid used to dissolve the metals except Sn, which contained 5% (v/v) hydrochloric acid. The ULTREX brand acids were manufactured by Baker Chemical Co. Ultrapure water of resistivity 18.3 megohms-cm was obtained direct from a Milli-Q2 water purification system (Millipore Corporation). All test solutions were prepared daily by serial dilution of the above stock solutions.

Gases and Gas Flow Control

High-purity argon gas (99.995% pure, Matheson Gas Products, Canada) was used both as purge gas and sheath gas for the graphite furnace. Two other gas mixtures were occasionally used as purge gas and sheath gas. One mixture contained 5.00% (v/v) hydrogen in argon (to be called the H_2/Ar purge gas), the other contained 2.00% (v/v) oxygen in argon (to be called the O_2/Ar purge gas)—both were supplied by Matheson Gas Products, Canada. The flow rate of the sheath gas and the purge gas was 1.5 L min^{-1} and 325 mL min^{-1} , respectively. Both the interrupt (off) and the normal (on) modes of purge gas flow were used. Under the interrupt mode of purge gas flow, the purge gas flow was ceased during the atomization cycle, but was restored immediately on the termination of the atomization cycle in order to provide an Ar gas atmosphere in which the probe was allowed to cool (to room temperature) inside the graphite atomizer before it was manually retracted. Under the normal mode of argon purge gas flow, the gas flow was continued throughout the atomization cycle.

Experimental and Operating Conditions

The experimental and operating conditions used for obtaining the atomization data for the eight elements are presented in Table 8. A spectral bandpass of 0.7 nm was used for all atomic absorption measurements. The hollow cathode lamps were allowed to warm up for ten minutes to attain a stable lamp current before any measurements were made.

Procedure

Test solutions were deposited on the probe and dried as described earlier. The oscilloscope was triggered at the start of the atomization step. After the furnace had attained a steady-state temperature, the probe was automatically inserted into the heated atomizer using the probe insertion device. To ensure the attainment of the preselected atomization temperature by the graphite furnace, a delay of 10 s was used prior to insertion of the probe into the heated atomizer.

Table 8. Experimental and operating conditions.

Element	Monochromator Wavelength, nm	HCL current, mA	Analyte mass, ng	Test Solution Matrix
Pb	283.3	5	1.0	1% HNO _{3(aq)}
Sn	224.6	5	100	5% HCl _(aq)
Se	196.0	15	10	1% HNO _{3(aq)}
As	193.7	15	10	1% HNO _{3(aq)}
Ag	328.1	5	0.1	1% HNO _{3(aq)}
Cu	324.8	5	0.4	1% HNO _{3(aq)}
Mn	279.5	5	0.1	1% HNO _{3(aq)}
Au	242.8	5	0.5	1% HCL _(aq)

RESULTS AND DISCUSSION

The exposure-time experiments, as described below, were carried out using aqueous solutions of the eight analyte elements. During these experiments test solutions were deposited on the graphite probe and dried with an infrared lamp. The graphite furnace was then heated to a constant temperature, T_e , and the probe was then automatically inserted as described earlier. After the elapse of the programmed exposure time, t_e , the power to the graphite furnace was automatically cut off; the furnace and the probe were then rapidly cooled in a convective flow (325 mL min^{-1}) of Ar gas. The probe was then removed from the furnace, the furnace was reheated to a high temperature, T_p , the probe was reinserted, and the atomic absorption pulse was recorded. Figure 38 shows the heating program for the exposure-time experiments. The atomic absorption signal obtained from this procedure is designated $[M_{(c)}]_t$ to denote that it was produced by the analyte species that remains on the probe at the end of the exposure time. The designation $[MX_{(c)}]_t$ is used for the molecular species of the elements. A reference atomic absorption pulse was obtained by omitting the first, low-temperature exposure, and this atomic absorption pulse is designated $[M_{(c)}]_0$ or $[MX_{(c)}]_0$ to denote that it was produced by the amount of metal species originally deposited on the probe – the subscript zero stands for the time equal to zero. Lead and tin were found to be vaporized as molecules at low temperatures and are discussed in Part I; selenium and arsenic were found to be vaporized as molecules which had a tendency to stick to the tube wall and the probe – they are discussed in Part II; silver, gold, manganese and copper were found to be vaporized as atoms and are discussed in Part III.

Figure 38. Temperature program for exposure time experiments. T_e , the temperature of the graphite tube wall when the probe is initially inserted at time, t_i ; T_r , the temperature of the graphite tube wall when the probe is re-injected at time, t_r .

Measurement of the temperature of the graphite probe, inserted into the graphite furnace, has been reported by Wu et al.⁴⁷. Wu et al.⁴⁷ measured the time at which bulk (powder) samples of pure metals, deposited on the graphite probe, melted and assumed that at that time the temperature of the surface of the graphite probe was equal to the melting temperature of the deposited metal. Wu et al.⁴⁷ obtained quantitative agreement between experimental results and a computer model used to calculate the temperature of the whole of the graphite probe. From the work of Wu et al.⁴⁷ and from this work it may be concluded that the temperature of the inside surface of the graphite tube and the temperature of the gas phase are in a steady-state condition when the probe is inserted into the furnace. Thus molecules and atoms on the surface of the probe are rapidly heated by radiation from the tube wall and from conduction from the gas phase. In this work the temperature of picogram masses of analyte elements deposited on the surface of the graphite probe are assumed to be equal to the temperature of the inside of the tube wall at the onset of vaporization or atomization. Thus vaporization and atomization from the probe in the graphite probe furnace are considered to be isothermal processes.

PART I

LEAD AND TIN

Loss of lead from the probe occurs with $T_e \geq 1000$ K but an atomic absorption signal is not observed unless $T_e \geq 1340$ K is used. Loss of tin from the probe occurs with $T_e \geq 1200$ K but an atomic absorption signal is not observed unless $T_e \geq 1800$ K is used. It is therefore reasonable to conclude that lead and tin form gas-phase molecules that do not yield atoms at low temperatures and are lost in the preatomization stage. Gas-phase oxides of lead and tin are therefore considered to be precursors to atom formation; this point was discussed in detail in Chapter 1. Here, it will be assumed that PbO and SnO are the predominant form of molecular lead and tin species. Figure 39 shows results typical of those obtained for lead and tin; exposure at T_e gives no atomic absorption pulses (curve A) and subsequent atomization at T_r produces a signal (curve B) that is smaller than that obtained without the exposure step (curve C). Figures 40 and 41 show the thermal stability curves for lead and tin, respectively, when tube wall atomization is used. In both cases, loss of sample occurs in the charring step, at least 150 K lower in temperature than that at which an atomic absorption pulse is seen in the atomization step. Figures 39–41 show that lead and tin vaporize as molecules prior to formation of their atoms in the graphite furnace.

The results of the exposure time experiments are shown in Figures 42 and 43 as plots of $-\ln \left[[MX_{(c)}]_t / [MX_{(c)}]_0 \right]$ vs time for lead and tin for three temperatures. If the vaporization of MX is a first-order process then according to equation 20 the rate constant is equal to the slope of the appropriate line in Figure 42 or 43. Exposure time experiments were also conducted with H_2/Ar purge gas and O_2/Ar purge gas. The H_2/Ar purge gas gave straight line plots for k , whereas the O_2/Ar purge gas gave results having high uncertainty. The irreproducible results in the O_2/Ar system was probably due to rapid degradation of the graphite probe and graphite tube by oxidation.

Figure 39. Loss of lead and tin from the graphite probe. A, the signal obtained when the probe was inserted at T_e ; B, the signal obtained when the probe was re-inserted at T_r , after exposure at temperature T_e for time t_e ; C, the signal obtained when the probe was injected directly at T_r without ever being inserted at T_e .

Figure 40. Thermal stability curves for lead. The charring curve shows the peak-area absorbance as a function of charring temperature (40 s char time) when an atomization temperature of 2200 K is used. The atomization curve shows the peak-area absorbance as a function of temperature when a charring temperature of 800 K is used. Tube wall atomization was used only in Figure 40 and 41 all other work on lead and tin reported in this chapter was done using the graphite probe furnace.

Figure 41. Thermal stability curves for tin. The charring curve shows the peak-area absorbance as a function of charring temperature (40 s char time) when an atomization temperature of 2700 K is used. The atomization curve shows the peak-area absorbance as a function of temperature when a charring temperature of 800 K is used. Tube wall atomization was used only in Figure 40 and 41 all other work on lead and tin reported in this chapter was done using the graphite probe furnace.

does the graphite surface without chemisorbed hydrogen.

As mentioned earlier activation energy values for vaporization of lead and tin from the tube wall were calculated using the data published by Byrne et al.²⁰, who conducted experiments in which aqueous test solutions containing lead and tin (as the nitrates) were dried and charred, then heated rapidly to temperatures up to and including the appearance temperature of lead in the graphite furnace. At a pre-selected cut-off temperature, power to the atomizer was cut off and the furnace was purged with argon. The sample was then rapidly heated to 2300 K and the lead or tin atomic absorption signal was recorded. Byrne et al.²⁰ concluded that lead and tin were lost as $\text{PbO}_{(g)}$ and $\text{SnO}_{(g)}$, respectively, below their appearance temperatures. From the data on loss of lead or tin vs cut-off temperature reported by Byrne et al.²⁰ the activation energy for the vaporization of PbO or SnO may be calculated. Since the initial temperature of the furnace and the heating rate are known, one may convert the temperature vs loss scale into time vs loss scale. If one considers small time increments then the temperature change during this increment is small and thus the uncertainty incurred by assuming a constant temperature over the time increment is small. Dividing the mass of lead lost during the small time increment ($-\Delta[\text{PbO}_{(c)}]$) by the time increment (Δt) gives the rate of vaporization during that time increment. For this small time increment, the following approximation may be made assuming a first-order reaction:

$$\frac{-d[\text{PbO}_{(c)}]}{dt} = \frac{-\Delta[\text{PbO}_{(c)}]}{\Delta t} = k_1[\text{PbO}_{(c)}] \quad 22$$

then

$$k_1 = \frac{-\Delta[\text{PbO}_{(c)}]}{\Delta t [\text{PbO}_{(c)}]} \quad 23$$

Figure 43. The results of the exposure time experiments for tin. Time on the x – axis is exposure time, t_e .

Tin oxide vaporizes at approximately 200 K higher temperature than does lead oxide, yet, the temperature at which a tin atomic absorbance signal is seen is 500 K higher than the temperature at which a lead atomic absorbance signal is seen, presumably because of the greater bond dissociation energy³⁹ (548 ± 21) kJ mol^{-1} for SnO , compared with (378 ± 4) kJ mol^{-1} for PbO . The higher bond dissociation energy causes most of the tin to remain in the oxide form at temperatures at which lead oxide has been almost completely dissociated.

According to equation 21, a plot of $\ln(k)$ vs $1/T$ should give a straight line with slope equal to the activation energy for the vaporization process. Figure 44 shows the Arrhenius plots for lead monoxide molecules vaporized with argon as the purge gas and with the H_2/Ar purge gas. Figure 44 also shows the line obtained when the results of percent loss (of lead using Ar purge gas) as a function of temperature published by Byrne et al.²⁰ are, as explained below, fitted to the Arrhenius plot. Figure 45 shows the Arrhenius plots for tin with argon purge gas, with H_2/Ar purge gas and the reworked data of Byrne et al.²⁰. Table 9 lists the activation energies obtained using this method. The activation energies for the vaporization of PbO and SnO from the probe in argon purge gas generally agree with those for vaporization of PbO and SnO from the tube wall. Table 10 shows thermochemical properties of the relevant lead and tin species. Comparison of Table 9 with Table 10 shows that the activation energies obtained are not indicative of any bulk properties of the oxides, and probably represent energies of desorption of the oxide molecules from the surface of the graphite probe. When hydrogen is present in the purge gas, the activation energies for desorption of both PbO and SnO are much higher, which suggests that hydrogen alters the release mechanism of these oxides. Hydrogen is known to form strong chemical bonds with carbon and to chemisorb to graphite surfaces^{48,49}. Probably, the graphite surface with hydrogen chemisorbed on it forms different bonds with the lead and tin oxides than

Figure 44. Arrhenius plots for the vaporization of lead species for various conditions. Ar and H₂/Ar denote the two different purge gases used in the graphite probe furnace. The % loss data reported by Byrne et al.²⁰ for tube wall atomization is also shown.

Figure 45. Arrhenius plots for the vaporization of tin species for various conditions. Ar and H₂/Ar denote the two different purge gases used in the graphite probe furnace. The % loss data reported by Byrne et al.²⁰ for tube wall atomization is also shown.

Table 9. Experimentally-measured activation energies for the vaporization of PbO and SnO in the graphite probe furnace with Ar purge gas and with H₂/Ar purge gas and in the graphite tube furnace with Ar purge gas.

Oxide	Activation energy for vaporization, kJ mol ⁻¹		
	Ar purge gas		H ₂ /Ar purge gas
	Probe	Wall	Probe
PbO	90 ± 6	105 ± 15	230 ± 30
SnO	130 ± 10	150 ± 20	180 ± 20

Table 10. Thermochemical data for some lead and tin species.

Reaction	Standard Enthalpy, kJ mol^{-1}	Temperature, K	Ref.
$\text{Pb}_{(l)} \rightarrow \text{Pb}_{(g)}$	178	2023	39
$\text{Sn}_{(l)} \rightarrow \text{Sn}_{(g)}$	230	2473	39
$\text{PbO}_{(l)} \rightarrow \text{PbO}_{(g)}$	213	1745	39
$\text{SnO}_{(l)} \rightarrow \text{SnO}_{(g)}$	251	1800	39
$\text{SnO}_{2(l)} \rightarrow \text{SnO}_{2(g)}$	314	2273	39
$\text{PbO}_{(l)} \rightarrow \text{Pb}_{(g)} + \text{O}_{(g)}$	629	1100	51,52
$\text{SnO}_{(l)} \rightarrow \text{Sn}_{(g)} + \text{O}_{(g)}$	753	1300	51,52
$\text{SnO}_{2(l)} \rightarrow \text{Sn}_{(g)} + \text{O}_{2(g)}$	756	1800	51,52
$\text{PbO}_{(l)} + \text{C}_{(s)} \rightarrow$ $\text{Pb}_{(g)} + \text{CO}_{(g)}$	263	1100	51,52
$\text{SnO}_{2(l)} + 2\text{C}_{(s)} \rightarrow$ $\text{Sn}_{(g)} + 2\text{CO}_{(g)}$	507	1800	51,52

does the graphite surface without chemisorbed hydrogen.

As mentioned earlier activation energy values for vaporization of lead and tin from the tube wall were calculated using the data published by Byrne et al.²⁰, who conducted experiments in which aqueous test solutions containing lead and tin (as the nitrates) were dried and charred, then heated rapidly to temperatures up to and including the appearance temperature of lead in the graphite furnace. At a pre-selected cut-off temperature, power to the atomizer was cut off and the furnace was purged with argon. The sample was then rapidly heated to 2300 K and the lead or tin atomic absorption signal was recorded. Byrne et al.²⁰ concluded that lead and tin were lost as $\text{PbO}_{(g)}$ and $\text{SnO}_{(g)}$, respectively, below their appearance temperatures. From the data on loss of lead or tin vs cut-off temperature reported by Byrne et al.²⁰ the activation energy for the vaporization of PbO or SnO may be calculated. Since the initial temperature of the furnace and the heating rate are known, one may convert the temperature vs loss scale into time vs loss scale. If one considers small time increments then the temperature change during this increment is small and thus the uncertainty incurred by assuming a constant temperature over the time increment is small. Dividing the mass of lead lost during the small time increment ($-\Delta[\text{PbO}_{(c)}]$) by the time increment (Δt) gives the rate of vaporization during that time increment. For this small time increment, the following approximation may be made assuming a first-order reaction:

$$\frac{-d[\text{PbO}_{(c)}]}{dt} = \frac{-\Delta[\text{PbO}_{(c)}]}{\Delta t} = k_1[\text{PbO}_{(c)}] \quad 22$$

then

$$k_1 = \frac{-\Delta[\text{PbO}_{(c)}]}{\Delta t [\text{PbO}_{(c)}]} \quad 23$$

where k_1 is a first-order rate constant, and $[\text{PbO}_{(c)}]$ is the amount of Pb in the form $\text{PbO}_{(c)}$ in the middle of the small time increment. If one assumes that $\text{PbO}_{(c)}$ exists as a monolayer on the graphite tube surface then the mass is proportional to the surface coverage. A plot of $\ln(k_1)$ vs $1/T$ should be a straight line with slope equal to the activation energy for vaporization of the oxide (since no atomic absorption occurs during the cut-off experiment). The uncertainty in the Arrhenius plot arises from the uncertainty in the value of k_1 . The uncertainty in the k_1 value may be calculated by considering the minimum and the maximum value of the rate constant over the small temperature (time) interval (where $T_1 > T_2$).

$$\frac{k_{T_1}}{k_{T_2}} = \exp \left[\frac{E_a}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right] \right] \quad 24$$

From equation 24 one finds that for $E_a = 100 \text{ kJ mol}^{-1}$, $T_1 = 990 \text{ K}$ and $T_2 = 1010 \text{ K}$, the ratio $k_{T_1}/k_{T_2} = 0.79$. The above method was used to calculate the uncertainty of the points shown in Figures 44 and 45 – a 50 ms interval was used for lead and a 10 ms interval was used for tin.

Figures 46–59 are for direct insertion of the probe at the temperature indicated and the purge gas flow off without an initial insertion at T_e . Figure 46 shows the effect of tube wall temperature, T_w , on the lead signal for T_w from 1340 K to 1620 K. The peak height and the peak area increase with increasing temperature, whereas atomization time (τ_1 , the time from the appearance of the atomic absorption pulse to the maximum absorbance) decreases with increasing temperature. The ten-fold increase in peak area for $T_w = 1620 \text{ K}$ over $T_w = 1340 \text{ K}$ is due to the greater degree of dissociation of $\text{PbO}_{(g)}$ molecules at 1620 K than at 1340 K. Figure 47 shows the effect of T_w on the lead atomic absorbance pulse for T_w from 1710 K to 1890 K. The

peak height increases with increasing T_w , whereas the peak area remains constant and τ_1 decreases. If dissociation of the PbO is virtually complete at 1710 K then there will be no increase in the peak area with increasing T_w , but the condensed-phase lead monoxide will vaporize at a greater rate giving the observed increase in the peak height and decrease in the atomization time. Figure 48 shows calculated profiles of the lead species for two different temperatures assuming that lead is vaporized as PbO, and exists in the gas phase in thermodynamic equilibrium with the gas phase. Figure 48 was drawn using experimentally determined rate constants and activation energies, which were used to model the supply of PbO, and the diffusion coefficients given by L'vov et al.⁵⁰ to model the removal of molecules and atoms from the furnace. A P_{O_2} scale similar to that used by Frech et al.²⁷ and the free energy minimization routine of Frech et al.²⁷ along with published thermodynamic data^{51,52} were used for the equilibrium calculations. Comparison of figure 46 with Figure 48 shows that the experimental results are consistent with the postulate that PbO vaporizes from the probe and is dissociated in the gas phase according to thermodynamic equilibrium, since the changes in peak heights, peak areas and appearance times with T_w follow the same trends.

Figure 49 shows the atomic absorption pulses obtained for lead atomized at 1620 K in argon purge gas and in H_2/Ar (5% H_2) purge gas. Peak areas are similar for the atomic absorption pulses indicating that complete dissociation of PbO occurs at 1620 K, but the greater peak height and shorter atomization time of the H_2/Ar pulse suggest that the rate of PbO vaporization is higher with this gas mixture. Figure 50 shows the effect of T_w on the lead atomic absorption pulse for T_w from 1230 K to 1530 K when H_2/Ar purge gas is used. The peak height and the peak area increase whereas the atomization time decreases with increasing temperature. The five-fold increase in peak area for $T_w = 1530$ K over $T_w = 1230$ K is due to decrease in the preatomization

Figure 46. Atomic absorbance pulses for lead when the probe is injected at tube wall temperatures: 1340 K; 1440 K; 1620 K. For these experiments no initial insertion at a lower temperature was done and the atomization time was ten seconds. Time on the x – axis is the time since the beginning of the atomization cycle, the probe was inserted at 10.8 seconds.

Figure 47. Atomic absorbance pulses for lead when the probe is injected at tube wall temperatures: 1710 K; 1800 K; 1890 K. For these experiments no initial insertion at a lower temperature was done and the atomization time was ten seconds. Time on the x-axis is the time since the beginning of the atomization cycle, the probe was inserted at 10.8 seconds.

Figure 48. Calculated temporal distribution of molecular and atomic lead species at tube wall temperatures: 1340 K and 1620 K. Time on the x - axis is time since the insertion of the probe.

loss of gas-phase PbO molecules at the higher temperature. Figure 51 shows the effect of T_w on the lead atomic absorbance pulse for T_w from 1530 K to 1800 K when H_2/Ar is used as purge gas. The peak height increases with increasing T_w , whereas the peak area remains constant and the atomization time decreases. If dissociation of PbO is virtually complete at 1530 K then there will be no increase in peak area with increase in T_w , for $T_w > 1530$ K, but the condensed-phase PbO will vaporize at a greater rate giving the observed increase in the peak height and decrease in the atomization time. Figure 52 shows calculated profiles of the lead species for two different temperatures assuming that lead is vaporized as PbO, and exists in the gas phase in thermodynamic equilibrium with the gas phase. Figure 52 was drawn using the experimentally determined rate constants and activation energies for lead in the H_2/Ar purge gas and the other parameters used in Figure 48. Comparison of Figures 50 with Figure 52 shows that the experimental results are consistent with the postulate that PbO vaporizes from the probe and exists in the gas-phase in thermodynamic equilibrium with the gas phase when H_2/Ar is used as purge gas. However, with H_2/Ar purge gas the atomic absorption pulses are detectable at lower temperatures and complete dissociation of PbO occurs at a lower temperature, the result of lower P_{O_2} levels shifting the equilibrium towards greater dissociation of PbO when H_2/Ar purge gas is used.

It was mentioned earlier that when the exposure time experiments were attempted using O_2/Ar purge gas there was a great deal of uncertainty in the results and no rate constants or activation energy could be determined. Figure 53 shows the lead atomic absorbance pulses with Ar purge gas and with O_2/Ar purge gas and $T_w = 1620$ K. In Figure 53 the atomic absorbance pulse with O_2/Ar purge gas lies completely inside the atomic absorbance pulse with argon purge gas and the trailing edges are nearly coincident. If the rate of vaporization of PbO were the same for both the atomic

Figure 49. Atomic absorbance pulses for lead when the probe is inserted into the furnace having tube wall temperature 1620 K for the case where argon purge gas is used and for the case where H_2/Ar purge gas is used. Time on the x — axis is the time since the beginning of the atomization cycle, the probe was inserted at 10.8 seconds.

Figure 50. Atomic absorbance pulses for lead when the probe is inserted at tube wall temperatures: 1230 K; 1340 K; 1440 K; 1530 K. For these experiments no initial injection lower temperature was done, the atomization time was ten seconds and H_2/Ar purge gas was used. Time on the x – axis is the time since the beginning of the atomization cycle, the probe was inserted at 10.8 seconds.

Figure 51. Atomic absorbance pulses for lead when the probe was inserted at tube wall temperatures: 1530 K; 1620 K; 1800 K. For these experiments no initial insertion lower temperature was done, the atomization time was ten seconds and H_2/Ar purge gas was used. Time on the x – axis is the time since the beginning of the atomization cycle, the probe was inserted at 10.8 seconds.

Figure 52. Calculated temporal distribution of molecular and atomic lead species for tube wall temperatures: 1230 K and 1530 K with H_2/Ar purge gas. For 1530 K the signal for lead in the absence of the spectrophotometer's RC time constant is designated the true signal and the signal produced by the spectrophotometer is designated the measured signal.

Figure 53. Atomic absorbance pulses for lead when the probe was inserted into the furnace having tube wall temperature 1620 K. Ar and O₂/Ar denote the pulses for Ar purge gas and for O₂/Ar purge gas, respectively. Time on the x - axis is the time since the beginning of the atomization cycle, the probe was inserted at 10.8 seconds.

absorbance pulses then one would expect that the higher partial pressure of oxygen with the O_2/Ar purge gas would result in a greater loss of lead as PbO . When O_2/Ar purge gas is used it is likely that PbO vaporizes as is does with Ar purge gas but the degree of dissociation is less for O_2/Ar purge gas due to the higher partial pressure of oxygen.

The above experiments were also done with tin and the results (not shown) are similar to those of lead, suggesting that tin vaporizes and atomizes in a manner similar to that of lead.

Figures 54 and 55 show the change in peak area and peak height, respectively, for the lead atomic absorbance pulse when the probe is inserted at different T_w . Figures 56 and 57 show the similar experiments for tin. For both lead and tin the peak area is greater when H_2/Ar is used as purge gas compared to that for Ar as purge gas; this effect is largest at the lowest temperatures; the curves tend to converge at high temperatures. Presumably at low temperatures, incomplete dissociation occurs and the analyte is lost as oxide molecules; added hydrogen lowers the partial pressure of oxygen, thereby shifting the equilibrium towards greater dissociation of the oxides. At high temperatures lowered oxygen levels and increased equilibrium constant give virtually complete dissociation of the oxides for both cases; hence, the peak area curves come closer together. Effects of added oxygen on the lead atomic absorption pulse are well documented¹⁸⁻²², the effects of O_2/Ar purge gas on the atomic absorption signal of tin is shown in Figures 56 and 57. Added oxygen has an effect opposite to that of added hydrogen presumably because higher oxygen levels shift the equilibrium away from dissociation of SnO . Figures 54-57 also show that the lead atomic absorption signals rise to maximum values over a smaller temperature interval than do the tin atomic absorption signals, presumably because of the differences in standard free

Figure 54. Peak-area absorbance atomization curves for lead when the probe technique was used. Ar and H_2/Ar denote the curves obtained for Ar and H_2/Ar purge gas, respectively.

Figure 55. Peak-height absorbance atomization curves for lead when the probe technique was used. Ar and H_2/Ar denote the curves obtained for Ar and H_2/Ar purge gas, respectively.

Figure 56. Peak-area absorbance atomization curves for tin when the probe technique was used. Ar and H₂/Ar denote the curves obtained for Ar and H₂/Ar purge gas, respectively.

Figure 57. Peak-height absorbance atomization curves for lead when the probe technique was used. Ar and H_2/Ar denote the curves obtained for Ar and H_2/Ar purge gas, respectively.

energy of the lead and tin oxides relative to the standard free energies of their atoms over the temperature ranges studied. In view of the results for tin one would expect that the volatilization and preatomization losses of tin would be greater than those of lead. In all cases (for lead and tin using Ar purge gas, H_2 /Ar purge gas and O_2 /Ar purge gas), the peak height increases with increasing temperature, reflecting the increasing rate of vaporization of the oxide molecules.

Figures 58 and 59 show the measured appearance times for lead and tin when Ar and H_2 /Ar purge gases are used. Hydrogen reduces the partial pressure of oxygen in the furnace, resulting in a greater extent of dissociation of the oxides at a low temperature, and producing the observed shift of the signals to earlier times. Figure 60 shows the calculated extent of dissociation of PbO and SnO molecules in the gas phase as a function of P_{O_2} according to gas-phase thermodynamic equilibrium. For a furnace temperature of 1200 K, PbO molecules start to dissociate when the P_{O_2} has reached 10^{-6} atm, and the dissociation of PbO is complete when the P_{O_2} has reached 4.5×10^{-10} atm. Addition of 0.05 atm of hydrogen to the purge gas has two effects on the atomic absorption pulses of lead and tin. Number one, hydrogen decreases the P_{O_2} in the furnace, causing an increase in the degree of dissociation of PbO and SnO molecules. Number two, as shown earlier, hydrogen, chemisorbed onto the surface of the graphite probe, causes an increase in the rate of vaporization of PbO and SnO. The combination of these two factors give the observed shift to earlier appearance time of the lead and tin atomic absorption pulses. When O_2 /Ar purge gas is used, increase in the P_{O_2} results in a decrease in the degree of dissociation of SnO molecules; hence more SnO must be vaporized to yield (by dissociation) the number of tin atoms required for the appearance of the tin atomic absorption pulse.

It has been proposed²² that PbO molecules undergo many episodes of

Figure 58. Appearance time of lead atomic absorbance pulses as a function of the temperature of tube wall upon insertion of the probe. Ar and H₂/Ar denote the curves obtained for Ar and H₂/Ar purge gas, respectively.

Figure 59. Appearance time of tin atomic absorbance pulses as a function of the temperature of tube wall upon insertion of the probe. Ar , H_2/Ar and O_2/Ar denote the curves obtained for Ar , H_2/Ar and O_2/Ar purge gas, respectively.

Figure 60. Distribution of lead and tin species as a function of the partial pressure of oxygen for a furnace heated to 1400 K for lead and 1800 K for tin.

desorption/adsorption with the graphite tube wall prior to reduction to $\text{Pb}_{(s/l)}$ on the tube wall. This mechanism may be written as :

where $\text{PbO}_{(a)}$ refers to PbO molecules adsorbed on the graphite surface carbon is supplied by the graphite surface, $T_1 < T_2$ and T_2 is the appearance temperature of lead. If this mechanism is correct then for a short exposure time and low exposure temperature PbO molecules should desorb from the probe and stick to the wall and not be lost during the atomization cycle. Subsequent heating of the tube to 2000 K would then produce an atomic absorption signal for lead that vaporizes from the tube wall. Such signals were not observed for lead and tin, but were observed for selenium and arsenic. These results are consistent with a mechanism in which PbO is vaporized from the graphite probe, followed by the gas-phase equilibrium dissociation of PbO. This mechanism may be written as follows:

Table 11 shows that more tin is lost when the purge gas flow is on than under stopped-flow conditions. The results for tin vaporization and atomization in the graphite probe furnace are consistent with a mechanism in which SnO has multiple episodes of vaporization – adsorption and exists in the gas phase tin thermodynamic equilibrium with the gas phase. This mechanism may be written as:

Table 11. The flow on/flow off experiment for lead and tin.

Element	Temperatures, K		Flow during initial exposure	Peak-area absorbance	
	Initial	Final		Initial	Final
Pb	1515	2200	On	0.00	0.077±0.004
			Off	0.03±0.02	0.044±0.007
Sn	1710	2430	On	0.00	0.057±0.005
			Off	0.00	0.090±0.010

PART II

SELENIUM AND ARSENIC

Loss of selenium from the graphite probe occurs with $T_e \geq 700$ K but an atomic absorption pulse is not seen unless $T_e \geq 1440$ K is used. Loss of arsenic from the probe occurs at $T_e \geq 915$ K but an atomic absorption signal is not seen unless $T_e \geq 1240$ K is used. It is therefore reasonable to conclude that selenium and arsenic form gas-phase molecules which do not yield analyte atoms at low temperatures. Figure 61 shows results typical of those obtained for selenium and arsenic; exposure at T_e gives no atomic absorbance pulse. Subsequent probe reinsertion at T_r produces a signal containing two temporally- and spatially-resolved absorbance pulses. The first atomic absorbance pulse (the left-hand-side peak of curve A) which occurs before the reinsertion of the probe at 10.8 seconds, is due to vaporization and atomization of analyte species adsorbed on the graphite tube wall. Probably, analyte species are vaporized from the probe during its exposure at T_e and condensed on the graphite tube wall and the graphite probe when power to the atomizer is cut off. The second pulse (the right-hand-side peak of curve A) which occurs after insertion of the probe, is due to the analyte species which has been adsorbed on the probe at the end of the previous exposure step. For selenium, if T_e is less than 1340 K and t_e is less than six seconds then the second pulse will be due in part to the analyte that has not been vaporized during the short time interval allowed during the exposure time experiment (this topic is covered in depth later); this will be in addition to the analyte species which will be adsorbed on the probe at the end of the exposure time experiment. This property of sticking to the tube wall is characteristic of selenium and arsenic among the eight elements studied. There is also an indirect evidence that copper sticks to the graphite tube wall but the extent of sticking is not sufficient to be measured directly using the above technique.

Figure 61. Loss of selenium species from the graphite probe: zero absorbance, the signal obtained when the probe was injected at T_e ; A, the signal obtained when the probe was re-injected at T_r (10.8 s), after exposure at temperature T_e for time t_e . B, the signal obtained when the probe was injected directly at T_r (10.8 s) without ever being injected at T_e .

The results of the exposure time experiments are shown in Figures 62 and 63 as plots of $-\ln \left[[MX_{(c)}]_t / [MX_{(c)}]_0 \right]$ vs time for selenium and arsenic, respectively. If the vaporization of the molecular species, MX (where M = selenium or arsenic and X = oxygen or another electronegative element), is a first-order process then according to equation 20 the rate constant is equal to the slope of the appropriate line in Figures 62 or 63. According to equation 21, a plot of $\ln(k)$ vs $1/T$ will give a straight line with slope equal to the activation energy for the vaporization process. Figure 64 shows Arrhenius plots for the vaporization of selenium and arsenic molecular species from the probe during the exposure-time experiments. Table 12 shows the experimentally-determined activation energies for vaporization of selenium and arsenic species obtained from figure 64 along with the thermochemical properties for the relevant chemical processes involving the selenium and arsenic species. Comparison of the values in Table 12 with the activation energy obtained for selenium shows that the latter is not indicative of any bulk property of selenium species, and probably represents the energy of desorption of the selenium molecules from the surface of the graphite probe.

The vaporization of arsenic in the graphite probe furnace has a low activation energy. Akman et al.³³ have proposed that AsO vaporizes from the graphite tube wall and that the gas-phase dissociation of AsO is the predominant process for arsenic atom formation in the graphite tube furnace. Akman et al.³³ also have stated that carbon reduction of the condensed-phase As_2O_3 provides an alternative mechanism for atom formation; this mechanism, deemed to be too slow by Akman et al.³³, may occur for arsenic atomization in the graphite probe furnace. Using thermodynamic equilibrium calculations Frech et al.²⁷ have concluded that the condensed-phase As_2O_3 is the precursor to the vapour-phase arsenic dimer. Since arsenic is vaporized as a molecular species (ie there is no atomic absorption signal) it is reasonable to conclude that

Figure 62. The results of the exposure time experiment results for selenium.

Figure 63. The results of the exposure time experiment results for arsenic.

Figure 64. Arrhenius plots for the desorption of selenium and arsenic species from the graphite probe.

Table 12. Thermochemical data for selenium and arsenic.

Reaction	Standard Enthalpy, kJ mol^{-1}	Temperature, K	Ref.
$\text{Se}_{(l)} \rightarrow \text{Se}_{(g)}$	230	900	51,52
$2\text{Se}_{(l)} \rightarrow \text{Se}_{2(g)}$	900	900	51,52
$2\text{As}_{(s)} \rightarrow \text{As}_{2(g)}$	14	886	39
$\text{SeO}_{(l)} \rightarrow \text{SeO}_{(g)}$	188	2075	39
$\text{SeO}_{2(l)} \rightarrow \text{SeO}_{2(g)}$	103	603	39
$\text{As}_2\text{O}_{3(l)} \rightarrow \text{As}_2\text{O}_{3(g)}$	30	738	39
Desorption of Se species	30 ± 3		This work
Desorption of As species	50 ± 10		This work

condensed-phase As_2O_3 is reduced by carbon or thermally decomposed to yield gas phase As_2 molecules.

Figure 65 shows the atomic absorption pulses for selenium when the probe was inserted at $T_w = 1620$ K, for ten seconds, after which the furnace was cooled and the probe was removed (pulse A). The furnace was then reheated to a higher temperature, $T_w = 2350$ K, which caused a pulse with two peaks (pulse B). Figure 65 can be explained as follows. When the probe was inserted at $T_w = 1620$ K, complete vaporization of the selenium from the probe occurred. Re-heating the furnace to the atomization temperature 2350 K caused the vaporization and atomization of the selenium species that have condensed on the graphite tube wall during the $T_w = 1620$ K exposure step. Re-inserting the graphite probe at $T_w = 2350$ K caused vaporization and atomization of the selenium species that had been adsorbed onto the probe at the end of the $T_w = 1620$ K exposure step. It is unlikely that the observed second atomic absorption pulse is due to selenium species that remain on the probe in the condensed-phase during the initial exposure at 1620 K. Using the experimentally-measured rate constant for the vaporization of selenium species at $T_w = 1085$ K and the experimentally-measured activation energy, the calculated rate constant for the vaporization of selenium at $T_w = 1620$ K is 0.57 s^{-1} . The half-life for selenium species on the graphite surface is 1.2 s at $T_w = 1620$ K thus an exposure of ten seconds is sufficient to vaporize more than 99.6 % of the sample. There is no known selenium species that can remain in the condensed-phase when heated to 1620 K. Further increase in exposure time, beyond ten seconds, did not diminish the second absorption peak, as expected for desorption process.

The experiment in Figure 66 was designed for further study of the short-range vaporization — adsorption of selenium species that occurs in GFAAS. First, the

Figure 65. Atomic absorbance pulses for selenium when: A – the probe was inserted at 10.8 seconds at tube wall temperature 1620 K for 10 seconds and B – reinserted at 10.8 seconds at 2350 K.

Figure 66 Transfer of selenium from the graphite tube wall to the graphite probe: zero absorbance – when selenium was deposited on the tube wall and the furnace heated to 1440 K with the probe inserted; left-hand-side peak – reheating the furnace to 2350 K before the probe is reinserted; right-hand-side peak – re-insertion of the probe (without any sample) at 10.8 seconds at tube wall temperature 2350 K.

selenium test solution was deposited on the graphite tube wall then dried. The furnace was then raised to 1440 K with the graphite probe in place (without any sample) – no atomic absorption pulse was seen during this step. At the end of this heating cycle the furnace was cooled and the probe was withdrawn. The furnace was then re-heated to 2350 K and yielded the left-hand-side peak before it reached the preset $T_w = 2350$ K. After the furnace reached $T_w = 2350$ K, the probe from the previous step was re-inserted into the furnace, which yielded the right-hand-side peak of the curve. Figure 66 can be explained as follows. Selenium species vaporize from the graphite wall but are not atomized at $T_w = 1440$ K. However, short-range vaporization from the furnace wall and adsorption onto the probe must occur in this first step, resulting in the right-hand-side peak of selenium at higher T_w (2350 K) due to the atomization of the condensed-phase selenium species from the probe at the higher $T_w = 2350$ K. Such short-range vaporization – adsorption is a characteristic feature of selenium vaporization in GFAAS.

Figures 67–72 are for atomization of selenium by insertion of the graphite probe at the indicated T_w without an initial insertion at T_e . Figure 67 shows the effect of T_w on the selenium signal for T_w equal to 1440 K, 1620 K and 1800 K. At T_w equal to or greater than 1800 K no sticking on the tube wall was observed when an atomization time of ten seconds is used. The peak height and peak area increase with increasing temperature because the degree of dissociation of the molecular species increases with increasing temperature. The appearance time lags behind the time of insertion of the probe by 600 ms and decreases slightly with increasing temperature. Also, the atomization time does not decrease with increasing temperature. The short appearance time indicates that selenium molecules are vaporized rapidly and that the rate of vaporization is only weakly influenced by temperature. Lack of a detectable decrease in the atomization time shows that the rate of vaporization is only weakly dependent on

temperature. This lack of temperature — dependence of the rate of vaporization, and hence the rate constant, is indicative of a vaporization process having a low activation energy. These results agree with the low activation energy for vaporization of selenium species determined by the exposure time experiments.

Figure 68 shows calculated profiles of the selenium species for two different temperatures, assuming that selenium is vaporized as SeO_2 , and exists in the gas phase in thermodynamic equilibrium with the gas phase. Experimentally — determined rate constants and activation energies were used to model the supply of SeO_2 ; diffusion coefficients given by L'vov et al.⁵⁰ were used to model the removal of molecules and atoms from the furnace. The gas—phase species considered for the thermodynamic equilibrium calculations were: H_2 , H_2O , CH_4 , C , C_2 , CO , CO_2 , O_2 , Se , Se_2 , SeO , SeO_2 , SeH and SeH_2 . The P_{O_2} scale mentioned earlier and the free energy minimization routine of Frech et al.²⁷ along with published thermodynamic data^{51,52} were used for equilibrium calculations. Comparison of Figure 67 with Figure 68 shows that the experimental results are consistent with the postulate that the species that vaporizes from the probe is SeO_2 , which exists in the gas phase in thermodynamic equilibrium with the gas phase.

Figures 69 and 70 show the change in peak area and peak height, respectively for the selenium atomic absorption pulse when the probe is inserted at different T_w . The atomization time was ten seconds, sufficient to allow complete vaporization of the analyte from the probe for the temperatures used. The decrease in both peak height and peak area at the high end of the temperature scale is probably due to the formation of selenium carbide either through linked thermodynamic equilibrium with gas—phase species or by heterogeneous reaction between gas—phase selenium atoms and condensed—phase carbon. Experiment showed that substituting H_2/Ar purge gas for Ar

Figure 67. Atomic absorbance pulses for selenium when the probe was inserted at tube wall temperatures: 1440 K; 1620 K; 1800 K. For these experiments no initial insertion lower temperature was done and the atomization time was ten seconds.

Figure 68. Calculated temporal distribution of molecular and atomic selenium species for tube wall temperatures 1440 K and 1800 K. Σ Se denotes all molecular forms of selenium these are predominantly: SeO_2 , SeO and Se_2 at 1440 K.

purge gas did not affect the peak area or peak height of the selenium atomic absorption signal. In the temperature range 1000 K to 1600 K thermodynamic equilibrium predicts that the selenium oxides (SeO and SeO_2) are the predominant forms of gas-phase selenium. The H_2/Ar purge gas probably caused the formation of selenium hydride and negates any beneficial effect that hydrogen may have by lowering the P_{O_2} . At temperatures above 1600 K thermodynamic equilibrium predicts that Se_2 becomes the predominant form of gas-phase selenium thus hydrogen will not affect the dissociation of the dimer through linked equilibrium. Figures 71 and 72 show similar experiments for arsenic. H_2/Ar purge gas causes a marginal increase in the peak area and the peak height of the arsenic atomic absorption pulses when $T_w < 2350$ K. Thermodynamic equilibrium calculations²⁷ and experimental evidence presented in Chapter One of this text suggests that arsenic is atomized by the decomposition of condensed phase As_2O_3 to yield $\text{As}_{2(g)}$. Thus hydrogen should not affect the dissociation of the arsenic dimer but it may affect the decomposition of the condensed phase arsenic oxide and cause less analyte to be lost before atomization. At high temperatures, lowered oxygen levels and increased equilibrium constant cause a greater degree of dissociation for selenium. The dissociation of arsenic species, which are initially dimers in the gas phase, will not be affected by lower oxygen levels but will be affected by increasing temperature, which will favour greater dissociation of the dimers.

Figure 69. Peak-area absorbance atomization curves for selenium when the probe technique was used.

Figure 70. Peak-height absorbance atomization curves for selenium when the probe technique was used.

Figure 71. Peak-area absorbance atomization curves for arsenic when the probe technique was used. Ar and H₂/Ar denote the signals obtained for Ar and H₂/Ar purge gas, respectively.

Figure 72. Peak-height absorbance atomization curves for arsenic when the probe technique was used. Ar and H₂/Ar denote the signals obtained for Ar and H₂/Ar purge gas, respectively.

Experimental evidence is consistent with the following mechanisms for vaporization and atomization of selenium and arsenic:

or

where there exists gas-phase thermodynamic equilibrium.

The activation energies obtained in this work for the vaporization of PbO , SnO , SeO_2 and As_2O_3 do not agree with the activation energies reported by other workers, using the kinetic approach⁴¹⁻⁴⁴, for the atomization of these elements. This is not surprising because vaporization of the condensed-phase oxide is not necessarily the rate limiting step in atomization of lead, tin, selenium and arsenic. Furthermore, other workers who used the kinetic approach often measured the atomization process indirectly from the shape of the atomic absorbance pulse. For an element that vaporizes as an oxide and then dissociates in the gas phase use of the atomic absorbance pulse for the kinetic approach will give results that are not related to the activation energy of the atomization process. Smets' method⁴⁴ uses the shape of the

atomic absorbance pulse to determine activation energy for the atomization of elements. A condition of Smets' method is that analyte atomization is a first order process, which is probably not the case for lead, tin, selenium and arsenic. Incorrect use of Smets' method to yield an activation energy can be seen by using Smets' method to determine the activation energy for the atomization of lead (equation 16). Smets' method (using the correct form of the equation) gives the rate constant for the vaporization of lead:

$$k = \frac{\beta A}{\int_t^{\infty} A dt} \quad 33$$

where β is atomization efficiency and A is absorbance. Applying the Arrhenius equation and plotting the natural log of the right hand side of equation 33 against the reciprocal of temperature, one would get a straight line, but the measured energy would not be the activation energy of the vaporization process, as shown below. The equilibrium constant K for reaction 16 is :

$$K = \frac{P_M P_X}{P_{MX}} \quad 34$$

where the subscripts for P indicate the partial pressure of the subscripted species and M , X , and MX are in the gas phase. The equilibrium constant may also be written as :

$$K = \exp(-\Delta G_T^0 / RT) \quad 35$$

where ΔG_T^0 is the standard Gibbs free energy change for reaction 16 at temperature T . Combining equations 34 and 35 one may rearrange terms to obtain an expression for

the partial pressure of the metal atoms. Assuming that absorbance is directly proportional to the partial pressure of the analyte atoms one gets:

$$A = \frac{\exp(-\Delta G_T^0 / RT) P_{MX} \alpha}{P_X} \quad 36$$

where α is the proportionality constant that links absorbance to the partial pressure of M i.e. $A = \alpha P_M$. Substituting equation 36 into equation 33 and equation 33 into equation 21 one can see that Smets' method, when applied to an analyte that exists in the furnace in thermodynamic equilibrium with one or more gas-phase species, will give a line corresponding to:

$$\frac{-\Delta G_T^0}{RT} - \ln(P_X) - \ln\left(\int_1^\infty A dt\right) + \ln(P_{MX}) + \ln(\alpha) \text{ vs } \frac{1}{T} \quad 37$$

When lead vaporizes as PbO and then dissociates in the gas phase ($X = \frac{1}{2} O_2$), the first and second terms of equation 37 are strongly dependent on temperature, whereas the third and the fourth terms have a smaller temperature dependence. Using thermodynamic data^{51,52}, atomic absorption pulses, experimental measurements of P_{PbO} made by Byrne et al.²⁰, and two different values for P_{O_2} ^{27,53}, equation 37 was plotted. Figure 73 shows that if indeed PbO vaporizes and then dissociates according to equation 16 then Smets' method would give an activation energy between 200 kJ mol⁻¹ and 270 kJ mol⁻¹ – values that are close to those reported in the literature by workers using the kinetic approach, but which are not indicative of the activation energy for the atomization of lead.

Figure 73. Calculated apparent Arrhenius plot for lead using Smets⁴⁴ method. The upper curve is that obtained when the oxygen partial pressures proposed by Frech et al.²⁷ are used and the lower curve is that obtained when the oxygen scale proposed by L'vov⁵² is used.

Figure 81. The results from the exposure-time experiments for copper.

Figure 74. The atomic absorption pulses for silver with tube-wall temperatures 1710 K and 2170 K.

Figure 75. Thermal stability curves for silver. The charring curve shows the peak-area absorbance as a function of charring temperature (40 s char time) when an atomization temperature of 2200 K is used. The atomization curve shows the peak-area absorbance as a function of temperature when a charring temperature of 800 K is used. Tube wall atomization was used only in Figures 75–79 all other work on silver, copper, manganese and gold reported in this chapter was done using the graphite probe furnace.

Figure 76. Thermal stability curves for copper. The charring curve shows the peak-area absorbance as a function of charring temperature (40 s char time) when an atomization temperature of 2500 K is used. The atomization curve shows the peak-area absorbance as a function of temperature when a charring temperature of 1100 K is used. Tube wall atomization was used only in Figures 75–79 all other work on silver, copper, manganese and gold reported in this chapter was done using the graphite probe furnace.

Figure 77. Thermal stability curves for manganese. The charring curve shows the peak-area absorbance as a function of charring temperature (40 s char time) when an atomization temperature of 2200 K is used. The atomization curve shows the peak-area absorbance as a function of temperature when a charring temperature of 1100 K is used. Tube wall atomization was used only in Figures 75–79 all other work on silver, copper, manganese and gold reported in this chapter was done using the graphite probe furnace.

Figure 78. Thermal stability curves for gold. The charring curve shows the peak-area absorbance as a function of charring temperature (40 s char time) when an atomization temperature of 2200 K is used. The atomization curve shows the peak-area absorbance as a function of temperature when a charring temperature of 1200 K is used. Tube wall atomization was used only in Figures 75–79 all other work on silver, copper, manganese and gold reported in this chapter was done using the graphite probe furnace.

Figure 79. Thermal stability curves for manganese. The charring curve shows the peak-height absorbance as a function of charring temperature (40 s char time) when an atomization temperature of 2700 K is used. The atomization curve shows the peak-height absorbance as a function of temperature when a charring temperature of 1100 K is used. Tube wall atomization was used only in Figures 75-79 all other work on silver, copper, manganese and gold reported in this chapter was done using the graphite probe furnace.

to the corresponding peak-area absorbance curves (Figures 75, 76 and 78), that is the atomization curve starts to rise at the same temperature that the charring curve starts to fall. However, for manganese the peak-height absorbance curve (Figure 79) is different from the peak-area absorbance curve (Figure 77) in that in Figure 79 the charring curve starts to fall off at a temperature lower than the temperature at which the atomization curve starts to rise. The difference in these two figures indicates that manganese is atomized by a mechanism which is different than that of silver, copper and gold.

Figures 80 and 81 show results of the exposure-time experiments for silver and copper, respectively. Note that for silver when the tube wall temperature is 1440 K the data points do not lie in a straight line, indicating that vaporization does not occur by a first-order process. Rayson and Holcombe⁵⁴ have suggested that silver forms islands or microdroplets prior to being atomized from the tube wall and thus has an order of release less than one. Formation of microdroplets may occur on the probe and persist after the insertion of the probe into the heated graphite furnace – with tube-wall temperatures up to 1440 K, but at higher temperatures it appears that silver atoms have rearranged on the probe surface to a monolayer or submonolayer distribution and follow first-order release. Figure 82 shows the activation energy plots for silver and copper. Note that the silver data point for 1440 K (the lowest data point) does not fall in line with the remaining data points. Activation energies for silver and copper were calculated to be $(126 \pm 12) \text{ kJ mol}^{-1}$ and $(131 \pm 6) \text{ kJ mol}^{-1}$, respectively, using the exposure-time technique.

If atomization of silver and copper is by vaporization of atoms direct from the graphite surface then the atomic absorption pulse may be used to study the vaporization process. For a first-order desorption process the surface coverage at time, t_1 , is

Figure 80. The results from the exposure-time experiments for silver.

Figure 81. The results from the exposure-time experiments for copper.

Figure 82. The activation energy plot for silver and copper using the exposure time experiments.

proportional to the number of atoms present on the graphite surface, which may be calculated by subtracting the number of atoms that have desorbed at t_1 from the number of atoms initially present on the probe surface. If the peak area is directly proportional to the number of atoms that have entered the gas phase and the number of atoms remaining on the probe surface is directly proportional to the surface coverage, then the number of atoms present on the probe surface at time, t_1 , is proportional to the difference of the total peak area and the peak area between time zero and time t_1 :

$$[M_{(c)}]_{t_1} \propto \int_{t=0}^{t=\infty} [M_{(g)}] dt - \int_{t=0}^{t=t_1} [M_{(g)}] dt \quad 38$$

where notations of the species are the same as those used previously and the first and second terms on the right hand side are the integrated gas-phase population between $t=0$ and $t=\infty$, and between $t=0$ and $t=t_1$, respectively. Unlike atomization from the tube wall, atomization from the probe is an isothermal process, so the rate constant for vaporization does not change during the atomization step. If the vaporization of $M_{(c)}$ in equation 38 is a first order process then the rate constant may be determined by plotting the right – hand side of equation 38 vs time and taking the slope of the line. Plotting the natural logarithm of the rate constant vs the reciprocal of temperature gives the activation energy for vaporization (equation 7). This method, henceforth to be called the "area technique", gives activation energies of $(118 \pm 5) \text{ kJ mol}^{-1}$ and $(123 \pm 6) \text{ kJ mol}^{-1}$ for silver and copper, respectively. The temperature ranges used for determination of the above activation energies were: 1800 K to 2170 K for silver and 2250 K to 2690 K for copper.

The activation energies obtained by the "area technique" agree with those obtained by the exposure–time experiments. This agreement re–inforces the

conclusion that silver and copper atoms are formed by vaporization direct from the graphite probe surface; hence, vaporization and atomization are the same process. Using thermodynamic calculations Frech et al.²⁷ have concluded that the condensed-phase metals are the precursors the gas-phase atoms of silver and copper. Smets⁴⁴ has reported that silver atoms are vaporized direct from the surface of a graphite strip atomizer and has correlated the experimentally-determined activation energy of $(276 \pm 12) \text{ kJ mol}^{-1}$ with the enthalpy of vaporization of silver metal. Rayson and Holcombe⁵⁴ have reported that silver may form islands or droplets in addition to a submonolayer distribution on the tube-wall surface of a graphite furnace. Rayson and Holcombe⁵⁴ have concluded that vaporization of silver atoms from the islands or droplets has an activation energy corresponding to the enthalpy of vaporization of silver metal, but the vaporization process has a kinetic order of less than one. Rayson and Holcombe⁵⁴ have also reported that the activation energy for the vaporization of silver from submonolayer coverage on the surface of the graphite tube wall is $(125 \pm 9) \text{ kJ mol}^{-1}$. The experimentally determined activation energy, for atomization from the graphite probe agrees with that reported by Rayson and Holcombe⁵⁴ for silver having submonolayer distribution on the surface of the graphite tube wall. Holcombe and co-workers^{55,56} have also reported that copper atoms have a submonolayer distribution on the surface of the graphite tube prior to atomization and that gas-phase copper atoms may be back-scattered and the atoms stick to the surface. The experimentally-determined activation energy for the vaporization and atomization of copper of this work agrees with that reported by Holcombe and co-workers⁵⁶ ($131 \pm 4 \text{ kJ mol}^{-1}$). If copper atoms have elastic collisions with the graphite surface and the desorption - adsorption process is in a state of pseudo-equilibrium⁵⁷⁻⁵⁹ (with reaction enthalpy of 121 kJ mol^{-1}):

then from the Clausius–Clapeyron equation⁶⁰ one may write the temperature dependence of P_{Cu} in equation 39 as follows:

$$\frac{\partial(\ln(P))}{\partial T} = \frac{\Delta H_{\text{vap}}}{RT^2} \quad 40$$

where H_{vap} is the molar enthalpy of vaporization. Assuming that ΔH_{vap} is independent of temperature over the limited range of temperature involved, equation 40 can be integrated to yield:

$$\ln(P) = \text{constant} - \frac{\Delta H_{\text{vap}}}{RT} \quad 41$$

From equation 41 it can be seen that the ratio of $\text{Cu}_{(\text{g})}/\text{Cu}_{(\text{ads})}$ will increase exponentially with temperature. Prior to atomization the oxides of silver and copper are probably thermally decomposed or reduced by carbon to silver and copper metal, respectively:

or:

Silver atoms then vaporize direct from the graphite surface and do not become adsorbed on the graphite surface:

where $M_{(out)}$ represents analyte atoms lost from the analysis volume. Copper atoms become re-adsorbed when they collide with the graphite surface:

Figures 83 and 84 show the change in the atomic absorption pulses for silver and copper, respectively, at various tube wall temperatures. For silver, in accordance with the proposed model, the peak height increases, whereas the peak area decreases with increasing temperature. Atomization time also decreases with increasing temperature. For copper, both the peak height and the peak area increase as the temperature is increased. At low temperatures, copper atoms may migrate along the tube wall and leave the graphite tube without giving any atomic absorption signal. Only at high temperatures ($T > 2600$ K), where the ratio $Cu_{(g)}/Cu_{(ads)}$ is much greater than one, does the peak area stop increasing with increasing temperature. The change in peak height and atomization time with temperature follows the expected trend. Figure 85 is the modelled silver atomic absorption pulse based on first-order vaporization of atoms from the probe surface and loss of atoms from the gas phase by diffusion out of the graphite tube ends. In modelling the atomic absorption pulses in Figure 85, and later in Figures 94 and 101, experimentally-determined rate constants and activation energies were used for the supply of analyte atoms, the diffusion coefficients were taken from L'vov et al.⁵⁰. The model for silver (Figure 85) gives results in quantitative agreement with the experimentally-measured atomization times and the change in peak height and peak area with changing temperature. Assuming that all of the copper atoms are desorbed for $T_w \geq 2600$ K one may calculate the fraction of copper desorbed from the graphite surface at lower temperatures. Figure 86 shows the fraction of copper desorbed vs T_w , note the similarity between the curve in Figure 86 and the copper

Figure 83. The atomic absorption pulses for silver with the probe inserted at tube-wall temperatures: 2000 K; 2090 K; 2170 K.

Figure 84. The atomic absorption pulses for copper with the probe inserted at tube-wall temperatures: 2350 K; 2520 K; 2690 K.

Figure 85. The modelled atomic absorption pulses for silver with the probe inserted at tube-wall temperatures. 2000 K, 2090 K; 2170 K.

Figure 86. The fraction of copper as a function of temperature modelled using the Clausius Claperon equation.

atomization curves (Figures 88 and 89) which are explained later.

Experimentally, addition of hydrogen to the argon purge gas had no effect on the atomic absorption signals of silver and copper. Addition of oxygen had no effect on the copper atomic absorption signal, but did cause a suppression of the silver signal when the oxygen was added to the graphite surface prior to the deposition of silver test solutions on the probe, resulting in oxygen being chemisorbed on the probe surface. A "first shot back" experiment, for silver test solutions, was conducted as follows: Atomization was done using argon purge gas, then the probe was allowed to cool in argon and removed from the furnace. The purge gas was then switched to O_2/Ar gas; the above probe was then reinserted into the heated graphite furnace. This reinsertion of the probe into this oxygen-containing atmosphere did not cause any change in the silver atomic absorption pulse. Oxygen was then chemisorbed to the probe by allowing it to cool down in the O_2/Ar mixture. Atomization of silver from the oxygenated probe in the O_2/Ar purge gas produced a suppressed signal, as shown in Figure 87. Using an oxygenated probe but switching back to an argon purge gas the same suppressed signal as for the oxygenated probe and O_2/Ar purge gas was observed. Hence, the suppression of the silver signal by oxygen was not due to the oxygen in the gas phase but to the oxygen chemisorbed on the probe surface. Silver is vaporized and lost from the furnace in the form of Ag_2O at a low temperature. Silver oxide can form and be lost in this manner only when the probe has oxygen chemisorbed on it. Loss of Ag_2O must occur at a temperature below 473 K because silver oxide decomposes to silver and oxygen at a temperature greater than 473 K.

Figures 88, 89 and 90 show the effect of temperature on the peak area, peak height and atomization time, respectively, for silver and copper. Peak area signals for both silver and copper reach a maximum, then fall off because of higher rates of

Figure 87. The effect of oxygen on the silver atomic absorbance pulse when the probe is inserted at 2000 K: A, silver atomized with Ar purge gas; B, silver atomized with an untreated probe but with O_2 /Ar purge gas; C, silver atomized with an oxygenated probe and O_2 /Ar purge gas; D, silver atomized with an oxygenated probe and Ar purge gas.

Figure 88. Atomization curves for silver and copper in the graphite probe furnace drawn using peak-area absorbance.

Figure 89. Atomization curves for silver and copper in the graphite probe furnace drawn using peak-height absorbance.

Figure 90. Atomization times for silver and copper in the graphite probe furnace as a function of tube-wall temperature.

diffusion of atoms from the furnace at higher temperatures. Peak height signals for silver initially increase, then reach a plateau, whereas peak height signals for copper increase steadily throughout the temperature range examined, indicating an increase in the rate of atomization with increasing temperature. Atomization time becomes shorter with increasing temperature, indicating an increase in the rate of atomization with increasing temperature. Atomization times for copper are always greater than those for silver because copper sticks to the graphite probe surface and to the graphite tube surface whereas silver does not.

Table 13 shows that for a given temperature and exposure time more silver is lost when there is a convective flow of argon in the furnace than when there is no convective flow in the furnace. The amount of copper lost is independent of whether the purge gas flow is on or off. If silver undergoes elastic collisions with the probe then, upon collision with the probe, a silver atom will reside on the graphite surface for only a brief time compared to the time spent by it in the gas phase between collisions with the graphite surface. In this case, a convective flow of gas over the graphite surface should strip atoms away, thereby increasing the loss compared to the loss when no convective flow is present. If copper, under similar circumstances, resides for a longer time on the graphite surface then the presence of a convective flow of gas will not have as great an effect on the amount of copper lost as on the amount of silver lost during the same exposure time. Hence, Table 13 suggests that silver has elastic collisions with the tube wall and the probe, whereas copper has inelastic collisions with the tube wall and the probe, which results in sticking.

Figure 91 shows the results of exposure-time experiments, as plots of $-\ln \left[[M_{(c)}]_t / [M_{(c)}] \right]$ vs time, for manganese for several temperatures. Figure 92 shows the activation energy plots of $\ln(k)$ vs $1/T$, for the exposure-time experiments

Table 13. The flow on/flow off experiment for silver and copper.

Element	Temperatures, K		Flow during initial exposure	Peak—area absorbance	
	Initial	Final		Initial	Final
Ag	1390	2250	On	0.00	0.060±0.005
			Off	0.00	0.085±0.007
Cu	1945	2250	On	0.00	0.042±0.007
			Off	0.00	0.047±0.005

and the area technique described for silver and copper. Activation energies for manganese were calculated to be $(36 \pm 2) \text{ kJ mol}^{-1}$ by the exposure time technique and $(46 \pm 5) \text{ kJ mol}^{-1}$ by the area technique. Sturgeon et al.⁷ and Genc et al.⁴⁶ have reported the activation energy for the atomization of manganese to be $(385 \pm 15) \text{ kJ mol}^{-1}$ and $(390 \pm 6) \text{ kJ mol}^{-1}$, respectively. These authors^{7,46} have correlated their experimentally-measured activation energies with the bond dissociation energy of MnO ³⁹, $(402 \pm 20) \text{ kJ mol}^{-1}$. They have therefore proposed that manganese is atomized in the graphite furnace by vaporization of MnO and its dissociation in the gas phase. Smets⁴⁴ has reported that the activation energy for the atomization of manganese from a graphite strip, $(590 \pm 40) \text{ kJ mol}^{-1}$, agrees with both carbon reduction of the $\text{MnO}_{(s)}$ and thermal dissociation of $\text{MnO}_{(s)}$. Frech et al.²⁷, using thermodynamic equilibrium calculations, have concluded that condensed-phase MnO is the precursor to gas-phase manganese atoms. Manganese oxides have not been observed in the gas phase and no high-temperature thermodynamic data has been found for gaseous oxides of manganese. Hence, manganese atoms are probably formed by thermal decomposition of the condensed-phase oxide or by carbon reduction of the condensed-phase manganese oxide:

or

Comparison of the activation energies obtained in this work with those obtained by other workers^{7,46} suggests that either the atomization mechanism for manganese in the graphite probe furnace is different from that for manganese in the graphite tube furnace, or that the atomization mechanisms are the same but the activation energy

Figure 91. The results of the exposure-time experiments for manganese.

Figure 92. $\ln(k)$ vs reciprocal temperature for manganese in the graphite probe furnace.

barrier is lower in the graphite probe furnace than it is in the graphite tube furnace. In the graphite tube furnace, the temperature of the gas phase is lower than the temperature of the graphite tube wall⁴⁷, whereas in the graphite probe furnace the temperature of the gas phase is greater than or equal to the temperature of the graphite probe. If manganese is atomized by thermal decomposition of $\text{MnO}_{(c)}$, then the temperature of the gas phase probably affects the activation energy barrier; hence, the graphite probe furnace may have a lower activation energy barrier to overcome for atomization.

Figure 93 shows that for the atomic absorbance pulses of manganese peak height increases with increasing temperature whereas peak area decreases. Atomization time decrease with increasing temperature. The decrease in peak area with increasing temperature is due to the increase in the diffusion coefficient with increasing temperature. The increase in peak height and the decrease in atomization time with increasing temperature are due to the increase in the rate of atomization with increasing temperature. Comparison of the results for manganese with those for silver and copper shows that for manganese changes in peak height and atomization time with increasing temperature are less than those for silver and copper. These results agree with the low activation energy for the vaporization and atomization of manganese compared to that of silver and copper reported earlier. Figure 94 shows the calculated atomic absorption pulses for 2180 K, 2250 K and 2460 K modelled in a manner similar to that used for the silver and copper atomic absorbance pulses. The rising portions and the peak heights of the modeled pulses are quite different from those of the experimental pulses. This discrepancy indicates that, initially, manganese atomization is not by a simple first-order mechanism, but later in the pulse first-order kinetics may apply. Figures 95–97 show the experimentally measured values of peak height, peak area and atomization time at various temperatures. Peak height increases with increasing

Figure 93. The manganese atomic absorbance pulses with the probe inserted at tube wall temperatures: 2180 K; 2250 K; 2460 K.

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Figure 94. The modelled manganese atomic absorbance pulses with the probe inserted at tube wall temperatures: 2180 K; 2250 K; 2460 K.

Figure 95. Atomization curves for manganese in the graphite probe furnace drawn using peak-area absorbance.

Figure 96. Atomization curves for manganese in the graphite probe furnace drawn using peak-height absorbance.

Figure 97. Atomization time of manganese in the graphite probe furnace as a function of tube-wall temperature.

temperature because of increase in the rate of vaporization with increasing temperature. Peak area initially increases, then decreases with increasing temperature because of increasing diffusion coefficient with increasing temperature. Atomization time decreases with increasing temperature because of the increasing rate of vaporization with increasing temperature.

Experimentally, addition of hydrogen to the argon purge gas causes an enhancement in the manganese atomic absorbance signal, whereas addition of oxygen to the argon purge gas causes a suppression of the manganese atomic absorption signal. The enhancement and suppression were only observed when hydrogen or oxygen were chemisorbed on the graphite probe surface prior to the deposition of the manganese test solutions on the graphite probe. A "first shot back" experiment for the manganese test solutions was conducted as follows: Atomization was done using argon purge gas, then the probe was allowed to cool in argon and removed from the furnace. The purge gas was then switched to O_2/Ar purge gas; the probe was then reinserted into the heated graphite furnace; this reinsertion of the probe into this oxygen-containing atmosphere did not cause any change in the manganese atomic absorption pulse. Oxygen was then chemisorbed on the probe by allowing it to cool down in the O_2/Ar mixture. Atomization of manganese from the oxygenated probe in the O_2/Ar purge gas produced a suppressed signal, as shown in Figure 98. Using an oxygenated probe but switching back to argon purge gas the same suppressed signal as for the oxygenated probe and the O_2/Ar purge gas was observed. Therefore, the suppression of the manganese signal by oxygen is not due to oxygen in the gas phase but to oxygen chemisorbed on the surface of the probe. The manganese atomic absorption pulse produced from the oxygenated probe has a lower peak height, longer atomization time and smaller peak area than that produced from the normal graphite probe. These changes are indicative of a lower rate of atomization. Probably, the presence of chemisorbed oxygen may suppress the rate

Figure 98. The manganese atomic absorbance profiles with the probe inserted at tube-wall temperature 2620 K with: H_2/Ar purge gas, Ar purge gas and O_2/Ar purge gas.

of thermal decomposition of condensed-phase MnO. Alternatively, when chemisorbed oxygen is present on the graphite probe, manganese may be vaporized and lost from the furnace in the form of MnO at a low temperature. Manganese oxide may be formed and lost in this manner only when the probe has oxygen chemisorbed on it. Loss of MnO must then occur at a low temperature because MnO cannot exist in the gas phase at its appearance temperature.

Similar experiments were done using H₂/Ar in place of O₂/Ar as an alternative purge gas. When hydrogen is chemisorbed on the graphite probe, the manganese atomic absorbance signal has a greater peak height and shorter atomization time than that produced in the absence of chemisorbed hydrogen. These changes are indicative of a higher rate of atomization. Hence, the presence of chemisorbed hydrogen may enhance thermal decomposition of the condensed-phase MnO.

Exposure-time experiments done with test solutions of gold produced highly uncertain results and none of the characteristics: rate constant, activation energy, reaction order could be determined by exposure-time experiments. It was found, however that for exposure temperatures of 1440 K and 1620 K and exposure time under ten seconds gold may be lost in molecular form, presumably as AuCl₃ or Au₂Cl₆³⁹. Using the area technique described earlier it was found that the atomic absorbance pulses of gold fit an atomization process having a kinetic order of negative one. For atomization of gold with kinetic order of negative one the rate of atomization may be written as:

$$-\frac{d[\text{Au}_{(c)}]}{dt} = k [\text{Au}_{(c)}]^{-1} \quad 48$$

Rearranging and integrating equation 48 gives:

$$\frac{1}{2}([Au_{(c)}]_0^2 - [Au_{(c)}]_t^2) = k t \quad 49$$

A plot of $\frac{1}{2}([Au_{(c)}]_0^2 - [Au_{(c)}]_t^2)$ vs time will give the rate constant for atomization (Figure 99). Smets⁴⁴ has reported that gold metal is atomized by a first-order process and that the activation energy for atomization of gold is $(326 \pm 14) \text{ kJ mol}^{-1}$, and has correlated the experimentally-measured activation energy with the enthalpy of sublimation of metallic gold. Sturgeon and Arlow⁶¹ agree with the mechanism proposed by Smets⁴⁴ for gold atomization and have obtained an activation energy of $(322 \pm 17) \text{ kJ mol}^{-1}$. Frech et al.²⁷, using thermodynamic calculations, have concluded that the condensed-phase gold is the precursor to gas-phase gold atoms. Comparison of the results obtained for gold with the graphite probe technique with those of Smets⁴⁴ and Frech²⁷ suggests that the mechanism of atomization in these two cases is different.

For gold the area technique was used without the supporting evidence of the results from the exposure time technique. Data were collected from the gold atomic absorption pulse and the vaporization of gold was not directly measured. By trial-and-error it was found that gold was not atomized by a first order process and that a kinetic order of negative one best fits the experimental data. Elementary reactions cannot have negative kinetic orders but several elementary reactions may occur simultaneously to yield an overall reaction order of negative one. Negative kinetic order means that initially, when the concentration of reactants is highest ($[M_{(c)}]_t \equiv [M_{(c)}]_0$), the rate of reaction will be slow whereas later, when the concentration of reactants has decreased, the rate of reaction will be faster. For gold one possible explanation is that atomization is inhibited by a condensed-phase gold species. This phenomenon warrants further investigation.

Since the atomization of gold in the graphite probe furnace is probably not an elementary reaction, calculating the activation energy in the manner used for the other elements studied would not be correct. Figure 99 shows that the rate of atomization of gold has a weak dependence on temperature.

Figure 100 shows the atomic absorbance pulses for gold for tube wall temperatures of 2350 K, 2520 K and 2690 K. The peak height, peak area and atomization time decrease with increasing temperature. Figure 101 shows the modelled pulses for the atomization of gold for a process where the rate constant for atomization is independent of temperature. Figures 102 – 104 show the change in peak area, peak height and atomization time for the atomic absorbance pulses of gold as a function of the tube wall temperature. The peak area and peak height of the gold atomic absorption pulse reach maximums, then fall off because of the increasing diffusion coefficient with increasing temperature.

Given the present results for gold atomization in the graphite probe furnace a mechanism for gold atomization cannot be proposed.

Figure 99. The vaporization of gold for insertion of the probe at tube wall temperatures: 2250 K; 2460 K; 2620 K; 2790 K.

Figure 100. The gold atomic absorbance pulses for insertion of the probe at tube wall temperatures: 2350 K; 2520 K; 2690 K.

Figure 101. The modelled gold atomic absorbance pulses for insertion of the probe at tube wall temperatures: 2350 K and 2690 K.

Figure 102. Atomization curves for gold in the graphite probe furnace drawn using peak-area absorbance.

Figure 103. Atomization curves for gold in the graphite probe furnace drawn using peak-height absorbance.

Figure 104. The atomization time for gold in the graphite probe furnace as functions of tube-wall temperature.

CONCLUSIONS

Lead, tin, selenium and arsenic are vaporized as molecular species, most likely as the monoxides for lead and tin, the dioxide for selenium, and the dimer for arsenic. These molecules exist in the gas phase in thermodynamic equilibrium with the gas phase. SnO is more stable in the gas phase than PbO presumably because of its greater bond strength, $(548 \pm 21) \text{ kJ mol}^{-1}$ for SnO compared with $(378 \pm 4) \text{ kJ mol}^{-1}$ for PbO. Selenium and arsenic species tenaciously stick to the tube wall and high-temperature atomization is required for quantitative recovery.

Silver and copper are atomized by vaporization of the metal atoms direct from the graphite probe surface. Manganese is atomized by thermal decomposition of condensed-phase MnO and vaporization of manganese atoms. Chemisorbed oxygen and hydrogen show opposite effect on the rate of thermal decomposition of condensed-phase MnO – the former suppresses whereas the latter enhances the rate. The atomization mechanism for gold in a graphite probe furnace probably differs from that in a graphite tube furnace. In the graphite probe furnace the atomization of gold has a kinetic order of negative one.

FUTURE WORK

In this thesis two new techniques have been introduced: 1) time resolved analysis of the gas phase using gas chromatography and 2) study of the kinetics of the vaporization of molecules using the exposure time experiments. Both these techniques should continued to be used to gain insight into the chemical and physical processes that operate in the graphite furnace during analysis.

The gas phase analysis should be applied to new systems including those with matrix interferences and chemical modifiers. This technique should be used in conjunction with mass spectrometry so that analyte molecular species may be detected along with the gases mentioned here.

The exposure time technique should be applied to new systems including those with matrix interferences and chemical modifiers. The effect of the type of graphite on the kinetics of vaporization and atomization should also be studied. This technique should be used in conjunction with surface analytical techniques and mass spectrometry for positive identification of condensed-phase species and gas-phase species.

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