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STUDIES ON ELECTROTHERMAL ATOMIZATION FROM GRAPHITE
AND METAL SURFACES IN ATOMIC ABSORPTION SPECTROMETRY

by

Ana H. Delgado

A thesis submitted to the Faculty of Graduate
Studies and Research in partial fulfilment
of the requirements for the degree of
Master of Science

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I dedicate this thesis to the memory of my parents

ABSTRACT

An experimental study was done on the following instrumental parameters that determine the sensitivity and selectivity of electrothermal atomizers in atomic absorption spectrometry - the effect of heating rates and atomization surfaces on the sensitivity of two pulse-heated atomizers: a tungsten atomizer (WETA-82), and a graphite atomizer (HGA-500). The selectivity was studied in terms of matrix interferences in two pulse-heated atomizers: a laboratory-made, constant-temperature graphite furnace and a tungsten atomizer (WETA-82). In order to gain insight into atomization processes, mechanisms of atomization of cobalt and titanium were studied - the former from a graphite platform in a graphite atomizer, and the latter from graphite and tungsten tube walls of the graphite and the tungsten atomizer, respectively. Mechanisms proposed for the atomization of Co and Ti from all the surfaces studied are reduction of the metal monoxide to the solid metals, followed by their sublimation. The study has given valuable insight into the problem that titanium forms refractory carbides (lamellar compounds) with the graphite atomizer (HGA-500); formation of refractory carbides is avoided when titanium is atomized from the tungsten atomizer (WETA-82).

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STUDIES ON ELECTROTHERMAL ATOMIZATION FROM GRAPHITE AND METAL SURFACES IN ATOMIC ABSORPTION SPECTROMETRY

INTRODUCTION

Electrothermal atomization has been lately used in atomic absorption spectrometry (AAS) because of some limitations of flame atomization. Electrothermal atomization technique possesses many advantages over flame atomization technique, some of which are: higher sensitivity, better detection limits, direct solid-sampling capability, smaller liquid sample volume required, and better control of the chemical and thermal environment of the atomic vapour than that achieved in flames. As a result, most of the significant developments in atomic absorption spectrometry in the last few years were especially centred on the development of electrothermal atomizers complementary to conventional flame atomizers. Electrothermal atomizers of various types as follows have been used: heated graphite tubes [1], carbon rods [2], glassy carbon tubes [3], metallic filaments such as tantalum [4], platinum [5], and tungsten [6], as well as the recently developed tantalum strip and tungsten tube atomizer [7,8]. These devices have made atomic absorption spectrometry with electrothermal atomizers a very popular technique for determination of trace and ultratrace elements.

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atomization will be studied by using the model proposed by Sturgeon et al. [9.27], in which a plot of the logarithm of the absorbance value from the rising part of the transient absorbance signal versus the reciprocal of the absolute temperature yields a straight line with a slope proportional to the sum of the activation energy and the heat of vaporization. Since the heated graphite platform inside the heated graphite tube is not a blackbody, its temperature could not be measured with an optical pyrometer. A computer program for calculating the theoretical temperature of the graphite platform which had been developed in this laboratory by Chakrabarti et al. (32) was therefore used. Such a program allowed predictions of the temperature of the platform as a function of the time of heating of an electrothermal atomizer. The mechanisms for titanium atomization will be studied using the decomposition/atomization curves for titanium as was done by Wahab and Chakrabarti [31] for the mechanisms of yttrium atomization in a graphite tube atomizer.

STUDIES ON ELECTROTHERMAL ATOMIZATION FROM GRAPHITE AND METAL SURFACES IN ATOMIC ABSORPTION SPECTROMETRY

INTRODUCTION

Electrothermal atomization has been lately used in atomic absorption spectrometry (AAS) because of some limitations of flame atomization. Electrothermal atomization technique possesses many advantages over flame atomization technique, some of which are: higher sensitivity, better detection limits, direct solid-sampling capability, smaller liquid sample volume required, and better control of the chemical and thermal environment of the atomic vapour than that achieved in flames. As a result, most of the significant developments in atomic absorption spectrometry in the last few years were especially centred on the development of electrothermal atomizers complementary to conventional flame atomizers. Electrothermal atomizers of various types as follows have been used: heated graphite tubes [1], carbon rods [2], glassy carbon tubes [3], metallic filaments such as tantalum [4], platinum [5], and tungsten [6], as well as the recently developed tantalum strip and tungsten tube atomizer [7,8]. These devices have made atomic absorption spectrometry with electrothermal atomizers a very popular technique for determination of trace and ultratrace elements.

Many authors have contributed to advances in electrothermal atomizers in AAS [9-20]. The most significant of these contributions was made by L'vov [20], who has developed a comprehensive theory of electrothermal atomization in a graphite cuvette. Because of the complexity of the analytical signal and the nature of the analyte atomic species [21] in graphite or metal atomizers, it is essential to have some knowledge of the process of vaporization, atom formation in and dissipation from atomizers in order to achieve improvements, not only in instrumentation but also in analytical applications of these atomizers to atomic absorption spectrometry. For a better understanding of the processes involved in atomization in electrothermal atomizers, many approaches such as thermodynamic, kinetic, combined thermodynamic-kinetic, as well as empirical approaches based on decomposition/atomization curves have been made by various authors [22-31].

This thesis has three objectives: 1) to study the effect of heating rates and atomization surfaces on the sensitivity of two pulse-heated atomizers: a tungsten atomizer (WETA-82), and a graphite atomizer (HGA-500); 2) to study matrix interferences in a pulse-heated and a constant-temperature atomizer; 3) to study mechanisms of atomization of cobalt and titanium - the former from a graphite platform in a graphite atomizer, and the latter from graphite and tungsten tube walls of the graphite and the tungsten atomizer, respectively. The mechanisms for cobalt

atomization will be studied by using the model proposed by Sturgeon et al. [9,27], in which a plot of the logarithm of the absorbance value from the rising part of the transient absorbance signal versus the reciprocal of the absolute temperature yields a straight line with a slope proportional to the sum of the activation energy and the heat of vaporization. Since the heated graphite platform inside the heated graphite tube is not a blackbody, its temperature could not be measured with an optical pyrometer. A computer program for calculating the theoretical temperature of the graphite platform which has been developed in this laboratory by Chakrabarti et al. (32) was therefore used. Such a program allowed predictions of the temperature of the platform as a function of the time of heating of an electrothermal atomizer. The mechanisms for titanium atomization will be studied using the decomposition/atomization curves for titanium as was done by Wahab and Chakrabarti [31] for the mechanisms of yttrium atomization in a graphite tube atomizer.

CHAPTER 1

EFFECT OF HEATING RATE OF A TUNGSTEN ELECTROTHERMAL ATOMIZER (WETA-82) ON THE ABSORBANCE OF SOME ELEMENTS

INTRODUCTION

In a pulse-heated electrothermal atomizer, the kinetics of atomization as well as many of the processes (e.g., diffusion, expulsion, convection, chemical reactions) by which the analyte is removed from the analysis volume, are determined by the atomizer temperature, which depends on its heating rate. Both the peak height and the shape of the transient atomic absorption signal are affected by the heating rate of the atomizer. In pulse-heated electrothermal atomizers, the transient atomic absorption signal is usually generated under non-isothermal conditions, making theoretical treatment of the transient signal complicated. Several models for this transient atomic absorption signal have been developed by other workers [15,16,27-30,33,34-36].

Fuller [33] has described the release and removal of Cu in The Perkin-Elmer atomizer (HGA-70) and concluded that, depending on the atomization temperature, the rate of removal exceeds 3-20 times the rate of supply. Paveri-Fontana et al. [15] have expressed the supply of the analyte atoms by an Arrhenius-type equation and related the removal of the analyte atoms to diffusion and convection. Later on,

van den Broek et al. [16] have used a convolution integral to express the time-dependent number of atoms as composed of two functions: a supply and a removal function. They have concluded that the heating rate, the frequency factor and the activation energy of the atomization process determine the supply function, whereas the removal function is determined by convection or by diffusion.

Zsako' [34] has proposed an equation for the transient atomic absorption signal from an electrothermal atomizer, taking into account only the supply function. He has reported that a linear increase in the peak-height absorbance and in the peak temperature with increasing heating rates of the atomizer should not be expected. Chakrabarti et al. [35] proposed a simplified model of atomization to describe the transient atomic absorption signal under thermal perturbation. They have concluded that increasing heating rates tend to increase the peak-height absorbance by shifting the absorption pulse towards the constant temperature region. Also, the heating rate that gives the maximum peak-height absorbance of a given element is determined by the final temperature and the kinetics of atom formation and loss. Moreover, higher heating rates do not significantly shift the absorption pulse of elements with high activation energies. On the basis of the van den Broek et al. model [16] Zhou et al. [36] have recently derived expressions that describe the relationship between the heating rate and the peak-height absorbance under

isothermal or non-isothermal conditions. They have found that the heating rates giving the maximum peak-height absorbance depend upon the vaporization characteristic of the element, and that the rate constant for the supply function effectively determines the peak-height absorbance.

The above models refer to transient atomic absorption signals generated by graphite electrothermal atomizers. In this thesis some of these models have been used to study the relationship between the heating rate and the atomic absorption signal generated by a tungsten electrothermal atomizer (WETA-82).

THEORY

A. Atomization under non-isothermal conditions

The theory of atomization under non-isothermal conditions has been developed by L'vov [20], van den Broek et al. [15], and Zhou et al. [36], as follows. The following symbols will be used. N_0 is the number of atoms in the sample and N is the total number of atoms in the analysis volume at any instant t .

The balance between the number of atoms entering the analysis volume, $n_1(t)$, and leaving it, $n_2(t)$, in unit time is given by

$$\frac{dN}{dt} = n_1(t) - n_2(t) \quad 1.1$$

Expressions derived from Eqn 1.1 have been used to

temperature, k and k_r are constant. In this case, the peak-height absorbance is given by [

$$A_p = \beta N_0 \frac{k_s}{k_r} \exp[-k_s(t_p - t_0)] \quad 1.13$$

where k_s and k_r are the rate constants for atom supply and atom removal, respectively, under isothermal conditions.

Regardless of the environment in which complete atomization of the analyte occurs, the integral of the time-dependent number of atoms, $N(t)$, gives the integrated absorbance Q_N

$$Q_N = \int_0^{\infty} N(t) dt \quad 1.14$$

If the conditions $\tau_m > \tau_s + 4\tau_R$ is satisfied (where τ_m is the length of time during which the signal is recorded), Eqn 1.14 can be rewritten as

$$Q_N = N_0 \tau_R \quad 1.15$$

with an accuracy up to 2 per cent [p. 119, 20].

Equation 1.15 shows that the integrated absorbance depends only on N_0 and the time constant, τ_R , for atom removal. Contrary to the peak-height absorbance, the integrated absorbance (given by Q_N) does not depend on the kinetics of atom supply (i.e., τ_R). Here, the only requirements are complete atomization of the sample and maintenance of the experimental conditions that ensure a

Hence, the shape of the experimental $A(t)$ curve is now equivalent to the shape of $R(t)$. The convolution integral thus expresses more clearly than the differential equation 1.1 the experimental conditions that must be fulfilled to measure the supply and the removal function independently [16].

The time constant for the supply function is given by [16]

$$\tau_S = \frac{\int_0^{\infty} S(t) dt}{S_{\max}} = \frac{N_0}{S_{\max}} \quad 1.5$$

The $\frac{\tau_R}{\tau_S}$ ratio is a measure of the efficiency of the furnace [20]. If $\frac{\tau_R}{\tau_S} \ll 1$, the atoms are slowly supplied and rapidly removed, so that Eqn 1.3 applies and the maximum number of atoms in the atomizer is given by

$$N_{\max} = S_{\max} \tau_R = \frac{N_0 \tau_R}{\tau_S} \quad 1.6$$

If, on the other hand, $\frac{\tau_R}{\tau_S} \gg 1$, the atoms are rapidly supplied and slowly removed, so that Eqn. 1.4 applies and the maximum number of analyte atoms are given by

$$N_{\max} = R_{\max} N_0 = N_0 \quad 1.7$$

This means that with increasing values of $\frac{\tau_R}{\tau_S}$, the efficiency of the furnace, $N_{\max}/N_0$ is first equal to $\frac{\tau_R}{\tau_S}$, and ultimately approaches unity. The exact correlation between $N_{\max}/N_0$ and $\frac{\tau_R}{\tau_S}$ depends upon the relative shapes

of the supply function, $S(t)$, and the removal function, $R(t)$.

The rate constant for atom formation, k , depends upon the temperature of the atomizer. When the atomizer temperature is increasing, the rate constant of atom formation, k , is a function of the heating rate and can be expressed as [15].

$$K = B e^{-E_a/R(T_0 + \alpha t)} \quad 1.8$$

where B is the frequency factor (s^{-1}), E_a is the activation energy ($kJ\ mol^{-1}$), R is the universal gas constant ($kJ\ mol^{-1}\ K^{-1}$), T_0 is the initial temperature (K), α is the linear heating rate of the atomizer ($K\ ms^{-1}$) and t is the time (ms). Using Eqn 1.8 the supply function $S(t)$ may be expressed as a function of the rate constant as follows [16]

$$S(t) = N_0 B e^{-E_a/R(T_0 + \alpha t)} \exp\left[-\int_0^t B e^{-E_a/R(T_0 + \alpha t')} dt'\right] \quad 1.9$$

Assuming that the rate of atom removal is constant over the absorption pulse peak, Eqn 1.9 has been formulated by Zhou et al. [36] as

$$N = N_0 \exp\left[-\int_0^t k dt'\right] = N_0 v_t \quad 1.10$$

where N is the number of atoms left on the surface of the atomizer tube at time t , and v_t is the surface coverage and is equal to the exponential value of the integral.

At the absorption pulse peak, the number of atoms entering the analysis volume is equal to the number of atoms leaving it. Therefore, the number of atoms, N_p , in the analysis volume at time of the peak maximum, t_p , can be written as [36]

$$N_p = \frac{k_p}{k_r} N_o \exp \left[- \frac{1}{\alpha} \frac{T_m^2 (T_p - T_o) K_m}{T_p \cdot T_o} \right] \quad 1.11$$

where k_p and k_m are the rate constants for atom supply at temperature T_p and T_m , respectively, where $T_o < T_m < T_p$, and k_r is the rate constant for atom removal.

Identifying A_p with N_p and using the approximation $T_m \approx T_p \cdot T_o$ which is valid for the usual experimental conditions, Eqn 1.11 may be described by Eqn 1.12

$$A_p = \beta N_o \frac{k_p}{k_r} \exp \left[- \frac{1}{\alpha} (T_p - T_o) k_m \right] \quad 1.12$$

where β relates the number of free atoms in the analysis volume to the absorbance and the exponential is the surface coverage at the absorption peak position. Equation 1.12 shows an exponential dependence of the peak-height absorbance on the heating rate of the atomizer. This accounts for the increase in the peak-height absorbance with increasing heating rates of the atomizer reported in RESULTS AND DISCUSSION. Equation 1.12 is valid only if the peak of the absorption pulse appears under non-isothermal conditions. If the atomization occurs at constant

temperature, k and k_r are constant. In this case, the peak-height absorbance is given by [

$$A_p = \beta N_o \frac{k_s}{k_r} \exp[-k_s(t_p - t_o)] \quad 1.13$$

where k_s and k_r are the rate constants for atom supply and atom removal, respectively, under isothermal conditions.

Regardless of the environment in which complete atomization of the analyte occurs, the integral of the time-dependent number of atoms, $N(t)$, gives the integrated absorbance Q_N

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If the conditions $\tau_m > \tau_s + 4\tau_R$ is satisfied (where τ_m is the length of time during which the signal is recorded), Eqn 1.14 can be rewritten as

$$Q_N = N_o \tau_R \quad 1.15$$

with an accuracy up to 2 per cent [p. 119, 20].

Equation 1.15 shows that the integrated absorbance depends only on N_o and the time constant, τ_R , for atom removal. Contrary to the peak-height absorbance, the integrated absorbance (given by Q_N) does not depend on the kinetics of atom supply (i.e., τ_R). Here, the only requirements are complete atomization of the sample and maintenance of the experimental conditions that ensure a

constant length of time spent by atoms in the analysis volume (i.e., τ_R is a constant). However, experimental studies have revealed [37,38] that in the commercial electrothermal atomizer, τ_R is often not a constant. Nevertheless, the integrated absorbance has been widely used for analytical determinations.

EXPERIMENTAL

Apparatus

A schematic diagram of the instrument used in this study is shown in Fig. 1. It consists of a single-beam spectrophotometer complete with a detection system and a tungsten electrothermal atomizer (WETA-82).

Spectrophotometer and detection system

The spectrophotometer and the detection system are as follows. Single-element hollow-cathode lamps (manufactured by Westinghouse, Cathodeon Ltd., and The Perkin-Elmer Corporation) were modulated with a frequency of 843 Hz to match the high heating rates of WETA-82. All atomic absorption measurements were made with a Varian-Techtron 0.5 m Ebert-mount monochromator (50 x 50 mm grating, ruled with 638 lines/mm) and a Hamamatsu R955 photomultiplier tube (Hamamatsu Corporation). The absorbance pulses from the photomultiplier were passed through a preamplifier and fed into a lock-in amplifier which has a reference signal of the

Figure 1. Box diagram of the spectrophotometer, the detection system, and the tungsten electrothermal atomizer, WETA-82.

same frequency as that of the hollow-cathode lamp. The amplified signal was then passed through a laboratory-made amplifier assembly (a logarithmic converter) of variable time constant from 4 to 10⁴ ms, located at the output of the logarithmic amplifier. The signal output was recorded with a two-channel digital oscilloscope, model 2090-III, fitted with a model 201 plug-in unit and a disk recorder (all from Nicolet Instrument Co.). The integrated absorbances were measured with a four-channel digital oscilloscope, model 4090 with a plug-in model 4562 (Nicolet Instrument Co.). A Hewlett-Packard plotter, model 7470A, was used to trace atomic absorption and temperature profiles.

Tungsten electrothermal atomizer (WETA-82)

WETA-82 is shown in Fig. 2. It consists of a work-head with a tungsten tube atomizer, a programmable control unit and gas control unit. These components have been already described in detail elsewhere [7]. However, a brief description of these components is given below.

Work-head with a tungsten tube atomizer

Figure 3 shows the work-head with a tungsten tube atomizer. It is connected permanently to both the programmable control unit and the gas control unit with a supply conduit which carries all the gas, water, power cables, light pipe and other electrical supplies.

The work-head has two brass electrodes, which are cut

Figure 2. Tungsten electrothermal atomizer (META-82) with gas control and power supply units

Figure 3. WETA-82 work-head

horizontally. The bottom part has two pins for securing the tungsten tube. The upper part with two locating holes is mounted together with the bottom part by means of two clamping screws. This demountable system allows easy replacement of tungsten tube and ensures a good electrical contact between the tungsten tube and the electrodes.

The cavity containing the tungsten tube is almost entirely enclosed by two special teflon masks fitted with two 5.5 mm circular quartz windows, which are mounted on a 1.0 mm thick quartz plate cover (with a 4.0 mm hole in the centre), located on both sides of the atomizer.

Figures 4 and 5 show two different types of tungsten tube atomizers used, called for simplicity laboratory-made and factory-made atomizers, respectively. Both atomizers consist of two profiled ultrapure tungsten strips (0.1 mm thick, 26 mm wide and 15 mm long). The former was made by the Institute of Chemical Technology, Department of Petroleum Technology and Petrochemistry, Laboratory for Atomic Absorption Spectroscopy, Prague, Czechoslovakia, and the latter by Metallwerk, Plansee, Austria. The strips form a cylindrical tube (15 mm long, 3.5 mm i.d.) with a 1.5-2.3 mm sampling hole in the centre of the upper strip. To ensure reproducible location of the sample in the atomizer, a small circular depression was made in the centre of the bottom strip of the laboratory-made atomizer. The factory-made atomizer (Fig. 5) also consists of two strips. Both strips have small grooves around and on both sides of the

Figure 4. Home-made atomizers: (a) Upper Strip, (b) Bottom Strip, (c) Side view of the atomizer. Dimensions are in mm.

ALL DIMENSIONS ARE IN MM

Figure 3. Factory-made atomizer: (a) Upper Strip. (b) Bottom Strip. (c) Side view of the upper strip. (d) Side view of the bottom strip.

half cylinder. The bottom part also has a boat-shaped depression in the middle to hold the sample - this ensures better reproducibility in the location of the sample than in the laboratory-made atomizer, resulting in higher precision in the absorbance measurements.

Power supply control unit

The power supply control unit (Fig. 2) has a transformer and provides six independent heating steps. Each step can be preset to the desired temperature and time within the following ranges:

	<u>Temperature</u>	<u>Time</u>
*Drying I Temperature	20 - 200 °C	0 - 30 s
*Drying II Temperature	100 - 400 °C	0 - 30 s
*Thermal Treatment I	200 - 1000 °C	0 - 30 s
*Thermal Treatment II	400 - 1800 °C	0 - 30 s
*Atomization Temperature	1200 - 3200 °C	0 - 4 s
*Cleaning Temperature	2000 - 3200 °C	0.5 s (fixed)

*These temperatures are dial settings on the instrument panel and not measured temperatures.

The control unit also provides two heating rates in the range of 0-3 K ms⁻¹ (slow) and 0-30 K ms⁻¹ (fast). The drying and charring temperatures are controlled by a voltage feedback; the atomization temperature is controlled by a temperature feedback circuit incorporated in a photodiode (Tesla I PP-75) which is attached to the work-head; the photodiode views the radiation emitted by the inner surface

of the atomizer. The output signal from the photodiode has been calibrated to give temperatures profiles of the atomizer.

Gas control unit

The gas control unit consisting of needle valves and a flowmeter controls and measures the argon and the hydrogen gas flow. This unit allows an argon flow rate of 0-4 L min⁻¹ in six steps throughout the duration of the heating cycle of the instrument and a hydrogen flow rate of 0-1.6 L min⁻¹ throughout the charring and the atomization cycle as well as the cleaning cycle. The supply of gas and cooling water is controlled by solenoid valves. The cooling period has a maximum duration of 5 s and the water flow has a maximum rate of 2.0 L min⁻¹. A schematic diagram of the unit is shown in Fig. 2.

Reagents

Stock solutions containing 1000 µg/mL of Pb and Cd were prepared by dissolving the appropriate mass of the pure metal oxide (99.99% pure) in ULTREX nitric acid. Stock solutions of Co and Mn containing 1000 µg/mL of each metal separately were prepared by dissolving the metal (99.99% pure) in ULTREX nitric acid. The above solutions were diluted with ultrapure water to make the stock solutions 1% (v/v) in nitric acid. A stock solution containing 1000 µg/mL of Ti was prepared by dissolving the metal (99.99%

pure) in 100 mL (1:1 v/v) ULTREX sulphuric acid and diluting the solution with ultrapure water to make the stock solution 10% (v/v) in sulphuric acid. All ULTREX acids were manufactured by Baker Chemical Co. Ultrapure water of resistivity 18.3 megohm-cm was obtained direct from a Milli-Q2 water purification system (Millipore Corporation). All test solutions were prepared by diluting the above stock solutions to the desired concentrations with ultrapure water immediately prior to determination. The test solutions for Ti were prepared in 1% (v/v) HF + 1% (v/v) HNO₃ aqueous solutions.

Gases

High-purity argon and hydrogen gases (99.995% pure) from Union Carbide Ltd. were used as atomizer purge and sheath gases.

General procedure

Test solutions (25 µL of Mn or Pb, 10 µL of Ti, or 5 µL of Cd or Co) were injected, one element at a time, in the middle of the lower tungsten strip with an adjustable microlitre syringe (Hamilton Company) fitted with a plastic tubing tip. During the injection, excessive contact between the plastic tip and the surface of the bottom tungsten strip was avoided as much as possible in order to improve reproducibility of the injection-volume and to prevent damage of the atomizer surface.

Single-element hollow-cathode lamps were operated at

Figure 9. Absorption pulses of 2.5×10^{-12} kg of Mn (as NO_3^-) as a function of heating rate. A: 1.0 K ms^{-1} . B: 10 K ms^{-1} . C: 20 K ms^{-1} . D: 30 K ms^{-1} . Tube wall temperature curves at different heating rates. a: 1.0 K ms^{-1} . b: 10 K ms^{-1} . c: 20 K ms^{-1} . d: 30 K ms^{-1} .

TABLE I. Optimum experimental conditions used for WETA-82

Parameters	Elements				
	Cd	Co	Mn	Pb	Tl
Mass (kg)	4.0×10^{-14}	1.0×10^{-12}	2.5×10^{-11}	1.5×10^{-10}	2.5×10^{-12}
Wavelength (nm)	228.8	240.7	279.5	283.3	365.3
Spectral Band Width	0.33	0.2	0.33	0.33	0.17
Lamp Current (mA)	10	10	8.0	5.0	20.0 ^e
*Dry I Temperature (°C)	90	110	75	100	100
Time (s)	30	30	30	30	30
*Dry II Temperature (°C)	110	140	85	110	110
Time (s)	30	25	30	30	30
*Thermal Treatment I (°C)	200	320	300	200	300
Time (s)	15	10 ^b	10	5	10
*Thermal Treatment II (°C)	400	630	500	400	1500
Time (s)	5	5	10	5	10
*Atomization Temperature (°C)	1200	2500	2200	2000	3000
Time (s)	0.8	0.6	0.5	0.5	1
Argon Flow Rate (L min ⁻¹)	2.5	2.5	2.5	2.5	2.5
Hydrogen Flow Rate (L min ⁻¹)	0.4	0.4	0.4	0.2	0.8

^aThese temperatures are dial settings on the instrument panel and not the measured temperatures.

RESULTS AND DISCUSSION

A. Effect of heating rate on the peak-height absorbance

Figure 5 shows the shape of the absorption pulse for Ti at different heating rates of WETA-82. It is important to mention here that the temperature values used in calculating the heating rates are the dial settings on the instrument panel and are not measured temperatures; therefore, the values of the heating rates used in the figures are relative. The heating rates were obtained by subtracting the initial temperature from the final temperature and dividing the difference by the heating time. In most cases, close agreement between the heating rate set on the instrument panel and that calculated was observed.

It can be seen from Fig. 6 that the absorbance peak not only becomes sharper with increasing heating rates but is also shifted to an earlier time and towards the isothermal region of the corresponding tube wall temperature curve. Similar shifts were observed for Cd, Co, Mn and Pb as shown in Figs. 7-10. Figure 7 shows that Cd absorption pulse undergoes the greatest shift towards the isothermal region.

Figure 11 shows the effect of heating rate on the peak-height absorbance of the same elements. With the exception of Ti, a maximum in the peak-height absorbance is reached between 5-15 K ms⁻¹. Titanium shows a continuous increase in the peak-height-absorbance throughout the range of heating rates studied (1-30 K ms⁻¹).

Figure 6. Absorption pulses of $\text{Tl } 2.5 \times 10^{-12} \text{ kg (as TlF}_6\text{)}$ as a function of heating rate. A: 1.0 K ms^{-1} . B: 10 K ms^{-1} . C: 20 K ms^{-1} . D: 30 K ms^{-1} . Tube wall temperature curves at different heating rates. a: 1.0 K ms^{-1} . b: 10 K ms^{-1} . c: 20 K ms^{-1} . d: 30 K ms^{-1} .

Figure 7. Absorption pulses of 4.0×10^{-14} kg of Cd (as NO_3^-) as a function of heating rate. A: 1.0 K ms^{-1} . B: 10 K ms^{-1} . C: 20 K ms^{-1} . D: 30 K ms^{-1} . Tube wall temperature curves at different heating rates. a: 1.0 K ms^{-1} . b: 10 K ms^{-1} . c: 20 K ms^{-1} . d: 30 K ms^{-1} .

Figure 8. Absorption pulses of 1.0×10^{-12} kg of Co (as NO_3^-) as a function of heating rate. A: 1.0 K ms^{-1} , B: 10 K ms^{-1} , C: 20 K ms^{-1} , D: 30 K ms^{-1} . Tube wall temperature curves at different heating rates. a: 1.0 K ms^{-1} , b: 10 K ms^{-1} , c: 20 K ms^{-1} , d: 30 K ms^{-1} .

Figure 9. Absorption pulses of 2.5×10^{-12} kg of Mn (as NO_3^-) as a function of heating rate. A: 1.0 K ms^{-1} . B: 10 K ms^{-1} . C: 20 K ms^{-1} . D: 30 K ms^{-1} . Tube wall temperature curves at different heating rates. a: 1.0 K ms^{-1} . b: 10 K ms^{-1} . c: 20 K ms^{-1} . d: 30 K ms^{-1} .

Figure 10. Absorption pulses of 1.5×10^{-10} kg of Pb (as NO_3^-) as a function of heating rate. A: 1.0 K ms^{-1} . B: 10 K ms^{-1} . C: 20 K ms^{-1} . D: 30 K ms^{-1} . Tube wall temperature curves at different heating rates. a: 1.0 K ms^{-1} . b: 10 K ms^{-1} . c: 20 K ms^{-1} . d: 30 K ms^{-1} .

Figure 11. Effect of heating rate on the peak-height absorbance at a constant final temperature.

$\triangle$ 2.5×10^{-11} kg of Mn (as NO_3^-). $\blacksquare$ 4.0×10^{-14} kg of Cd (as NO_3^-). $\square$ 1.5×10^{-10} kg of Pb (as NO_3^-). $\blacktriangle$ 1.0×10^{-12} kg of Co (as NO_3^-). $\circ$ 2.5×10^{-12} kg of Tl (as TlF_6^{-2}).

The constant, final temperatures for different elements are the dial settings on the instrument panel and have been reported in Table I.

The general trend observed for the peak-height absorbance as a function of heating rates is similar to that reported by Püschel et al. [7] in the evaluation of WETA-82. These authors have observed greater enhancement in the peak-height absorbance of low-volatility elements (Er and Ba) relative to high- and medium- volatility elements. Suzuki et al. [39], who have studied the effect of heating rates of a molybdenum microtube on the shape and peak-height absorbance, have reported an increase in the peak-height absorbance of Cu and Mn with increasing heating rates and no variation in the peak-height absorbance for Pb. No information has been given by the latter authors about the atomization environment (isothermal or non-isothermal) used.

The work done by Chakrabarti et al. [35] with the capacitive discharge technique has shown that increasing heating rates enhances the peak-height absorbance of Co, Cd, Mn, Pb, Ni and Mo. Zhou et al. [36] have reported that both the peak-height absorbance and the sharpness of the absorption pulse peak increase with increasing heating rates in non-isothermal conditions.

The shape of the curves in Fig. 11 may be explained as follows. Table II lists the τ_S and τ_R values obtained from Fig. 12 [40]. It can be seen that τ_S decreases more rapidly than τ_R for heating rates $< 10 \text{ K ms}^{-1}$ for all elements. As expected from Eqn 1.12, the most rapid increase in the peak-height absorbance in Fig. 11 was

TABLE II. Experimental values of τ_S and τ_R

Heating Rate (K ms ⁻¹)	Elements											
	Cd		Co		Mn		Pb		Ti			
	τ_S	τ_R	τ_S	τ_R	τ_S	τ_R	τ_S	τ_R	τ_S	τ_R	τ_S	τ_R
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
1	88	113	125	218	262	274	208	211	116	132	158	-
3	58	81	69	80	100	99	92	122	115	108	100	170
5	53	83	61	73	83	89	37	63	65	60	64	65
10	52	72	55	52	71	79	34	54	61	47	58	62
15	45	78	60	55	70	76	29	53	58	38	56	59
20	43	72	46	53	69	75	29	53	61	40	56	59
25	50	78	67	52	66	71	30	53	62	38	55	57
30	39	70	70	50	64	70	29	53	61	44	57	56
											83	112

τ_S and τ_R are in ms measured according to reference No. 40. $\tau_S = t_p - t_0$. (a) values of τ_R have been measured as shown in Fig. 12; (b) values of τ_R have been measured as follows:

$$\tau_R = \frac{\int_0^\infty A_t dt}{A_p}$$

Figure 12. Illustration of procedure used for obtaining τ_{R-11} signal was obtained from 2.5×10^{-12} kg of Tl

observed for heating rates $< 10 \text{ K ms}^{-1}$. For heating rates $> 10 \text{ K ms}^{-1}$ the τ_S and τ_R values do not vary significantly and the peak-height absorbances remain nearly constant for all elements excepting Ti.

It is expected that the peak-height absorbance for medium-volatility elements such as Co and Mn (elements which have relatively high activation energies) should not be very sensitive to changes in heating rates since their absorption pulse peaks appear closer to the isothermal region, as can be seen in Figs. 8 and 9. When the absorption pulse peak appears close to or inside the isothermal region, the surface temperature and the vapour temperature are no longer changing much. Therefore, heated gases inside the atomizer should have nearly completed their expansion. Hence, analyte vapour forming at this time is not appreciably lost with expanding gases (i.e., no appreciable loss by expulsion). Hence, the loss of analyte vapour is almost wholly by diffusion at a constant temperature. Such loss follows first-order kinetics: a constant fraction of the analyte species is lost in a given time interval.

Therefore, in a nearly constant-temperature environment both τ_S and τ_R values and the $\frac{\tau_R}{\tau_S}$ ratios tend to have constant values and become independent of further increases in the heating rates. At nearly constant τ_R values, the peak-height absorbance tends to attain a nearly constant value. This may explain the small effect of heating rates $> 10 \text{ K ms}^{-1}$ on the peak-height absorbance of Co and Mn.

However, relatively volatile elements such as Cd and Pb,

(elements which have lower activation energies than Co and Mn) should be more sensitive to changes in the heating rate, as has been observed in graphite atomizers [35]. The loss of analyte vapour by expulsion should be more important for relatively volatile elements, Cd and Pb, at high heating rates [41]. However, no significant effect of high heating rates on Cd and Pb was observed experimentally in WETA-82.

Titanium has the lowest volatility of the elements studied, and hence, the highest activation energy for atomization. For a given temperature, the higher the activation energy, the more difficult it is to overcome the energy barrier to chemical reaction, resulting in a slow rate of atom formation. According to Eqn 1.8, at the lowest heating rate, a high activation energy should result in a broader absorption pulse peak (as shown in Fig. 6 for Ti) than for the other relatively more volatile elements. In order to obtain a maximum peak-height absorbance for elements with high activation energies, such as Ti, it is necessary to employ high temperatures coupled with high heating rates [35] to minimize the time during which the analyte vapour can be lost by diffusion. However, τ_S and τ_R remain nearly constant for heating rates $> 10 \text{ K ms}^{-1}$ (Table II), yet the peak-height absorbance for Ti continues to increase (Fig. 11). This may suggest a possible increase in the frequency factor in the Arrhenius-type equation. High activation energies and low frequency factors reduces the peak height absorbance and makes it broader [15]. As the

frequency factor increases the absorbance peak becomes sharper and taller. This is consistent with the experimental results shown in Fig. 6.

Since the absorbance signal of the elements studied appears under non-isothermal conditions even for Ti (the absorption pulse peak for Ti at heating rates $> 15 \text{ K ms}^{-1}$ occurs just when the atomizer reaches the maximum temperature), the peak-height absorbance is determined by several parameters, including the rate of atom supply as shown by Eqn 1.12.

B. Effect of heating rates on the integrated absorbance

According to Eqn 1.14, the integrated absorbance should depend on N_0 (total number of analyte atoms) and τ_R (the time constant for atom removal). To test whether the atomization of Cd, Co, Mn, Pb, and Ti in WETA-82 follows the relationship given by Eqn 1.14, the effect of heating rate of WETA-82 on the integrated absorbance of Cd, Co, Mn, Pb and Ti was studied. Results are shown in Fig. 13.

Figure 13 shows that for Cd and Mn, the integrated absorbance decreases rapidly with increasing heating rates up to about 5 K ms^{-1} , above which the integrated absorbance remains constant up to a heating rate of 30 K ms^{-1} . For Co and Pb, the integrated absorbance decreases rapidly with increasing heating rates up to about 10 K ms^{-1} , above which the integrated absorbance decreases slightly up to a heating rate of 30 K ms^{-1} . Sturgeon et al. [9] have reported

Figure 13. Effect of heating rate on the integrated absorbance at a constant final temperature.

△ 2.5×10^{-11} kg of Mn (as NO_3^-). ■ 4.0×10^{-14} kg of Cd (as NO_3^-). □ 1.5×10^{-10} kg of Pb. ▲ 1.0×10^{-12} kg of Co (as NO_3^-). ○ 2.5×10^{-12} kg of Ti (as TiF_6^{-2}).

The constant, final temperatures for different elements are the dial settings on the instrument panel and have been reported in Table I.

mechanisms of Cd and Mn atomization from a graphite furnace as follows: the mechanism of atomization of Cd and Mn is the same and involves the condensed-phase decomposition of their monoxides to gaseous metal atoms; also, the mechanism of atomization of Co and Pb is the same and involves carbon reduction of their monoxides in the condensed-phase to gaseous metal dimers and then to gaseous metal monomers. Since at relatively high temperatures, solid tungsten is a strong reducing agent like solid carbon, both reducing the analyte metal oxides to metals and forming oxides of tungsten and carbon, respectively, it is reasonable to assume that the atomization mechanisms of these elements from tungsten surface are similar to those from graphite surface in the respective furnaces.

In Table II, the great decrease in T_R values with increasing heating rates up to 5 K ms^{-1} for Cd and Mn, and up to 10 K ms^{-1} for Co and Pb is reflected in a rapid decrease in their integrated absorbance values up to these limiting heating rates. However, the cause for these rapid changes in T_R and Q_H values for Cd, Mn, Co, and Pb up to these limiting heating rates is probably the loss of analyte atoms by expulsion with the rapidly expanding gas phase.

The similarity in the trend for these four elements despite the above difference in their atomization mechanisms is due to their common features: condensed-phase reactions giving rise to gaseous analyte species. Table II shows that for Cd, Mn, Co and Pb, with increasing heating rates, the T_R values decreases in a parallel fashion with

the corresponding Q_N value up to heating rates of 5 K ms^{-1} for Cd and Mn, and 10 K ms^{-1} for Co and Pb. This parallel decrease suggests that the decrease in τ_R value is responsible for the decrease in Q_N , and the results are consistent with Eqn 1.14.

Figure 13 shows that the integrated absorbance for Ti increases linearly up to the highest heating rate measured (30 K ms^{-1}). Table II shows that the τ_R value for Ti, after an initial large decrease from the heating rate of 3 to 5 K ms^{-1} becomes almost constant (within the experimental uncertainty). The inescapable conclusion from the above experimental evidence and from Eqn 1.14 is that with increasing heating rates the number of analyte atoms (N_0) in Eqn 1.14 is increasing in a parallel fashion with the increasing integrated absorbance value. Such a continuous increase in the N_0 value for Ti in Eqn 1.14 may be rationalized as follows. Increasing heating rates make additional sources of Ti atoms available, presumably because of the fact that a part or the whole of the tungsten surface changes in its reactivity and/or the partial pressure of oxygen or of tungsten oxide vapour, which determine the equilibrium concentration of Ti (assuming local thermodynamic equilibrium), changes, with increasing heating rates, in the direction which makes atomization of Ti thermodynamically more favourable.

CONCLUSIONS

High heating rates of WETA-82 have a greater effect in shifting the absorption pulses of relatively volatile elements towards the isothermal region of the tube wall temperature curve than in shifting those of medium- and low-volatility elements. In addition, increasing heating rates enhance the peak-height absorbance up to a limiting heating rate which is specific for each element; beyond the limiting heating rate, further increase in the heating rates of WETA-82 does not have a significant effect on the peak-height absorbance except for elements with high activation energies, such as Ti.

The values of integrated absorbance as a function of heating rates of WETA-82 generally support the dependence of Q_H on τ_R , as predicted by the theory.

Changes in heating rates of WETA-82 have similar effects on the peak-height and the integrated absorbance as those observed in graphite furnace atomic absorption spectrometry. However, in WETA-82, expulsion losses of analyte vapour may be less severe, even for relatively volatile elements such as Cd, the loss of which by expulsion has been found to play an important role in determining its peak-height absorbance in graphite furnaces.

CHAPTER II

EFFECT OF ATOMIZATION SURFACE ON THE SENSITIVITY OF TITANIUM

INTRODUCTION

Sturgeon et al. [9] have reported that the mechanism of atomization can be influenced by the atomization surface. Standard graphite have many limitations such as high porosity and low resistance to oxidation. L'vov [20] recommended pyrolytic graphite for the construction of electrothermal atomizers on the basis of its low permeability to gases, low porosity, high purity, high thermal conductivity, high sublimation point (3970 K), and high resistance to oxidation. These advantages of the pyrolytic graphite should reduce the penetration of the analyte through the pores of the graphite tube, ensure uniform heating of the graphite tube, and increase its lifetime. However, adequate sensitivity cannot be achieved using pyrolytic graphite tubes for elements that form carbides and/or lamellar or intercalation compounds, which are involatile even at the highest temperature achievable in graphite electrothermal atomizers [14].

In order to overcome some of the limitations of electrothermal graphite atomizers, different approaches such as the use of metal linings, metal-carbidized surface, metal

filaments and tubes, and glassy carbon tubes were used by earlier workers. Baird et al. [42] reported an increase in the sensitivity of As and Se using a graphite tube lined with a tantalum foil. L'vov [14] reported an increase in sensitivity for 32 of 40 elements studied (e.g., Ti, Al, Ba, U, V, Zr) by using a tantalum-lined HGA-76B graphite tube atomizer. Moreover he found a reduction in the memory effect for most of the elements studied, and a decrease in atomization temperatures as well. A 59.7 fold enhancement in the sensitivity (relatively to that in a graphite atomizer) of U atomized from a 0.05 mm thick tantalum foil lining of the same graphite atomizer was reported by Grégoire and Chakrabarti [43]. Wahab and Chakrabarti [44] reported 4.5 and 6.4 fold enhancements in the sensitivity of Y by using Ta and W linings, respectively, and a 1.4-2.3 fold enhancements in the sensitivity of Y from various metal-carbidized surfaces. A great increase in the useful lifetime of Ta-carbidized graphite tubes was reported by Zatka [45]. A significant enhancement in the sensitivity of Ti and other elements was reported by Wall [46] when a rigid collar of tungsten was used in a graphite atomizer. Aggett [8] reported an increase in the sensitivity of Cr when atomized from a tantalum strip.

The above publications indicate that metal or metal-carbidized surfaces have a significant advantage of preventing carbide formation and elimination of or decrease in the loss of the analyte by diffusion through porous graphite tubes.

EXPERIMENTAL

Apparatus

The Perkin-Elmer atomic absorption spectrophotometer, model 5000, equipped with a Tungsten/Deuterium Arc Background Corrector, an HGA-500 graphite atomizer, and an, AS-1 autosampler, was used. The HGA-500 graphite atomizer has a temperature control assembly, which monitors the applied power to prevent overshooting of the preset temperature. The temperature control assembly contains a silicon photodiode sensor positioned above the graphite tube. This sensor monitors the emission from the outside wall of the graphite tube; constant temperature is maintained by voltage control. In this study two different modes of heating were used: Maximum Power Heating and Normal Power Heating. The former provides more rapid heating of the graphite tube to the preset atomization temperature than the latter. The Perkin-Elmer pyrolytically-coated graphite tubes, 25 mm long, 6 mm i.d., and 7 mm o.d., (part number B0091-1504) were used.

The tungsten electrothermal atomizer (WETA-82) was used with the atomic absorption spectrophotometer fitted with the detection system described in Chapter I. Tungsten tube atomizers described earlier were used.

Titanium hollow-cathode lamps (Westinghouse) were used with both instruments.

TABLE IV. Characteristic mass of titanium atomized from different surfaces under optimum experimental Conditions^a

Atomizer and Surface	^a Characteristic Mass (kg)	Enhancement in ^b Sensitivity
HGA-500, pyrolytically-coated graphite	1.1×10^{-13}	-
WETA-82, tungsten tube	2.8×10^{-14}	3.9

^aListed in Table III

^aCharacteristic mass is the mass of element which gives an absorbance of 0.0044 by the peak-height absorbance mode.

^bEnhancement relative to the sensitivity values given by HGA-500, pyrolytically-coated graphite tube.

heated to high temperature (2800 K) to expand the lining to form a good contact with the graphite tube surface.

Six percent (w/v) tantalum soaking solution

Three grams of Ta metal (99.998% pure) was dissolved in 10 mL diluted HF (1:1 v/v) in a 100 mL Teflon beaker. Three grams of oxalic acid dihydrate and 0.5 mL of 30% (v/v) hydrogen peroxide were added to the above solution. The solution was heated carefully, hydrogen peroxide was added when the reaction became slow until the metal was completely dissolved. After complete dissolution, four grams of oxalic acid and 30 mL of ultrapure water were added to the above solution. After the oxalic acid dissolved, the solution was diluted with ultrapure water to 50 mL and stored in a high-density polyethylene bottle.

Surface treatment of pyrolytically-coated graphite tube

The procedure prescribed by Zatka [45] for coating of the graphite tube was followed. The tube was immersed vertically in the above tantalum solution in a plastic vial for 24 hours under atmospheric pressure. The tube was then removed from the bath and dried, first at room temperature for 30 minutes and then, at 105 °C for one hour. After drying the tube, it was mounted in the atomizer (HGA-500) fitted with new graphite contact rings. While the argon gas and cooling water were on, the temperature was raised gradually over a period of 30 s to 1273 K and then to 1773 K.

over a period of 5 s. For a second coating, the entire procedure was repeated.

General procedure

Sample volumes of 10 $\mu\text{g/mL}$ of Ti solution were injected in the centre of the graphite or the tungsten tube with either an autosampler or a Hamilton syringe fitted with a plastic tubing tip, depending on the instrument used. Great care was taken to avoid excessive contact between the tip and the surface of the tungsten tube during injection. When working with the HGA-500, the gas-stop mode was used during the atomization step. To ensure reproducible experimental conditions, the resistance across the workhead terminal of the atomizer was monitored with a milliohmeter (Hewlett-Packard). The Maximum-Power-Heating mode was set carefully by means of the temperature sensor to obtain the desired atomization temperature, which was checked with an Ircon 1100 series automatic optical pyrometer (Ircon Inc.). Optimum experimental conditions used in this study are shown in Table III. The measured absorbances were corrected for blank absorbances to obtain net absorbances, which were reported. All values reported were the averages of at least three replicate determinations.

TABLE III. Optimum experimental conditions for titanium

Analytical Parameters	^a HGA-500	^b WETA-82
Wavelength (nm)	365.3	365.3
Spectral Band Pass (nm)	0.2	0.2
Lamp Current (mA)	16	12
*Drying I Temperature (°C)	130	90
Time (s)	30	30
*Drying II Temperature (°C)	-	110
Time (s)	-	30
*Charring I Temperature (°C)	-	300
Time (s)	-	10
*Charring II Temperature (°C)	1500	1500
Time (s)	10	10
*Atomization Temperature (°C)	2800	2800
Time (s)	6	0.6
Heating Rate (K/ms)	^c MP	15
Argon Gas Flow (L/min)	^d GS	2.5
Hydrogen Gas Flow (L/min)	-	0.8

^aHeated Graphite Atomizer^bTungsten Electrothermal Atomizer^cMaximum Power Mode^dGas-Stop Mode

*These temperatures are dial settings on the instrument panel and are not measured temperatures.

RESULTS AND DISCUSSION

A. Effect of surface on the sensitivity of titanium

Figure 14 shows the absorbance of Ti as a function of the lamp current with The Perkin-Elmer atomic absorption spectrophotometer, model 5000. The lamp current of 16 mA corresponding to the maximum absorbance was chosen as the optimum lamp current for further experimental work.

Table IV shows the characteristic mass of Ti atomized from both the graphite and the tungsten surface. The characteristic mass of Ti from pyrolytically-coated graphite tube is higher than that of WETA-82. It is possible that with graphite Ti starts to form TiC_xO_y at about 1273 K [47]. As the temperature and heating rate increase the formation of TiC (m.p. 3410 °C) is favoured [47]. Probably, some Ti atoms are tied up by C as TiC formed at the charring step (1773 K), resulting in a decrease in the characteristics mass value.

According to Sturgeon and Chakrabarti [9, p. 128], loss of atomic vapour (of the elements studied by them) through the wall of pyrolytically-coated graphite tubes is probably negligible and that at atmospheric pressure the major loss mechanism in the graphite tube atomizer is diffusion of the atomic vapour from the hotter central part towards the coldest ends of the tube, where the analyte vapour condenses. For low-volatility elements, such as Ti, the

Figure 14. Absorbance of 5.0×10^{-14} kg of Ti (as TiF_6^{-2}) as a function of hollow-cathode lamp current.

TABLE IV. Characteristic mass of titanium atomized from different surfaces under optimum experimental Conditions^a

Atomizer and Surface	^a Characteristic Mass (kg)	Enhancement in ^b Sensitivity
BGA-500, pyrolytically-coated graphite	1.1×10^{-13}	-
WETA-82, tungsten tube	2.8×10^{-14}	3.9

^aListed in Table III

^aCharacteristic mass is the mass of element which gives an absorbance of 0.0044 by the peak-height absorbance mode.

^bEnhancement relative to the sensitivity values given by BGA-500, pyrolytically-coated graphite tube.

atomization temperature used was not sufficient to reevaporate any condensate deposited at the colder ends of the graphite tube. However, an absorbance signal was observed in the subsequent atomization cycles (memory effect). Diffusion through the pores of the tube wall may also occur. Especially when high temperatures are used, the pyrolytic graphite layer is partly destroyed with each atomization cycle by vaporization of the layer graphite [48]. This results in an increase in the porosity of the graphite tube. As the porosity increases, more analyte solution penetrates into the pores, and vaporization of the analyte occurs from the pores of the bulk graphite.

The temperature dependence of the diffusion coefficient for diffusion through pores of a solid material may be expressed by [49]

$$D = D_0 \exp\left(-\frac{Q}{RT}\right) \quad 2.1$$

where D_0 is the frequency factor (s^{-1}), Q is the activation energy of the diffusion process ($kJ\ mol^{-1}$), and R is the universal gas constant ($kJ\ mol^{-1}\ K^{-1}$). The value of Q was found to be $87\ kJ\ mol^{-1}$ for Ti and the other elements studied by Weisweiler and Nageshwar [49]. Equation 2.1 shows that high temperatures favour increase in diffusion coefficient of the analyte through the pores of graphite tube wall. The diffusion coefficient of Ti for a porous surface was reported by these authors to be 163 and $144\ cm^2\ s^{-1}$, the calculated and experimental values,

respectively. The diffusion coefficient of analyte atoms through the wall of a cuvette is related to the residence time of the atoms in the analysis volume by [20, p. 205]

$$\tau_2' = \frac{t_w V_w}{D S_w} \quad 2.2$$

where t_w is the thickness of the walls, V_w is the volume of the cuvette, S_w is the area of the walls of the cuvette. Consequently, if the porosity of the surface increases, the diffusion coefficient will also increase causing a decrease in the residence time of the analyte atoms, and hence, a decrease in the characteristic mass (i.e., sensitivity) by the peak-height absorbance mode.

Despite the fact that the pyrolytic layer of the graphite tube reduces diffusion of the analyte through the wall, the porosity of the graphite tube is still greater than that of tungsten tube. Figures 15a and 15b show the Scanning Electron micrographs (SEM) of the interior surface of the unused pyrolytically-coated graphite tube and the tungsten tube, respectively. It is observed that graphite surface is rougher than the tungsten surface. Moreover, the graphite surface grains are not uniform. This may favour penetration of the analyte solution through grooves and pores. Figures 16a and 16b show the SEM of the graphite and tungsten tube after ten atomization cycles at 3073 K. It can be seen that both graphite and tungsten surfaces have become rougher than the surfaces in Fig. 15. However, considering the unused surfaces, the increased porosity of

Figure 15a. Scanning electron micrograph (x1500) of the interior surface of an unused pyrolytically-coated graphite tube

Figure 15b. Scanning electron micrograph (x3000) of the interior surface of an unused tungsten tube

Figure 16a. Scanning electron micrograph (x1500) of the interior surface of a pyrolytically-coated graphite tube after ten atomization cycles at 3073 K

Figure 16b. Scanning electron micrograph (x3000) of the interior surface of a tungsten tube after ten atomization cycles at 3073 K

the graphite surface favours more penetration of the analyte solution. Figures 17a and 17b show the fracture edges of the unused and used graphite tubes. In the latter, the graphite layers are not as compact as in the former, and the latter will allow readily diffusion of the analyte towards the empty spaces where it will be trapped between graphite layers forming lamellar or intercalation compounds.

Complete atomization is not achieved once the analyte is trapped between graphite layers forming lamellar or intercalation compounds, resulting in loss of sensitivity and in the memory effect observed.

Figure 18 shows the absorbance of Ti atomized from the HGA-500 as a function of the number of atomization cycles (firings) using the two different modes of heating. Figure 18 shows that after the initial atomization cycle, more than ten firings are required in order to eliminate or reduce the memory effect. It may be also seen that the sensitivity obtained with the Maximum Power Heating mode is almost twice as great as that of the Normal Power Heating mode. The Maximum Power Heating mode heats the graphite tube to the preset temperature at a faster rate than the Normal Power Heating mode, resulting in a faster atomization rate which produces an increase in the sensitivity.

The problem of memory effect encountered with the HGA-500 was not observed with WETA-82, even when the mass of Ti injected was doubled because carbide formation was completely eliminated by atomization from the tungsten

Figure 17b. Scanning electron micrograph (x2000) of the fracture edge of a pyrolytically-coated graphite tube after ten atomization cycles.

Figure 17a. Scanning electron micrograph (x2000) of the fracture edge of an unused pyrolytically-coated graphite tube

Figure 18. Absorbance of 1.0×10^{-11} kg of Ti as a function of number of atomization cycles.

○ Normal Power Mode. □ Maximum Power Mode

furnace.

Because of the low mass of the tungsten tube, the temperature gradient generally found along the HGA-500 graphite tube length is probably smaller in the tungsten tube. Therefore, the loss by condensation at the ends of the tungsten tube may be small in WETA-82. Diffusion through the pores of the tungsten tube wall may be considered negligible because of the low porosity of the tungsten surface. Moreover, regeneration of the tungsten surface by hydrogen gas, as it will be explained in the next section, may contribute to the low porosity of the tungsten surface. As a result of this, an enhancement in the sensitivity of Ti should be observed. In fact, when Ti was atomized from WETA-82 a 3.9 fold enhancement in the sensitivity was obtained.

B. Effect of hydrogen gas on the absorbance of Ti

In order to prevent oxidation of the tungsten tube of WETA-82, it is necessary to provide a reducing environment by making hydrogen gas flow through the tube especially when high temperature is used. Tungsten is rapidly oxidized in the presence of oxygen at about 770 K, forming a series of protective layer oxides, e.g., WO_3 , WO_2 , $W_{18}O_{49}$ or $W_{20}O_{58}$, through which oxygen may penetrate to reach the metal [50]. However, when tungsten is heated in a hydrogen atmosphere, tungsten oxides are not formed, or if formed are reduced to tungsten metal. Reduction of WO_3 by hydrogen has been reported to be a four-step process [51] as shown in the

following reactions.

Since these reactions are reversible, their rates as well as the thermodynamic stability of W and its oxides are determined by the equilibrium partial pressures of hydrogen and water vapour by the following relation [52] which assumes unit activity for solid WO_3 and W.

$$K_p = \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} \quad 2.3$$

where K_p is the equilibrium constant for the reduction reaction (reaction 5). If the rate of formation of tungsten oxides is faster than the rate of formation of Ti atoms, vaporization of Ti may be somewhat hindered by the growth of the tungsten oxides, covering the tungsten surface with the result that the absorbance signal of Ti will decrease or even be absent. This may explain the complete absence of Ti signal from WETA-82 observed when hydrogen flow is not used.

Since the equilibrium of the above reactions are governed by the $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ ratio, the presence of water vapour inside the atomizer not only shifts the equilibrium of the

reaction 5 to the left but also favours the formation of the refractory $\text{TiO}_2(\text{s})$. Increasing hydrogen concentration in the vapour phase drives the reaction 5 extensively to the right, making the reduction of WO_3 to W approach completion.

As the metallic surface of the tungsten tube is regenerated by hydrogen gas, the possible hindering of the atomization of Ti atoms mentioned earlier is reduced or eliminated. It is also possible that hydrogen gas regenerates the tungsten surface continuously; the etching of the tungsten surface is reduced as recrystallization of the tungsten particles, vaporized during the atomization step, occurs. Figure 19 shows an area of the tungsten tube slightly off the sample target. It is observed that the surface has a structure which is different from that in Fig. 17b. This difference probably originated from the above-mentioned recrystallization process. Also, the rate of reduction of TiO_2 to the lower oxide or the metal by W may increase. As a result of this, more titanium is atomized. This explanation is consistent with experimental results shown in Fig. 20, which shows that the peak-height absorbance of Ti increases with increasing hydrogen gas flow rate. Similar effect was also observed with the integrated absorbance (Fig. 21).

In Figs. 20 and 21, the fact that both the peak-height and the integrated absorbance of Ti are still increasing at the maximum hydrogen gas flow rate used may suggest any or

Figure 19. Scanning electron micrograph (x3000) of a tungsten tube area slightly off the sample target after ten atomization cycles

Figure 20. Absorbance of 5.0×10^{-12} kg of Ti (as TiF_6^{-2}) as a function of hydrogen gas flow rate of WETA-82

CHAPTER III

MATRIX INTERFERENCES IN PULSE-HEATED AND CONSTANT-TEMPERATURE ATOMIZERS

INTRODUCTION

Since the introduction of commercial electrothermal atomizers (pulse-heated) as atom reservoirs in atomic absorption spectrometry, these atomizers have undergone a continuous process of modification and refinement to make use of the full potential of the electrothermal atomization technique. Despite increasing improvements and sophistication of these atomizers, most of them are still based on the furnace design introduced by Massmann [1], i.e., the sample is deposited on the wall of the graphite tube prior to its being rapidly heated (called pulse-heated) to the predetermined atomization temperature. These atomizers are called pulse-heated atomizers to differentiate them from constant-temperature atomizers.

In pulse-heated atomizers, the analyte is atomized from a surface which is rapidly increasing in temperature; the result is that serious matrix interferences occur [55,56], particularly in the determination of highly volatile elements, e.g., Cd and Pb in chloride matrices. The atomization of Cd and Pb occurs almost at the same

both of the two following things: the rate of reduction of $\text{TiO}_2(\text{s})$ to Ti is still increasing; the position of equilibrium in the reaction 5 is shifting increasingly to the right. In addition, even with the maximum flow rate of hydrogen gas used, the partial pressure of hydrogen gas in the vapour phase probably has not reached that required to ensure complete reduction of $\text{WO}_3(\text{s})$ to W.

In order to obtain more information about the contribution of diffusion (through the pores of the graphite tube wall) to the memory effect problem, the tube was lined with 0.1 mm thick W-foil. However, no Ti signal was observed. This is contrary to the results obtained with WETA-32, which shows an enhancement in the sensitivity of Ti (Table III). The results obtained from the effect of hydrogen gas flow rate in WETA-82 on the absorbance of Ti have shown that in order to obtain a measurable Ti signal, at least 0.1 L min^{-1} hydrogen gas flow rate must be used. This knowledge may be applied to explain the absence of Ti absorbance signal in a W-lined graphite tube. However, no work has been reported on the role of hydrogen gas on the absorbance of Ti in metal-lined graphite tubes. There is clearly a need for further work on this subject.

Attempts were made to atomize Ti from a tantalum-carbidized graphite tube which had been subjected to the Zatka pretreatment process [45]. However, an absorbance signal, which was about 10-15 times smaller than that obtained for graphite tubes without the pretreatment, was

observed. Similar results were obtained by Slavin et al. [53], who reported that Ti and Mo did not give any absorbance signal when a graphite tube subjected to the Zatka pretreatment [45] was used. However, when they used a tantalum-carbidized graphite tube coated by the Norval et al. [54] process (coating the graphite surface with Ta metal generated by cathodic sputtering technique) a superior performance was obtained, although the sensitivity was slightly lower than that obtained with the untreated Perkin-Elmer graphite tubes (part number B009-1504). Therefore, they were of the opinion that tantalum alone was not the reason for the poor performance of the graphite tubes treated by the Zatka pretreatment process [45]. They noted that during the manufacture of the graphite tubes, a fluorinated compound had been used, followed by a firing at high temperature to eliminate the fluorine. They found that the sensitivity was unusually low for some graphite tubes during the first few firings. They concluded that the graphite tubes had not been heated long enough to eliminate all fluorine.

It should be noted that the tantalum soaking solution for the Zatka pretreatment process [45] is prepared in hydrofluoric acid (aqueous) solutions. This may increase the concentration of fluorine in the graphite surface, presumably resulting in the formation of volatile TiF_4 . The volatile TiF_4 may be partly or wholly lost in the charring cycle, causing a decrease in the sensitivity. In fact, when the tube was twice-carbidized, it was observed that the

sensitivity was even lower, probably because of the accumulation of more fluorine on the graphite tube surface from successive carburizations. However, no attempt was made to find out if the sensitivity improved with subsequent firings as observed by Slavin et al. [53].

CONCLUSIONS

From the comparison of results of the characteristic mass of titanium obtained with HGA-500 and WETA-82 furnaces, the following conclusions can be drawn.

1. Formation of lamellar compounds and/or carbides with the graphite surface are responsible for the poor sensitivity and memory effect of Ti atomized from the graphite surface of electrothermal atomizers.
2. Provided that a sufficiently high temperature is used, the Maximum Power Heating mode of The Perkin-Elmer HGA-500 furnace enhances the sensitivity of titanium (relative to that of the Normal Power Heating mode) almost by a factor of 2.
3. Tungsten electrothermal atomizers should be used to determine titanium because it forms low-volatility carbides and/or lamellar compounds with graphite electrothermal atomizers.
4. Hydrogen gas increases the peak-height and the integrated absorbance of titanium in WETA-82.

CHAPTER III

MATRIX INTERFERENCES IN PULSE-HEATED AND CONSTANT-TEMPERATURE ATOMIZERS

INTRODUCTION

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equilibrium of the vapour with the graphite tube wall may not occur throughout the tube. Manning et al. [72] have suggested that a graphite platform delays the vaporization of the sample for only a limited time; the vapour phase within the graphite tube may not have reached the analyte atomization temperature by the time that the graphite platform reaches the temperature at which vaporization of the analyte occurs. To solve the above problem Livov [73] has introduced the third approach, which is introduction of a sample into a pulse-heated atomizer after it has attained a preset atomization temperature. Livov has used tungsten wire or graphite as a probe. Reduction of matrix interferences by using wires or filaments as probes has been reported by other authors [72,74]. This technique is called the probe technique.

Slavin and Manning [75] have reported on the sensitivity and selectivity of the probe technique. They have also found that the probe technique permits the atomization temperature to be selected independently of the charring temperature. Moreover, there is no need for matrix modifiers. By using the probe technique, Giri et al. [76] have observed reduction of vapour phase interferences in the determination of Pb in $MgCl_2$ and $CaCl_2$ matrices and substantial reduction in matrix interferences in the determination of Pb in diluted blood samples [57].

Another variation of the third approach was the development of graphite tube atomizers which are operated at

interferences. Manning and Slavin [62] used ammonium nitrate to reduce interferences when determining Pb by using molybdenum-coated and pyrolytically-coated graphite tube. Bertenshaw et al. [63,64] reported reduction of matrix interferences in the determination of Pb in drinking waters by combining a lanthanum pretreatment procedure with acid matrix modifier. Hodges and Skelding [65] reported reduction of matrix interferences in the determination of Pb by using a Mo-precoated graphite tube together with orthophosphoric acid as a matrix modifier.

Despite these advances, the problem of matrix interferences has remained largely unsolved. More recently, many attempts have been made to increase the vapour phase temperature of the atomizer. These attempts can be identified with three general approaches: very rapid heating of the atomizer surface; delay of vaporization process by vaporizing samples from a platform surface; and introduction of samples into an atomizer after it has attained a high, constant temperature.

In the first approach, the atomizer is very rapidly heated in such a way that constant atomization temperature is achieved during the lifetime of the analyte absorbance pulse. An example is the capacitive discharge technique, used by Chakrabarti et al. [66] which achieves a constant atomization temperature by using heating rates up to 100 K ms^{-1} . They [66] have also demonstrated that the capacitive discharge technique eliminates or reduces

interferences caused by chloride matrix. Commercial electrothermal atomizers can achieve heating rates only up to about 2 K ms^{-1} . Recently, a tungsten electrothermal atomizer (WETA-82) has been developed, which achieves heating rates up to 30 K ms^{-1} [7]. However, no systematic studies of matrix interferences have yet been published for WETA-82.

In the second approach, delay of vaporization process by vaporizing samples from the surface of a graphite platform was suggested by L'vov [10]. The sample is vaporized from the platform at a time when the vapour phase has attained a nearly constant vapour phase temperature. Several authors have directed their work to the application of and for the improvement in graphite platform. Slavin and Manning [67] have demonstrated that a graphite platform reduces matrix interferences arising from change in the appearance temperature of Pb from different matrices. These authors have also reported [68] a great reduction of matrix interferences for Pb, Cd, and Tl using the L'vov graphite platform [10]. Also, they have reported very few matrix interferences in the determination of Al [69]. Chakrabarti et al. [70] have reported a 100% recovery of Cd and Pb from chloride matrix using a graphite platform. This technique is called the platform technique.

Ottaway [71] has reported that the use of heating rate alone is not sufficient to eliminate completely matrix interferences completely because local thermodynamic

equilibrium of the vapour with the graphite tube wall may not occur throughout the tube. Manning et al. [72] have suggested that a graphite platform delays the vaporization of the sample for only a limited time; the vapour phase within the graphite tube may not have reached the analyte atomization temperature by the time that the graphite platform reaches the temperature at which vaporization of the analyte occurs. To solve the above problem Livov [73] has introduced the third approach, which is introduction of a sample into a pulse-heated atomizer after it has attained a preset atomization temperature. Livov has used tungsten wire or graphite as a probe. Reduction of matrix interferences by using wires or filaments as probes has been reported by other authors [72,74]. This technique is called the probe technique.

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Another variation of the third approach was the development of graphite tube atomizers which are operated at

constant temperature but are much simpler in design and less complicated in operation than the L'vov furnace [77] and the Woodruff furnace [78]. Frech and Jonsson [17] have developed a system using two CRA 90 carbon rod atomizers and two power supplies to heat the graphite tube and the graphite sample cup separately. Siemer [18] has developed a graphite tube atomizer with independent control of volatilization and atomization conditions by introducing a graphite cup in the middle of the graphite tube. He has reported that matrix interferences observed with conventional furnaces have been greatly reduced with his furnace design. Chakrabarti and Jotov [19] have reported a great reduction in chloride interferences in the determination of Pb, Cu, and Mn in synthetic seawater samples by using their laboratory-made constant-temperature graphite furnace. The furnace was so designed as to separate vaporization process physically from atomization process, by doing the former in a detachable sample cup and the latter in a long, tube furnace, both made of standard graphite.

It is clear that the matrix interference problem in pulse-heated atomizers is more difficult to overcome than in a constant-temperature furnace. A few papers comparing matrix interferences with both types of atomizer have been published [79,80]. It would be interesting to compare matrix interferences in two recently developed atomizers: the pulse-heated tungsten atomizer (WETA-82), which provides heating rates up to 30 K ms^{-1} , and the constant-temperature

furnace developed by Chakrabarti and Jotov [19] mentioned earlier. Cadmium and Pb were chosen for this study because matrix interferences have often reported to be severe for these two elements [55,56].

EXPERIMENTAL

Apparatus

The WETA-82 apparatus has been described in Chapter I. A constant-temperature furnace [19] was also used in this study. It consists of a spectrophotometer equipped with a detection system complete with a Deuterium-Arc Background Correction system. The atomizer consists of two detachable parts: a main (graphite tube) furnace and a graphite sample cup. Two separate power supplies were used to heat these two parts separately and independently of each other.

Figure 22 shows a schematic diagram of the apparatus - the components and manufacturers are listed in Table V. Graphite tubes (Fig. 23a) were fabricated from high purity graphite rods RW-0 (Ringsdorff, Spektakhlen, West Germany). Sample cups (Fig. 23b) were fabricated from ULTRA PURITY rods grade 12 (Ultracarbon Corporation, Bay City, Michigan, USA).

Cadmium and Pb hollow-cathode lamps (Westinghouse) were used with both instruments. A deuterium-arc lamp, model L544-20 (Hamamatsu), and a deuterium-hollow-cathode lamp, model L233-1DQ (Hamamatsu), were used as continuum sources

Figure 22. Schematic diagram of the components of the constant-temperature furnace. Reproduced from [19], with permission of the authors

TABLE V. Description of the instrumental components
of the diagram in figure 22

1. Hollow-cathode lamp
2. Deuterium-Arc lamp
- 3,4,9 Lenses
5. Beam Splitter
6. Main furnace
7. Sample cup
8. Chamber housing the atomizer in an inert gas environment
10. Monochromator (Varian 31-02-SPEC)
11. Photomultiplier (R-156)
12. Deuterium-Arc lamp power supply, model C 1518
(Hamamatsu)
13. Logic control system
14. Hollow-cathode lamp power supply, 800 V, model IR1
15. 11 x 30 series Ircon optical pyrometer (Ircon Inc.
Skokie, Illinois, USA)
16. Water supply
17. Gas supply
18. Plotter, model 7470A, Hewlett-Packard
19. Four-channel digital oscilloscope, model 4094 with two
4562 plug-in and an XP44 disc recorder (Nicolet
Instrument Co., Madison, Wisconsin).
20. Electronics, (pre-amplifier, amplifier, pulse
generator).
21. Temperature programmer
22. Main furnace power supply, 10 KW step-down transformer
with silicon controlled rectifier (SCR).
23. Stepping motor, type M062-FD03 (Superior Electric)
24. Power supply for the stepping motor, type MPS 1000
(Superior Electric)

DIMENSIONS ARE IN mm

Figure 23. a: Front view the graphite main tube furnace
b: Front view of the sample cup

in the Background Correction system - the former with the constant-temperature furnace, and the latter with the META-82.

Reagents

Stock solutions containing 1000 µg/mL of Cd and Pb were prepared by dissolving an appropriate mass of the metal oxide (99.99% pure) separately in ULTREX nitric acid (Baker Chemical Co.) and diluting with ultrapure water. Ultrapure water of resistivity 18.3 megohm-cm was obtained direct from a Milli-Q2 water purification system (Millipore Corporation). A stock solution containing a mixture of NaCl, MgCl₂ and CaCl₂ was prepared by dissolving appropriate masses of the pure salts (ACS reagent grade purity) in ultrapure water to make the solution contain 5×10^4 µg/mL NaCl, 5×10^3 µg/mL MgCl₂, and 2×10^3 µg/mL CaCl₂. Test solutions were prepared by diluting the above stock solutions to the desired concentrations with ultrapure water immediately prior to determination.

Gases

Argon and hydrogen gases of 99.995% purity (Union Carbide Canada Ltd.) were used.

General procedure

Samples of 5 µL volume were injected into the tungsten tube atomizer and the graphite sample cup, respectively,

with a 10 μ L Hamilton syringe fitted with a plastic tubing tip. Experimental conditions used with the respective apparatus are shown in Tables VI and VII. Time steps of the temperature program for the constant-temperature furnace are shown in Fig. 24.

When using the constant-temperature furnace the sample cup temperature was measured with a 300 series optical pyrometer, and the main furnace tube temperature with the optical pyrometer specified in Table V. The stepping motor was synchronized such that the sample cup was inserted after the main furnace attained a constant atomization temperature. The sample cup position was carefully chosen to maximize the height of the analyte absorption pulse.

For WETA-82 the temperature profiles were recorded direct from the photodiode as described in Chapter I. The laboratory made and the factory-made atomizer (Chapter I) were used for determination of Pb and Cd, respectively.

The analyte absorbances were corrected for the blank and the background absorbance. Sequential background correction was used in WETA-82 by subtracting the matrix background from the total absorbance signal (analyte plus matrix), whereas with the constant-temperature furnace a simultaneous background correction system was used.

All data reported are averages of three to four replicate determinations.

TABLE VI. Optimum experimental conditions for the study of Cd and Pb recovery with WETA-82.

Experimental Parameter	Cd	Pb
Mass (kg)	4.0×10^{-14}	6.0×10^{-13}
Wavelength (nm)	228.8	383.3
Spectral Band Pass (nm)	0.17	0.17
Lamp Current (mA)	10.0	5.0
*Drying I Temperature ($^{\circ}\text{C}$)	100	120
Time (s)	30	30
*Drying II Temperature ($^{\circ}\text{C}$)	120	140
Time (s)	30	30
*Charring I Temperature ($^{\circ}\text{C}$)	200	200
Time (s)	30	10
*Charring II Temperature ($^{\circ}\text{C}$)	400	500
Time (s)	15	30
*Atomization Temperature ($^{\circ}\text{C}$)	1500	1800
Time (s)	0.8	0.6
Heating Rate (K ms^{-1})	12.5	20
Argon Flow Rate (L min^{-1})	2.5	2.5
Hydrogen Flow Rate (L min^{-1})	0.4	0.2

*These temperatures are dial settings on the instrument panel and not the measured temperature

Figure. 26. Effect of 4.0×10^{-8} kg NaCl + 0.48×10^{-8} kg MgCl_2 + 0.16×10^{-8} kg CaCl_2 matrix on the absorbance of 6.0×10^{-13} kg of Cd (as NO_3^-) in WETA-82 without any matrix modifier. A: Pb signal alone.

B: Cd + matrix, not corrected for background (matrix). C: Background (matrix) alone. D: Pb signal, corrected for background (matrix).

E: Tube wall temperature curve.

TABLE VII. Optimum experimental conditions for the study of Cd recovery with the constant-temperature furnace

Experimental Parameter	Cd
Mass (kg)	1.2×10^{-12}
Wavelength (nm)	228.8
Spectral Band Pass (nm)	0.17
Lamp Current (mA)	6.0
Drying Temperature of the Sample Cup ($^{\circ}\text{C}$)	120
Time (s)	40
Heating Temperature of the Sample Cup ($^{\circ}\text{C}$)	400
Time (s)	20
Vaporisation Temperature of the Sample Cup ($^{\circ}\text{C}$)	1800-1850
Chamber Gas Flow (L min^{-1})	5.0
Convective Gas Flow under the Sample Cup (L min^{-1})	1.1
Background Corrector	D ₂ Lamp

Figure 24. Time-steps of the temperature program for the constant-temperature furnace. Reproduced from reference No. 19 with permission of the authors.
 SC = sample cup. MF = main furnace. SM = stepping motor.

RESULTS AND DISCUSSION

A. Effect of the NaCl-MgCl₂-CaCl₂ matrix on Cd and Pb absorbance signal in WETA-82.

Figures 25 and 26 show the atomic absorption pulses of Cd and Pb, respectively, in aqueous solution without the matrix (Figs. 25A and 26A) and in the NaCl-MgCl₂-CaCl₂ matrix (Figs. 25D and 26D) without use of any matrix modifier. Two important observations can be made: 1) the matrix depresses both the peak-height and the peak-area absorbance; 2) the matrix shifts the peak of the absorption pulse along the time axis.

The depression in the absorbance of Cd and Pb, both peak-height and peak-area, increases with increasing concentrations of the matrix, as can be seen in Figs. 27 and 28. The curves for Cd and Pb show different trends. For matrix concentrations 8.00×10^{-8} kg NaCl + 0.96×10^{-8} kg MgCl₂ + 0.32×10^{-8} kg CaCl₂, the Cd peak-height absorbance remains constant; with higher concentrations of the matrix, the Cd peak-height absorbance rapidly decreases. However, the Cd peak-area absorbance curve steadily decreases with increasing matrix concentrations starting from the lowest matrix concentration. On the other hand, the Pb recovery drops to about 60% for both the peak-height and the peak-area absorbance at the matrix mass: 12×10^{-8} kg NaCl + 1.44×10^{-8} kg MgCl₂ + 0.48×10^{-8} kg CaCl₂, and then

Figure 25. Effect of 5.0×10^{-8} kg NaCl + 0.6×10^{-8} kg MgCl_2 + 0.2×10^{-8} kg CaCl_2 matrix on the absorbance of 4.0×10^{-14} kg Cd (as NO_3^-) in WETA-82 without any matrix modifier. A: Cd signal alone. B: Cd + matrix, not corrected for background. C: Background (matrix) alone. D: Cd signal, corrected for background (matrix). E: Tube wall temperature curve.

Figure. 26. Effect of 4.0×10^{-8} kg NaCl + 0.48×10^{-8} kg MgCl_2 + 0.16×10^{-8} kg CaCl_2 matrix on the absorbance of 6.0×10^{-13} kg of Cd (as NO_3^-) in WETA-82 without any matrix modifier. A: Pb signal alone.

B: Cd + matrix, not corrected for background (matrix). C: Background (matrix) alone. D: Pb signal, corrected for background (matrix).

E: Tube wall temperature curve.

remains nearly constant up to the matrix mass: 14×10^{-8} kg NaCl + 1.68×10^{-8} kg HgCl₂ + 0.56×10^{-8} kg CaCl₂; above this matrix mass, the Pb recovery gradually decreases.

In Figs. 27 and 28, the large decrease in the Cd and Pb recoveries may be explained as follows. The decrease may be due to the chloride vapour-phase interference [10,81] caused either by recombination of the analyte atoms with the chloride or by incomplete dissociation of the analyte chloride vapour. Vaporization of the bulk chloride matrix starts within the temperature range of 900-1000°C [67] at a time when the analyte atoms are being released in the vapour phase (the boiling points of CdCl₂ and PbCl₂ are 960°C and 950°C, respectively). It may be observed from Figs. 25 and 26 that the maxima in the atomic absorption pulses of Cd and Pb occur at the same time as the chloride matrix begins to vaporize.

Loss of the analyte vapour by expulsion may also occur. In WETA-82 (as in any other pulse-heated atomizers), vaporization and atomization of the sample occur when the temperature of the tube surface, and hence, the vapour-phase temperature is increasing rapidly. Therefore, in the case of high concentrations of volatile matrix (such as the chloride matrix), the effect of loss of analyte species by expulsion with expanding gases when the temperature is rapidly rising (besides increasing diffusional loss with increasing temperatures) may become significant; this is known as the carrier effect [82]. In fact, white fumes

Figure 27. Recovery of 4.0×10^{-14} kg of Cd (as NO_3^-) from the NaCl-MgCl₂-CaCl₂ matrix in WETA-82.

□ Peak-height. ○ Peak area

Figure 28. Recovery of 6.0×10^{-13} kg of Pb (as NO_3^-) from the $\text{NaCl-MgCl}_2\text{-CaCl}_2$ matrix in VETA-82.

coming out through the injection hole were observed during the atomization step, especially for high concentrations of the chloride matrix. Moreover, the inside walls of the atomizer were found to be coated with a layer of salt probably resulting from condensation of the chloride matrix.

From Figures 25 and 26, it may be seen that whereas the atomic absorption pulse of Cd in the presence of the matrix appears slightly later than that in the absence of the matrix, the Pb atomic absorption pulse appears earlier. An analogous shift of the Pb atomic absorption pulse in a similar matrix in a graphite atomizer has been reported in the literature [19,61,83]. It has been reported [9,30] that in graphite atomizers, Cd atoms are formed by thermal dissociation either of oxide or chloride, followed by vaporization of the metal, whereas Pb atoms are formed by carbon reduction of $PbO_{(s)}$ (which is thermodynamically favourable at the appearance temperature of Pb), followed by vaporization of the metal to form either the monomeric or dimeric lead species.

A reason for the above difference in the atomic absorption pulse shifts of Cd and Pb may be the fact that for Cd a hydrogen gas flow rate twice that for Pb was used. Hydrogen was reported by Frech et al. [60] to be effective in reducing chloride interference in the determination of Pb in steel.

Effect of nitric acid on the recovery of Cd and Pb

Figures 29 and 30 show absorption pulses of Cd and Pb, respectively, in the presence of the $\text{NaCl-MgCl}_2\text{-CaCl}_2$ matrix, with HNO_3 as a matrix modifier. It can be seen that the molecular absorption due to the matrix is reduced compared to that in Figs. 25 and 26. This is because a part of the matrix is eliminated as volatile HCl during the charring step, and a part is converted into the respective nitrates, e.g., NaNO_3 , which is decomposed at low temperatures. Thus, the chloride interference is reduced with consequent increase in the analyte recovery.

In the peak-height absorbance mode, 100% recoveries were obtained for both elements only for the low matrix mass (e.g., 10×10^{-8} kg NaCl + 1.2×10^{-8} kg MgCl_2 + 0.4×10^{-8} kg CaCl_2) and high concentrations of HNO_3 as shown in Figs. 31-32. However, for the matrix mass higher than the above, the recoveries were low even when high concentrations of HNO_3 were used. Similar trends are shown by the integrated absorbances (peak area) (Figs. 33-34), although recoveries in the integrated absorbance mode were slightly lower than those of the peak-height absorbance mode.

Addition of nitric acid also shifts Cd and Pb atomic absorption pulses to later times, especially for low concentrations of the acid, as shown in Table VIII. The atomic absorption pulse shifts in the presence of nitric acid probably indicate stabilization of the Cd and/or Pb by

Figure 29. Effect of 5.0×10^{-8} kg NaCl + 0.6×10^{-8} kg MgCl_2 + 0.2×10^{-8} kg CaCl_2 matrix on the absorbance of 4.0×10^{-4} kg of Cd (as NO_3^-) in 1% (v/v) HN_3 in WETA-82. A: Cd signal alone. B: Cd + matrix, not corrected for background (matrix). C: Background (matrix) alone. D: Cd signal, corrected for background (matrix). E: Tube wall temperature curve.

Figure 30. Effect of 4.0×10^{-8} kg NaCl + 0.48×10^{-8} kg MgCl_2 + 0.16×10^{-8} kg of CaCl_2 on the absorbance of 6.0×10^{-13} kg of Pb (as NO_3^-) in 1% (v/v) HNO_3 in WETA-82. A: Pb signal alone. B: Pb + matrix, not corrected for background (matrix). C: Background (matrix) alone. D: Pb signal, corrected for background (matrix). E: Tube wall temperature curve.

Figure 31. Effect of nitric acid on the recovery from peak-height of 4.0×10^{-14} kg of Cd (as NO_3^-) in WETA-82 from the following matrices.

- 5.0×10^{-8} kg NaCl + 0.60×10^{-8} kg MgCl_2 + 0.20×10^{-8} kg CaCl_2
- 10×10^{-8} kg NaCl + 1.2×10^{-8} kg MgCl_2 + 0.4×10^{-8} kg CaCl_2
- △ 15×10^{-8} kg NaCl + 1.8×10^{-8} kg MgCl_2 + 0.6×10^{-8} kg CaCl_2
- 20×10^{-8} kg NaCl + 2.4×10^{-8} kg MgCl_2 + 0.8×10^{-8} kg CaCl_2

Figure 32. Effect of nitric acid on the recovery from peak-height of 6.0×10^{-13} kg of Pb (as NO_3^-) in WETA-82 from the following matrices:

○ 2.0×10^{-8} kg NaCl + 0.24×10^{-8} kg MgCl_2
+ 0.08×10^{-8} kg CaCl_2

□ 4.0×10^{-8} kg NaCl + 0.48×10^{-8} kg MgCl_2
+ 0.16×10^{-8} kg CaCl_2

△ 6.0×10^{-8} kg NaCl + 0.72×10^{-8} kg MgCl_2
+ 0.24×10^{-8} kg CaCl_2

Figure 33. Effect of nitric acid on the recovery from peak area of 4.0×10^{-14} kg of Cd (as NO_3^-) in WETA-82 from the following matrices: ○ 5.0×10^{-8} kg NaCl + 0.6×10^{-8} kg MgCl_2 + 0.2×10^{-8} kg CaCl_2 . □ 10×10^{-8} kg NaCl + 1.2×10^{-8} kg MgCl_2 + 0.4×10^{-8} kg CaCl_2 . △ 15×10^{-8} kg NaCl + 1.8×10^{-8} kg MgCl_2 + 0.6×10^{-8} kg CaCl_2 . ● 20×10^{-8} kg NaCl + 2.4×10^{-8} kg MgCl_2 + 0.8×10^{-8} kg CaCl_2 .

Figure 34. Effect of nitric acid on the recovery from peak area of 6.0×10^{-13} kg of Pb (as NO_3^-) in WETA-82 from the following matrices:

- 2.0×10^{-8} kg NaCl + 0.24×10^{-8} kg MgCl_2
+ 0.08×10^{-8} kg CaCl_2
- 4.0×10^{-8} kg NaCl + 0.48×10^{-8} kg MgCl_2
+ 0.16×10^{-8} kg CaCl_2
- △ 6.0×10^{-8} kg NaCl + 0.72×10^{-8} kg MgCl_2
+ 0.24×10^{-8} kg CaCl_2

TABLE VIIIA. Effect of 10×10^{-8} kg NaCl + 1.2×10^{-8} kg MgCl_2 + 0.4×10^{-8} kg CaCl_2 on the appearance time of 4.0×10^{-14} kg Cd (as NO_3^-) in WETA-82 in different concentrations of nitric acid.

HNO_3 % (v/v)	Cd without the matrix Appearance Time	Cd with the matrix Appearance Time
	(ms)	(ms)
0	91	106
1	101	123
3	98	125
5	114	127

TABLE VIIIB. Effect of 6.0×10^{-8} kg NaCl + 0.72×10^{-8} kg MgCl_2 + 0.24×10^{-8} kg CaCl_2 on the appearance time of 6.0×10^{-13} kg Pb (as NO_3^-) in WETA-82 in different concentrations of nitric acid.

HNO_3 % (v/v)	Pb with the matrix Appearance Time	Pb with the matrix Appearance Time
	(ms)	(ms)
0	80	50
1	80	73
3	81	83
5	84	85

formation of nitrates, e.g., $\text{Cd}(\text{NO}_3)_2$, which are decomposed at low temperatures producing the respective oxides which are less volatile than the chlorides. This explanation is supported by the fact that appearance times for Cd and Pb from the matrix tend to converge towards the appearance times without the matrix as the acid concentration increases.

It is important to mention that the nitric acid may not change the mechanism of atomization; it may prevent the covoatilization of the analyte with the matrix by forming volatile HCl with the chloride matrix. The nitric acid may also form analyte nitrates which undergo thermal decomposition to relatively nonvolatile oxides, followed by atomization by carbon reduction or thermal decomposition of the analyte oxides.

Precision of measurements

The precision with WETA-82 (expressed as per cent relative standard deviation) is 10-15% for peak-height absorbance and 18-22% for peak-area (integrated) absorbance for both elements. The peak-height absorbance depends on the relative rates at which atoms are formed and lost, whereas the peak-area absorbance depends on the rate at which atoms leave the analysis volume. Because the volatile analytes are vaporized while the atomizer temperature is rapidly increasing, the matrix may alter the atomization time of the analyte, and hence, the atomization temperature. This in turn will alter the residence time of the analyte

atoms [67], and hence, the peak-area absorbance to a greater extent (relative to the peak-height absorbance). The poorer precision of the peak-area absorbance relative to that of the peak-height absorbance also suggests that the peak-height absorbance mode is preferable to the peak-area absorbance mode for determination of these elements.

A major factor affecting the precision of WETA-82 is its lack of a simultaneous background correction system. In this study, net absorbance was obtained by taking the difference between two sequential measurements of absorbances: one, by the analyte plus the matrix, and the other by the matrix alone. In this case, good reproducibility from run to run is not likely as surface conditions, vaporization rates of analyte and bulk matrix, temperature and other factors change from run to run. As Figs. 25, 28, 29, and 30 show, the matrix alone gives an absorbance of about 2 absorbance units. When absorption pulse-heights are subtracted, one from the other, to obtain the net absorbance due to the analyte alone, the two absorption pulses may not be completely and reproducibly resolved in time from run to run. All of these factors affect precision.

B. Effect of $\text{NaCl-MgCl}_2\text{-CaCl}_2$ matrix on the Cd absorbance signal in the constant-temperature furnace

The large interference effect of the $\text{NaCl-MgCl}_2\text{-CaCl}_2$ matrix on the Cd absorbance signal observed in WETA-82 was virtually eliminated when the same solutions were atomized from the constant-temperature furnace. However, the shape of the atomic absorption pulse shown in Fig. 35, with and without the matrix are slightly different. The Cd absorption pulse in the presence of the matrix appears at a slightly earlier time. A similar matrix showed the same effect on the Pb absorption pulse when atomized from the same atomizer [19]. The shift for Cd in the constant-temperature furnace was opposite to that observed in WETA-82, which might indicate a surface effect.

One hundred per cent recovery of Cd, both by peak-height and by peak-area (Fig. 36), was obtained even when the undiluted matrix was used without any matrix modifier. Similar recovery was obtained for Pb in presence of almost the same concentrations of matrix in the same atomizer [19], and for both elements by platform atomization [70] and by the probe atomization [84]

The better recovery of Cd from the constant-temperature furnace may be primarily due to the fact that volatilization and atomization of the sample are spatially separated in this atomizer. The drying and the charring step are done with the sample cup in the down position.

Figure 35. Effect of 5.0×10^{-8} kg NaCl + 0.6×10^{-8} kg MgCl_2 + 0.2×10^{-8} kg CaCl_2 on the absorption pulse of 1.2×10^{-12} kg Cd (as NO_3^-) in the constant-temperature furnace. A: Pb signal alone. B: Cd + matrix, not corrected for background (matrix). C: Background (matrix) alone. D: Cd signal, corrected for background (matrix). E: Tube wall temperature curve.

Figure 37. Effect of the sample cup position on the absorbance of

1.2×10^{-12} kg Cd (as NO_3^-) in the presence of 25.0×10^{-8} kg NaCl + 3.0×10^{-8} kg MgCl_2 + 1.0×10^{-8} kg CaCl_2 matrix. A: Cd signal alone. B: Cd + matrix, not corrected for background (matrix),

C: Background (matrix) alone. D: Cd signal, corrected for background. E: Tube wall temperature curve.

The sample cup is lifted to the bottom part of the main furnace after the latter has reached a constant temperature. Since volatilization occurs from the sample cup into the main furnace of much larger (~ 50 times) volume at constant temperature, loss of the analyte by expulsion with the expanding gases should be negligible. Also, high temperature experienced by the analyte vapour inside the main furnace should allow more complete dissociation of the analyte molecular vapour. Moreover, the loss of analyte by diffusion at the constant temperature should be less because the relatively long (75 mm) main furnace tube ensures a large effective path length through which the sample must diffuse to be lost from the tube ends. Molecules of Cd cannot escape from the tube ends of the main furnace without being subjected to the high, constant atomization temperature of 1800-1850 °C. Consequently, at this temperature, the analyte molecular vapour is extensively dissociated. In WETA-82, however, the short length of the tube (15 mm), as well as the design of the atomizer cavity which contains the tube (open at the ends), may allow part of the analyte molecular vapour to escape after volatilization and before sufficiently high temperature is achieved for its dissociation.

It is important to realize that almost complete temporal separation between the analyte and the matrix absorption pulse may be achieved with the constant-temperature furnace, as shown in Fig. 37. It was observed

TIME, ms

Figure 37. Effect of the sample cup position on the absorbance of 1.2×10^{-12} kg Cd (as NO_3^-) in the presence of 25.0×10^{-8} kg NaCl + 3.0×10^{-8} kg MgCl_2 + 1.0×10^{-8} kg CaCl_2 matrix. A: Cd signal alone. B: Cd + matrix, not corrected for background (matrix). C: Background (matrix) alone. D: Cd signal, corrected for background. E: Tube wall temperature curve.

that the design of the sample cup length, the position of the electrodes for the sample cup, and the timing of the commencement of the atomization cycle are critical in determining the shape and the peak-height of the analyte absorption pulse. Sample cups of (internal) depth greater than 12 mm are not recommended. Best results were obtained when the electrodes contacted the sample cup at the bottom (see Fig. 24, Experimental Section). Finally, the vaporization cycle of the sample cup should be controlled to begin a few ms after the sample cup has been lifted up and introduced into the main furnace. This will prevent premature vaporization and loss of the analyte vapour in the sample vaporization step.

It should be noted that the relative standard deviation for both peak-height and peak-area modes of measurement in Fig. 36 is $\pm 10\%$.

C. Effect of heating rate of WETA-82 on the recovery of Pb from the $\text{NaCl-MgCl}_2\text{-CaCl}_2$ matrix

The use of high heating rates in the capacitive discharge technique has been reported [66] to eliminate or reduce the MgCl_2 interference with the Pb peak-height absorbance as the analyte absorption pulse is shifted into the isothermal region of the tube wall temperature curve. Consequently, vapour-phase interferences by chloride matrix are greatly reduced if not eliminated [66]. This prompted a study of the effect of heating rates of WETA-82 on the

Figure 38. Effect of heating rate of WETA-82 on the recovery of 6.0×10^{-13} kg of Pb (as NO_3^-) from 2.0×10^{-8} kg NaCl + 0.24×10^{-8} kg MgCl_2 + 0.08 kg CaCl_2 .

○ Peak-height; □ Peak area; △ % pulse area under the isothermal region of the tube-wall temperature curve.

recovery of Pb 6×10^{-13} kg in a 5 μ L test solution of a diluted matrix of synthetic seawater. The synthetic seawater consisted of an aqueous solution of 5×10^4 μ g/mL NaCl_2 + 6×10^3 μ g/mL MgCl_2 + 2×10^3 μ g/mL CaCl_2). A 12.5 fold diluted matrix was chosen in order to avoid the use of a matrix modifier to reduce molecular absorption.

Figure 38 shows the recovery of the Pb from the above matrix, using the peak-height and the peak-area mode of measurement. Also shown is the percentage of peak-area inside the isothermal region of the tube wall temperature curve. The similarity of trends in these curves should be noted. Both peak-area and peak-height recoveries, especially the former, increase with increasing heating rates, the peak-area recovery reaching 100% at heating rates $> 10 \text{ K ms}^{-1}$ and above. This tends to confirm the arguments by many authors [19,57,66-68,70,73,76,79-80] that sufficiently high heating rates achieve higher recoveries of analytes by shifting the absorption pulses more into the isothermal region of the tube wall temperature curve, which is also higher temperature. This also confirms the explanation given in the previous section that higher atomization temperatures reduce vapour-phase interferences.

CONCLUSIONS

Shifts of the Cd absorption pulse by the matrix to an earlier time in WETA-82 suggests a mechanism of atomization from a tungsten surface different from that from a graphite surface.

This study has also shown that despite all the improvements in designs of pulse-heated atomizers, they have not yet provided a complete solution to matrix interference problem in atomic absorption spectrometry, especially those occurring in the vapour-phase, even with the use of matrix modifiers and high heating rates and high atomization temperatures. However, the constant-temperature furnace represents one of the best approaches to the possible solution of the matrix interference problem.

CHAPTER IV

MEASUREMENT OF TEMPERATURE OF THE TUNGSTEN TUBE ATOMIZER, WETA-82

INTRODUCTION

A. Surface temperature

Determination of the true temperature of an electrothermal atomizer by optical pyrometry is a difficult task because emissivity is highly dependent on both the target material and on the operational wavelength of the pyrometer.

Attempts have been made to overcome the problem of temperature measurements by optical pyrometry. De Witt and Kung [85] have measured the temperature ratios and emissivities at two wavelengths. Ruffino [86] has measured the surface temperature through radiance temperature and emissivities at two wavelengths. Unlike a single-wavelength pyrometer, a two-wavelength pyrometer does not require a knowledge of absolute values for emissivity, but only a knowledge of the ratio of the emissivities at the two chosen wavelengths [87, 88]. This ratio is usually known to much better accuracy than is the absolute value, particularly for metal rapidly heated in reactive atmospheres [89].

To avoid the effect of emissivity on the temperature

of a graphite tube measured by optical pyrometry, Falk [90] has suggested measurement of the blackbody spectral radiance of the graphite tube atomizer emitted through the ~~injection~~ hole in the centre of the tube because this minimizes the effect of the emissivity of the target.

Real bodies such as a tungsten tube deviate from an ideal blackbody. Therefore, it is necessary to make adequate corrections for the temperature of a real body measured by optical pyrometry. In this work the "apparent" temperature of a tungsten tube was measured by using optical pyrometers which had been calibrated for blackbody radiation by the manufacturers, and necessary corrections were applied to obtain the spectral radiance temperature of the tungsten tube, which will be henceforth called its true temperature.

B. Vapour temperature

Rief et al. [91] have critically reviewed the theoretical concepts underlying spectroscopic measurement of flame temperatures and their physical significance. The vapour temperature, as determined by the two-line atomic absorption method [92] reflects the population of the lower (electronic energy) levels of the line pair of the same element and is thus a more significant parameter of the lower-level atom population used in atomic absorption spectrometry than the methods based on the excited state population [32, 92]. The vapour temperature in a pulse-heated graphite furnace, as determined by the two-line atomic

absorption method, depends on many factors including the temperature gradient along the inside surface of the furnace, and the spatial distribution of the concentration of the thermometric species. However, the vapour temperature thus determined represents neither the average nor the weighted average temperature [91] of the vapour in a pulse-heated furnace, such as the Tungsten Electrothermal Atomizer (WETA-82), and will be called the effective (vapour) temperature (T_{eff}) [32, 93, 94].

Measurement of the tube wall temperature and the vapour temperature of WETA-82 has not been reported in the literature. Since these temperatures are vitally important for the study of the mechanisms for atomization in WETA-82, described in the following chapter, it was decided to determine them experimentally and to use these temperatures in the study of atomization mechanisms.

THEORY

A. Temperature of the tungsten tube wall of WETA-82

The spectral radiance of a blackbody at temperature T is related to the wavelength by the Planck equation [90].

$$L_b(\lambda, T) = 2 c_1 \lambda^{-5} \left[\exp\left(\frac{c_2}{\lambda T}\right) - 1 \right]^{-1} \quad 4.1$$

where $L_b(\lambda, T)$ = spectral radiance of a blackbody
($W m^{-3} sr^{-1}$).

- c_1 = Planck's first radiation constant
 $= 5.95 \times 10^{-17} \text{ m}^2 \text{ W}$
 c_2 = Planck's second radiation constant
 $= 1.4388 \times 10^{-2} \text{ m K}$
 λ = wavelength (m)
 T = absolute temperature (K)

No real body exists with a surface emitting blackbody radiance, and the radiance of the real body L_r is always smaller, by a factor of L_r/L_b (i.e., emissivity, ϵ), than the radiance of the blackbody at the same temperature. Therefore, the radiance of a real body is given by [90]

$$L_r(\lambda, T) = \epsilon(\lambda, T) L_b(\lambda, T) \quad (\text{W m}^{-3} \text{ sr}^{-1}) \quad 4.2$$

where $\epsilon(\lambda, T)$ = emissivity of the real body
 (dimensionless).

Generally, the signal of an optical pyrometer is proportional to [90]

$$\int_{\lambda_2}^{\lambda_1} L(\lambda, T_t) d\lambda \quad 4.3$$

where $L(\lambda, T_t)$ = spectral radiance of the real body
 $(\text{W m}^{-3} \text{ sr}^{-1})$

T_t = true temperature of the real body (K)
 λ_1 to λ_2 = the spectral wavelength working range of
 the pyrometer (m)

Usually, optical pyrometers have a narrow spectral band width, and consequently, the integration in Eqn 4.3 can

be omitted and all radiance values can be referred to a "central" wavelength inside the interval $\lambda_2 - \lambda_1$. An optical pyrometer with a broad spectral response cannot be calibrated in a unique way while the emissivity of the real body under study is changing with wavelength. Therefore, in the following section only narrow-band pyrometers are considered, and λ stands for the central wavelength. Such pyrometers are calibrated in "black" temperatures which means that the output of the pyrometer is the temperature of a blackbody with the same radiance as the object to be measured (see Eqn 4.2) [90].

The radiant energy measured by the pyrometer through the injection hole is given by [95]

$$L_b = \Omega_p A_r \int_0^\tau \int_{\lambda_1}^{\lambda_2} \epsilon(\lambda, T) \eta(\lambda) L_b(\lambda, T_t) d\lambda dt \quad 4.4$$

where L_p = radiant energy measured by the pyrometer (W s)

Ω_p = solid angle at the body subtended by the entrance optics of the pyrometer (sr)

A_r = observed area of the body (m²)

τ = time constant of the pyrometer (s)

$\eta(\lambda)$ = sensitivity function of the pyrometer (dimensionless)

T_t = true temperature of the real body (K)

$\lambda_1 \leq \lambda \leq \lambda_2$ = wavelength range of the pyrometer (m)

The output signal of the pyrometer S_p is proportional

to the measured radiant energy L_p [96]

$$S_p \propto L_p \quad 4.5$$

With a narrow-band pyrometer and for a body temperature which is changing slowly, the following equation can be derived [95]

$$S_p = \frac{\pi c_p d_o^2 A_r \Delta\lambda}{4 r_p^2} \epsilon(T_r, \lambda_m) \eta(\lambda_m) L_{\lambda b}(T_r) \quad 4.6$$

where S_p = pyrometer signal (V)

c_p = response constant of the pyrometer ($V W^{-1}$)

d_o = optical aperture of the pyrometer (m)

A_r = observed area of the body (m^2)

r_p = distance of the body from the entrance optics of the pyrometer (m)

ϵ = emissivity (dimensionless)

η = sensitivity of the pyrometer (dimensionless)

T_r = temperature of the real body (K)

$\Delta\lambda$ = spectral band width of the pyrometer (m)

λ_m = "central" (mean) wavelength of the pyrometer (m)

It is possible to express the radiance L_p in terms of a measured temperature of a blackbody, the so-called "black" temperature and calibrate the output signal S_p of the pyrometer by applying the following equation [95]

$$S_p = c_{np} L_b(T_b) = \frac{c'_{np}}{[\exp(c_2/T_b) - 1]} \quad 4.7$$

where c_{np} = calibration constant of the narrow-band
pyrometer ($V W^{-1} m^3 sr$)

$$c'_{np} = 2 \pi c^2 h \lambda^5 c_{np}$$

c = velocity of electromagnetic radiation in
vacuum

$$= 2.997925 \times 10^8 m s^{-1}$$

$$h = \text{Planck constant} = 6.62618 \times 10^{-34} J s$$

$$c'_2 = c_2 / \lambda k, \text{ where } k \text{ is Boltzmann constant}$$

$$T_b = \text{temperature of the blackbody (K)}$$

For $T \leq 3000 K$ and $\lambda < 1 \mu m$, Eqn 4.1 may be
simplified by neglecting the -1 in the brackets leading to
Wien's Law (approximation), which has been done to get the
right side of Eqn 4.7.

The true temperature T_t of a body is given by Eqn 4.8

[96]

$$T_t = \left(\frac{1}{T_{br}} + \frac{\lambda_p}{c_2} \ln \epsilon \right)^{-1}$$

where T_{br} = the "black" temperature of a real body (K)

λ_p = the operational wavelength of the pyrometer (m)

Equation 4.8 shows that the smaller the wavelength at
which the measurement is made and the closer the
approaches the value 1, the closer is the measured
temperature (T_{br}) to the true temperature (T_t). The measured
temperature is always lower than the true temperature.

When Wien's Law (approximation) is valid, from Eqn 4.7

we get the following expression for the pyrometer signal,

S_{pb} , calibrated with a blackbody [95]

$$S_{pb} = c_{np}' \exp(-c_2/T_b) \quad 4.9$$

Equation 4.9 shows that a plot of S_{pb} versus $1/T_b$ should give a straight line, from the slope of which the operational wavelength of the pyrometer can be evaluated. This procedure has been used to determine the operational wavelength of the pyrometer used in the measurement of the temperature.

The spectral radiance temperature (true temperature) of the tungsten tube wall was then determined by using Eqn 4.8 and the emissivity value of the tungsten from reference No. 97.

B. Vapour temperature of WETA-82

The two-line atomic absorption method used by Chakrabarti et al. [32] and L'vov [93] to determine the vapour-phase temperature in graphite furnace atomic absorption spectrometry with the graphite platform technique was used. Lead was used as the thermometric species with the 368.3 and 280.2 nm line pair. The vapour-phase temperature was calculated from the equations 4.10 and 4.11 [32,93].

$$T_{eff} = \frac{\log e}{k} \frac{E_2 - E_1}{\log \frac{A_1 g_2 f_2}{A_2 g_1 f_1}} \quad 4.10$$

$$T_{\text{eff}} = \frac{1770}{\log \left(3.68 \frac{A_1}{A_2} \right)} \quad 4.11$$

where T_{eff} = effective vapour temperature (K)
 k = Boltzmann constant ($1.38066 \times 10^{-23} \text{ J K}^{-1}$)
 E_1, E_2 = energy of the upper and the lower electronic level (cm^{-1})
 A_1, A_2 = absorbance at the two wavelengths used
 g_1, g_2 = statistical weight of the electronic energy level (dimensionless)
 f_1, f_2 = oscillator strength for the two wavelengths used (dimensionless).

EXPERIMENTAL

Apparatus

The tungsten electrothermal atomizer, WETA-82, described in chapter I-III, was used.

A two-channel digital oscilloscope, model 2090, fitted with a model 201 plug-in unit and a disk recorder (all from Nicolet Instrument Co., Madison, Wisconsin, USA) were used to record the output signals.

The surface temperature was measured with two optical pyrometers - one 300 series for temperature $\leq 1000 \text{ K}$, and the other 11x30 series for temperatures $> 1000 \text{ K}$ - both were manufactured by Ircon Inc. (Skokie, Illinois, USA).

General procedure

The temperature was measured at the surface of the tungsten strips (which together make up the tungsten tube) at the points shown in Fig. 39.

The pyrometer was focussed on the point 1 (outside the upper strip) and the output signal recorded. Then the strips were inverted and the pyrometer was focussed on the point 2 (outside the lower strip) and the input power to the tungsten tube was increased until the output signal attained the same voltage as for the point 1. This input power was kept constant and the temperature was measured at the points 3 and 4; the former (point 3) which is T_{br} of the Eqn 4.8, was measured directly below the injection port on the outside of the lower strip, and the latter (point 4) on the same point on the inside of the lower strip. It is important to mention that the pyrometer was focussed on the point 4 at an angle corresponding to the tangent of the ratio of the diameter of the injection port and the diameter of the tungsten tube (i.e., 1.5 mm/5mm). The pyrometer thus accepted light from a cone having a vertex angle of 16 degrees at the point 4. Such a position of the pyrometer was chosen in order to increase the radiation intensity received by the pyrometer relative to that received when it was focussed perpendicular to the surface [98]. Since the emissivity value of the tungsten used in this work was taken from Touloukian and De Witt [97], the temperature at the

(a)

(b)

Figure 39. Schematic diagram of the points at which the temperature of the tungsten tube was measured. a: End of view of the tungsten tube. B: Side view of the tungsten tube.

Figure 42. Correlation of the (uncorrected) tube wall temperature at the point 4 with the calculated (true) temperature.

Charring temperature = 610 K . Heating rate: $\circ 15 \text{ K ms}^{-1}$, $\square 5 \text{ K ms}^{-1}$.

Dashed part of the curve marks the high-temperature region in which Wien's approximation is not valid.

TABLE IX. Measurement of the surface temperature of WETA-82

Output of the Photodiode (Voits)			Temperature Set on WETA-82 (K)			Temperature Measured at Point 4 (K)			Calculated (True) Temperature (K)		
Heating Rate Setting 15 K ms ⁻¹	Heating Rate Setting 5 K ms ⁻¹	Heating Rate Setting 15 K ms ⁻¹	Heating Rate Setting 5 K ms ⁻¹	Heating Rate Setting 15 K ms ⁻¹	Heating Rate Setting 5 K ms ⁻¹	Heating Rate Setting 15 K ms ⁻¹	Heating Rate Setting 5 K ms ⁻¹	Heating Rate Setting 15 K ms ⁻¹	Heating Rate Setting 5 K ms ⁻¹	Heating Rate Setting 15 K ms ⁻¹	Heating Rate Setting 5 K ms ⁻¹
Atomization Temperature (with above heating rates)											
6.98 ± 0.45	9.25 ± 0.65	2770 ± 0.3	2820 ± 0	3210 ± 0.3	3200 ± 0.3	3350 ± 0.2	3350 ± 0.2	3350 ± 0.2	3350 ± 0.2	3350 ± 0	3350 ± 0
7.84 ± 0.50	7.88 ± 0.60	2540 ± 0.1	2560 ± 0.2	2950 ± 0.3	2920 ± 0.2	3080 ± 0.4	3080 ± 0.4	3080 ± 0.4	3080 ± 0.4	3110 ± 0.3	3110 ± 0.3
7.20 ± 0.55	7.00 ± 0.85	2410 ± 0	2410 ± 0.2	2729 ± 0	2680 ± 0.2	2830 ± 0.3	2830 ± 0.3	2830 ± 0.3	2830 ± 0.3	2780 ± 0.4	2780 ± 0.4
5.85 ± 0.85	6.00 ± 1.20	2160 ± 0	2210 ± 0.5	2420 ± 0	2440 ± 0.2	2550 ± 0.2	2550 ± 0.2	2550 ± 0.2	2550 ± 0.2	2570 ± 0.2	2570 ± 0.2
5.20 ± 0.90	5.46 ± 0.90	2050 ± 0	2090 ± 0.2	2270 ± 0	2290 ± 0.8	2360 ± 0	2360 ± 0	2360 ± 0	2360 ± 0	2460 ± 0.4	2460 ± 0.4
4.82 ± 1.00	4.40 ± 1.10	1960 ± 0	1880 ± 0.3	2130 ± 0	2080 ± 1.0	2280 ± 0.2	2280 ± 0.2	2280 ± 0.2	2280 ± 0.2	2190 ± 0.2	2190 ± 0.2
3.90 ± 0.00	*	1760 ± 0	*	1970 ± 0	*	2050 ± 0	2050 ± 0	2050 ± 0	2050 ± 0	*	*
3.20 ± 0.00	3.40 ± 0.00	1650 ± 0.3	1690 ± 0.3	1820 ± 0	1870 ± 0	1920 ± 0	1920 ± 0	1920 ± 0	1920 ± 0	1960 ± 0	1960 ± 0
2.20 ± 0.00	*	1570 ± 0.3	*	1720 ± 0	*	1800 ± 0	1800 ± 0	1800 ± 0	1800 ± 0	*	*
1.95 ± 3.00	1.94 ± 1.60	1380 ± 0	1410 ± 0.4	1520 ± 0	1520 ± 0	1550 ± 0.3	1550 ± 0.3	1550 ± 0.3	1550 ± 0.3	1530 ± 0	1530 ± 0
Charring Temperatures (with unknown heating rates)											
2.7 ± 0.00		1920 ± 0		1710 ± 0		1770 ± 0		1770 ± 0		1770 ± 0	
no signal		1040 ± 0		980 ± 0		890 ± 0		890 ± 0		890 ± 0	
no signal		800 ± 0		610 ± 0		610 ± 0		610 ± 0		610 ± 0	

* not measured

± values represent uncertainties expressed as percent relative standard deviation

temperature at the point 4 approaches the calculated (true) value. The atomization temperature set on the dial on the instrument panel of WETA-82 was much lower than the measured and the calculated (true) temperature.

As mentioned above, the atomization temperatures set on the dial on the instrument panel of WETA-82 did not agree with the measured nor with the calculated (true) temperature. However, for a given dial setting, the output voltage of the photodiode does not change appreciably. Therefore, a calibration curve can be made using the output voltage of the photodiode as a function of the measured (inside) surface temperature (Fig. 40), and of the calculated (true) temperature (Fig. 41). Correlation of the measured temperature with the calculated (true) temperature is presented in Fig. 42. A similar correlation with the charring (i.e., pre-atomization) temperature is presented in Fig. 43.

The error in the calculated (true) temperature at 3000 K due to an error in the emissivity value has been calculated to be 5.6 K, which is negligible. Therefore, the error in the calculated (true) temperature would be essentially that resulting from reproducibility of the measurement, and has been determined to be $\leq \pm 20$ K (taken as one standard deviation) for six-to-ten replicate measurements.

Figure 40. Correlation of the (uncorrected) tube wall temperature at point 4 with the output of the photodiode.

Charring temperature = 610 K. Heating rates: $\circ$ 15 K ms⁻¹,
 $\square$ 5 K ms⁻¹.

Dashed part of the curve marks the high-temperature region in which Wien's approximation is not valid.

Figure 41. Correlation of the voltage output of the photodiode with the calculated (true) temperature.

Charring temperature = 610 K. Heating rates: ○ 15 K ms⁻¹,
 □ 5 K ms⁻¹.

Dashed part of the curve marks the high-temperature region in which Wien's approximation is not valid.

Figure 42. Correlation of the (uncorrected) tube wall temperature at the point 4 with the calculated (true) temperature.

Charring temperature = 610 K. Heating rate: $\circ$ 15 K ms⁻¹, $\square$ 5 K ms⁻¹.

Dashed part of the curve marks the high-temperature region in which Wien's approximation is not valid.

Figure 43. Correlation of the charring temperature of the tungsten tube wall measured at point 4 with the calculated (true) temperature.

B. Vapour temperature

Figure 44 shows effective vapour temperature (T_{eff}) at three tube wall temperatures (true) as a function of the heating time of the tungsten furnace (WETA-82) obtained by using lead (the line pair at the wavelengths 368.3 and 280.2 nm) as the thermometric species. The charring temperatures have been taken to be the initial temperatures of the tube wall temperature curves. The figure shows that at relatively long time both the tube wall temperatures (true) and the effective vapour temperatures attain nearly steady-state values. The figure also shows that effective, steady-state, vapour temperatures at the three tube wall temperatures (true) are lower (200-300 K) than the steady-state, tube wall temperatures (true) and follow the same trend as the tube wall temperatures (true).

The T_{eff} values are the average of three to five replicate determinations. However, partly because of the high heating rates used ($> 10 \text{ K ms}^{-1}$) noisy absorbance signals of lead were obtained especially for the tail-parts of the absorption pulses.

It has been reported [32] that in a graphite furnace, the T_{eff} depends on many factors such as heating rates, geometry and design of the atomizer, water-cooling and convective gas flow. Therefore, distribution of the tungsten tube wall (true) temperature along the tube length and across the tube diameter was measured at the points numbered

Figure 44. Temperature of the WETA-82 as a function of heating time.

Charring temperature = 500 K. Heating rate = 12.5 K ms^{-1} .

○ Tube wall (true) temperature = 2120 K.

● Effective vapour temperature.

Charring temperature = 610 K. Heating rate = 15 K ms^{-1} .

□ Tube wall (true) temperature = 2460 K.

■ Effective vapour temperature.

Charring temperature = 700 K. Heating rate = 15 K ms^{-1} .

△ Tube wall (true) temperature = 3240 K.

▲ Effective vapour temperature.

Figure 44

in Fig. 39. It was found that at 2830 K at the point 1, the temperature at the point 2 was ≈ 50 K lower, but there was no difference between the temperatures at the points 1 and 1'; similarly, the difference between the temperatures at the points 5 and 5' was ≤ 30 K. The temperature at the point 2 was ~ 30 K higher than that at the point 3. However, the temperature at the point 5" was ≈ 160 K lower than that at the point 1.

CONCLUSIONS

The tube wall temperature (true) has shown that the output signal obtained from the photodiode does not correspond to the dial setting of WETA-82. Therefore, in order to determine the true temperature of the tungsten tube wall it is necessary to measure this by optical pyrometry and to correct the measured temperature for the emissivity. The tungsten tube wall temperature (true) has been observed to remain almost unchanged from firing to firing for the same tungsten tube and for long-term work period, which results in very good precision and day-to-day reproducibility of the measurements.

As in other pulse-heated atomizers, the effective vapour temperature of WETA-82 has been found to lag behind the tube wall temperature and to reach a steady-state value at the latter part of the atomization cycle; the steady-state vapour temperature is about 200-300 K lower than the steady-state temperature of the tungsten tube wall.

CHAPTER V

MECHANISM OF COBALT AND TITANIUM ATOMIZATION IN GRAPHITE AND TUNGSTEN ELECTROTHERMAL ATOMIZERS

INTRODUCTION

The process of atom formation in electrothermal atomizers has been discussed by several authors. By assuming that the vapour temperature is equal to the graphite tube wall temperature, Fuller [23,99], has proposed a kinetic model of atom formation of Cu in The Perkin-Elmer Heated Graphite Atomizer, HGA-70. Campbell and Ottaway [26] have suggested that the appearance temperature of the analyte signal may be correlated with the temperature at which reaction 5.1 becomes thermodynamically feasible ($\Delta G^{\theta} < 0$).

These authors (26) have reported good agreement between the experimental and the calculated temperature for 18 of 27 elements studied. Aggett and Sprott [25] have compared the appearance temperature of 16 elements in both graphite and tantalum atomizers to determine whether or not the above reduction would occur. They have observed that from the graphite surface, the appearance temperatures for Co, Fe,

Ni, and Sn are lower than those from the tantalum surface and have concluded that graphite probably acts as a reducing agent in the atomization of these elements. They have also observed that the appearance temperatures for Pb, Cu and Cr are essentially the same from a carbon rod as from a tantalum strip.

Sturgeon et al. [9,27] are of the opinion that Campbell and Ottaway [26] overestimated the appearance temperatures and have shown that the graphite tube wall temperatures that the latter used as the appearance temperatures are too high because the vapour temperature lags behind the tube wall temperature. Sturgeon et al. [9,27] have proposed a thermodynamic-kinetic approach to the study of mechanisms of atomization from the Heated Graphite Atomizer (HGA-2100). From their results, they have concluded that thermal dissociation or reduction of the metal oxide, or thermal dissociation of the halides or the carbides are the major pathways that lead to the formation of gaseous analyte atoms in the graphite atomizer.

On the basis of a simple thermodynamic model, Byrne [29] has suggested that the role of carbon in the atomization process has been over-emphasized. He has reported that only 4 (Co, Fe, Ni, and Sn) of 15 elements studied appear to have significantly higher appearance temperatures in a tantalum atomizer, and attributes this to an inhibiting effect of the tantalum surface rather than to carbon reduction.

To assess the role of carbon in the atomization of cobalt, the atomization model proposed by Sturgeon et al. [9,27] has been used in this work. Sychra et al. [100] have reported a mechanism for the atomization of cobalt and other elements from a tungsten surface, which will be compared in this work with the proposed mechanism for the cobalt atomization from a pyrolytic graphite platform. The pyrolytic graphite platform has been chosen because atomization of cobalt from the platform occurs at a constant vapour temperature; therefore, the rate of loss of Co atoms by diffusion at the constant vapour temperature should be constant, which will simplify the study of cobalt atomization mechanisms.

Atomization mechanism can be studied also by using empirical approaches, e. g., using decomposition/atomization curves [31]. By using decomposition/atomization curves, Wahab and Chakrabarti [31] have reported the mechanism of yttrium atom formation from pyrocoated graphite, and tantalum- and tungsten-lined surface of graphite tubes. The same approach has been used in this work to elucidate the mechanism of titanium atomization from both graphite and tungsten surfaces.

Since mechanisms of atomization from a graphite platform placed inside a heated graphite atomizer have also been studied in this work, it is necessary to provide a theory for the heating of the graphite platform. This is provided below.

THEORY

A. Heat transfer by radiation from a heated graphite tube to a graphite platform placed inside a heated graphite tube atomizer

It has been established by Chakrabarti et al. [32] that the graphite platform is heated primarily by radiation heat transfer from the heated graphite tube wall - the heat transfer by conduction and convection has been shown to contribute only a small fraction of the total heat transfer to the graphite platform.

The rate of heat transfer ($\dot{q}_r$) from the tube wall to the platform (both considered as gray bodies) is [100]

$$\dot{q}_r = \sigma A_1 \mathcal{F}_{1-2} (T_1^4 - T_2^4) \quad 5.2$$

where $\dot{q}_r$ = rate of heat transfer (W)

A_1 = surface area of the tube (m^2)

T_1 = absolute temperature of the tube wall (K)

T_2 = absolute temperature of the platform (K)

σ = Stefan-Boltzmann constant

$$= 5.677 \times 10^{-8} \text{ W } m^{-2} K^{-4}$$

$\mathcal{F}_{1-2}$ = Interchange Factor (a factor which modifies the equation for a perfect radiator and takes into account the emissivity and the relative geometries of the graphite platform and the tube wall).

Since both the tube wall and the platform are heated from the room temperature in pulse-heated graphite furnaces, and since the temperature of the platform is much lower than that of the heated tube wall except at relatively long heating time of the tube wall, T_2^4 in the term $(T_1^4 - T_2^4)$ can be ignored during the initial period of heating of the tube wall and Eqn 5.2 can be rewritten as Eqn 5.3

$$\dot{q}_r = \sigma A_1 T_{1-2}^4 T_1^4 \quad 5.3$$

The rate of heat storage, $\dot{q}_s$, in the graphite platform is given by [32]

$$\dot{q}_s = m C_{p_2} \frac{dT_2}{dt} \quad 5.4$$

where m = mass of the platform (g)

C_{p_2} = specific heat of the platform ($J \text{ kg}^{-1}$)

According to Eqn 5.3, the rate of heat transfer, $\dot{q}_r \propto T_1^4$ (since all other terms in Eqn 5.3 are constant for a given furnace and platform). Therefore, the platform begins to be heated significantly only when the tube wall has reached a high temperature (i.e., at a relatively long heating time of the tube wall). This results in a delay of the atomization of the analyte from the platform, shifting the analyte absorption pulse into the constant temperature region of the tube wall temperature curve, and hence, into the constant temperature region of the gas temperature curve

since the gas temperature curve runs parallel to the tube wall temperature curve at relatively long heating time of the tube wall [32]. The magnitude of the absorption pulse shift depends on the mass of the platform. The constant gas temperature is also significantly higher than what would have been the gas temperature had the analyte been atomized from the tube wall instead of the platform. Also, atomization of the analyte from the tube wall would have occurred much earlier at a time when the tube wall temperature would have been much lower (than its steady-state temperature at a much later heating time) and when the tube wall temperature would have been rising very rapidly, causing a great expansion of the gas phase with the resulting partial loss of the gas-phase analyte species by expulsion with the expanding gas phase.

In platform atomization, as the absorption pulse is shifted into a steady-state, higher temperature of the gas, the extent of dissociation of the analyte molecules should increase. This should result in an enhancement in the sensitivity, especially for relatively volatile elements, such as Cd and Pb, which would have been partly lost by expulsion with the expanding gas phase had they been atomized from the tube wall. Moreover, by the time that atomization from the platform occurs, the gas has expanded to its final volume at its steady-state temperature. Hence, in platform atomization, loss of analyte species by expulsion with the expanding gas phase is eliminated or reduced, which is the cause for enhancement in the sensitivity and

for elimination or reduction in matrix interferences.

B. Mechanism of atomization

Several mechanisms of atomization are possible in electrothermal atomizers. According to Sturgeon et al. [9,27], the majority of precursors to gas phase atoms are either metal oxides (generally, MO) or halides which may undergo the following atomization mechanisms.

a. Dissociation of the oxide vapour

b. Reduction of the solid oxide by solid carbon

c. Dissociation of the halide

where M = analyte atom

O = oxygen atom

C = carbon atom

X = a halogen atom

The combined thermodynamic-kinetic approach of

Sturgeon et al. [9.27] assumes a gas phase-condensed-phase equilibrium between $\text{MO(s/l)}/\text{M}_x\text{O}_y\text{(s/l)}$, M(s/l) , and $\text{M}_2\text{(g)}$. Such an equilibrium should be more properly labelled quasi-equilibrium [9.27].

where k_f and k_r are rate constants for the forward and reverse reactions, k_f/k_r is the equilibrium constant for the phase equilibrium, and k_d is the rate constant for the diffusional loss of gas-phase analyte molecules.

For Eqn 5.5, the rate of production of atoms at any given temperature T (K) may be expressed as

$$\frac{dp_{\text{M(g)}}}{dt} = \frac{1}{x} k_1 P_{\text{M}_x\text{O}_y\text{(g)}} \quad 5.9$$

where $P_{\text{M}_x\text{O}_y\text{(g)}}$ is the partial pressure of the metal oxide, and k_1 is the rate constant for the dissociation of $\text{M}_x\text{O}_y\text{(g)}$.

According to transition-state theory [104], the rate constant k_1 can be formulated in thermodynamic terms, by introducing the standard free energy change for the reaction

$$k_1 = \frac{kT}{h} e^{-\Delta G^\ddagger/RT} = \frac{kT}{h} e^{-\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT} \quad 5.10$$

where k and h are Boltzmann constant and Planck constant, respectively, $\Delta G^{\theta\dagger}$, $\Delta S^{\theta\dagger}$ and $\Delta H^{\theta\dagger}$ are the free energy of activation, the entropy of activation and the enthalpy of activation, respectively, T is the absolute temperature (K), and R is the gas constant.

Since the measured absorbance is proportional to the partial pressure of the analyte vapour $P_M(g)$, Sturgeon et al. [9,27] combined the van't Hoff equation [102] and equation 5.10 to develop an equation that relates the measured absorbance, A_T , to the energy associated with the production of analyte atomic vapour

$$\log A_T = - \frac{E_a + \Delta H^{\theta}}{2.3 RT} + A_0 \quad 5.11$$

where E_a is the activation energy of the process (kJ mol^{-1}), ΔH^{θ} is the standard enthalpy change for the phase transition, and A_0 is the sum of the entropy of activation term and the log of several physical constants.

It may be seen from Eqn 5.11 that a plot of the $\log A_T$ versus the reciprocal of the absolute temperature should yield a straight line with slope equal to $-(E_a + \Delta H^{\theta})/2.3R$ and intercept $= A_0$. The slope of the plot may be identified with the sum of the activation energy and the enthalpy change for the phase transition. According to Szwarc [104], the E_a value is an excellent approximation to the bond dissociation energies of the gaseous species, and will be identified with the latter in this work.

The energy term in Eqn 5.11 may be correlated with the following values [9]: the dissociation energy of the metal oxide, the dissociation energy of the metal halide, the heat of atomization of the metal, the dissociation energy of the metal-metal bond or the dissociation energy of the metal-carbon bond. In the model of Sturgeon et al. [9,27], $\log A_T$ versus $1/T$ plots may sometimes appear as a composite of two or more intersecting straight lines of different slopes. Such plots represent the possible transitions that may occur as the temperature increases and the major supply of analyte atoms $M(g)$ changes from one species to another. If the appearance temperature of the analyte is higher than its melting point or boiling point, then the enthalpy change of the phase transition will not be observable by this technique, and the slope of the straight line plot will be simply equal to $-E_a/2.3 R$.

Since the intercept A_0 in Eqn 5.11 includes the entropy change factor (a variable quantity) and some physical constants and temperature-dependent parameters, its magnitude cannot be evaluated by extrapolation. Hence, this term will not be considered further in this discussion.

EXPERIMENTAL

Apparatus

The WETA-82 and The Perkin-Elmer spectrometer model 5000, described in chapter I and II, respectively, were used. A modified atomic absorption spectrometer: The Perkin-Elmer model 503, equipped with a Deuterium-Arc Background, Corrector and an HGA-74 atomizer, was also used. The atomizer was fitted with a laboratory-made power supply with independent control of the heating rate and the temperature. The details of this instrument have been published earlier [70]. The temperature of the graphite tubes was measured with an Ircan model 11x30 series automatic optical pyrometer (Ircan, Inc., Skokie, Illinois).

Absorbance and temperatures profiles were recorded with a Nicolet two-channel digital oscilloscope, model 2090-III, fitted with a model 201 plug-in (Nicolet, Instrument Co., Madison, Wisconsin). A four-channel digital oscilloscope, model 4090, with two plug-in, model 4562 (Nicolet Instrument Co., Madison, Wisconsin), and a Hewlett-Packard plotter, model 7470A, were used to trace the absorbance and the temperature profile.

Cobalt and titanium hollow-cathode lamps (Cathodeon and The Perkin-Elmer, respectively) were operated at the recommended lamp current.

Experimental conditions for each element are

presented in Tables X and XI.

Reagents

A stock solution containing 1000 $\mu\text{g/mL}$ of Co was prepared by dissolving the metal (99.99% pure) in ULTREX nitric acid. A stock solution containing 1000 $\mu\text{g/mL}$ of Ti was prepared by dissolving the metal (99.99% pure) in 100 mL (1:1 v/v) ULTREX sulphuric acid and water. The above stock solutions were diluted with ultrapure water to make the solutions 1% (v/v) in nitric acid and 10% (v/v) in sulphuric acid, respectively. The acids were manufactured by Baker Chemical Co. Ultrapure water of resistivity 18.3 megohm-cm was obtained direct from a Milli-Q2 water purification system (Millipore Corporation). All test solutions of Co and Ti were prepared in 0.2% (v/v) HNO_3 and in 1% (v/v) $\text{HF} + 1\%$ (v/v) HNO_3 , respectively, by diluting the above stock solutions to the desired concentration with ultrapure water immediately prior to use.

Pyrolytic graphite platform

Rectangular platforms of pyrolytic graphite (manufactured by Super-Temp, Santa Fe Springs, California, USA) of dimensions: 18 mm long, 0.40 mm wide, 0.26 mm thick, and weighing 41 mg, were used. To prevent physical contact between the sides of the platform and the tube wall, 0.5 mm-deep cuts were made along the lateral edges of the platform. The platform was placed inside a pyrolytically-coated

TABLE I. Optimum experimental conditions used for the study of cobalt atomization mechanism

Experimental Parameters	Atomizers	
	HGA-74	WETA-82
Mass (kg) of Co.	1.0×10^{-12}	1.0×10^{-13}
Wavelength (nm).	240.7	240.7
Spectral Band Pass (nm)	0.2	0.2
Lamp Current (mA)	10	20
Drying I Temperature ($^{\circ}\text{C}$)	120	90
Time (s)	40	30
Drying II Temperature ($^{\circ}\text{C}$)	-	120
Time (s)	-	30
Charring I Temperature ($^{\circ}\text{C}$)	-	330
Time (s)	-	5
Charring II Temperature ($^{\circ}\text{C}$)	460	440
Time (s)	20	5
Atomization Temperature ($^{\circ}\text{C}$)	2800	2950
Time (s)	3	0.6
Argon Flow Rate (L min^{-1})	65 ^a	2.5 ^a
Hydrogen Flow Rate (L min^{-1})	-	0.4
Heating Rate (K ms^{-1})	1.4	15

^a Gas flow mode of operation

TABLE XI. Optimum experimental conditions used for the study of titanium atomization mechanism

Experimental Parameters	Atomizers	
	BGA-74	WETA-82
Mass (kg) of Ti	1.0×10^{-11}	5.0×10^{-12}
Wavelength (nm)	365.3	365.3
Spectral Band Pass (nm)	0.2	0.2
Drying I Temperature ($^{\circ}\text{C}$)	120	100
Time (s)	35	30
Drying II Temperature ($^{\circ}\text{C}$)	-	120
Time (s)	-	30
Charring I Temperature ($^{\circ}\text{C}$)	-	300
Time (s)	-	10
Charring II Temperature ($^{\circ}\text{C}$)	1500	1350
Time (s)	5	5
Atomization Temperature ($^{\circ}\text{C}$)	2800	3350
Time (s)	5	0.8
Argon Flow Rate (L min^{-1})	CS^a	2.5
Hydrogen Flow Rate (L min^{-1})	-	0.8
Heating Rate (K ms^{-1})	HP^b	15

^aGas Stop mode of operation

^bMaximum Power Mode of operation

graphite tube (The Perkin-Elmer part number B0091-1504) between the grooves cut inside the tube.

Gases

Argon and hydrogen gas of 99.995% purity (Union Carbide Canada Ltd.) were used.

General procedure

The Co test solution (5 μ L) was carefully deposited on the platform with a 5 μ L Eppendorf pipet (fitted with disposable plastic tips) in such a way as to prevent spilling of the solution over the platform during the drying step. The Ti solution (10 μ L) was carefully deposited on the graphite tube or the tungsten tube with an autosampler, model AS-1 (The Perkin-Elmer), or manually with a 10 μ L Hamilton syringe, respectively.

Absorbance values reported are corrected for the blanks and represent the mean value of two to five replicate determinations.

RESULTS AND DISCUSSION

A. Mechanism of cobalt atom formation

Cobalt nitrate, when heated, is converted into cobalt monoxide, which is the most stable species at high temperatures [105-107]:

The activation energy, E_a , for the above atomization reaction may be compared with one of the following processes: a) the heat of vaporization of the metal, b) the heat of sublimation of the metal, c) the dissociation energy of the metal-oxygen bond, d) the carbon reduction of the metal oxide, and e) the dissociation energy of the metal dimer.

Figure 45 shows the activation energy (E_a) plot obtained by plotting the $\log A_T$ versus $1/T$ for atomization of cobalt taken as nitrate (in an aqueous solution). Activation energy values of 418, 429 and 425 kJ mol^{-1} for atomization from the platform, the graphite tube wall and the tungsten tube wall, respectively, were obtained from Fig. 45. The values represent the average of five (for the platform and for the tungsten tube) and three (for the graphite tube) replicate determinations. Table XII lists the literature (energy) values and the experimental activation energy values.

Tables XIII, and XIV show the appearance temperatures and the standard free energy change for carbon reduction of $\text{CoO}(\text{s})$, respectively. Table XII shows that the activation energy values agree fairly well with the heat of sublimation of cobalt. The activation energy values also agree closely with those reported by Sturgeon et al. [9,27] for the Co atomization from graphite tube wall and those

Figure 45. Arrhenius plot for 1.0×10^{-11} kg Co (as NO_3^- in an aqueous solution) for atomization from: $\square$ Graphite tube wall.
 $\circ$ Platform. $\triangle$ Tungsten tube wall

Figure 45.

TABLE XI. ΔH° for cobalt sublimation, carbon reduction of the oxide, and dissociation of the oxide compared with the experimental activation energy

Element	ΔH° , kJ mol ⁻¹					Activation Energy kJ mol ⁻¹
	$H_{(s)} \rightarrow H_{(g)}$	$H_{(g)} \rightarrow H_{(g)}$	$MO_{(s)} \rightarrow H_{(g)} + O_{(g)}$	$MO_{(s)} + C \rightarrow H_{(g)} + CO_{(g)}$	$H_{2(g)} \rightarrow H_{(g)}$	
Co	439	389	368	568	167	^a 418 ± 24% ^b 429 ± 6% ^c 425 ± 10%

^a Graphite platform

^b Graphite tube wall

^c Tungsten tube wall

Thermodynamic data taken from references No. 107-110

± values represent uncertainties expressed as percent relative standard deviation

TABLE XIII. Appearance temperature of cobalt atomization from various atomizer surfaces

Atomizer and Surface	Appearance Temperature (K)
Graphite platform, BGA-74	1640 $\pm$ 4%
Pyrolytically-coated graphite tube wall, BGA-74	1800 $\pm$ 1%
Tungsten tube wall, WETA-82	2050 $\pm$ 0.8%

$\pm$ values represent uncertainties expressed as per cent relative standard deviation

TABLE XIV. Standard free energy change for the reduction of $\text{CoO}_{(s)}$ by solid carbon

$$\Delta G_R^\theta = \Delta G_{f, \text{Co}}^\theta + \Delta G_{f, \text{CO}}^\theta - \Delta G_{f, \text{CoO}}^\theta - \Delta G_{f, \text{C}}^\theta$$

Temperature (K)	$\Delta G_{f, \text{Co}}^\theta$	$\Delta G_{f, \text{CO}}^\theta$	$\Delta G_{f, \text{CoO}}^\theta$	$\Delta G_{f, \text{C}}^\theta$	ΔG_R^θ
	kJ mol ⁻¹				
1400	0	- 235.19	- 136.10	0	- 98.89
1500	0	- 243.77	- 128.94	0	- 114.83
1600	0	- 252.31	- 121.96	0	- 130.35
1700	0	- 260.80	- 114.92	0	- 145.88
1800	0	- 269.25	- 107.60	0	- 161.98

Thermodynamic data taken from references No. 107-110

reported by Sychra et al. [100] for the Co atomization in WETA-82. It is also clear from Tables XIII and XIV that reduction of $\text{CoO}_{(s)}$ is thermodynamically favourable well below its appearance temperatures in the graphite furnace and in the WETA-82. However, the energy values for these reduction reactions which occur below the appearance temperatures are not observable with the present technique, since measurable absorbance values can be obtained only above the appearance temperatures. It is therefore, reasonable to conclude that reduction of $\text{CoO}_{(s)}$ by solid carbon to $\text{Co}_{(s)}$ must have occurred at temperatures below the appearance temperatures, followed by sublimation of cobalt. It has been reported in the literature [105] that at 900°C $\text{CoO}_{(s)}$ may be completely reduced to $\text{Co}_{(s)}$ by an excess of carbon.

In WETA-82, there are two possibilities: reduction of $\text{CoO}_{(s)}$ either by solid tungsten (Table XV) or by H_2 gas (Table XVI). The reduction of $\text{CoO}_{(s)}$ by solid tungsten is thermodynamically favourable ($\Delta G^\theta < 0$) even below the appearance temperature of Co, as shown in Table XV. However, it is reasonable to suppose that when argon is used as the purge gas, this reaction is not very probable since the oxygen in the air inside the tungsten tube forms a stable film of WO_3 on the tungsten surface and hinders the diffusion of the $\text{CoO}_{(s)}$ through the film of WO_3 to reach the underlying tungsten surface [100]. However, when the reducing environment inside the atomizer is improved by introduction of hydrogen gas, as was done in this work,

TABLE XV. Standard free energy change for the reduction of $\text{CoO}_{(s)}$ by solid tungsten

$$\Delta G_R^0 = \Delta G_{f,\text{Co}}^0 + \Delta G_{f,\text{WO}_3}^0 - \Delta G_{f,\text{CoO}}^0 - \Delta G_{f,\text{W}}^0$$

Temperature (K)	$\Delta G_{f,\text{Co}}^0$	$\Delta G_{f,\text{WO}_3}^0$	$\Delta G_{f,\text{CoO}}^0$	$\Delta G_{f,\text{W}}^0$	ΔG_R^0
			kJ mol ⁻¹		
1500	0	- 446.00	- 386.82	0	- 79.18
1600	0	- 442.53	- 365.88	0	- 76.65
1700	0	- 439.18	- 344.76	0	- 74.42
1800	0	- 395.97	322.80	0	- 73.13

Thermodynamic data taken from references No. 107-110.

TABLE XVI. Standard free energy change for the reduction of $\text{CoO}_{(s)}$ by hydrogen gas

$$\Delta G_R^\theta = \Delta G_{f, \text{Co}}^\theta + \Delta G_{f, \text{H}_2\text{O}}^\theta - \Delta G_{f, \text{CoO}}^\theta - \Delta G_{f, \text{H}_2}^\theta$$

Temperature (K)	$\Delta G_{f, \text{Co}}^\theta$	$\Delta G_{f, \text{H}_2\text{O}}^\theta$	$\Delta G_{f, \text{CoO}}^\theta$	$\Delta G_{f, \text{H}_2}^\theta$	ΔG_R^θ
	kJ·mol ⁻¹				
1400	0	- 170.83	- 136.10	0	- 34.73
1500	0°	- 165.14	- 128.94	0	- 36.20
1600	0	- 159.41	- 121.96	0	- 37.43
1700	0	- 152.75	- 114.92	0	- 37.80
1800	0	- 147.86	- 107.60	0	- 40.26

Thermodynamic data taken from references No. 107-110

reduction of the $\text{CoO}_{(s)}$ becomes thermodynamically very favourable, as shown in Table XVI. Therefore, provided that a reducing atmosphere (i.e., Ar/H_2) inside the atomizer is present, the precursor to $\text{Co}_{(g)}$ in the tungsten furnace (WETA-82) is probably the same as that in the graphite furnace, i.e., reduction of $\text{CoO}_{(s)}$ to $\text{Co}_{(s)}$ followed by sublimation of $\text{Co}_{(s)}$.

Based on the above results, a mechanism of $\text{Co}_{(g)}$ formation from the platform and the tube wall surface is proposed as follows:

The proposed mechanism and the activation energy values are in good agreement with those reported by Sturgeon et al. [9,27]. However, they also reported another activation energy values, suggesting the formation of $\text{Co}_2_{(g)}$. This was not observed in this work. The formation of $\text{Co}_2_{(g)}$ is well documented [9,111]. However, L'vov et al. [112] suggested that the additional lower activation energy value obtained by Sturgeon et al. [9,27] from the activation energy plot for cobalt (which they attributed to the formation of $\text{Co}_2_{(g)}$) was very likely the result of slowing down of diffusion of the analyte through pores of the graphite tube wall into which the aqueous solution of the analyte had penetrated.

B. Mechanism of titanium atom formation

The decomposition and atomization curves for titanium from the graphite and tungsten surfaces (shown in Figs. 46 and 47), respectively), were obtained by atomizing an aqueous solution of Ti in 1 (v/v) HF + 1% (v/v) HNO_3 . The left-hand curves in both figures show the net absorbance values obtained by using a fixed (optimum) atomization temperatures and variable charring temperatures; the right-hand curves show the net absorbance values obtained by using a fixed (optimum) charring temperature and variable atomization temperatures.

Titanium was introduced into the furnaces as its hexafluoride complex in aqueous solution; the complex on heating formed $\text{TiO}_2(\text{s})$ [113]. According to Samsonov and Rozinova [114], reduction of $\text{TiO}_2(\text{s})$ by carbon starts at 935 °C, and between 1000-1500 °C it proceeds through the following steps:

It has been reported [115] that reduction of $\text{TiO}_2(\text{s})$ by hydrogen gas in a Mo-boat (on heating for three hours) at 1250 °C produces $\text{Ti}_3\text{O}_5(\text{s})$. Titanium dioxide (solid) may also be reduced by hydrogen gas to $\text{TiO}(\text{s})$ at 2000 °C by using high pressures [116].

Figure 46. Decomposition/atomization curves for titanium (as TiF_6^{-2} in an aqueous solution) in HGA-500. □ Charring curve. △ Atomization curve.

Figure 47. Decomposition/atomization curves for titanium (as TiF_6^{2-}) in an aqueous solution in WETA-82. $\square$ Charring curve. $\circ$ Background signal from 1% (v/v) HF + 1% (v/v) HNO_3 aqueous solution. $\triangle$ Atomization curve.

The charring (left-hand) curve from the graphite surface (Fig. 46) has poor reproducibility in the temperature range 900-1000 °C, and starts to drop in absorbance values above 1800 °C. The trend of the curve appears to be consistent with the fact that in the temperature range of poor reproducibility, different titanium oxides having variable thermal stability are formed. Another possible explanation for the above observation is that Ti starts to form TiC_xO_y at 1200 °C (Chapter II). With increasing temperatures, the TiC_xO_y is converted into carbon-deficient TiC and $Ti(s)$. However, no significant decrease in the absorbance values was observed in the above temperature range (900-1500 °C). From the Ti-C phase diagram [117], the C/Ti ratio is < 0.5 at temperatures lower than 1670 °C. Formation of TiC has been reported in a furnace at 1800 °C [118] which is probably consistent with the drop in absorbance values in the charring curve at 1800 °C, a temperature at which no Ti signal is observed in the atomization (right-hand) curve (Fig. 46).

Figure 48 shows the absorbance signal of Ti in 1% (v/v) HF + 1% (v/v) HNO_3 aqueous solution, and the blank (mixture of the acids alone) atomized from the tungsten surface after charring at temperatures 230-830 °C. Two absorption peaks were observed. The first peak is the blank signal and it decreases with increasing temperatures till it almost disappears (Figure 48, curve g) at a charring temperature of 830 °C, whereas the peak-height absorbance of

Figure 48. Absorption pulses with charring temperature as a parameter

A: Absorbance signal of 5.0×10^{-12} kg of titanium (as TiF_6^{-2}) in an aqueous solution of 1% (v/v) HF + 5% (v/v) HNO_3 in WETA-82. B: Absorbance signal of the [1% (v/v)HF + 1% (v/v) HNO_3] aqueous solution in WETA-82.

- a: Charring temperature = 230 °C
- b: Charring temperature = 330 °C
- c: Charring temperature = 430 °C
- d: Charring temperature = 530 °C
- e: Charring temperature = 630 °C
- f: Charring temperature = 730 °C
- g: Charring temperature = 830 °C

TABLE XVII. ΔH° for titanium metal sublimation, titanium metal vaporization, dissociation of the titanium oxygen bond and reduction of solid titanium dioxide by hydrogen gas compare with the experimental activation energy

Literature Values		Experimental Values taken from the Curves in Fig. 19	
Process	ΔH° KJ mol ⁻¹	Temperature Region Used for Activation Energy Calculation	Activation Energy KJ mol ⁻¹
$Ti(l) \rightarrow Ti(g)$	429	High	463 ± 32
$Ti(s) \rightarrow Ti(g)$	470		
$TiO(s) \rightarrow Ti(g) + O(g)$	662	Low	720 ± 31
$TiO(s) + H_2 \rightarrow Ti(g) + H_2O(g)$	745		

*Thermodynamic data taken from references No. 107-110

the right-hand peak (which is due to Ti) increases greatly from the charring temperature of 630 °C, and then to a still greater value at 830 °C (Fig. 48, curves e, f, and g).

Figure 48 shows the importance of investigating the thermal stability and the atomization characteristics of samples by studying the (charring) temperature dependence of both the analyte signal and the blank signal, so as to determine the optimal charring temperature. The optimal charring temperature is defined as the charring temperature that gives the highest absorbance value for the analyte and the lowest absorbance value for the blank at the atomization cycle, so that the net absorbance value of the analyte is maximum.

Figure 47 (the left-hand) curve shows that the net value of Ti absorbance increases rapidly with increasing temperatures up to about 1570 °C, and then starts to drop rapidly at higher charring temperatures. Figure 48 also shows that the optimal charring temperature for the above titanium solution is 1500 °C.

The charring curve in Fig. 47 shows that in the WETA-82 the peak-height absorbance increases more rapidly with increasing charring temperatures (up to 1460 °C) than in the graphite furnace (Fig. 46). The increase in the peak-height absorbance with increasing charring temperatures up to 1460 °C may be rationalized by considering the fact that a layer of WO_3 is formed on the tungsten surface at lower

temperatures, hindering the availability of the tungsten surface for reduction of the solid titanium oxides. With increasing temperatures, more and more of the WO_3 is vaporized, stripping the WO_3 layer off the tungsten surface, thereby facilitating the reduction of solid titanium oxides by solid tungsten, which results in increasing formation of Ti(g) , and hence, in increasing absorbance. Above 1460°C and up to 1660°C , the trend of the curve is similar to that of the graphite furnace. The reason for the decrease in absorbance values of Ti at charring temperatures $> 1580^\circ\text{C}$ is not clear; it may be related to an enhanced activity of the tungsten surface or to the presence of the H_2 gas when the tungsten surface is heated for a prolonged period (during charring) at temperatures $> 1580^\circ\text{C}$, leading to premature formation and loss of Ti(g) in the charring cycle; hence, the observed decrease in the absorbance.

It is important to note that the charring curve from tungsten surface (Fig. 47, left-hand curve) does not continue beyond 1660°C . This is because of the instrumental limitations of WETA-82, in which charring temperatures higher than 1660°C are not available.

The drop in both the charring curves (Fig. 46 and Fig. 47) at 1800°C and 1660°C , (for the graphite and the tungsten surface, respectively), may suggest that titanium atoms begins to form at these temperatures. However, no absorbance signal was observed until temperatures of 2000°C

and 2500 °C (appearance temperatures) were attained in the graphite and the tungsten furnace, respectively. The absorbance values in the atomization (right-hand) curves increase with increasing temperatures (without reaching a plateau up to the maximum temperature setting (3000 °C) obtainable from the instrument panels. It is evident that a higher sensitivity for Ti would be obtainable if the atomization temperature of the graphite and the tungsten furnace is increased above 3000 °C, up to a temperature corresponding to the onset of the (missing) plateau in the atomization curve or to the beginning of a significant loss of the graphite or the tungsten surface by vaporization as the atomization temperature approaches the sublimation point of pyrolytic graphite (3700 °C - reference 20, p. 206) or the melting point of tungsten (3410 °C - reference 20, p. 298).

In order to compare the mechanism of Ti atomization in the tungsten and the graphite furnace, the model of Sturgeon et al. [9,27] was used to determine the activation energy of the atomization reaction. Figure 49 shows the activation energy plot for Ti from the tungsten surface. It is important to note that no activation energy plot from the graphite surface was obtained. This was because of the poor reproducibility of the absorbance measurements and high memory effects observed in the atomization of Ti from the graphite surface, which made it very difficult to obtain reproducible activation energy plots.

Figure 49. Arrhenius plot for atomization of titanium 5.0×10^{-12} kg
(as TiF_6 in an aqueous solution) from tungsten tube
wall

Activation energy values of $729 \pm 3\%$ and $487 \pm 5\%$ for low ($< 2800^\circ\text{C}$) and high ($> 2800^\circ\text{C}$) temperature ranges, respectively, were obtained for the atomization of Ti in WETA-82. The latter agrees fairly well with the ΔH° value for the sublimation reaction: $\text{Ti(s)} \longrightarrow \text{Ti(g)}$, as shown in Table XVII. It might be expected that the activation energy would show correlation with the enthalpy change in vaporization: $\text{Ti(l)} \longrightarrow \text{Ti(g)}$, since the appearance temperature is above the melting point of Ti (1660°C). However, in this study, the Ti sample was rapidly atomized (heating rate 15°C ms^{-1}) from a charring temperature of 1350°C , possibly before melting of Ti could occur.

The activation energy value for the low temperature range of Fig. 49 could only be roughly correlated with the reduction of $\text{TiO}_2(\text{s})$ by H_2 (Table XVII) in WETA-82. This is because the Ti signal was very low at $T = 2700^\circ\text{C}$ and noisy; therefore, the data were not very reproducible, which made it difficult to obtain reproducible activation energy plots, and hence, a more reliable activation energy value.

Mass-spectrometric analysis of Ti oxides has shown that at temperatures below the appearance temperatures of Ti from the graphite and the tungsten surface, the gaseous species in equilibrium with $\text{Ti}_3\text{O}_5(\text{s})$ are $\text{TiO}^+(\text{g})$ (the predominant species), $\text{Ti}^+(\text{g})$, and $\text{TiO}_2^+(\text{g})$ [119-124]. Berkowitz et al. [120] reported that, when Ti oxides were vaporized from Th or Mo pellets, results showed the same gaseous species. Gilles et al. [121] and Yuan Wu et al. [123]

TABLE XVII. ΔH° for titanium metal sublimation, titanium metal vaporization, dissociation of the titanium oxygen bond and reduction of solid titanium dioxide by hydrogen gas compare with the experimental activation energy

Literature Values		Experimental Values taken from the Curves in Fig. 19	
Process	ΔH° KJ mol ⁻¹	Temperature Region Used for Activation Energy Calculation	Activation Energy KJ mol ⁻¹
$Ti(l) \rightarrow Ti(g)$	429	High	460 $\pm$ 32
$Ti(s) \rightarrow Ti(g)$	470		
$TiO(s) \rightarrow Ti(g) + O(g)$	662	Low	720 $\pm$ 32
$TiO(s) + H_2 \rightarrow Ti(g) + H_2O(g)$	745		

^aThermodynamic data taken from references No. 107-110

reported that $Ti^+(g)$ resulted from fragmentation of $TiO_2(g)$. Therefore, it is reasonable to expect that $TiO(g)$ is the precursor to Ti atoms. However, Hampson and Gilles (1967) reported that the appearance potential for Ti^+ and TiO^+ seemed to indicate that the detected $Ti^+(g)$ did not result from fragmentation of TiO . They also observed that the TiO/Ti ratio decreased during the analysis which indicated that the amount of Ti increased.

Based on the above facts, a mechanism for Ti atomization from the tungsten surface is proposed as follows:

Since reduction of $TiO(s)$ by carbon is thermodynamically favourable at the appearance temperature (Table VIII), and the same gaseous species are observed by mass spectrometry, it is reasonable to conclude that the mechanism of Ti atomization from the graphite surface would be similar to that proposed for the tungsten surface.

CONCLUSIONS

Because of the rather large uncertainties in the knowledge of the platform temperature, definite conclusions cannot be drawn on the differences or similarities in the activation energy values between the platform atomization

TABLE VIII. Standard free energy change for reduction of solid titanium oxide by solid carbon

$$\Delta G_R^\circ = \Delta G_{f,\text{Ti}}^\circ + \Delta G_{f,\text{CO}_2}^\circ - \Delta G_{f,\text{TiO}_2}^\circ - \Delta G_{f,\text{C}}^\circ$$

Temperature (K)	$\Delta G_{f,\text{Ti}}^\circ$	$\Delta G_{f,\text{CO}_2}^\circ$	$\Delta G_{f,\text{TiO}_2}^\circ$	$\Delta G_{f,\text{C}}^\circ$	ΔG_R°
	kJ mol ⁻¹				
1600	0	-120.60	-94.64	0	-25.90
1700	0	-124.70	-93.03	0	-31.70
1800	0	-129.20	-91.43	0	-37.80
1900	0	-132.20	-90.00	0	-42.70
2000	0	-135.70	-88.74	0	-48.50
2100	0	-140.70	-86.00	0	-54.70
2200	0	-144.68	-83.70	0	-60.00
2300	0	-148.64	-81.60	0	-64.00

Thermodynamic data taken from reference No. 107-110

and the atomization from other surfaces. However the results suggest that the reaction leading to the production of Co atoms occurs on the atomizer surface, i.e., condensed-phase reduction of $\text{CoO}_{1.5}$ either by C or by W/H_2 rather than a vapour-phase dissociation. Mechanism of cobalt atomization from the graphite platform, the graphite tube wall, and the tungsten surface (WETA-82) appears to be the same as that reported by Sturgeon and Chakrabarti [9] for the graphite tube wall.

Mechanism of titanium atomization probably depends on both the nature of the atomization surface and the strength of the reducing environment. For the graphite and the tungsten surface, the results show that the reaction leading to production of $\text{Ti}(\text{g})$ occurs on the atomizer surface as follows:

The results of the above study of titanium atomization mechanism suggests that further work is necessary to elucidate more fully the atomization mechanism of the complex Ti-O system, and to confirm the proposed mechanism of atomization from the graphite surface.

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