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**LA THÈSE A ÉTÉ
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A THEORETICAL AND EXPERIMENTAL STUDY OF PLATFORM FURNACE AND
PROBE FURNACE IN GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY

by

(C) Shaole Wu

A thesis submitted to the Faculty of Graduate Studies
in partial fulfilment of the requirements
for the degree of Doctor of Philosophy

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December of 1986

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The undersigned recommend to the Faculty of
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ABSTRACT - The heating characteristics and analytical performance of a commercial, pulse-heated, semi-enclosed graphite furnace with a graphite platform or a graphite probe insert have been studied as follows.

Theoretical models have been proposed for the time-dependent temperature field, including the temperature of the graphite platform, temperature distribution of the tube wall in the axial direction and of the gas phase in the axial and the radial direction, in the absence of a forced, convective flow of argon purge gas. The predictions of the models have been compared with experimental results. The extent of the temporal and the spatial nonisothermality of the above atomizer has been found to depend on the geometry and design of the atomizer, thermal properties of the purge gas, and temperature program of the furnace. A low initial tube wall temperature and a high tube wall heating rate (both at the furnace centre) reduce the temperature gradient of the tube wall and of the gas in the axial direction and delay heating of the platform.

A theoretical model for the time-dependent analyte atom distribution in the graphite platform furnace which takes into account the time-dependent temperature field of the graphite platform furnace has also been proposed. Predictions of the model have been tested experimentally using silver as the test analyte. Effects of some physical and chemical parameters of the analyte, experimental parameters, and nature of matrices on the absorbance signal from platform atomization have been studied and critically discussed. The results show relative insensitivity of the mean residence time of

analyte atoms to many of the above parameters.

The graphite probe furnace atomic absorption spectrometric technique has been found to be similar in its heating characteristics and analytical performance to the graphite platform furnace atomic absorption spectrometric technique. The former technique has been applied to direct analysis of solid samples of airborne particulates for quantitative determination of their toxic metal content. The technique gives high sensitivity, short analysis time and is relatively free from contamination. The platform technique, in conjunction with X-ray diffraction spectrometry, scanning electron micrography, energy dispersive X-ray spectrometry, and Auger Electron spectrometry, was used to elucidate mechanisms of molybdenum atomization in graphite furnace atomic absorption spectrometry.

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INTRODUCTION

Since L'vov's pioneering work [1-2], applications of electrothermal atomic absorption spectrometry really gained wide acceptance only after the graphite furnace design proposed by Massmann [3-4] was commercialized. Graphite furnaces of the Massmann-type are compact and simple to operate. However, samples, which are deposited direct on the tube wall prior to the heating of the furnace, are volatilized at a time when the furnace temperature is increasing rapidly, and the analyte species enter a gas phase which is both temporally and spatially non-isothermal. As a result, atomization efficiency is often low and is matrix-dependent [5-9].

In order to reduce the temporal nonisothermality of the conventional, pulse-heated furnace, L'vov proposed three approaches as follows: to heat the furnace at a high rate using the capacitive discharge technique [5]; to use the probe technique [10]; to use the platform technique [5, 11]. In the capacitive discharge technique [12-14], a furnace made of anisotropic pyrolytic graphite is heated rapidly (up to 75 K ms^{-1}) by discharge of a bank of capacitors in which electrical energy is stored prior to its discharge. In the probe technique, samples are atomized from a probe which is inserted into the furnace after the temperature of the furnace tube wall has reached a steady state. In the platform technique, samples are atomized from a graphite platform, located inside the furnace, at a time when the temperature of the tube wall approaches a steady state. The

atomization from a graphite platform has been called isothermal (temporal) atomization [15]. Soon after L'vov proposed the above three approaches, sufficient progress had been made in their use as to produce significant reduction or elimination of matrix interferences [7, 12-44]. Also, various other attempts have been made to reduce the temporal and/or spatial nonisothermality of conventional, pulse-heated graphite furnaces [45-52], which have been successful to different degrees.

Amongst these approaches, only the platform technique does not require any modification in the furnace design or in the measurement procedure and has gained the widest application, as can be seen from a recently published survey paper [53]. In addition, graphite platforms with a dual-cavity have been used to distinguish interferences in the gas phase from those in the condensed phase [44, 54]. Also, the platform technique has been used in conjunction with other techniques to elucidate the mechanism of atomization and of matrix interferences [54-56]. However, even with the use of the platform technique, some problems with the pulse-heated graphite furnace have remained unsolved, especially some matrix interferences. Only by integrating other developments in electrothermal atomic absorption spectrometry with the platform technique, will a system which provides a remarkably interference-free performance be achieved. These developments include use of signal integration, matrix modifiers, and Zeeman-effect background correction (to all but the simplest situation) [43, 53, 57].

Despite the widest application of the platform technique, there is as yet only a small amount of theoretical background material

which has been published. One important reason for this is the lack of detailed information regarding the temperature field in a graphite platform furnace, including time-dependent temperature distribution of the furnace tube wall, of the gas phase and of the platform. The temperature field in a graphite platform furnace is more complex than that in a conventional graphite furnace without a platform. The above knowledge is essential, however, since all physical and chemical processes occurring in the graphite platform furnace are temperature-dependent.

This research was undertaken in order to understand the atomization processes occurring in a commercial, pulse-heated graphite furnace with the platform technique and with the probe technique. The focus was mainly on the platform technique in an attempt to lay down some fundamental framework for atomization processes in graphite platform furnace atomic absorption spectrometry. In the first three chapters, theoretical models of the time-dependent temperature distribution of the tube wall, the time-dependent platform temperature, and the time-dependent temperature distribution of the gas inside the graphite platform furnace, respectively, have been developed. The temperature field of the graphite tube furnace (without the platform or the probe) is also presented and discussed. With the knowledge of the temperature field, a simplified theoretical model of the time-dependent analyte atom distribution in the graphite platform furnace has been developed and presented in Chapter 4, which serves, on a fundamental level, to predict characteristics of the atomic absorption signal profile, optimization protocol that should be

adopted mechanisms of atomization and matrix interferences. The performance of the graphite probe furnace has been compared with that of the graphite platform furnace in Chapter 5. Finally, Chapter 6 presents some applications of the platform technique in conjunction with the following surface-analytical techniques - X-ray diffraction spectrometry, scanning electron micrography, energy dispersive X-ray spectrometry and Auger electron spectrometry - to elucidate the mechanisms of molybdenum atomization in the graphite furnace.

Chapter 1

TIME-DEPENDENT TEMPERATURE DISTRIBUTION OF THE FURNACE WALL IN A PULSE-HEATED GRAPHITE TUBE FURNACE AND IN THE SAME FURNACE WITH A GRAPHITE PLATFORM

1.1. Introduction

In a Massmann-type, pulse-heated graphite tube furnace (which will be henceforth called the graphite tube furnace), temperatures of the tube wall and the gas phase inside the furnace are inter-related. In the above furnace with a graphite platform inside it (to be henceforth called the graphite platform furnace), temperatures of the tube wall, the platform and the gas phase are also inter-related. However, for a given graphite furnace, it is the time-dependent temperature distribution of the tube wall on which the temperature of the platform and/or of the gas phase mainly depends. Therefore, knowledge and modelling of time-dependent temperature distribution of the tube wall in the graphite tube furnace and in the graphite platform furnace is important for understanding and for modelling the temperature of the platform and/or of the gas phase.

No studies on time-dependent temperature distribution of the tube wall in a graphite platform furnace have been reported. Experimental and theoretical studies on the tube wall temperature distribution in a Massmann-type graphite furnace have been made by several researchers [58-65]. Existence of a temperature gradient in the tube wall of

Massmann-type graphite furnaces in the axial direction during their heating (both steady-state and non-steady-state systems) has been confirmed experimentally by indirect and direct measurements.

The indirect measurements include optical pyrometric measurement of the temperature of a small piece of graphite inserted inside the furnace on the assumption that the graphite piece is in equilibrium with the tube wall with which it is in thermal contact [58-59]. They also include methods based upon measurement of absorbance signals [60]. For non-steady-state systems, the optical pyrometric method suffers from a systematic error resulting from the tube wall radiation reflected from the test piece of graphite.

The direct measurements include the earlier method of employing a thermocouple in direct contact with the inner surface of the furnace wall [61] to measure the temperature distribution at steady state, and the later method of using an optical pyrometer to measure the outer surface temperature of the furnace wall at steady state [62-63], or at non-steady state [64-65]. In these measurements, the graphite tube was located either in a modified contact ring of a commercial atomizer [62, 64], or in a specially-designed atomizer [63, 65] in order to measure temperatures along the axial length of the graphite tube. In addition to confirming the non-isothermal nature of the tube wall, Falk et al. [65] also reported the dependence of temperature distribution of the tube wall on the tube wall heating parameters at the furnace centre. When the heating rate of the tube wall at the furnace centre was above 1 K ms^{-1} and the initial temperature of the furnace tube was the ambient temperature, a nearly constant temperature over most of the tube length during the early heating

period was reported [65].

Theoretical modelling of the temperature distribution along the tube length of a Massmann-type graphite furnace based on a simplified Heat transfer theory and thermal equilibrium (steady state) was given by Slavin et al. [62]. The model was used to calculate the steady-state temperature distribution of a contoured tube - the contoured tube resulted in a reduction of the temperature gradient in the axial direction. Human et al. [63] improved the model of Slavin et al. [62] to calculate the time-dependent temperature distribution of the furnace tube wall in the axial direction and compared the calculated and the experimental temperature of several types of contoured tubes. By fitting the property values of the graphite, a moderately good agreement between the theoretical and the experimental temperature distribution in the axial direction at thermal equilibrium (steady state) as well as between the theoretical and the experimental time-dependent temperature variations at the furnace centre was obtained. In the model of Human et al. [63], maintenance of a constant electrical current was assumed and was used as input to control the heating of the furnace in order to reflect the observed monotonic decrease in the heating rate at the centre of their furnace. The model was subsequently modified [66-68] to adopt the voltage as input in order to simulate the heating at the furnace centre in the 'maximum power' mode of the Perkin-Elmer Heated Graphite Atomizer. Unfortunately, with both electrical current and voltage control modes of the furnace heating in references 66-68, the predicted time-dependent temperature distribution of the furnace wall with various heating parameters is not directly observable. This was probably the

reason why the effects of the tube wall heating rate and the initial temperature of the tube wall at the furnace centre on the transient temperature distribution reported by Falk et al. [65] were not fully discussed in references 63 and 66-68. Also, in the models of Human and Rademeyer et al. [63, 66-68], a constant value for the thermal resistance at the furnace ends, derived from experimental results at thermal equilibrium (steady state), was used to calculate the time-dependent temperature distribution (non-steady-state) along the furnace length.

In the present study, a simplified thermal analysis of the tube wall of a graphite platform furnace has been developed. The model has been used to set up a computer program to allow prediction of the time-dependent temperature distribution in the axial direction of the tube wall in the graphite platform furnace for various tube wall heating parameters (tube wall heating rate, initial and final tube wall temperatures at the furnace centre) as well as for various furnace geometries. This theoretical model can predict the time-dependent temperature distribution in the axial direction of the graphite tube (without a platform) as well. By fitting the boundary temperatures at the furnace centre and at the furnace ends, the results of the model have been compared with the experimental results to establish confidence in the thermal analysis. The time-dependent temperature distribution of the furnace wall predicted by this theoretical model has been used in the following two chapters for calculating the time-dependent temperature of the platform and the time-dependent temperature distribution of the gas phase.

1.2. Theoretical model

This model calculates the time-dependent tube wall temperature distribution of a graphite platform furnace in the absence of forced convection (i.e., in the internal purge gas flow interrupt mode). Figure 1 shows the schematic diagram of the graphite platform furnace. The furnace is a commercial pulse-heated Massmann-type. The cylindrical graphite tube has an inner diameter d_i , outer diameter d_o and length l_w , and is located inside a concentric graphite contact shield of inner diameter $(d_o + 2\Delta s)$ with a stagnant gas inside the furnace and a sheath gas flowing between the furnace tube and the shield. An anisotropic pyrolytic graphite platform of length l_p , thickness b , and width w (except at two ends where the width is $w + \Delta w$ to minimize the physical contact between the platform sides and the tube wall), is placed inside the furnace tube in its middle section. This model can also be used to calculate the time-dependent tube wall temperature distribution of the graphite tube furnace (without the platform) as a special case in which the radiation heat transfer from the inner surface of the furnace tube wall to the platform is zero.

The following major assumptions are made in the analytical model regarding the thermal behaviour of the tube wall of the graphite furnace.

(a) The one-dimensional geometric configuration as shown in Fig. 2 can be used to model the thermal behaviour of the tube wall of the graphite platform furnace and the graphite tube furnace (without the platform).

Figure 1. Schematic diagram of the graphite platform furnace.

Figure 2. Geometric configuration assumed for calculating the temperature distribution of the furnace tube wall.

In Fig. 2, the inner diameter of the graphite tube is assumed to be uniform, whereas the outer diameter is allowed to vary with the axial position to account for the variation of the tube wall thickness. The existence of the sample injection hole in the furnace tube is ignored. Although the graphite platform is a rectangular plate and not a cylindrical rod, the model assumes that the platform is a cylindrical rod (having the same mass) located along the centre line (in the axial direction) of the graphite tube. The cylindrical symmetry of the graphite tube and of the rod allows the assumptions to be made that the graphite furnace has neither azimuthal nor radial temperature dependence. Its temperature only varies along the length of the furnace tube. While these assumptions are not exactly true, they considerably simplify an otherwise complex mathematical problem without seriously impairing the validity of the results.

(b) Mechanisms of heat transfer which are significant for the temperature distribution of the tube wall (which is heated electrically) are thermal conduction along the length of the furnace tube, thermal conduction in the radial direction through the sheath gas and radiation from the outer surface of the furnace tube to the surrounding cylindrical graphite shield, and thermal radiation from the inner surface of the furnace tube to the platform. Other mechanisms of heat transfer which can possibly contribute to the temperature of the furnace tube are natural convection of the internal gas, convection to and from the sheath gas, thermal conduction from the furnace tube to the internal, stagnant gas, multiple internal radiation heat transfer from one part to another part of the furnace by reflection and absorption.

Natural convection of the internal gas does not occur in the furnace in spite of the relatively large temperature differences across the gas or between the tube wall and the platform during the heating of the furnace because the small dimensions of the furnace effectively suppress natural convection. This assumption is confirmed by the Rayleigh numbers of the internal gas calculated during the heating of the furnace using the model described in Chapter 3. The Rayleigh numbers for argon gas calculated at all times are of the order of 400 or less, considerably below 1300, the value at which natural convection effects would be expected to begin [69].

Thermal conduction from the tube wall to the internal gas has only a minor effect on the temperature of the tube wall. This is because the thermal capacity of the internal gas in the furnace is negligible compared to that of the furnace and because the rate of heat transfer to the gas by thermal conduction is very low compared to that along the length of the tube.

The contribution of the heat transfer from one part to other parts of the tube wall by multiple internal radiation will be significant if the temperature gradient of the tube wall is large. However, the experimentally measured temperature distribution shows that there is about 8 mm of the middle part of the 28 mm-long-tube (having uniform thickness) in which the temperature is nearly constant [65]. Therefore, its contribution may be neglected.

In developing the radiation heat transfer analysis, the following assumptions are made in addition to the assumptions numbered (a) and (b) made earlier.

(c) The tube wall, the platform and the shield are considered to

be gray bodies, i.e., their emissivities are not functions of the wavelength of the radiation. Although most bodies are not gray, this assumption produces reasonable results provided that the absorptivity of a body in the wavelength band of the incident radiation is approximately equal to its emissivity in the wavelength band of the incident radiation [70]. For the graphite surfaces (the tube wall, the platform and the contact cylinder shield) and the temperature ranges of concern here, this requirement is reasonably well satisfied [42].

(d) The surfaces of the tube wall, the platform and the contact cylinder shield emit and reflect radiation diffusely. This is a reasonable assumption for the graphite surfaces.

(e) The internal gas of the furnace does not emit nor absorb radiation. This is an excellent assumption for the monatomic gas (argon) in the temperature ranges considered. Even for some heteropolar gas molecules (vaporized from the sample) in the furnace gas phase which may absorb infrared radiation in certain wavelength bands, radiation absorption by the gas phase will be negligible because of the very short radiation beam length and the probable very low partial pressures of the component gases.

The following assumptions are used in considering the boundary and the initial condition.

(f) The platform has a uniform temperature at each instant. Its time-dependent temperature is known at each instant as calculated from the model described in Chapter 2, in which the actual cross-sectional position of the platform relative to the furnace tube wall has been considered.

(g) The temperature of the graphite contact cylinder shield

remains uniform at a constant value of T_s during the transient.

This assumption may be justified because the graphite contact cylinder shield is located inside the water-cooled metal jacket to prevent it from overheating. Also, there is a sheath gas flowing between the tube and the shield to prevent the oxidation of the graphite tube. In addition, the mass of the graphite contact cylinder shield is much larger than that of the furnace tube.

(h) The transient temperatures of the tube wall at its ends where it contacts the graphite contact cylinder are pre-determined functions.

This assumption converts the difficult and complex problem of calculating the thermal contact resistance and thermal resistance of the heat flow path to the cooling water into a boundary value problem at the furnace ends which is relatively easy to be determined from the experimentally measured temperature distributions.

(i) The central temperature of the tube wall is controlled either by the experimentally measured temperature of the interior surface of the furnace at its centre or by the pre-selected temperature program.

This assumption is valid for a real heating process where the tube wall heating parameters at the furnace centre (the tube wall heating rate, the initial and the final tube wall temperature) are normally programmed and the transient temperature at the furnace centre is monitored or measured. This approach enables the model to approximate the real heating process accurately since the experimentally measured (with an optical pyrometer) temperature of the tube wall at the furnace centre is fairly accurate [71-72]. This approach has the advantage that effects of the tube wall heating

parameters at the furnace centre on the temperature distribution of the tube wall will be directly observed. It also enables the model to be simplified by expressing the electrical resistive heating power in terms of the rate of temperature change at the centre of the furnace tube. Thus, the temperature-dependent resistivity of the graphite [73-74] is much less important than it would be if an electrical current or voltage were controlled as in references 63 and 66-68.

(j) When the tube wall temperature at the furnace centre is the room temperature, the temperature of the furnace tube is the room temperature and is uniform. When the initial tube wall temperature at the furnace centre is higher than the room temperature, there will be initially a non-uniform temperature distribution along the furnace tube length. To determine this initial temperature, the model itself is used, assuming quasi-steady state, with the known initial tube wall temperature at the furnace centre to establish this initial temperature distribution in the axial direction.

Finally, the following assumption is made regarding the temperature-dependent property values.

(k) The temperature-dependent property values of the graphite furnace tube, the graphite platform, the sheath gas and the internal gas are allowed to vary with temperature in order to achieve accurate analysis for the large temperature range encountered in the furnace during a transient. Since the temperatures of the tube wall, the platform and the gas vary with coordinates and/or time, these temperature-dependent property values will be functions of coordinates and/or time.

With the above assumptions and considerations, an energy balance between the rate of heat storage, $\dot{Q}_{s,w}$, plus the rate of heat transfer, $\dot{Q}_{t,w}$, and the input electrical power, P_{in} , on an infinitesimal ring of the furnace tube located at the position x with an axial length of dx (the origin of the x coordinate is at the furnace tube centre), as shown in Fig. 3, yields the following equation:

$$\dot{Q}_{s,w} + \dot{Q}_{t,w} = P_{in} \quad 1.1$$

The rate of heat storage on the graphite ring is given by:

$$\dot{Q}_{s,w} = \rho_w A_{c,w}(x) dx c_{p,w}(x,t) \frac{\partial T_w(x,t)}{\partial t} \quad 1.2$$

where $c_{p,w}$, ρ_w , $A_{c,w}$ and T_w are the heat capacity, density, cross-sectional area, and the tube wall temperature of the graphite ring, respectively.

The rate of heat transfer from the graphite ring is expressed by:

$$\begin{aligned} \dot{Q}_{t,w} = & \dot{Q}_{cond\ w-w}(x,t) + \dot{Q}_{cond\ w-s}(x,t) \\ & + \dot{Q}_{rad\ w-g}(x,t) + \dot{Q}_{rad\ w-p}(x,t) \end{aligned} \quad 1.3$$

The terms at the right-hand side of equation 1.3 are defined as follows.

The rate of heat transfer by thermal conduction along the furnace tube wall length, $\dot{Q}_{cond\ w-w}$, is expressed by:

$$\dot{Q}_{cond\ w-w}(x,t) = - A_{c,w}(x) \frac{\partial}{\partial x} \left[\kappa_w(x,t) \frac{\partial T_w(x,t)}{\partial x} \right] dx \quad 1.4$$

where κ_w is the thermal conductivity of the graphite ring.

The rate of heat transfer by thermal conduction from the outer surface of the tube in the radial direction to the surrounding graphite shield, $\dot{Q}_{\text{cond } w-s}$, is given by

$$\dot{Q}_{\text{cond } w-s}(x, t) = A_{o, w}(x) \kappa_{g, s}(x, t) \frac{T_w(x, t) - T_s}{\Delta s}, \quad 1.5$$

where $A_{o, w}$ is the outer surface area of the ring; $\kappa_{g, s}$ is the thermal conductivity of the sheath gas; T_s is the temperature of the surrounding graphite shield.

Figure 3. Infinitesimal graphite ring of the furnace tube located at position x with axial length dx . The graphite contact cylinder shield is not shown.

The rates of radiation heat transfer from the outer surface of the graphite ring to the surroundings, $\dot{Q}_{\text{rad } w-s}$, and from the inner surface of the graphite ring to the platform, $\dot{Q}_{\text{rad } w-p}$, are given by [75]:

$$\dot{Q}_{\text{rad } w-s} = \sigma \mathcal{F}_{w-s}(x, t) A_{o, w}(x) [T_w^4(x, t) - T_s^4] , \quad 1.6$$

$$\dot{Q}_{\text{rad } w-p} = \sigma \mathcal{F}_{w-p}(x, t) A_{i, w} [T_w^4(x, t) - T_p^4(t)] , \quad 1.7$$

where σ is the Stefan-Boltzmann constant for radiation, $A_{i, w}$ is the inner surface area of the ring, T_p is the platform temperature, $\mathcal{F}_{w-s}$ and $\mathcal{F}_{w-p}$ are the total radiation interchange factors [75] for the radiation heat transfer from the outer surface of the ring to the surrounding and from the inner surface of the ring to the platform, respectively. They may be expressed as follows [75].

$$\mathcal{F}_{w-s}(x, t) = \left[\frac{1}{\epsilon_w(x, t)} + \frac{d_o(x)}{d_o(x) + 2\Delta s} \left(\frac{1}{\epsilon_s} - 1 \right) \right]^{-1} , \quad 1.8a$$

$$\text{for } \frac{l_w}{2} \geq x > 0, \quad t > 0 .$$

$$\mathcal{F}_{w-p}(x, t) = \left[\frac{1}{\epsilon_w(x, t)} + \frac{A_{i, w}}{A_p(x)} \left(\frac{1}{\epsilon_p(t)} - 1 \right) \right]^{-1} , \quad 1.8b$$

$$\text{for } \frac{l_p}{2} \geq x > 0, \quad t > 0 .$$

$$\mathcal{F}_{w-p}(x, t) = 0, \quad \text{for } \frac{l_w}{2} \geq x > \frac{l_p}{2}, \quad t > 0 . \quad 1.8c$$

If it is a graphite tube furnace, then equations 1.8b and 1.8c become

$$\mathcal{F}_{w-p}(x, t) = 0, \quad \text{for } \frac{l_w}{2} \geq x \geq 0, \quad t > 0. \quad 1.8d$$

In the above equations, ϵ_w , ϵ_p and ϵ_s are the emissivities of the tube wall, platform, and the contact cylinder shield, respectively, and A_p is the surface area of the platform segment of length dx .

The input electrical power, P_{in} , is given by

$$P_{in}(x, t) = I^2 R_w(x, t) \quad 1.9a$$

where I is the electrical current passing through the ring and $R_w(x)$ is the electrical resistance of the graphite ring. Since the heating of the furnace tube is controlled by the rate of temperature change at the centre of the tube, it can be determined by applying equation 1.1 to the central ring to calculate the power input at this ring, i.e., $P_{in}(0, t)$, and taking into account the resistance ratio of the ring at (x, t) to that at the centre $(0, t)$, i.e.,

$$P_{in}(x, t) = \frac{R_w(x, t)}{R_w(0, t)} P_{in}(0, t) \quad 1.9b$$

Since graphite rings at different position of x have the same length dx , equation 1.9b can be expressed as

$$P_{in}(x, t) = \frac{A_{c, w}(0) \gamma_w(x, t)}{A_{c, w}(x) \gamma_w(0, t)} P_{in}(0, t) \quad 1.9c$$

where γ_w is the resistivity of the graphite tube wall.

Substituting equations 1.2-1.9 into equation 1.1, the following partial differential equation is obtained:

$$\begin{aligned}
\rho_w A_{c,w}(x) \frac{\partial T_w(x,t)}{\partial t} &= A_{c,w}(x) \frac{\partial}{\partial x} \left[\kappa_w(x,t) \frac{\partial T_w(x,t)}{\partial x} \right] \\
&- A_{o,w}(x) \kappa_{g,s}(x,t) \frac{T_w(x,t) - T_s}{\Delta s} \\
&- \sigma [F_{w-s}(x,t) A_{o,w}(x) [T_w^4(x,t) - T_s^4] \\
&- \sigma F_{w-p}(x,t) A_{i,w} [T_w^4(x,t) - T_p^4(t)] \\
&+ \frac{A_{c,w}(0) \gamma_w(x,t)}{A_{c,w}(x) \gamma_w(0,t)} P_{in}(0,t) ,
\end{aligned} \tag{1.10}$$

subject to the following boundary conditions:

$$T_w(x,t) = B_{1w}(t), \quad \text{for } x = 0, \quad t > 0; \tag{1.11a}$$

$$T_w(x,t) = B_{2w}(t), \quad \text{for } x = \frac{l_w}{2}, \quad t > 0; \tag{1.11b}$$

and the initial conditions:

$$T_w(x,0) = I_w(x), \quad \text{for } \frac{l_w}{2} \geq x \geq 0; \tag{1.12a}$$

$$T_p(0) = T_p, \quad \text{for only the platform furnace.} \tag{1.12b}$$

In the above equations $I_w(x)$ is the initial temperature distribution of the tube wall, $B_{1w}(t)$ and $B_{2w}(t)$ are the prescribed boundary conditions at the tube centre and at the tube end. $T_p(t)$ is the temperature of the platform as calculated from the model described in Chapter 2. $P_{in}(0,t)$ is the input electrical power applied to the furnace centre, which, knowing the boundary condition at the furnace centre, can be calculated from equation 1.10 as

$$P_{12}(0, t) =$$

$$\begin{aligned} & \rho_w A_{c,w}(0) dx c_{p,w}(0, t) \frac{\partial T_w(0, t)}{\partial t} - A_{c,w}(0) dx \frac{\partial}{\partial x} \left[\kappa_w(0, t) \frac{\partial T_w(0, t)}{\partial x} \right] \\ & + A_{o,w}(0) \kappa_{g,s}(0, t) \frac{T_w(0, t) - T_s}{\Delta s} + \sigma \mathcal{F}_{w-s}(0, t) A_{o,w}(0) [T_w^4(0, t) - T_s^4] \\ & + \sigma \mathcal{F}_{w-p}(0, t) A_{i,w} [T_w^4(0, t) - T_p^4(t)] . \end{aligned} \quad 1.13$$

In the above equations, only the temperature distribution of the furnace over its half length is considered because of the symmetry of the graphite furnace.

A computer program has been written to solve equation 1.10 (subject to the initial and boundary conditions). In the computer program, equation 1.10 has been approximated by a numerical method of analysis using forward finite-difference approximations, as given in Appendix II. Using this approximation the temperature distribution of the tube wall at a series of axial nodes at each time step has been expressed explicitly in terms of the temperature distribution of the tube wall at these nodes at the preceding time step and in terms of the platform temperature at the preceding time step. The temperature of the platform is obtained by applying a subroutine program in which the temperature of the platform is calculated using the model described in Chapter 2. The number of axial nodes for the half length of the tube furnace is taken as 15 (including the nodes both at the centre and at the one end of the furnace tube). Therefore, for a furnace tube with a length of 28 mm the distance between the axial nodes is 1 mm. The time step used in the forward finite-difference approximation is an input value in the computer program. At each time

step for each node a check is made to ensure that numerical stability requirement of the explicit finite-difference method [75-77] is satisfied (see Appendix II). For the property values which are temperature-dependent, their variations with temperature are allowed for by polynomial curve fitting to tabulated values or given curves. The temperature-dependent property values used in the computer program are given in Table 1. However, the property values at any node are considered to be constant over the control volume and over each time step. For the adjacent nodes the arithmetic mean value of the temperatures at these two nodes is used for calculating the property values.

In order to take care of the temperature gradient in the axial direction at the end of the charring stage or at the beginning of the atomization stage, a provision has been made in the computer program to allow the calculated temperature distribution at a preselected time to be an input value for the program as the initial temperature distribution.

Table 1. Temperature-dependent property values of electrographite, pyrolytic graphite and argon

Property	Values	Reference
Electrographite (isotropic)		
Density ^a , ρ (g cm ⁻³)	$\rho(T) = 1.87$	
Heat capacity, c_p (J g ⁻¹ K ⁻¹)	$c_p(T) = 3.59 + 2.03 \times 10^{-3} T - 8.20 \times 10^{-7} T^2 + 1.14 \times 10^{-10} T^3$	[78] [†]
Thermal conductivity, κ (W cm ⁻¹ K ⁻¹)	$\kappa(T) = 2.17 - 2.08 \times 10^{-3} T + 9.08 \times 10^{-7} T^2 - 1.34 \times 10^{-10} T^3$	[79] [§]
Electrical resistivity, γ (ohm-cm)	$\gamma(T) = 2.80 \times 10^{-3} - 7.37 \times 10^{-6} T + 1.29 \times 10^{-8} T^2 - 1.15 \times 10^{-11} T^3 + 3.99 \times 10^{-13} T^4$ (1500 K > T > 200 K)	[73] [‡]
	$\gamma(T) = 7.60 \times 10^{-4} + 1.58 \times 10^{-7} T$ (T > 1500 K)	[73] [‡]
Pyrolytic graphite (anisotropic)		
Density ^a , ρ (g cm ⁻³)	$\rho(T) = 2.20$	[80]
Heat capacity, c_p (J g ⁻¹ K ⁻¹)	$c_p(T) = 3.59 + 2.03 \times 10^{-3} T - 8.20 \times 10^{-7} T^2 + 1.14 \times 10^{-10} T^3$	[78] [†]
Emissivity, ϵ (ab-plane)	$\epsilon(T) = 0.675 - 2.56 \times 10^{-4} T + 2.45 \times 10^{-7} T^2 - 4.20 \times 10^{-11} T^3$	[80]
Argon gas		
Density, ρ (g cm ⁻³)	$\rho(T) = 1.784 \times 10^{-3}$ (273/T)	[81]
Heat capacity, c_p (J g ⁻¹ K ⁻¹)	$c_p(T) = 0.521$	[82]
Thermal conductivity, κ (W cm ⁻¹ K ⁻¹)	$\kappa(T) = 5.84 \times 10^{-5} + 4.48 \times 10^{-7} T - 9.11 \times 10^{-11} T^2 + 1.29 \times 10^{-14} T^3$	[83]

(continued)

Table 1 (continued)

- * The density of graphite is only slightly dependent on temperature [84] and is therefore considered constant.
- † Least-square fit for the numerical data for curves 1-7, 19-20 shown in Fig. 2R-1 in [78].
- ‡ Least-square fit for the recommended value for 875S graphite, taking the arithmetic mean of the values parallel and perpendicular to the axis of extrusion.
- ‡ Least-square fit for the curve reported for POCO graphite, grade AXF-Q1.

1.3. Experimental

1.3.1. Apparatus

Computation was done with a Honeywell CP-6 computer. Programs were written in FORTRAN 77.

A Perkin-Elmer Heated Graphite Atomizer (HGA), model 400 (The Perkin-Elmer Corporation, Norwalk, CT., USA), equipped with a laboratory-made power supply and controller was used. The laboratory-made power supply and controller allowed the final steady-state temperature (at the furnace centre) to be controlled separately from and independently of the rate of heating. The power supply and controller also permitted the heating rate of the furnace tube wall (at its centre) to be varied from 0.5 to 7.0 K ms⁻¹.

Both Perkin-Elmer pyrocoated graphite tubes (part No. 0290-1766) and pyrolytically coated (long-lasting) graphite tubes (part No. B0091-504) were used. Their dimensions are given in Fig. 4. The dimensions of these tubes used in the computer program are listed in Table 2. The difference between the pyrolytically-coated tube and the pyrocoated tube lies in the difference between the pyrolytic graphite coating processes used by the manufacturers, which result in the former having a better coating and longer useful life than the latter.

A laboratory-made platform made of anisotropic pyrolytic graphite was used. The geometric dimensions of the platform (shown in Fig. 1) used in the experiment are given in Table 3; the same dimensions were used in computing the platform temperature.

Figure 4. Geometry of the Perkin-Elmer graphite tubes: (a) pyrocoated graphite tube, (b) pyrolytically-coated graphite tube.

Table 2. Geometric dimensions of the graphite tubes
used in the computer program

Type of tube	Distance from the centre (mm)	Outer diameter (mm)	Inner diameter (mm)	Length (mm)
Perkin-Elmer pyrocoated graphite tube	0 - 8	8.00	6.0	28
	9 - 12	7.80	6.0	28
	13 - 14	8.00	6.0	28
Perkin-Elmer pyrolyti- cally-coated graphite tube (long-lasting)	0 - 8	8.15	6.0	28
	9 - 10	7.95	6.0	28
	11 - 12	7.80	6.0	28
	13 - 14	8.00	6.0	28
Standard graphite tube	0 - 14	8.00	6.0	28

Table 3. Geometric dimensions of the anisotropic pyrolytic
graphite platforms used in the experiments

Length of platform, l_p (mm)	18
Width of platform at ends, $w+\Delta w$ (mm)	0.53
Width of platform, w (mm)	0.43
Thickness of platform, b (mm)	0.20 - 0.55
Mass of platform, m_p (mg)	35 - 96

The standard graphite contact cylinders of the H3A-400 were replaced with modified ones in order to measure the axial temperature distribution of the furnace tube with an optical pyrometer. In the modified graphite contact cylinders, the graphite tube was shifted to the right into the right contact cylinder so that left half of the graphite tube was not covered by the water-cooling metal jacket. A lateral groove, 2.2 mm wide at the top, 1.8 mm wide at the bottom, and 13.8 mm long was cut on the contact cylinder along its longitudinal axis to expose a narrow zone of the outer surface of the graphite tube. During temperature measurements, graphite wedges of suitable dimensions were inserted into the groove, leaving only $1.8 \times 1.8 \text{ mm}^2$ area of the outer surface of the graphite tube uncovered at the desired positions where temperature was measured. This instrumental arrangement made the graphite tube approach an ideal blackbody against which the optical pyrometer was calibrated.

The following automatic optical pyrometers were used for measurements of temperature: one Ircon series 300, model 300, and two identical Ircon series 1100, model 11x30 (Ircon Inc., Skokie, Ill., USA) in the way described in the following section. They were installed in a mechanical device which allowed them to be manually moved parallel to the longitudinal axis of the graphite tube. The technical details of these optical pyrometers are listed in Table 4.

A Nicolet 2090-III dual-channel, digital oscilloscope, fitted with a model 201 plug-in unit and a disk recorder (Nicolet Instrument Co., Madison, Wis., USA), was used to record the voltage outputs of the pyrometers. Oscilloscopic traces were converted into temperature readings using the pyrometer calibration curves supplied by the

manufacturer.

Table 4. Particulars of the optical pyrometers used

Particulars	Ircon series 300 model 300	Ircon series 1100 model 11x30
Temperature range available (K)	380-3050	1320-3670
Temperature range used (K)	380-1400	1320-3500
Spectral response characteristics:		
Mean wavelength (μm)	2.3	0.85
Bandpass (μm)	0.6	0.3
Focussing range (cm)	43- 4 (for L-1 lens)	10-18 (for P-3 lens)
Minimum target diameter (cm)	0.14 (for L-1 lens)	0.043 (for P-3 lens)
Calibration accuracy	2% of full scale temperature	1% of full scale temperature
Repeatability	0.5% of full scale temperature	0.5% of full scale temperature
Time constant (ms)	5	1.5
Emittance adjustment (dimensionless)	0.2-1.0	none

1.3.2. Measurement of the tube wall temperature distribution in the axial direction, and determination of the boundary conditions at the furnace ends

Of the two identical automatic optical pyrometers, Ircon series 1100, model 11x30, the first pyrometer was used to measure sequentially the outer surface temperature of the graphite tube at different positions along the longitudinal axis; the second pyrometer was used to measure and monitor the inner surface temperature at the furnace centre. Using the temperature measured by the second pyrometer, the outer surface temperature measured by the first pyrometer was converted into the inner surface temperature. The temperature distributions reported in later sections were those of the inner surface of the furnace tube wall.

Even using the modified graphite contact cylinder, the temperature of the furnace end could not be measured with the optical pyrometer directly. This was because the lateral groove on the graphite contact cylinder was so designed as to maintain intimate physical contact between the graphite contact cylinder and the end of the furnace tube, resulting in the end of the furnace tube being not exposed for the temperature measurement. The temperature at the furnace ends was determined by extrapolating the curve for the measured temperature distribution in the axial direction to the tube end under various experimental conditions. Empirical functions describing boundary temperatures at the furnace ends were then extracted from these determined values and were used in the computer program.

1.4. Results and discussion

1.4.1. Boundary conditions

The theoretical model shows that for a furnace of given dimensions, the temperature-dependent property values of the graphite used in constructing the furnace and the boundary conditions for the tube wall temperature are the most important parameters determining the time-dependent temperature distribution of the furnace. The temperature-dependent property values of electrographite, pyrolytic graphite, and of argon gas used in the computer program have been listed in Table 1.

The boundary temperature at the furnace centre was measured with the automatic optical pyrometer focussed through the centrally-located sample injection hole. The graphite tube furnace departs from ideal blackbody radiation because of the existence of its two open ends, and also because of contributions from the temperature gradients along the tube length [71-72]. However, calculations by Falk [71] indicate that errors in the temperature measured through the sample injection hole using an optical pyrometer having its operational wavelength in the visible region is less than one percent for a diffusely-reflecting graphite tube provided that it has constant temperature over a tube length three times the inner diameter. With the optical pyrometer used in this study - Iacon series 1100 of mean wavelength $0.85 \mu\text{m}$ (Table 4) - and with the furnace tube in which the length of the constant-temperature segment at the end of a temperature transient is close to three times the inner diameter (as will be seen later), the

temperature at the furnace centre can be measured fairly accurately (within 2%). When the optical pyrometer, Ircon series 300, of mean wavelength of $2.3 \mu\text{m}$ was used to measure temperatures lower than 1320 K emissivity adjustment was set at 0.85 [71] to obtain accurate measurement.

The actual boundary temperature at the furnace ends was very difficult to measure. The optical pyrometer could not measure it because the water-cooling metal jacket and the graphite contact cylinder blocked its view. Viewing from the open end would have produced inaccurate results because of the reflected radiation received from other parts of the furnace. The temperature at the furnace ends was determined using the modified graphite contact cylinder and the extrapolation method described in the experimental part. However, the temperatures at the furnace ends measured by the above procedure would be higher than what they actually were in this furnace. In the normal use of the furnace, the graphite tube end is located at a position where cooling by water in the metal jacket is much more effective and hence its temperature should be lower. However, as described earlier, the graphite tube was shifted from its normal position and was moved away from the cooling water in the experimental set-up required and used for the temperature measurement.

It was found that the boundary temperatures at the furnace ends were related to the temperature and the instantaneous heating rate at the furnace centre, which in turn were related to the input electrical power. These relationships may be described by the empirical functions listed in Table 5, which were extracted from the experimentally determined furnace-end temperatures in the graphite platform furnace

and in the graphite tube furnace. The functions listed in Table 5 will be applied to these two furnaces as boundary conditions at the furnace ends. In Table 5, b_1 , b_2 and b_3 are empirical constants obtained at an initial tube wall heating rate of $b_0 = 2 \text{ K ms}^{-1}$ at the furnace centre. C_1 , C_2 and $T_{w, \text{plateau}}$ are empirical parameters which are functions of the initial heating rate at the furnace centre, and have been normalized to the value obtained by using an initial tube wall heating rate of $b_0 = 2 \text{ K ms}^{-1}$ at the furnace centre. The following three cases have been considered in Table 5.

Case No. 1. Steady state. If the instantaneous tube wall heating rate at the furnace centre is smaller than C_1 the temperature distribution of the furnace tube will be called steady-state. Figure 5 shows the experimentally determined furnace-end temperatures as a function of tube wall temperature at the furnace centre at steady state. The experimental points (symbols) were least-square-fitted by a third-order polynomial curve, S (solid line in Fig. 5), whose function is given in Table 5. Also shown in Fig. 5 are the end temperatures of the tube wall at steady state assumed by Slavin et al. [62] and by Human et al. [63], respectively. The temperature distribution in the axial direction at steady state is shown in Fig. 6(a). Figures 5 and 6(a) show that with increasing tube wall temperature at the furnace centre at steady state, the end temperature of the tube wall initially increases linearly, then increases at a continuously decreasing rate, and finally levels off. This trend was mainly due to the cold graphite contact cylinder (surrounded by the water-cooling metal jacket) which acted as a heat sink and limited the temperature increase at the furnace ends with increasing temperature at the furnace centre (i.e.,

Table 5. Boundary temperatures of the tube wall at the furnace ends

Case	Boundary temperature (K)
Steady state	$B_{2w}(t) = S = 1.476 \times 10^2 + 4.564 \times 10^{-1} T_w(0, t) + 4.868 \times 10^{-5} T_w^2(0, t) + 2.440 \times 10^{-8} T_w^3(0, t).$ $\text{for } \frac{\partial T_w(0, t)}{\partial t} < C_1, \quad 3400 \geq T_w(0, t) \geq 300.$
Non-steady state A	$\frac{\partial B_{2w}(t)}{\partial t} = 0.9 \frac{\partial T_w(0, t)}{\partial t}$ $\text{for } \frac{\partial T_w(0, t)}{\partial t} > C_2, \quad B_{2w}(t) < T_{w, \text{plateau}}$ $B_{2w}(t) = T_{w, \text{plateau}}$ $\text{for } \frac{\partial T_w(0, t)}{\partial t} > C_2, \quad B_{2w}(t) \geq T_{w, \text{plateau}}$
Non-steady state B	$B_{2w}(t) = S + \frac{T_{w, \text{plateau}} - S}{C_2 - C_1} \left(\frac{\partial T_w(0, t)}{\partial t} - C_1 \right).$ $\text{for } C_2 \geq \frac{\partial T_w(0, t)}{\partial t} \geq C_1, \quad 3400 \geq T_w(0, t) \geq 300.$
	$b_0 = 2.0 \text{ K ms}^{-1}, \quad C_1 = \left[b_0 / \frac{\partial T_w(0, 0)}{\partial t} \right] b_1.$ $b_1 = 0.08 \text{ K ms}^{-1}, \quad C_2 = \left[b_0 / \frac{\partial T_w(0, 0)}{\partial t} \right] b_2.$ $b_2 = 0.2 \text{ K ms}^{-1},$ $b_3 = 150 \text{ K},$ $T_{w, \text{plateau}} = 1300 + b_3 \left[\frac{\partial T_w(0, 0)}{\partial t} / b_0 \right].$

* $\partial T_w(0, 0)/\partial t$ is the initial wall heating rate at the furnace centre in K ms^{-1} .

Figure 5. Tube wall temperatures at the furnace ends at steady state as a function of the tube wall temperature at the furnace centre.

The solid curve, S, is the least-square-fitted polynomial function of the experimental points of this study.

(o) experimental points of this study.

(□) data assumed by Slavin et al. (taken from Fig. 3 in [62]).

(Δ) data assumed by Human et al. (taken from Fig. 3 in [63]).

with increasing input electrical power). In addition, the contact resistance of the graphite-graphite type has always a negative temperature effect caused by the thermal expansion of the graphite at high temperatures [85]. Thus, with increasing temperatures at the furnace ends, the contact resistance at the furnace ends decreases, resulting in a smaller input electrical power at the furnace ends than it would have been if the contact resistance had no negative temperature effect.

Case No. 2: Non-steady state A. If the instantaneous tube wall heating rate at the furnace centre is higher than C_2 and the instantaneous temperature at the furnace ends is lower than the plateau temperature (defined below), the temperature distribution of the furnace tube will be called non-steady state A. Table 5 shows that at non-steady state A, the input electrical power will be large enough to raise the end temperatures at a rate which is 90% of the rate at the furnace centre until the temperature at the furnace ends has reached a certain temperature, called the plateau temperature. Afterwards, because of the large temperature difference developed between the furnace ends and the cold graphite contact cylinders, and hence, because of the high rate of heat dissipation by thermal conduction from the furnace ends to the cold contact cylinders and the negative temperature effect of the contact resistance, the end temperature remains at the plateau temperature until the instantaneous tube wall heating rate at the furnace centre is no longer larger than C_2 . The experimental results show that the plateau temperature, $T_{w, \text{plateau}}$ and C_1 and C_2 are all related to the initial tube wall heating rate at the furnace centre. The higher the initial tube wall

heating rate at the furnace centre, the higher the plateau temperature at the furnace ends and the lower the C_1 and C_2 .

Case No. 3: Non-steady state B. If the instantaneous tube wall heating rate at the furnace centre is higher than C_1 but smaller than C_2 , the temperature distribution of the furnace tube will be called non-steady state B. Table 5 shows that at non-steady state B, the temperatures at the furnace ends are considered to be between that obtained at steady state and at non-steady state A. For simplicity, the end temperatures are considered to be a linear function of the instantaneous tube wall heating rate at the furnace centre. This assumes the end temperature function at steady state, S , and the plateau temperature, $T_{w, \text{plateau}}$ as the low and high limits for the temperature at the furnace ends, respectively, and C_1 and C_2 as the low and high limits for the instantaneous tube wall heating rate at the furnace centre, respectively.

Admittedly, the empirical functions summarized in Table 5 for the boundary temperature at the furnace ends, are oversimplified. Nevertheless, they basically reflect the variations in the furnace-end temperatures with variations in the temperature and the heating rate at the furnace centre. With these boundary conditions applied to the analytical model, the calculated temperature distributions of the furnace tube wall at different heating parameters at the furnace centre show a fair agreement with the measured ones, as will be seen below.

1.4.2. Comparison of the measured and the computed, time-dependent temperature distribution of the furnace tube wall

Henceforth, for the sake of simplicity, the tube wall heating

parameters including the tube wall temperature, the initial and the final tube wall temperature, the tube wall heating rate will be those at the furnace centre, unless otherwise specified.

Figures 6(a)-6(g) show the experimentally measured (symbols) and the theoretically computed (solid lines) temperature distributions of the pyrolytically-coated graphite tube (Perkin-Elmer) at selected times at various tube wall heating parameters at the furnace centre in the graphite tube furnace. The tube wall heating parameters for curves shown in Fig. 6 are summarized in Table 6. The computed temperature distributions of the tube wall in the axial direction were calculated using the dimensions of pyrolytically-coated graphite tube (Perkin-Elmer) listed in Table 2, the experimentally determined boundary temperature functions at the furnace ends listed in Table 5, and the measured temperature vs. time curves at the furnace centre [Fig. 6(h)]. The Perkin-Elmer graphite tube used was, in fact, a kind of contoured tube, i.e., the tube wall was thinner towards the ends because of inside threads, which produced temperature shoulders in the computed and experimental curves. The term 'contoured tube' will be used in this study to mean a tube having a pronounced non-uniform thickness (deliberately made) in order to increase its electrical resistance towards the furnace ends, and hence their heating rate.

The above figures show that there are generally fair agreements between the measured and the computed temperature distribution for the various tube wall heating parameters. This agreement lends confidence to the theoretical model, the boundary conditions and the property values used. However, it has to be kept in mind that the measured temperature distribution and the extracted boundary temperatures at

Figure 6. Curves in 6(a) to 6(g) are the measured (symbols) and the computed (solid lines) temperature distribution of the furnace tube wall in the axial direction at three steady state tube wall temperatures at the furnace centre [6(a)] and at selected times at various heating parameters of the tube wall at the furnace centre [6(b)-6(g)]. Curves in 6(h) are the corresponding measured tube wall temperature (at the furnace centre) vs. time curves. See Table 6 for the numerical values of the tube wall heating parameters used.

Figure 6 (a)-(d)

Figure 6 (e)-(h)

Table 6. Experimental tube wall heating parameters at the centre of the graphite tube furnace used in Fig. 6*

Figure No.	Initial wall temperature T_i (K)	Final wall temperature T_f (K)	Heating [†] rate α (K ms ⁻¹)
6(a) (I)	1170	1170	0
(II)	1770	1770	0
(III)	3000	3000	0
6(b)	470	1770	~ 2.1
6(c)	470	2970	Various [‡]
6(d)	870	2970	Various [‡]
6(e)	470	3000	~ 2.6
6(f)	1270	3000	~ 2.1
6(g)	470	3000	~ 5.7

* Perkin-Elmer pyrolytically-coated graphite tubes were used.

[†] The tube wall heating rate reported here was obtained from the linear segment of the time-dependent temperature curve.

[‡] The initial tube wall heating rate was about 2 K ms⁻¹; after that $\alpha(t)$ decreased continuously until the preset T_f was reached.

the furnace ends were both obtained from a modified furnace in which the relative position of the graphite tube to the water-cooling metal jacket had been changed, resulting in the end temperatures being higher than it would actually be in the normal furnace, as explained previously. However, the use of the boundary temperatures at the furnace ends obtained from the modified furnace should not influence the temperature distribution at the centre part of the normal furnace, nor should it influence the general trend in variations of the temperature distribution of the graphite tube with variations in the heating parameters or in the furnace dimensions.

1.4.3. Time-dependent temperature distributions of the tube wall in the graphite tube furnace and in the graphite platform furnace

Figure 7 shows the computed temperature distributions of the tube wall (a contoured tube) in the graphite tube furnace (dashed line) and in the graphite platform furnace (solid line) at selected times for given heating parameters. Figure 7 shows that when the tube wall temperature is increasing, the tube wall temperature gradient in the axial direction in the graphite platform furnace is similar to that in the graphite tube furnace. However, after the tube wall temperature at the furnace centre has reached steady state, the temperature gradient in the axial direction in the graphite platform furnace is reduced compared to that in the graphite tube furnace. This is caused by the fact that the temperature of the platform is now higher than the tube wall temperature at the furnace ends. The radiation heat transfer between the platform and the tube wall reduces the temperature gradient of the tube wall in the axial direction in the graphite platform furnace.

Figure 7. Computed tube wall temperature distributions in the axial direction in the graphite platform furnace (—) and in the graphite tube furnace (- - -) at selected times. The tube wall heating rate at the furnace center $\alpha = 2.0 \text{ K ms}^{-1}$. The initial and the final tube wall temperature at the furnace centre were: $T_i = 300 \text{ K}$ and $T_f = 2870 \text{ K}$, respectively. Dimensions of the pyrolytically-coated graphite tube (Perkin-Elmer) given in Table 2 and of the platform given in Table 3 were used in the computing. The platform thickness $\delta = 0.035 \text{ mm}$ (mass 60 mg).

1.4.4. Temperature distributions of the tube wall of a contoured tube

Contoured tubes have been investigated in graphite furnace atomic absorption spectrometry in attempts to improve matching of the analysis volume in the furnace with the cross-section of the incident radiation [86], and/or to reduce temperature gradients in the axial direction [58, 62-63, 66-68, 87], and to obtain better analytical results. Human and Rademeyer and co-workers [63, 66-68] have used a computer model to study the temperature distributions of a contoured tube furnace. Based on these studies, a 'temperature stabilized' contoured tube furnace has been designed in which heating rate at the furnace centre is much lower than that at other parts of the furnace tubes [66-67]. Atomization of analyte from the graphite contoured tube is delayed compared to that from standard tubes, similar to atomization from a graphite platform in a graphite platform furnace. Rademeyer et al. [66-67] have reported that the analytical performance of the 'temperature-stabilized', contoured furnace is competitive with that of the graphite platform furnace with respect to reduction or elimination of matrix interferences for the elements and matrices studied.

Figure 8 shows the computed temperature distributions of the Perkin-Elmer pyrocoated and pyrolytically-coated graphite tubes (both are really contoured tubes), and of the standard tubes (of uniform wall thickness) in the graphite platform furnace. Compared to the standard furnace tube (of uniform wall thickness), the temperature distributions of the contoured tube furnace (in which the tube wall is thicker at the centre and thinner at the ends) have generally the following characteristics. The heating of the tube wall is slower at

Figure 8. Computed tube wall temperature distributions of the Perkin-Elmer pyrolytically-coated graphite tube (—), pyrocoated graphite tube (- - -), and the standard graphite tube (- · - · -) in the graphite platform furnace at selected times. $\alpha = 2 \text{ K ms}^{-1}$, $T_i = 300 \text{ K}$ and $T_f = 2870 \text{ K}$. (a) $t = 1.285 \text{ s}$. (b) $t = 2.285 \text{ s}$ (1 s after the tube wall temperature at the furnace centre had remained at 2870 K). The dimensions of the tubes are given in Table 2. The dimensions of the platform given in Table 3 with thickness $b = 0.035 \text{ mm}$ (mass 60 mg) were used in computing the platform temperature.

the thicker parts than at the thinner parts, resulting in tube wall temperature showing shoulders at the latter, especially during fast heating. For a given tube wall temperature at its centre, the length of the furnace tube over which the tube wall temperature is higher than a given value is greater and the average tube wall temperature is higher than those for the non-contoured tubes. After the tube wall temperature at the furnace centre becomes constant, the temperature gradient in the axial direction at the middle part of the furnace is reduced. The extent to which these characteristics develop depends on the actual distribution of the tube wall thickness of the contoured tube and the tube wall heating parameters used with the contoured tube.

1.4.5. Effects of heating parameters of the tube wall at the furnace centre on the time-dependent temperature distributions of the tube wall

These effects will be studied in this section because of their importance in selecting optimum heating conditions. As stated earlier, whenever tube wall heating parameters are mentioned, including the tube wall temperature, the initial and the final tube wall temperature, and the tube wall heating rate, they refer to those at the furnace centre, unless otherwise specified. Figures 9 and 10 show the computed wall temperature distributions of the standard tube (of uniform wall thickness) and of the contoured tube in the graphite platform furnace at a given final tube wall temperature, T_f , but at different initial tube wall temperatures, T_i , or at different tube wall heating rates, α . The tube wall temperature at the furnace centre was

assumed to increase with increasing time at a selected rate to reach a specified maximum temperature and to remain at this temperature (called final tube wall temperature, T_f). The following observations are made from these figures.

When the temperature at the furnace centre increases with increasing time, the temperature gradient of the tube wall develops gradually. For the same initial tube wall temperature and a given tube wall temperature (Fig. 9), the higher the tube wall heating rate, the smaller is the temperature gradient at the central part of the standard tube, and the higher is the tube wall temperature-shoulder of the contoured tube. This is due to the fast rise in the input electrical power which maintains a high tube wall heating rate and also produces a relatively high temperature at the furnace ends. For the same tube wall heating rate and at a given tube wall temperature (Fig. 10), the lower the initial tube wall temperature, the smaller is the tube wall temperature gradient at the central part of the standard furnace, and the higher is the tube wall temperature-shoulder of the contoured tube. This is due to the poor thermal contact and the small initial temperature difference between the furnace ends and the graphite contact cylinders in the early stage of the transient for a low initial tube wall temperature, and hence, the small rate of heat dissipation from the furnace ends to the cold contact cylinders. For the same wall heating rate and the same initial tube wall temperature (Figs. 9 and 10), the higher the tube wall temperature at the furnace centre, the larger is the tube wall temperature gradient, caused by the much lower temperature at the furnace ends compared to

Figure 9. Effect of the tube wall heating rate (at the furnace centre) on the temperature distributions of a standard graphite tube (filled symbols) and in a contoured graphite tube (Perkin-Elmer pyrolytically-coated) in the graphite platform furnace at selected tube wall temperatures (at the furnace centre): (a) 2270 K, (b) 2870 K, (c) 1 s after the tube wall temperature at the furnace centre had remained at 2870 K. $T_i = 300$ K. $S = 1.0$ (Δ , $\triangle$), 2.0 ($\circ$, $\bullet$), and 6.0 ($\square$, $\blacksquare$) K ms^{-1} . The dimensions of the tube and the platform used in the computing were the same as given in Fig. 8.

Figure 10. Effect of the initial tube wall temperature (at the furnace centre) on the temperature distributions of a standard graphite tube (filled symbols) and of a contoured graphite tube (Perkin-Elmer pyrolytically-coated) (empty symbols) in the graphite platform furnace at selected tube wall temperatures (at the furnace centre): (a) 300 and 870 K, (b) 1270 K, (c) 2270 K (I) and 2870 K (II), (d) 1 s after the tube wall temperature at the furnace centre had remained at 2270 K (I) and 2870 K (II). $\alpha = 2.0 \text{ K ms}^{-1}$. $T_f = 2870 \text{ K}$. $T_i = 300 \text{ K}$ (o, e), 870 K (Δ , Δ), and 1200 K ($\square$, $\square$). The dimensions of the tube and the platform used in the computing were the same as given in Fig. 8.

that at the furnace centre.

Differences in the temperature gradient of tube wall caused by different tube wall heating rates or by different initial tube wall temperatures disappear with increasing time. The temperature gradient of the tube wall along its length is fully developed at steady state. However, when the tube wall heating rate is high and the initial tube wall temperature is low, there is about an 8 mm section in the middle part of the 28-mm-long-tube in which the temperature difference is less than 50 K over most of the heating cycle. This prediction from the theoretical model also agrees with the experimental results of Faly et al. [65]

Because of the temperature-shoulder given by the contoured tube, it is difficult to evaluate the effects of the initial tube wall temperature and the tube wall heating rates on the wall temperature gradient along its length. In the contoured tube, the average tube wall temperature and the length in the middle part of the furnace over which the wall temperature is higher than a given value increase with increasing wall heating rates and with decreasing initial tube wall temperatures.

Although the above predictions of the temperature distribution of the furnace tube wall have been obtained from the graphite platform furnace, they are also applicable to the graphite tube furnace (without the platform).

1.4.6. Importance of setting a cooling cycle before the atomization cycle and before the cleaning cycle

As discussed earlier, a low initial tube wall temperature and a high tube wall heating rate result in a high average tube wall

temperature and a high tube wall temperature at the furnace ends during the heating. Therefore, these experimental conditions are beneficial in the atomization cycle in order to achieve a more isothermal (spatial) atomization. They are also beneficial in the cleaning cycle in order to remove the memory effect completely, especially from the furnace ends. To obtain a low initial tube wall temperature, adoption of a cooling cycle before the atomization and cleaning cycles is necessary and is recommended.

Adoption of a cooling cycle before the atomization cycle has been suggested in our earlier papers [15, 42] for atomization from a platform in graphite platform furnace atomic absorption spectrometry since at a low initial tube wall temperature the heating of the platform is delayed longer than at a high initial tube wall temperature. The atomic absorption signal profile of the analyte is, thus, shifted more towards the isothermal region in the temperature vs. time curve of the tube wall (at the furnace centre). A reduced temperature gradient during a temperature transient obtained at a low initial tube wall temperature makes this cycle even more necessary, not only for atomization from a platform in the graphite platform furnace but also for atomization from the tube wall in the graphite tube furnace (without a platform), as has been pointed out by Slavin et al. [88]. A lower initial tube wall temperature results in a larger total volume of gas expelled by expansion and in a higher maximum gas velocity. However, at a given tube wall temperature in the graphite tube furnace or at a given platform temperature in the graphite platform furnace, variations in the gas velocity at different initial tube wall temperatures are negligible, as will be seen in Chapter 3.

In the cleaning cycle with a low initial tube wall temperature and a fast tube wall heating rate, the final tube wall temperature should be made high, but not necessarily maintained high for a long time because the temperature gradient increases at longer times under steady-state conditions. For persistent memory effects, the cooling and the cleaning cycle should be repeated until the memory effects have been completely removed or reduced to low, constant values.

Chapter 2

TIME-DEPENDENT TEMPERATURE OF THE GRAPHITE PLATFORM IN A GRAPHITE PLATFORM FURNACE

2.1. Introduction

In graphite platform furnace atomic absorption spectrometry, processes that occur in the condensed phase, including formation of pre-atomization analyte species, vaporization and/or atomization of analyte species and matrix interferences, are affected by the time-dependent surface temperatures of the platform from which samples are volatilized and atomized. Therefore, knowledge of the platform temperature is essential for understanding the characteristics of the analyte atomic absorption signal in graphite platform furnace atomic absorption spectrometry. However, publications on graphite platform temperature [15, 67, 42, 89-90] are few, perhaps because of difficulties involved in measuring the temperature of a graphite platform inside a heated graphite atomizer.

A graphite platform in the pulse-heated graphite furnace is heated mainly by radiation heat transfer from the heated furnace tube wall [5, 11]. Its temperature, therefore, lags behind that of the furnace tube wall until thermal equilibrium is established. The radiation emitted by an object whose temperature is lower than that of its surroundings is not blackbody radiation. However, its temperature measured with an optical pyrometer which has been calibrated against

blackbody radiation, (i.e., its brightness temperature, T_b), can be related to the temperature of the object (platform) and the temperature of the surroundings (furnace tube wall) by [91]:

$$\frac{1}{\exp(c_2/\lambda_c T_b) - 1} = \frac{\epsilon_p}{\exp(c_2/\lambda_c T_p) - 1} + \frac{1 - \epsilon_p}{\exp(c_2/\lambda_c T_w) - 1}$$

where c_2 is the second radiation constant in Planck's equation for the spectral emissive power of a blackbody, λ_c is the operational spectral wavelength of the pyrometer, and ϵ_p is the emissivity of the platform. The term containing T_b (the first term) is the total radiation measured by the optical pyrometer. The terms containing T_p and T_w (the second and the third term) are the emitted and the reflected radiation, respectively, received by the optical pyrometer.

The above equation shows that the emitted radiation term represents the surface temperature of the platform. When an optical pyrometer is used to measure the surface temperature of the platform through the sample injection hole of the furnace tube, a positive systematic error results from the reflected term. The magnitude of this error depends on the operational wavelength of the optical pyrometer and the temperature difference between the furnace tube wall and the platform. At long operational wavelengths, the contribution from the reflected term and the resulting systematic error is relatively small. For a large temperature difference between the furnace tube wall and the platform, the systematic error is large. Since the temperature difference between the furnace tube wall and the platform varies with time during a temperature transient, and since the variation of such temperature difference with time is different

from one temperature transient to another in which heating parameters are different, the systematic error will vary with time in a temperature transient and will be different from one temperature transient to another.

Falk [89] measured the platform temperature with an optical pyrometer having long wavelength (7 μm) and corrected for the systematic error. The platform had two sides which were inserted into the grooves made in the inside tube wall of the furnace. Falk [89] reported that electrical heating of the platform should be included in calculation of the platform temperature. In order to compare the heating of a platform with the heating of a contoured graphite tube, which, like a graphite platform delays atomization, Rademeyer et al. [67] calibrated an optical pyrometer for direct measurement of the platform temperature at quasi-steady state against the melting points of a set of pure metal pieces which had been deposited on the surface of the platform. The optical pyrometer calibrated at this quasi-steady-state temperature was used to measure the transient platform temperature [67]. However, systematic errors in the above measured platform temperature during a temperature transient still occurred because the reflected radiation received by the pyrometer at non-steady state was higher than that at the quasi-steady state. Koirtychann et al. [90] indirectly measured the platform temperature by comparing the appearance times of selected analyte elements atomized from a graphite platform with those atomized from the tube wall whose temperature had been measured with an optical pyrometer. Assuming that the appearance temperatures from both the surfaces were the same, they determined the time-dependent temperature curves of the

platform heated by the maximum-power mode of heating of the Perkin-Elmer HGA-500 at three different, final tube wall temperatures. In their experiment, the surface of the graphite furnace tube wall was chemically treated with an aqueous solution of tantalum salt, and the platform was fabricated from the above tantalum-carbidized tubes. Thus, comparable conditions were maintained for both the atomization surfaces. However, since the heating histories of the two surfaces (the platform and the tube wall) at the appearance time of the element were different, it was uncertain that the appearance temperatures from the two surfaces were the same. Such indirect measurement of the platform temperature was usually ~~time-consuming~~ and laborious and had to be repeated for each different temperature transient.

Systematic errors involved in direct measurement of platform temperature with an optical pyrometer and the inconvenience and uncertainties involved in such indirect measurement have hampered systematic studies of the heating characteristics of a graphite platform in a graphite platform furnace; this, in turn, has hampered development of a sound theoretical framework for platform atomization.

In the present study, a simplified thermal analysis of a graphite platform in the graphite platform furnace has been developed, in which the thermal analysis of the furnace tube wall is as developed in Chapter 1, and the thermal analysis of the gas phase is as developed in Chapter 3. The thermal analysis has been used to write up a computer program to allow prediction of the platform temperature as a function of time. A method for indirect measurement of the platform temperature has also been developed by using reflection of a laser beam from a pure metal powder placed on the graphite platform surface.

in intimate physical contact with it. A series of pure metals with melting points covering the whole range of temperature of interest was used. An abrupt change in the reflected radiation from the pure metal powder was correlated with the melting point of the metal [15, 42]. Predictions of the model were compared with the experimental results to establish confidence in the thermal analysis. The model was then used to determine the effects of various tube wall heating parameters and platform geometric parameters on the heating of the platform. The knowledge so gained was used to optimize experimental parameters and to understand the temperature distribution of the gas phase and the distribution of the analyte atoms in the graphite platform furnace.

2.2. Theoretical model

In Chapter 1, to simplify the mathematics of the modelling of the time-dependent temperature distribution of the furnace tube wall, the platform was assumed to be a graphite rod located at the central (longitudinal) line of the furnace. However, the temperature of the platform is calculated using the actual geometric configuration as given in Fig. 11, which shows the cross-sectional position and the dimensions of the platform relative to the furnace tube wall. Since in this model the temperature distribution of the tube wall calculated from the previous model in Chapter 1 will be used as the heat source for the platform, all the assumptions of the previous model will be also made in this model.

Additional major assumptions made in this model regarding the

temperature of the platform, are given below.

(a) A two-dimensional geometric configuration as shown in Fig. 11 can be used to model the thermal behaviour of the platform.

Although there will be significant temperature gradient in the axial direction in the furnace (Chapter 1) and thus in the platform from the axial centre line to the end planes, it has been seen from both the experimentally measured and the theoretically predicted results given in Chapter 1 that the temperature distribution of the furnace tube wall in the graphite platform furnace is rather flat over the middle 8 mm of the 28-mm-long-tube during the temperature transient. It is typically less than 50 K, at the maximum. Therefore, particularly

Figure 11. Cross-section of the graphite platform furnace and the geometric configuration assumed for calculating the platform temperature.

considering that the temperature of the platform at the middle part where the samples will be deposited is of most concern, the two-dimensional analytical model is justified. However, to take into account the temperature gradient in the axial direction of the furnace tube wall and of the gas phase, the average radiation energy emitted by the furnace tube wall and the average heat transferred from the tube wall to the platform through the inner gas by thermal conduction will be considered.

In addition, in the two-dimensional model, it is assumed that there is no circumferential variation of temperature in the furnace tube wall nor lateral variation of temperature across the width of the platform. While these assumptions are not exactly true, they are reasonably valid for the present conditions and dimensions.

(b) Electrical resistive heating of the platform is not considered in the model. There is only a very small cross-sectional area of the four bottom corners of the platform which are in physical contact with the tube wall. The contact resistance at these corners is relatively large. In addition, the electrical resistivity of the anisotropic graphite in the C direction (normal to the flat surface of the platform) is about 800 times larger than that in the AB plane (flat surface of the platform) [80]. Therefore, the effect of the electrical resistive heating on the temperature of the platform is neglected as a first order approximation. However, if the contact area of the platform with the graphite furnace tube wall is significantly large, such as in the case of a platform inserted into the grooves specially cut in the inside wall of a graphite tube (such as the Perkin-Elmer platform), the electrical resistive heating of the

platform will become relatively important, as reported by Falk [89]. Since the contact resistance varies during the temperature transient, the electrical resistive heating has not been taken into account in this model in order to keep the model mathematically simple.

(c) Radiation is the major mechanism of heat transfer. Thermal conduction through inner gas from the furnace tube wall to the platform is also taken into account. Conduction to the platform through its four corners will not be taken into account because of the very small cross-sectional areas of these corners near their tips. Natural convection through the inner gas is negligible, as explained in Chapter 1.

(d) The thermal capacity of the internal purge gas in the furnace is negligible compared to that of the platform. This is a valid assumption since the energy stored in the gas in the furnace at the maximum (expected) equilibrium temperature at the end of the heating transient (~ 3170 K) with respect to its initial temperature is about 0.1 Joule, whereas the energy stored in the platform at this equilibrium temperature with respect to its initial temperature is about 550 Joules. Therefore, heat transfer to the internal purge gas in the furnace from either the furnace tube wall or the platform has only a minor effect on the temperature transient of the platform, particularly considering the very low rates of heat transfer to the gas by conduction.

(e) Temperature gradients across the thickness of the platform are ignored. This assumption is justified by the small thickness and relatively high thermal conductivity of the graphite platform. This is

true even considering the lower value of thermal conductivity normal to the platform resulting from the anisotropic properties of the pyrolytic graphite used [79-80]. A simple but reliable criterion for justifying the neglect of internal temperature gradients is that the Biot number for the platform, representing the ratio of internal to external thermal resistances, should be less than 0.1 [75]. For the present case, the maximum value of the Biot number, based on the half-thickness of the platform and the highest equivalent radiation heat transfer coefficient (which will give the maximum Biot number) during a typical temperature transient is about 0.0063, well below the value at which internal temperature gradients must be taken into account [42].

(f) The temperature of the tube wall used in the model is the average temperature which is decided by the average radiation energy of that part of the furnace tube wall in which the platform is located, as given by equation 2.6 below. The corresponding tube wall temperature distribution is calculated using the previous model described in Chapter 1, in which the temperature of the tube wall at its centre is controlled either by the pre-described (experimentally measured) or the pre-selected, time-dependent temperature program.

(g) The temperature of the gas phase at a radial distance Δr away from the platform is given by equation 2.10 below. It is the average gas temperature of that part of the gas which is located at a radial distance Δr away from the platform and has the same axial position as the platform. The temperature distribution of the gas phase is calculated from the model described in Chapter 3 (the model of the time-dependent temperature distribution of the gas phase).

With the above assumptions and the assumptions made earlier in Chapter 1, a thermal analysis of the platform in the furnace has been developed. A heat balance on the platform yields:

$$\dot{Q}_{s,p} = - \dot{Q}_{t,p} \quad 2.1$$

The rate of heat storage in the platform at time t is given by

$$\dot{Q}_{s,p} = m_p c_{p,p} \frac{dT_p(t)}{dt} \quad 2.2$$

where $c_{p,p}$ is the specific heat capacity of the platform; m_p is the mass of the platform and can be expressed as

$$m_p = \rho_p w b l_p \quad 2.3$$

in which ρ_p is the density of the platform and is assumed constant.

The rate of heat transfer from the platform consists of two terms, i.e.,

$$\dot{Q}_{t,p} = \dot{Q}_{\text{rad},p-w}(t) + \dot{Q}_{\text{cond},p-g}(t) \quad 2.4$$

The rate of heat transfer by radiation from the platform to the furnace tube wall is given by

$$\dot{Q}_{\text{rad},p-w}(t) = \sigma A_{p,\text{total}} \mathcal{F}_{p-w}(t) [T_p^4(t) - T_{w,\text{avg}}^4(t)] \quad 2.5$$

where $A_{p,\text{total}}$ is the total surface area of the platform; $T_{w,\text{avg}}$ is the average temperature of the tube wall over the length of the platform, and is given by

$$T_{w,avg}^4(t) = \frac{\int_0^{\frac{l_p}{2}} T_w^4(x,t) dx}{\frac{l_p}{2}} \quad 2.6$$

in which $T_w(x,t)$ is calculated from the previous model described in Chapter 1.

$\mathcal{F}_{p-w}$ is the total radiation interchange factor [75] between the platform and the tube wall. It can be determined for the two-dimensional configuration shown in Fig. 11, using the radiation thermal network resistance diagram [75] shown in Fig. 12, where the surfaces are identified by the subscripts shown in Fig. 11.

In determining $\mathcal{F}_{p-w}$ from Fig. 12, one should take into account the following factors.

(1) Since there is no circumferential variation of temperature in the furnace wall, the blackbody emissive powers, and hence, the emissivities of surfaces 1w and 2w are the same at all times, i.e.,

$$E_{b,1w} = E_{b,2w} = E_{b,w} = \sigma T_{w,avg}^4 \text{ and } \epsilon_{1w} = \epsilon_{2w} = \epsilon_w.$$

(2) Since the platform is at a uniform temperature, the blackbody emissive powers and the emissivities of the top surface 1p and the bottom surface 2p are the same at all times, i.e., $E_{b,1p} = E_{b,2p} = E_{b,p} = \sigma T_p^4$, and thus $\epsilon_{1p} = \epsilon_{2p} = \epsilon_p$.

Conditions 1 and 2 account for points 1w and 2w being shown at the same potential and points 1p and 2p being shown at the same potential in Fig. 12.

(3) Since surface 1p can only 'see' surface 1w with the two-

dimensional model assumption, $F_{1p-1w} = 1.0$. Similarly, $F_{2p-2w} = 1.0$.

From the network diagram, we see that:

$$\begin{aligned} Q_{\text{rad}, p-w} &= Q_{\text{rad}, 1p-1w} + Q_{\text{rad}, 2p-2w} \\ &= (E_{b,p} - E_{b,w}) \left(\frac{1}{R_{1p-1w}} + \frac{1}{R_{2p-2w}} \right) \end{aligned} \quad 2.7$$

Determining the thermal resistances R_{1p-1w} and R_{2p-2w} by using the component resistances given in Fig. 12 and the above conditions, and by using the approximation that $A_{p, \text{total}} = A_{1p} + A_{2p}$, it can be shown by comparing equations 2.5 and 2.7 that the total radiation interchange factor, F_{p-w} , is given by:

Figure 12. Thermal network resistance diagram for the graphite platform furnace.

$$\mathcal{F}_{p-w} = \frac{1}{2} \left[\frac{1}{\frac{1}{\epsilon_p} + \frac{A_{1p}}{A_{1w}} \left(\frac{1}{\epsilon_w} - 1 \right)} + \frac{1}{\frac{1}{\epsilon_p} + \frac{A_{2p}}{A_{2w}} \left(\frac{1}{\epsilon_w} - 1 \right)} \right] \quad 2.8$$

Consistent with the assumption of a two-dimensional model, the area ratios in equation 2.8 are, strictly speaking, areas per unit length. However, to allow approximately for the fact that the platform is shorter than the furnace, the actual area ratios are used in equation 2.8 in the computer program.

The rate of heat transfer from the furnace tube wall to the platform by thermal conduction through the internal gas located at a distance of Δr away from the platform is given by

$$\dot{Q}_{\text{cond, p-g}}(t) = \kappa_g(t) A_{p, \text{total}} \frac{T_p(t) - T_{g, \text{avg}}(r', t)}{\Delta r} \quad 2.9$$

where κ_g is the thermal conductivity of the gas phase at the arithmetic mean temperature of $T_p(t)$ and $T_{g, \text{avg}}(r', t)$. $T_{g, \text{avg}}(r', t)$ is the average gas temperature at a radial position r' , which is Δr away from the platform in the radial direction and is given as

$$T_{g, \text{avg}}(r', t) = \frac{\int_0^{\frac{l_p}{2}} T_g(x, r', t) dx}{\frac{l_p}{2}} \quad 2.10$$

in which $T_g(x, r', t)$ is calculated from the model for the temperature

distribution of the gas phase described in Chapter 3.

From the foregoing equations, equation 2.1 can be expressed as

$$\begin{aligned} m_p c_{p,p} \frac{dT_p(t)}{dt} = & \sigma A_{p, \text{total}} \mathcal{F}_{p-w}(t) [T_{w, \text{avg}}^4(t) - T_p^4(t)] \\ & + \kappa_g(t) A_{p, \text{total}} \frac{T_{g, \text{avg}}(r', t) - T_p(t)}{\Delta r}, \end{aligned} \quad 2.11$$

To enable a digital computer solution for the temperature transient of the platform to be developed, equation 2.11 is written in the following finite-difference form:

$$\begin{aligned} T_p(t+\Delta t) = & \frac{2}{b \rho_p c_{p,p}} \left[\sigma \mathcal{F}_{p-w}(t) [T_{w, \text{avg}}^4(t+\Delta t) - T_p^4(t)] \right. \\ & \left. + \kappa_g(t) \frac{T_{g, \text{avg}}(r', t) - T_p(t)}{\Delta r} \right] + T_p(t), \end{aligned} \quad 2.12$$

in which approximation $A_{p, \text{total}}/m_p = 2/b$ has been used, and $t+\Delta t$ is the time expressed explicitly in terms of the previous time, t , plus a finite increment of time, Δt .

A computer program was written using equations 2.6, 2.8, 2.10 and 2.12 under the assumptions given earlier. In the computer program, the platform temperature at each time step was calculated in terms of the platform temperature and $T_{g, \text{avg}}$ at the previous time step and in terms of $T_{w, \text{avg}}$ at the present time step. $T_{w, \text{avg}}$ and $T_{g, \text{avg}}$ were calculated by calling the corresponding subroutine programs in which the temperature distribution of the furnace tube wall and the gas phase were calculated as described in Chapters 1 and 3, respectively. The temperature-dependent property values, $c_{p,p}$, ϵ_w , ϵ_p and κ_g used

in the computer program are given in Table 1, which, however, are considered constant over each time step. Using this program, studies were made to establish the sensitivity of the platform thermal behaviour to the platform geometric dimensions and to the heating parameters of the tube wall (at the furnace centre) including the tube wall heating rate, the initial and the final tube wall temperature.

2.3. Experimental

2.3.1. Apparatus

The experimental set-up is shown in Fig. 13.

A Perkin-Elmer Heated Graphite Atomizer (HGA), model 74, equipped with a laboratory-made power supply and controller and a laboratory-made anisotropic pyrolytic graphite platform described in Chapter 1 were used for this study.

A He-Ne laser (10 mW max. cw) model No. CR-80-5HMM (COHERENT, Palo Alto, California 94304) was used as the radiation source. A mechanical chopper was used to modulate the laser radiation.

A Nicolet 2090-III, dual-channel digital oscilloscope fitted with a model 201 plug-in unit and a disk recorder was used to record the voltage output of the lock-in amplifier.

Two automatic optical pyrometers - one Ircon series 1100, model 11x30, and one Ircon series 300, model 300 (Ircop, Inc., Skokie, Ill., USA) - were used. The former was used for measuring the tube wall temperature at the furnace centre and the latter for measuring the platform temperature at the end of a 30 s charring cycle through

Figure 13. Schematic diagram of the apparatus for measuring the reflection signal of a He-Ne laser beam from the platform surface. L_1 and L_2 are lenses. I_1 and I_2 are iris diaphragms with apertures set between 1-2 mm.

the sample injection hole of the furnace tube wall. The technical details of these optical pyrometers are listed in Table 4.

Computation was done with a Honeywell CP-6 computer. The program was written in FORTRAN 77.

2.3.2. Measurement procedure

The platform temperatures were measured as follows. Pure metals (99.999% pure), Sb, Ag, Cu, Ni, Co, and Pt were used. A small quantity of the chemically pure metal (in a finely powdered form) was spread on the surface of the platform at its central part in such a way as to make intimate physical contact with the platform. The reflection signal of the laser beam from a layer of the above-mentioned metal powder was measured through the sample injection hole and was plotted as a function of time of heating. A typical oscilloscopic trace of the signal given by platinum metal is shown in Fig. 14, in which the time, t_m , corresponds to the half-height of the abrupt rise in the signal. The platform temperature at this instant is taken to be the melting point of this metal. The highest platform temperature of 2045 K (the melting point of Pt) that could be measured was limited by the background signal of the present apparatus. At a tube wall temperature higher than 2300 K, the background signal due to the emission from the heated tube wall became larger than the laser signal. Therefore, at a tube wall temperature higher than 2300 K, measurement of the platform temperature by this technique was unsatisfactory.

The experimentally measured transient temperatures of the platform reported here were all obtained for platforms which had been

2

Micro-D

Figure 14. An oscilloscopic trace of the change in reflection of the laser beam from the platinum metal deposited on the platform surface. V_i and V_f are the average signal intensities before and after the melting of the metal, respectively. t_m is the time corresponding to the melting of the metal.

gas (argon) flow on (300 mL min^{-1}). This initial platform temperature was measured with an optical pyrometer having an operational wavelength of $2.3 \mu\text{m}$ (Ircon series 300, model 300), which had been calibrated against the platform temperature measured by the laser beam reflection-melting point experiments for platform temperatures 900–2100 K as described above. For platform temperatures lower than 900 K, the same pyrometer was simply calibrated against the melting points of metals using pure metal pieces ($>99.9\%$ pure) of In, Pb, Sn, and Zn. The melting points were determined visually from the physical change of the metals while the tube wall temperature was raised using a series of increments.

2.4. Results and discussion

As in the previous chapter, for simplicity, whenever the tube wall heating parameters including the tube wall temperature, the initial and the final tube wall temperature, and the tube wall heating rate are mentioned, they refer to those at the furnace centre, unless otherwise specified.

2.4.1. Comparison of the measured and the computed temperature of the platform

Figure 15 shows the calibration curve of the optical pyrometer (having an operational wavelength of $2.3 \mu\text{m}$) vs. the platform temperature at a quasi-steady state, i.e., after the platform has been pre-heated for 30 s with the internal gas (argon) flow of 300 mL min^{-1} . The platform temperature was measured as described in section 2.3.

Figure 15. Calibration curve for the optical pyrometer (Ircon series 300, model 300) for direct measurement of the platform temperature at the end of a 30 s preheating period, with an internal argon gas flow rate of 300 mL min⁻¹. The dashed line shows perfect correlation where the two temperatures are equal.

Figure 15 shows that at this quasi-steady state, the temperature measured by the optical pyrometer is higher than that determined from the melting points of the metals, and the difference in temperature increases with increasing platform temperature. This indicates a lack of thermal equilibrium between the platform and its environment under the experimental conditions used. For reasons given in section 2.1, the calibration curve shown in Fig. 15 is not applicable if the experimental conditions are different from those used in obtaining the calibration curve. Figure 16 shows the measured platform temperature vs. the tube wall temperature at the above quasi-steady state, i.e., at the end of a 30 s heating period with the internal gas (argon) flow of 300 mL min^{-1} . The platform temperature was measured with the optical pyrometer and corrected using the calibration curve shown in Fig. 15. Figure 16 also shows the computed platform temperature at quasi-steady state. The results show that at this quasi-steady state the platform temperature is lower than the tube wall temperature, resulting from the temperature gradient in the axial direction of the tube wall and of the gas phase. The temperature difference is 0–200 K for the tube wall temperature ranging from 300–2300 K. Figure 16 was used to determine the initial platform temperature at a given initial tube wall temperature in the atomization cycle.

Figure 17 shows the measured (symbols) and the computed (solid lines) platform temperatures as a function of time during temperature transients at several tube wall heating rates and initial tube wall temperatures using the gas-flow-interrupted mode. The main source of error in the measured platform temperature is the variable physical contact between the metal powder and the platform. A loose physical

Figure 16. The experimentally determined platform temperature as a function of the tube wall temperature (at the furnace centre) at the end of a 30 s preheating period, with an internal argon gas flow rate of 300 mL min^{-1} (empty symbols) and the computed platform temperature at various tube wall temperatures (at the furnace centre) at quasi-steady state (filled symbols). The dashed line shows perfect correlation where the two temperatures are equal.

Figure 17. Computed (solid line) and measured (symbols) platform temperature as a function of time at different tube wall heating parameters at the furnace centre. The dashed-lines are the measured tube wall temperature (at the furnace centre) vs. time curves. The Perkin-Elmer pyrocoated graphite tube, and the platform with dimensions given in Table 3 and with platform thickness 0.30 mm (mass 50 mg) were used. (o) $T_i = 870 \text{ K}$, $\alpha \approx 3.0 \text{ K ms}^{-1}$. (Δ) $T_i = 570 \text{ K}$, $\alpha \approx 3.4 \text{ K ms}^{-1}$. ($\square$) $T_i = 570 \text{ K}$, $\alpha \approx 0.8 \text{ K ms}^{-1}$.

contact causes systematic error of the measured platform temperature. This systematic error may be positive or negative depending on the extent of physical contact of the metal powder with the platform surface and the radiation energy received by the metal powder. A variable physical contact results in scatter of the experimental data points. The relative standard deviation of a single measurement of the time (determined as described in section 3.3.2) corresponding to the melting point of various pure metals is $\pm 8\%$. The corresponding relative standard deviation of a single value of the various measured temperatures of the platform as obtained from Fig. 17 is $< \pm 5\%$. A measure of the uncertainty in this procedure may be obtained by considering the two extreme cases - taking the times corresponding to the average reflection signal of the laser beam just before and after the abrupt rise of the signal (shown in Fig. 14) as the melting times. These two values differ by 20%. In Fig. 17 the computed temperatures agree with the measured temperatures within $\pm 10\%$.

In a recent paper presented at Carleton University, Falk [92] has shown that electrical resistive heating is important to a pyrolytic graphite platform (The Perkin-Elmer platform) which fits tightly in the grooves cut in the inside wall of a graphite tube as well as to the platform used in this study (Fig. 1). Only for the 'pin platform' that Falk [92] has developed, electrical resistive heating could be neglected. However, the 'pin platform' was made of glassy carbon. Admittedly, the neglect of the electrical resistive heating of the platform in this model results in an under-prediction of platform temperature, especially at the initial heating stage. The maximum

under-estimation of the platform temperature by this model is probably within 10-20%, depending on the heating parameters of the tube wall and the platform temperature considered. When the platform temperature obtained from the model is used to predict the appearance time and the rate of analyte atom formation from the platform, the theoretical predictions is expected to be affected. (see Chapter 4, section 4.4.1, for the discussion).

It should be mentioned that the theoretical model presented in section 2.2 is an improvement over our earlier model [42]. The improvements are: the average tube wall temperature over the length of the platform calculated using the measured tube wall temperature (at the furnace centre) vs. time curve as input is used as the temperature of the tube wall instead of the programmed behaviour of the tube wall temperature. The latter resulted in an over-prediction of the platform temperature at long heating times. Also, gas conduction is not neglected in the improved model. Neglect of gas conduction would have resulted in an under-estimation of the platform temperature by about 10% at low platform temperatures (~900 K) and 1% at high platform temperatures (~2400 K) [42]. In addition, platform temperature at the end of the charring cycle determined from the given initial tube wall temperature using Fig. 16 or calculated from the model was used as the initial platform temperature instead of using the initial tube wall temperature, which resulted in an over-estimation. These improvements in the theoretical model resulted in a better prediction of the computed platform temperature at long heating times. The fair agreement between the measured and the computed platform temperature shown in Fig. 17 means that the simplifying assumptions made in the

above model have not impaired its predictive ability.

The indirect measurement of the platform temperature presented here is limited to tube wall temperatures lower than 2300 K and is also time-consuming and laborious; whereas the model gives results in fair agreement with the measured temperature. Hence, the platform temperatures reported hereafter are the computed ones using the theoretical model.

2.4.2. Effects of mass and geometric dimensions of the platform on platform temperatures

The heating rate of a platform, dT_p/dt , is inversely proportional to its mass, and directly proportional to its total surface area (equation 2.11). As a result, the thickness of the platform has a major effect on the platform heating rate, whereas the length and the width of the platform have only a slight effect (equation 2.12). Figure 18 shows that the thicker the platform is, the longer is the delay in the platform heating and the smaller is the heating rate of the platform. The decrease in the heating rate of the platform with increasing platform thickness is greater at a relatively high platform temperature e.g., 2000 K than at a relatively low platform temperature e.g., 1000 K.

Figure 18. Computer plots of the platform temperature (solid lines) as a function of time with the platform thickness as a parameter. From left to right: $b = 0.20$ mm, 0.35 mm, and 0.75 mm (corresponding masses 35, 60, and 96 mg). The dashed line is the tube wall temperature (at the furnace centre) vs. time curve. $\alpha = 2.0 \text{ K ms}^{-1}$. $T_f = 2870 \text{ K}$. $T_i = 300 \text{ K}$. The dimensions of the pyrolytically-coated (Perkin-Elmer) graphite tubes given in Table 2 and the platform dimensions given in Table 3 were used in the computing.

2.4.3. Effect of tube wall heating parameters (at the furnace centre) on platform temperatures

Figures 19-21 show the computer plots of the effect of the tube wall heating rate and of the initial and the final tube wall temperature on the platform temperature. The following points are of interest.

(a) The heating of the platform is nonlinear. It is extremely slow in the initial and the final stage of the heating cycle. At longer heating times, the platform temperature even decreases slightly with increasing time because of the decreased $T_{w,avg}$ caused by the temperature gradient in the axial direction of the tube wall. Because of the temperature gradient in the axial direction of the tube wall as well as of the gas, the platform temperature is lower than the tube wall temperature at the furnace centre even at quasi-steady state which prevails at long heating times.

(b) The higher the tube wall heating rate, the lower is the platform temperature at the time when the tube wall temperature at the furnace centre reaches the steady-state temperature. Also, the higher the tube wall heating rate, the higher is the heating rate of the platform at any given platform temperature, and the lower is the platform temperature at which the heating rate of the platform during a temperature transient has its maximum value (Fig. 19).

(c) The lower the initial tube wall temperature, the longer is the delay in the initial heating of the platform, and the higher is the maximum heating rate of the platform (Fig. 20).

(d) After the initial heating stage, the final tube wall temperature has an effect on the heating of the platform. The higher

Figure 19. Computer plots of the tube wall temperature (at the furnace centre) (dashed lines) and the corresponding platform temperature (solid lines) as a function of time at different tube wall heating rates (at the furnace centre). (a) From left to right: $\alpha = 6.0, 2.0,$ and 1.0 K ms^{-1} . $T_i = 300 \text{ K}$. $T_f = 2270 \text{ K}$. (b) From left to right: $\alpha = 3000, 6.0, 2.0,$ and 1.0 K ms^{-1} . $T_i = 300 \text{ K}$. $T_f = 2870 \text{ K}$. The dimensions of the tube and the platform used in the computing were the same as given in Fig. 18. The platform thickness was 0.35 mm (mass 60 mg).

Figure 20. Computer plots of the tube wall temperature (at the furnace centre) (dashed lines) and the corresponding platform temperature (solid lines) as a function of time at different initial tube wall temperatures (at furnace centre), from left to right: $T_i = 1270, 870, \text{ and } 300 \text{ K}$. $\alpha = 2.0 \text{ K ms}^{-1}$.

(a) $T_f = 2270 \text{ K}$; (b) $T_f = 2870 \text{ K}$. The dimensions of the tube and the platform used in the computing were the same as given in Fig. 19.

Figure 21. Computer plots of the tube wall temperature (dashed lines) and the corresponding platform temperature (solid lines) as a function of time at different final tube wall temperatures, from top to bottom: $T_f = 2870, 2570, 2270$ and 1970 K. $\alpha = 2.0 \text{ K ms}^{-1}$. $T_i = 300$ K. Dimensions of the tube and the platform used in the computing were the same as given in Fig. 19.

the final tube wall temperature, the higher is the highest platform temperature achieved, the faster is the heating of the platform at a given platform temperature, and the shorter is the delay in the platform heating (Fig. 21).

(c) The heating rates of a given platform can be higher or lower than the heating rate of the tube wall depending on the tube wall heating parameters and the platform temperatures considered, as can be seen from Table 7. However, in the temperature range of interest of the platform (800–2200 K, where the analyte atomic absorbance signal appears), they are of the same order. At low final wall temperatures

Table 7. Heating rates of the platform* at different platform surface temperatures calculated from the computed platform temperatures at various tube wall heating parameters

Tube wall heating parameters			Platform heating rate (K ms^{-1})			
T_i	T_f	α	At platform temperature (K)			
(K)	(K)	(K ms^{-1})	600	1200	1600	2000
300	2270	1.0	0.7	1.2	0.9	0.2
300	2270	2.0	1.2	1.0	0.9	0.2
300	2270	6.0	2.3	1.5	1.0	0.2
300	2870	1.0	0.7	1.2	1.6	2.2
300	2870	2.0	1.4	2.5	3.5	2.6
300	2870	6.0	2.5	3.6	3.5	2.8
300	2870	3000.0	6.5	4.5	4.0	3.0

* Platform 18 mm long, 5.2 mm wide, 0.35 mm thick and weighing 60 mg, with cuts 0.5 mm deep along its lateral edges.

and at high platform temperatures, the platform heating rate is rather insensitive to the tube wall heating rate. For example, as seen from Table 7, an increase in the tube wall heating rate from 6 to 3000 K ms⁻¹ does not result in any substantial increase in the platform heating rate at high platform temperatures (> 1000 K). This is because the rate of platform heating by radiation heat transfer depends on the difference between the temperature of the donor (furnace tube wall) and the receiver (platform), each raised to the power four. This difference in temperature is limited, at an extremely fast wall heating rate, e.g., 3000 K ms⁻¹ by the final tube wall temperatures used, and by the maximum tube wall temperature attainable in practice with a graphite tube furnace.

2.4.4. Optimization of the tube wall heating parameters and the platform thickness in graphite platform furnace atomic absorption spectrometry

Previous discussions indicate that, generally speaking, the delay in the heating of the platform relative to the heating of the tube wall is long for a thick platform heated at a low initial tube wall temperature, a low final tube wall temperature and a high tube wall heating rate. The heating rate of the platform is high for a thin platform heated at a low initial tube wall temperature, a high final tube wall temperature and a high tube wall heating rate. Therefore, a low initial tube wall temperature and a high tube wall heating rate should be used in graphite platform furnace atomic absorption spectrometry in order to achieve fast heating of the platform and to prolong the delay in the analyte atomization from a platform to such time as the tube wall and the gas phase have reached (or

closely approached) steady-state temperatures. Besides, as discussed in Chapter 1, when a low initial tube wall temperature is used in combination with a relatively high tube wall heating rate, the tube wall temperature gradient in the axial direction is small at the initial stage of heating, which is beneficial. For the sample which requires a high charring temperature in order to reduce or to eliminate matrix interferences, a cooling cycle between the charring and the atomization cycle should be inserted in order to achieve a low initial tube wall temperature. It is unnecessary to use any tube wall heating rates higher than, say, 10 K ms^{-1} because the increase in the platform heating rate at high tube wall heating rates is limited by the maximum tube wall temperature ($\sim 3300 \text{ K}$) attainable in practice with a graphite furnace, as mentioned earlier.

For relatively volatile elements, the atomic absorption signals of which usually appear at low platform temperatures, atomization from a relatively thick platform heated at a high final tube wall temperature should shift the atomic absorption signal of the analyte towards the high, constant-temperature region of the tube wall. For low-volatility elements, the atomic absorption signals of which usually appear at high platform temperatures (where the heating rate of the platform is low), atomization of the analyte from a relatively thin platform heated at a high final tube wall temperature is recommended for rapid heating of the platform and for complete atomization. However, a platform thinner than 0.20 mm is not practical because such a light platform (unless it is firmly held) is liable to change its position in the furnace tube during sudden thermal expansion of the gas phase on rapid heating. A final tube wall

temperature higher than 2970 K is normally not desirable because repeated heating at higher temperatures would shorten the useful life of the graphite tube by oxidation.

It appears from the above discussion that the charring curve [i.e., absorbance of the analyte vs. variable charring temperatures at a constant (optimal) atomization temperature] is the combined result of three separate factors: 1) shift of the atomic absorption pulse towards the isothermal region of the tube wall temperature curve with decreasing charring temperature; 2) decrease in the heating rate of the platform with increasing charring temperatures; 3) effect of the charring temperature itself (i.e., effect of the temperature used in charring on the analyte species) - only the last effect is present in the charring curve obtained in tube wall atomization. In platform atomization, the combined result of the above three factors may cause the peak-height absorbance of relatively volatile elements to decrease with increase charring temperatures at relatively low tube wall (atomization) temperatures, as shown in Fig. 22. However, this problem can and should be avoided by inserting a cooling cycle between the charring and the atomization cycle.

Figure 22. Charring curves for Pb (taken as the nitrate) without a cooling cycle (Δ) and with a cooling cycle (o) at 470 K. The Perkin-Elmer Heated Graphite Atomizer (HGA), model 500, and maximum power heating mode were used. $T_f = 2270$ K.

Chapter 3

TIME-DEPENDENT TEMPERATURE DISTRIBUTION OF THE GAS PHASE IN A GRAPHITE TUBE FURNACE AND IN A GRAPHITE PLATFORM FURNACE

3.1. Introduction

Knowledge of the temperature of the gas phase experienced by an analyte vapour in a semi-enclosed, pulse-heated graphite furnace is essential for predicting the characteristics of the atomic absorbance signal of the analyte, for understanding transport processes of the analyte atoms, mechanisms of atomization, and matrix interferences in the gas phase. This is because of the fact that after the analyte is vaporized from the graphite surface, physical and chemical processes involving the analyte are governed by the temperature of the gas phase inside the graphite furnace. Such physical and chemical processes are: transport of analyte atoms by diffusion and by forced convection (in the presence of a purge gas flow), or by convection due to expansion of the heated gas (in the absence of a purge gas flow), adsorption, desorption, condensation, re-vaporization, dissociation of analyte species, ionization of neutral atoms and chemical reactions of analyte species with gaseous species present or produced in the graphite furnace.

The temperature distribution of the gas phase inside the graphite furnace depends upon a number of factors, including the temperature distribution of the furnace wall (which results from geometry and

design features of the furnace, and heating program of the furnace wall), thermal properties of the internal gas used, and presence or absence of a forced convective flow of a purge gas. In a graphite platform furnace, the temperature distribution of the gas phase also depends upon the temperature of the graphite platform in addition to the above factors. Because the tube wall temperature of a Maassmann-type, pulse-heated graphite furnace is time-dependent and has a temperature gradient in the axial direction, the temperature of the gas phase inside the furnace is also time-dependent. The gas phase has also gradients in both the axial and radial directions. Generally speaking, the temperature gradient in the radial direction in a graphite platform furnace is expected to be even larger than in the graphite tube furnace (without the platform) because of the large differences in temperature between the furnace tube wall and the platform, as shown in Chapter 2.

Spectroscopic determination of gas temperature in a graphite furnace by the two-line atomic absorption method has been reported [93-100]. The gas temperature in a graphite platform furnace has been determined by the two-line atomic absorption method [42, 101] and the line-reversal method [90]. However, these methods offer temporal but not spatial resolution. Rief et al. [102] have critically reviewed the theoretical concepts underlying the spectroscopic flame temperature measurement and their physical significance. The authors have pointed out that for the gas phase which is spatially nonisothermal the gas temperature determined by the above spectroscopic methods represents neither the average gas temperature nor the weighted-average gas temperature. The temperature, so

determined has been called 'effective gas temperature' [102-103]. The effective gas temperature, $T_{g, \text{eff}}$, depends on the particular temperature gradient present in the gas phase, the measurement method employed, the concentration distribution of the thermometric species, and the energy of the spectroscopic terms involved in the transition producing the line. Therefore, even for the same gas phase, with the same measurement method but different thermometric species or different lines of the same thermometric species, measured effective gas temperatures can be different, as has been reported in the literature.

In contrast to the two-line atomic absorption method or the line-reversal method, the two-line atomic fluorescence method permits spatially-resolved measurement of local temperature in the gas phase [104-106]. The advent of tunable cw dye lasers and development of dyes covering the visible and near ultraviolet spectrum have enabled application of the two-line atomic fluorescence method to non-steady-state conditions [107], offering both temporal and spatial resolution. For spatial resolution in the axial direction, small holes have to be cut at different axial positions of the furnace tube wall to let the laser radiation pass through the holes. So far, the laser-excited two-line atomic fluorescence method has not been used to determine the gas temperature in a graphite furnace.

Theoretical models for gas temperature in the Massmann-type graphite tube furnace [68, 97, 100] have demonstrated their capability for predicting quantitative time-dependent temperature distribution of the gas phase. The main features of these models are summarized in Table 8.

Table 8. Features of various theoretical models for gas temperature distribution in a pulse-heated graphite tube furnace

Features considered in the model		
Description	van den Broek et al. [97]	Charrabart et al. Rademeyer et al. [100] [68]
Pressure inside the furnace	Constant	Constant
Internal gas flow mode	For stopped-flow mode and forced-flow mode	For stopped-flow mode and forced-flow mode
Time-dependence of tube wall temperature	Yes	Yes
Gradient in tube wall temperature in the axial direction	No	No
Thermal conduction in the axial direction	No	Yes
Thermal conduction in the radial direction	No	No
Heat transfer from tube wall to gas	By thermal conduction only	By thermal conduction only

(continued)

Table 8 (continued)

Description	Features considered in the model	
	van den Broek et al. [97]	Chakrabarti et al. [100]
Heat transfer coefficient from wall to gas, h	<p>Stopped-flow mode: $h = 4 \kappa_g / (d_1/2)$</p> <p>Forced-flow mode: $h = 2.5 \kappa_g / (d_1/2)$</p>	<p>Stopped-flow mode: no heat transfer coefficient at the tube wall is necessary</p> <p>Forced flow mode: $h = 2.5 \kappa_g / (d_1/2)$</p>
Natural convection	No	No
Temperature-dependence of property values of gas	Yes	Yes
The amount of gas heated	Constant	Variable according to Ideal Gas Law
Expansion velocity of stagnant gas	Not calculated	<p>Calculated at the furnace centre with</p> $\frac{\partial T_g}{\partial x} = 0 \text{ at the furnace centre}$
Direction of forced flow	From the furnace ends to its centre	From the furnace ends to its centre

The model of van den Broek et al. [97] has many over-simplified assumptions. It predicts that in the absence of a forced, convective gas flow, the gas temperature follows the wall temperature of the heated furnace to within a few degrees. When a significant flow of a protective, cold (internal) gas is forced through the furnace, the gas temperature varies greatly along the furnace length and its average value can be several hundred degrees (300-1150 K) lower than the wall temperature.

The model proposed by Chakrabarti et al. [100] is also an over-simplified one, in which the furnace wall temperature is assumed to be uniform in the axial direction, and thermal conduction in the axial direction in the gas phase is not taken into account. Therefore, the model gives an approximation of the gas temperature distribution in the radial direction at the furnace centre. The model [100] predicts that the time-dependent gas temperature distribution in the radial direction is affected by the tube wall heating rate, the initial and the final tube wall temperature. It also predicts a maximum temperature difference of about 100 K between the tube wall and the gas phase at the furnace centre (for a tube wall heating rate of 2 K s^{-1} and an initial tube wall temperature of 470 K), occurring near the beginning of the heating cycle. Thereafter, the gas temperature asymptotically approaches the tube wall temperature (within a few degrees), and the gas temperature gradient in the radial direction diminishes after the tube wall temperature attains a steady-state value.

In a recently developed model by Rademayer et al. [68], the tube wall temperature gradient and the thermal conduction in the gas, both

in the axial direction, have been taken into account. In this respect, the model of Rademeyer et al. [68] is a significant improvement on the previous models. Unfortunately, as in the model of van den Broek et al. [97], in the model of Rademeyer et al. [68], thermal conduction in the radial direction in the gas phase has not been taken into account and the temperature gradient in the radial direction has been neglected. This neglect, in the absence of a forced convective gas flow, is equivalent to assuming a lumped-thermal-capacity model [75] of the gas in order to predict an effective heat transfer coefficient. A simple rule-of-thumb that can be used to establish conditions under which the lumped-thermal-capacity model can be used is that the Biot number, $(h d_i)/2\kappa_g$ (where h , d_i and κ_g are the heat transfer coefficient, the inner diameter of the tube, and the thermal conductivity of the gas, respectively,) must be less than 0.1 [75], whereas the models of van den Broek et al. [97] and Rademeyer et al. [68] explicitly set this parameter equal to 4 and 2.5, respectively. The model of Rademeyer et al. [68] predicts, in the absence of a forced, convective gas flow, a temperature difference between the tube wall and the gas (at the furnace centre) as a function of time, similar to the prediction of the model of Chakrabarti et al. [100]. The model [68] also predicts similar trends in the presence of a forced, convective gas flow, but with an even larger temperature difference between the tube wall and the gas. Using the model [66-68] they have calculated the time-dependent temperature distribution of the gas phase in the axial direction in differently-shaped, contoured, graphite tubes, and have reported that the gas temperature at the central part of the contoured tube is higher than the tube wall

temperature at the furnace centre.

Heating of the gas results in its expansion. This means that time-dependent gas temperature distribution is accompanied by time-dependent gas velocity distribution, which plays an important role in the transport process for analyte atoms. The gas (expansion) velocity at the furnace ends reported by the earlier model of Chakrabarti et al. [100] is over-estimated because of the neglect of the temperature gradient of the gas phase in the axial direction. In the model of Rademeyer et al. [68], the direction of gas expansion in the absence of a forced, convective gas flow has been considered to be from the furnace ends towards the furnace centre, whereas it follows from symmetry that the gas velocity at the furnace centre is zero [100, 108-109]. Based on a simplified model in which temperature distributions of the gas phase in the radial and the axial direction have not been taken into account and in which the gas is assumed to be heated at a constant rate as is the tube wall, Holcombe [108] calculated the relative amount of gas expelled at the furnace ends and estimated the relative rates of analyte loss by diffusion, thermal expansion of the gas and expulsion caused by gas evolution from the vaporized matrix. In a theoretical model of the transport process of analyte atoms in a semi-enclosed, graphite tube furnace in atomic absorption spectrometry, Gilmutdinov et al. [109] formulated analytical expressions for the gas (expansion) velocity in the absence of a forced, convective gas flow, using mass balance of the heated gas and allowing for spatial and temporal nonisothermality of the furnace. Using the analytical expressions, they have predicted a general trend in the gas velocity with time and with nonisothermality of the

furnace.

— Although theoretical models for the time-dependent temperature distribution of the gas phase in the graphite tube furnace have been reported [66-68, 97, 100], no studies on the temperature distribution of the gas phase in a graphite platform furnace have been reported in the literature.

This chapter presents a sophisticated model for the heating characteristics of the gas phase in the gas flow interrupt-mode in the graphite platform furnace as well as in the graphite tube furnace. In this theoretical model, the tube wall temperature gradient in the axial direction has been taken into account, as described in Chapter 1, and temperature gradients of the gas phase in both the axial and the radial direction have been considered. The theoretical model has been used in a computer program to predict temperatures and velocity distributions of the gas at various tube wall heating parameters. The time-dependent, weighted-average gas temperatures predicted by the theoretical model have been compared with the time-dependent, effective gas temperatures determined by the two-line atomic absorption method. The time-dependent temperature and velocity distributions of the gas will be used in Chapter 4 to simulate transport processes of analyte atoms in the graphite platform furnace.

3.2. Theoretical model

This model calculates the time-dependent temperature distribution of the gas inside the graphite tube furnace and the graphite platform furnace in the absence of a forced, convective gas flow. The geometric configurations considered in the model are the same as described in Chapter 1 and in Fig. 1. In this model, the temperature distribution of the furnace tube wall and of the platform are as calculated using the models described in Chapters 1 and 2, respectively. Hence, all the assumptions made in the previous models in Chapters 1 and 2 are also made here.

The following additional major assumptions regarding thermal behaviour of the gas inside the graphite furnace are made.

Figure 23. Geometric configuration assumed for calculating the temperature distribution of the gas phase in the graphite platform furnace.

(a) The geometric configuration shown in Fig. 23 can be used to model the thermal behaviour of the gas phase in the graphite platform furnace. The same geometric configuration (but without the graphite platform) can be used to represent the thermal behaviour of the gas phase in the graphite tube furnace. In the geometry assumed, the existence of the sample injection hole in the furnace tube wall is ignored. Also, the rectangular platform is assumed to be a cylindrical rod (having the same mass, similar volume and surface area as the actual platform) located along the central line (longitudinal axis) of the furnace. Considering the symmetry of the assumed geometry the temperature of the gas phase is assumed to vary with the axial and radial coordinates, x and r , at each instant. Thus, the model allows for temperature gradients in the gas phase in both the axial and the radial direction.

Whereas these assumptions are not exactly valid, they are consistent with the corresponding assumptions made in the previous model for temperature distribution of the furnace tube wall and they will be reasonably valid for the present conditions and dimensions. The assumption that the platform takes the form of a cylindrical rod greatly simplifies the mathematics of the model without seriously impairing the validity of the results.

(b) The gas contained inside the furnace is an ideal gas at constant atmospheric pressure. The flow of the gas caused by its expansion as it is heated is laminar, which will be satisfied if the Reynolds number is below 2300 [75].

(c) Heat transfer from the furnace wall or the platform to the gas phase and within the gas phase in the furnace is by thermal

conduction only. The effect of heat transfer by natural convection in the gas phase and the effect of radiation heat transfer to the gas phase are negligible, as have been explained in the model given in Chapter 1.

(d) Any laminar boundary layer development [75] on the wall of the furnace or on the platform resulting from the expansion of the gas as it is heated will have no significant effect on the heat transfer rate from the wall or the platform to the gas because of the very low transient gas velocity and very short half-length of the furnace. This assumption is consistent with the assumption that heat transfer from the tube wall to the gas is by conduction only.

(e) Molecules of gas impinging on the furnace wall or on the platform rapidly reach thermal equilibrium with the wall of the platform. That is, there is no temperature discontinuity between the furnace wall, the platform and the adjacent gas. This condition will be satisfied if the ratio of the mean free path of the molecules to the furnace diameter, the Knudsen number, is well below unity [75].

(f) The heat dissipation by the expansion of the gas through the sample injection hole is neglected. The area of the sample injection hole is relatively small compared with the transverse cross-sectional area of the gas-filled furnace tube.

(g) The temperature-dependent property values of the graphite, the sheath gas and the gas inside the furnace are allowed to vary with temperature, i.e., to vary with coordinates and with time because the temperature is a function of both coordinates and time.

The following assumptions are made regarding the boundary and the initial condition.

(h) Time-dependent temperature distribution of the tube wall and time-dependent temperature of the platform are as calculated by the previous models in Chapters 1 and 2.

(i) The temperature distribution of the gas phase in the radial direction at the furnace tube ends at each instant is dependent on the heat conduction at the tube ends in the radial and axial directions. The gas temperatures just outside the tube ends are assumed as the arithmetic mean of 370 K (the boiling point of water in the water-cooling metal jacket) and the temperatures at the furnace ends.

(j) If the initial tube wall temperature at the furnace centre is the room temperature, then the initial temperature distribution of the gas phase is uniform and the initial temperature is the room temperature. When the initial tube wall temperature at the furnace centre is higher than the room temperature, there will be initially a non-uniform temperature distribution of the gas phase. To determine this initial gas temperature, the model itself is used, assuming quasi-steady state, with the known initial tube wall temperature at the furnace centre to establish the initial temperature distribution of the gas phase.

With the above assumptions, an energy balance and a mass balance for an infinitesimal gas ring located at position (x, r) with axial length Δx , radial width Δr , as shown in Fig. 24, are considered. An energy balance between the rate of heat storage, and the rate of heat transfer yields the following equation:

$$\dot{Q}_{s, g} = - \dot{Q}_{t, g} \quad 3.1$$

The rate of heat storage at the gas ring at (x, r, t) is

$$\dot{Q}_{s,g} = \frac{\partial}{\partial t} [\rho_g(x, r, t) c_{v,g} 2\pi r dr dx T_g(x, r, t)] \quad 3.2$$

The rate of heat transfer from the gas ring at (x, r, t) is

$$\begin{aligned} \dot{Q}_{t,g} = & - \frac{1}{r} \frac{\partial}{\partial r} \left[\kappa_g(x, r, t) r \frac{\partial T_g(x, r, t)}{\partial r} \right] dr 2\pi r dx \\ & - \frac{\partial}{\partial x} \left[\kappa_g(x, r, t) \frac{\partial T_g(x, r, t)}{\partial x} \right] dx 2\pi r dr \\ & + 2\pi r dr c_{p,g} \frac{\partial}{\partial x} [\rho_g(x, r, t) u_{x,g}(x, r, t) T_g(x, r, t)] dx, \end{aligned} \quad 3.3$$

where $u_{x,g}$ is the gas velocity in the x direction.

Substituting equations 3.2-3.3 into equation 3.1 and noting that

Figure 24. Infinitesimal ring of gas located at position (x, r) with length (axial direction) dx and width (radial direction) dr .

for a perfect gas

$$\rho_g(x, r, t) = \frac{M_g P}{R T_g(x, r, t)} \quad 3.4$$

in which M_g and R are the molar mass of the gas and the gas constant, respectively, and the pressure P is assumed to be constant, we have

$$c_{p, g} \rho_g(x, r, t) T_g(x, r, t) \frac{\partial u_{x, g}(x, r, t)}{\partial x} = - \frac{1}{r} \frac{\partial}{\partial r} \left[\kappa_g(x, r, t) r \frac{\partial T_g(x, r, t)}{\partial r} \right] + \frac{\partial}{\partial x} \left[\kappa_g(x, r, t) \frac{\partial T_g(x, r, t)}{\partial x} \right] \quad 3.5$$

A mass balance on the infinitesimal gas ring yields the following equation:

$$\frac{\partial}{\partial t} [\rho_g(x, r, t) 2\pi r dr dx] = - \frac{\partial}{\partial x} [\rho_g(x, r, t) 2\pi r dr u_{x, g}(x, r, t)] dx \quad 3.6$$

Substituting equation 3.4 into equation 3.6, the latter can be expressed as

$$\frac{\partial u_{x, g}(x, r, t)}{\partial x} = \frac{1}{T_g(x, r, t)} \frac{\partial T_g(x, r, t)}{\partial t} + \frac{u_{x, g}(x, r, t)}{T_g(x, r, t)} \frac{\partial T_g(x, r, t)}{\partial x} \quad 3.7$$

Equation 3.7 is subject to the boundary condition that the gas velocities at the furnace centre and well outside the furnace ends are assumed to be zero, the gas velocities at the furnace wall and at the platform are also assumed zero (which allows approximately for the effect of viscous drag).

It should be mentioned that it has been assumed that the total

pressure is constant throughout the semi-enclosed furnace, and hence, the momentum conservation equation has not been explicitly solved for the motion of the gas.

Substituting equation 3.7 into equation 3.5, we have

$$c_{p,g} \rho_g(x, r, t) \left[\frac{\partial T_g(x, r, t)}{\partial t} + u_{x,g}(x, r, t) \frac{\partial T_g(x, r, t)}{\partial x} \right] - \frac{1}{r} \frac{\partial}{\partial r} \left[\kappa_g(x, r, t) r \frac{\partial T_g(x, r, t)}{\partial r} \right] + \frac{\partial}{\partial x} \left[\kappa_g(x, r, t) \frac{\partial T_g(x, r, t)}{\partial x} \right] = 0 \quad 3.8$$

for the gas phase in both the graphite tube furnace and the graphite platform furnace.

In the graphite tube furnace, equation 3.8 is subject to the following boundary conditions:

$$T_g(x, r, t) = T_w(x, t), \quad \text{for } \frac{l_w}{2} \leq x \leq 0, \quad r = \frac{d_i}{2}, \quad t > 0; \quad 3.9a$$

$$T_g(x, r, t) = B_g(x, r, t), \quad \text{for } x = \frac{l_w}{2}, \quad \frac{d_i}{2} > r > 0, \quad t > 0; \quad 3.9b$$

$$\frac{\partial T_g(x, r, t)}{\partial r} = 0, \quad \text{for } \frac{l_w}{2} \leq x \leq 0, \quad r = 0, \quad t > 0; \quad 3.9c$$

$$\frac{\partial T_g(x, r, t)}{\partial x} = 0, \quad \text{for } x = 0, \quad \frac{d_i}{2} > r > 0, \quad t > 0; \quad 3.9d$$

and the following initial condition:

$$T_g(x, r, 0) = I_g(x, r), \quad \text{for } \frac{l_w}{2} \leq x \leq 0, \quad \frac{d_i}{2} \geq r \geq 0. \quad 3.10a$$

In the graphite platform furnace, the following equations are substituted for equations 3.9c and 3.9d.

$$T_g(x, r, t) = T_p(t), \quad \text{for } \frac{l_p}{2} \geq x \geq 0, \quad r = r_p, \quad t > 0; \quad 3.9e$$

$$\frac{\partial T_g(x, r, t)}{\partial r} = 0 \quad \text{for } \frac{l_g}{2} \geq x \geq \frac{l_p}{2}, \quad r = 0, \quad t > 0; \quad 3.9f$$

$$\frac{\partial T_g(x, r, t)}{\partial x} = 0, \quad \text{for } x = 0, \quad \frac{d_i}{2} \geq r \geq r_p, \quad t > 0. \quad 3.9g$$

And the following equation is substituted for equation 3.10a.

$$T_g(x, 0) = I_g(x, r), \quad \text{for } \frac{l_w}{2} \geq x \geq \frac{l_p}{2}, \quad \frac{d_i}{2} \geq r \geq 0,$$

$$\text{and for } \frac{l_p}{2} \geq x \geq 0, \quad \frac{d_i}{2} \geq r \geq r_p. \quad 3.10b$$

In the above equations, $c_{p,g}$, ρ_g , κ_g are the heat capacity of the gas at constant pressure, the density and the thermal conductivity of the gas, respectively. These values for argon gas (which is commonly used in pulse-heated graphite furnace atomic absorption spectrometry) have been listed in Table 1. B_g is the boundary temperature at the tube end given by assumption (i). I_g is the initial temperature distribution of the gas phase. T_w and T_p are prescribed functions, which can be calculated using the models given in Chapters 1 and 2, respectively. In the above equations, only the temperature distribution of the gas phase over its half length is considered because of the cylindrical symmetry of the graphite furnace.

From the temperature distribution of the gas phase, the weighted-average gas temperature of the furnace, $T_{g,w \text{ avg}}$, can be obtained in cylindrical coordinates as follows:

$$T_{g,w \text{ avg}}(t) = \frac{\int \int_{\text{(furnace volume)}} \rho_g(x, r, t) T_g(x, r, t) 2\pi r \, dx \, dr}{\int \int_{\text{(furnace volume)}} \rho_g(x, r, t) 2\pi r \, dx \, dr} \quad 3.11$$

A computer program has been written using equations 3.7-3.11 to obtain temperature and velocity distributions of the gas, as well as the weighted-average gas temperature of the furnace. In the computer program, equation 3.8 has been approximated by a numerical method using the splitting technique [110-111]. With this technique, the two-dimensional problem of equation 3.8 is reduced to two steps which involve difference approximation in only one dimension at a time, i.e., temperature distribution of gas due to the thermal conduction in the radial direction, and due to the thermal expansion and conduction in the axial direction. In each step, the backward or implicit finite-difference approximation method was used at a set of nodal points. The Crout Reduction method for Tridiagonal Linear Systems was used for solving the above problem [76]. Because equations 3.7 and 3.8 are interrelated, they were approximated as follows. The velocity and temperature distributions of the gas were calculated assuming $\partial T_g / \partial x = 0$ at first. The gas velocity thus obtained was then used in equation 3.8 (without assuming $\partial T_g / \partial x = 0$) to calculate the gas temperature distribution, which was then used in equation 3.7 to calculate the gas velocity. This procedure was repeated until the velocity and the temperature distribution of the gas phase were

stabilized within 0.1%. The details of the numerical approximation of equations 3.7-3.10 with the splitting technique used in the computer program are given in Appendix III.

In the computer program, there are 15 nodes in the axial direction (including the central node and the end node), and there are 10 nodes in the radial direction. The radial boundary conditions for equation 3.8 were obtained at each time step by calling the subroutine programs which calculated the time-dependent temperature distribution of the furnace tube wall and of the platform according to the models in Chapters 1 and 2. The property values which are temperature-dependent are the same as listed in Table 1. As explained earlier, these property values at any nodes in the computer program were considered to be constant over the control volume and the time step. For adjacent nodes, the arithmetic mean value of the temperature of the two nodes was used as the temperature at which the property values were evaluated.

The numerical stability of the approximation by the backward or implicit finite-differences was generally ensured by the method itself [76-77]. The time step used in the program (which was an input value) was limited only by the approximation of the temperature distribution of the furnace tube wall in which the explicit finite-difference approximation method was used, as discussed in Chapter 1 and in Appendix II. However, the accuracy of the calculation by the implicit finite-difference approximation method depended on the magnitude of the time step once the increment in the space coordinates had been decided.

3.3. Experimental

3.3.1. Apparatus, reagents and sampling procedure

The apparatus used was the same as described in Chapter 2.

Stock solutions containing $1000 \mu\text{g mL}^{-1}$ of Pb and Ni were prepared separately by dissolving the appropriate mass of pure metal oxides (99.99% pure) or metal (99.999% pure) in ULTREX nitric acid (Baker Chemical Co.). The stock solution containing $1000 \mu\text{g mL}^{-1}$ of Sn was prepared by dissolving 1.000 g of pure Sn metal (99.999%) in 100 mL concentrated HCl and diluting the solution to 1 L with ultrapure water. 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 serial dilution of the above stock solutions with ultrapure water immediately before determination. In all cases, 5 μL volume of the sample solution was injected into the furnace on the inner surface of the tube wall for tube wall atomization or on the upper surface of the platform for platform atomization. The solutions were injected with an Eppendorf microlitre pipette fitted with disposable plastic tips. Great care was required for sampling on the platform so as to prevent the sample solution from spilling over the platform during the drying of the sample.

3.3.2. Measurement of the effective gas temperature, $T_{g, \text{eff}}$, by the two-line atomic absorption method

Tin, nickel and lead were used as the thermometric species for

determining the effective gas temperature, $T_{g,eff}$, by the two-line atomic absorption method. The particulars of the line pairs of Sn, Ni, and Pb and the reduced equations used in calculating $T_{g,eff}$ are presented in Table 9.

3.4. Results and discussion

3.4.1. Validity of the assumptions made in formulating the theoretical model

Results of the computer simulation confirm the validity of some of the assumptions made in formulating the theoretical model.

In all cases up to the highest wall heating rate (6 K ms^{-1}) studied, the maximum Ar gas velocities predicted by the computer program are below 30 cm s^{-1} in both the graphite tube furnace and the graphite platform furnace. The Reynolds numbers for the Ar gas in the furnace at all times are of the order 10 or less, considerably below 2300, the value at which turbulent flow in a tube would be observed [75]. This confirms assumption (b) that the flow of the Ar gas is laminar. For such low values of Reynolds number and because of the short tube length, no significant boundary layer near the furnace wall will be produced. This confirms assumptions (c) and (d).

In all cases up to the highest heating rate (6 K ms^{-1}) studied, the Rayleigh number for the Ar gas in the furnace at all times are of the order of 400 or less, considerably below 1500, the value at which natural convection effects would be expected to begin [69]. This confirms assumption (c).

Table 9. Physical data and equations used in the determination of $T_{g, \text{eff}}$

Element	Wavelength (nm)	Difference in lower level of energy ΔE (cm^{-1})	$\frac{g_2 f_2}{g_1 f_1}$	λ_2 $\gamma(-)$ λ_1	Reduced equations used in calculating $T_{g, \text{eff}}$ (K)	Temperature range covered [†] (K)
Sn	286.3	3428	4.9 ± 0.2 [‡]	0.996	2143 $\frac{\log(4.9 \frac{\lambda_2}{\lambda_1})}{\log(4.9 \frac{\lambda_2}{\lambda_1})}$	1600-3100
	284.0					
Ni	229.0	1332	2.18 [‡]	1.008	833 $\frac{\log(2.18 \frac{\lambda_2}{\lambda_1})}{\log(2.18 \frac{\lambda_2}{\lambda_1})}$	1600-2450
	232.6					
Pb	368.3	2831	3.68 [‡]	0.872	1770 $\frac{\log(3.68 \frac{\lambda_2}{\lambda_1})}{\log(3.68 \frac{\lambda_2}{\lambda_1})}$	1100-3100
	280.2					

* The approximation $\gamma(\lambda_2/\lambda_1) = \sqrt{(\lambda_2/\lambda_1)}$ was used.

† The lower limit of the temperature range was determined by the appearance temperature of the elements.

‡ Reference No. [114].

‡ Reference No. [97].

‡ Reference No. [99,101].

The Knudsen number [75] for the gas in the furnace at all time is of the order of 10^{-7} at the most, well below the value of unity at which non-continuum effects would become significant in the Ar gas. This confirms assumption (e).

As mentioned earlier, to simplify mathematical formulation, the theoretical model has assumed that the rectangular, flat platform is a cylindrical rod (with the same mass, similar volume and surface area as the real platform has), located at the central line (longitudinal axis) of the furnace. The predicted temperature and the velocity distributions of the gas in the graphite platform furnace based on this geometric assumption will certainly depart from the real ones, especially for the radial distribution at the axial positions where the platform is located. It is likely that the predicted temperature distribution in the radial direction at the axial positions where the platform is located will approximate the one at the central plane (perpendicular to the horizontal plane of the rectangular, flat platform) where the assumed geometry is closer to the real one.

3.4.2. Measurement of the effective gas temperature, $T_{g, \text{eff}}$ with the thermometric species, Sn, Ni, and Pb

Following references 93, 96, 103, and 112, and using a hollow-cathode lamp or another narrow-line source to measure the relative population of two atomic energy levels, the effective gas temperature, $T_{g, \text{eff}}$ can be obtained from the expression:

$$T_{g, \text{eff}} = \frac{\Delta E}{2.303 k \log \left[\frac{A_1 s_2 f_2 \lambda_2}{A_2 s_1 f_1 \lambda_1} \gamma \left(\frac{\lambda_2}{\lambda_1} \right) \right]} \quad 3.12$$

where ΔE is, the electronic energy difference of the lower levels of the two atomic absorption lines, k is the Boltzmann constant, A_1 and A_2 are the measured narrow-line absorbances, $g_1 f_1$ and $g_2 f_2$ are the products of the statistical weight and oscillator strength for each transition, $\gamma(\lambda_2/\lambda_1)$ is a function of the Doppler half-width, Δv_D , and of the Voigt integral of each absorption line

$$\gamma(\lambda_2/\lambda_1) = \frac{\Delta v_{D1} H_2(a, w=0.725a)}{\Delta v_{D2} H_1(a, w=0.725a)} \quad 3.13$$

where a is the damping parameter [113].

It has been reported in the literature [93, 96-97] that the accuracy in $T_{g, \text{eff}}$ determined by the two-line atomic absorption method increases with increasing difference in the energy of the lower levels of lines used in the measurement. However, because of the sensitivity loss involved in the line arising from the less-populated energy level, determination of $T_{g, \text{eff}}$ should be made with the line pair of which the line with higher energy of the lower level has a higher gf value, which will minimize the difference in the sensitivity of the two lines. The lines (of the line pair) should be as close as possible so that the dependence of the Voigt integral on the a -parameter is minimal and the difference in their wavelengths does not affect the sensitivity appreciably. Furthermore, reliable values for the ratio of the oscillator strengths of the line pair must be available, and the thermometric species selected should behave reproducibly in the furnace. Also, to cover the full range of temperature of a graphite furnace, several thermometric elements having atomization temperatures covering the full range of temperature

to be measured should be used. In this work Sn, Ni and Pb have been used as the thermometric species. The details of the line pairs of Sn, Ni and Pb and the reduced equations used for calculating $T_{g, \text{eff}}$ have been given in Table 9. Table 10 shows the reproducibility of the absorbance measurement at a tube wall heating rate of 3.0 K ms^{-1} . Table 11 shows the percentage relative (random) errors for a given percentage (random) error in the absorbance measurement for each line pair. The calculation of relative (random) errors is based on the following equation [99, 103]

$$\frac{\Delta T_{g, \text{eff}}}{T_{g, \text{eff}}} = \frac{0.695 T_{g, \text{eff}}}{\Delta E \ln} \sqrt{\left[\frac{\Delta \left(\frac{g_2 f_2}{g_1 f_1} \right)}{\frac{g_2 f_2}{g_1 f_1}} \right]^2 + \left(\frac{\Delta A_1}{A_1} \right)^2 + \left(\frac{\Delta A_2}{A_2} \right)^2} \quad 3.14$$

where ΔE is the difference in lower levels of energy of the line pair in cm^{-1} , n is the number of measurements made. In calculating the percentage relative (random) errors using equation 3.14, the relative uncertainty in the gf ratio has been taken as 4% for Sn (as shown in Table 9) and this value has been applied to Pb and Ni as a minimum; the $\Delta A_1/A_1$ has been taken as $\approx \Delta A_2/A_2$. In equation 3.14, the relative error arising from $\gamma(\lambda_2/\lambda_1)$ has been ignored. Also, no allowance has been made for the error contributed by the sequential measurement technique used in this work.

The following observations are made on the basis of the reproducibility of absorbance measurement and the relative (random)

Table 10. Standard deviation* of a single measurement of
absorbance at a wall heating rate of 3.0 K ms^{-1}

Element	Wave-length (nm)	Final tube wall temperature (K)	Relative standard deviation (%)			
			Wall atomization		Platform atomization	
			Peak†	Tail§	Peak†	Tail§
Sn	286.3	2970	2-3	~ 4	3-4	6-8
Ni	229.0	2500	1-2	~ 4	3-5	6-8
Pb	368.3	2270	2-3	~ 4	2-3	~ 6

* Of 5-7 replicate measurements

† Absorbance ~ 0.4

§ Absorbance ~ 0.1

Table 11. Percentage relative error in $T_{g, \text{off}}$ at $T_{g, \text{off}} = 2500 \text{ K}$
for various percentage errors in the absorbance measurement ($\Delta A/A\%$)

Element	Wavelength (nm)	$\Delta \left(\frac{S_2 f_2}{S_1 f_1} \right)$ (%)	Percentage relative error of $T_{g, \text{off}}$					
			$\Delta A/A\%$					
			1.0	2.0	4.0	6.0	8.0	10
Sn	286.3	4	2.2	2.4	3.5	4.8	6.0	7.5
	284.0							
Ni	229.0	4	5.5	6.3	9	12	16	19
	232.6							
Pb	368.3	4	2.6	2.9	4.3	5.8	7.4	9
	280.2							

errors in effective gas temperature presented in Tables 10 and 11. Tin, nickel and lead show comparable reproducibility in the absorbance measurements in both wall and the platform atomization; but because tin has a relatively large ΔE value, it gives small relative (random) error. For the tube wall atomization, at a high atomization temperature ($>2500^\circ \text{K}$) and a high heating rate ($>3 \text{ K ms}^{-1}$), lead is not recommended as a thermometric species because it is atomized at a relatively low temperature and is partly lost by expulsion with the rapidly expanding gas phase caused by rapid heating of the furnace wall. Because the maximum gas temperature that can be measured with Ni is limited to $\sim 2450 \text{ K}$ and because of the relatively slow heating of the platform at 2450 K , the reproducibility of Ni peak absorbance measurement is poor and the total relative (random) error for Ni as the thermometric species is larger with atomization from the platform than that from the tube wall, and is larger than those for Sn and Pb as the thermometric element for atomization from the platform. Therefore, nickel is not recommended as a thermometric species for atomization from the platform. In addition, the gf ratio for Ni and a similar constant for Pb which is a composite of the gf ratio and of the function $\gamma(\lambda_2/\lambda_1)$ were obtained from the temperature of an air-acetylene flame using Sn as the thermometric element [97, 99, 101]. Therefore, the gf ratios for Ni and Pb have larger relative uncertainties than those for Sn. The $T_{g, \text{eff}}$ values reported later in this chapter were mostly obtained using Sn as the thermometric species.

Tin, Ni and Pb have different volatilities, different atomization temperatures and different residence times - the residence time

determines the time during which there is measurable absorbance in the tail of the atomic absorption signal profile. Each of the three thermometric species has applications in determining $T_{g, \text{eff}}$ in which it is better suited than the other two; together they can be used to cover different time and temperature ranges. Figure 25 shows $T_{g, \text{eff}}$ as a function of time obtained using Sn, Ni and Pb as thermometric species in the graphite tube furnace and in the graphite platform furnace. The differences among $T_{g, \text{eff}}$ determined by using these elements are mainly caused by their different time-dependent concentration distributions in the furnace and by their different spectroscopic properties [102].

3.4.3. The effective gas temperature, $T_{g, \text{eff}}$, and the computed weighted-average gas temperature, $T_{g, w \text{ avg}}$

Figure 26 shows the effective gas temperature, $T_{g, \text{eff}}$ (measured), and the computed weighted-average gas temperature, $T_{g, w \text{ avg}}$ with tube wall heating rate as a parameter, in the graphite tube furnace. Figure 27 shows $T_{g, \text{eff}}$ and $T_{g, w \text{ avg}}$ with the final tube wall temperature as a parameter, in both the graphite tube furnace and the graphite platform furnace. Rief et al. [102] have pointed out that the effective gas temperature determined by the two-line atomic absorption method may differ by as much as 200 to 500 K from the weighted-average gas temperature or the average gas temperature, depending on the temperature gradient and the concentration distribution of the thermometric species. Figures 26 and 27 show similar trends in $T_{g, \text{eff}}$ and $T_{g, w \text{ avg}}$ with increasing time. In the graphite tube furnace, both of them increase with increasing tube wall temperature, and then decrease gradually with increasing time

Figure 25. T_{eff} as a function of time in the graphite tube furnace (empty symbols) and in the graphite platform furnace (filled symbols) determined by the two-line atomic absorption method using line pairs: Sn 286.3/284.0 nm (o, e), Ni 229.0/232.6 nm (□, ■) and Pb 368.3/280.2 nm (Δ, ▲). The dashed line is the measured temperature vs. time curve of the tube wall at the furnace centre. $\alpha \approx 3 \text{ K ms}^{-1}$ and $T_i = 470 \text{ K}$.

Figure 26. $T_{g,eff}$ (open symbols) determined using the Sn 286.3/284.0 nm line pairs, and $T_{g,w,avg}$ (filled symbols) computed as a function of time in the graphite tube furnace at different tube wall heating rates. The experimental tube wall temperature (at the furnace centre) vs. time curves (dashed lines) were used in computing $T_{g,w,avg}$. $T_i = 470$ K. From left to right: $\alpha \approx 7 \text{ K ms}^{-1}$ (o, ●), 3 K ms^{-1} (□, ■) and 1 K ms^{-1} (Δ, ▲). The error bars represent one standard deviation.

Figure 27. $T_{g,eff}$ (open symbols) determined using the Sn 286.3/284.0 nm line pairs, and $T_{g,w avg}$ (filled symbols) computed as a function of time in the graphite tube furnace (A,A) and in the graphite platform furnace (o,e) at different, final tube wall temperatures. The experimental tube wall temperature (at the furnace centre) vs. time curves were used in computing $T_{g,w avg}$. $T_i = 470$ K. $\alpha \approx 3$ K ms⁻¹.

(a) $T_f = 2270$ K. (b) $T_f = 2550$ K. (c) $T_f = 2760$ K.
(d) $T_f = 2970$ K. The error bars represent one standard deviation.

Figure 27 (a)-(b)

Figure 27 (c)-(d)

after the tube wall temperature at the furnace centre has attained and remained at a steady state. In the graphite platform furnace, both of them remain relatively stable with increasing time.

3.4.4. Computed temperature and velocity distributions of the gas phase

Figures 28-30 show the computed time-dependent temperature distribution in the gas phase in the graphite tube furnace, and Figs. 31-33 that in the graphite platform furnace. These results have been obtained using a set of typical computing parameters as follows. The tube dimensions are those of the Perkin-Elmer pyrolytically-coated graphite tube given in Table 2. The tube wall heating parameters (at the furnace centre) are: $u = 2 \text{ K ms}^{-1}$, $T_i = 300^\circ\text{K}$, and $T_f = 2870 \text{ K}$. In computing the platform temperature, the platform has the dimensions given in Table 3 and has a thickness of 0.35 mm (mass 60 mg). In computing the gas temperature in a graphite platform furnace, it is assumed that the graphite platform has the geometry of a graphite rod of the same length and of 0.79 mm radius, and is located at the furnace central line (longitudinal axis). In Figs. 28 and 31, points 1-3 represent locations adjoining the tube wall, as shown in the inset of the figures. The gas temperature at points 1-3 are, therefore, equal to the corresponding tube wall temperatures. In Fig. 31, point 4 adjoins the platform, and the gas temperature at point 4 is equal to the platform temperature. Therefore, in Figs. 28 and 31, the temperature differences between the curves 1-3 and 4-6 at every instant represent the instantaneous temperature gradient in the axial direction of the gas at radial positions adjacent to the tube wall and at the furnace centre, respectively. The temperature differences at

Figure 28. Computed temperature vs. time curves of Ar gas at selected points in the graphite tube furnace. $\alpha = 2 \text{ K ms}^{-1}$, $T_i = 300 \text{ K}$, $T_f = 2870 \text{ K}$. The dimensions of the Perkin-Elmer pyrolytically-coated tube are given in Table 2. Points 1-3 were adjacent to the tube wall at axial coordinates: $x = 0, 10$ and 14 mm , respectively. Points 4-6 were on the axial central line of the tube at axial coordinates: $x = 0, 10$ and 14 mm , respectively.

Figure 29. Computed temperature distributions of Ar gas in the axial direction in the graphite tube furnace at radial coordinates: $r = 0$ mm (---) and 3 mm (—) and at selected times: (a) 0.105, 0.285, 0.485, 0.835 and 1.135 s when the tube wall temperature at the furnace centre reached 510, 870, 1270, 1970 and 2570 K, respectively; (b) 1.285 s when it reached 2870 K, and 2.285 s after it had remained at 2870 K for 1 s. The computing parameters used were the same as given in Fig. 28.

Figure 30. Computed temperature distributions of Ar gas in the radial direction in the graphite tube furnace at axial coordinates: $x = 0, 10$ and 14 mm, and at selected times: (a) $0.105, 0.285, 0.485$ and 0.835 s when the tube wall temperature at the furnace centre reached $510, 870, 1270$ and 1970 K, respectively. (b) 1.285 s when it reached 2870 K, and at 2.285 s after it had remained at 2870 K for 1 s. The same computing parameters as given in Fig. 28 were used.

Figure 31. Computed temperature vs. time curves of Ar gas at selected points inside the graphite platform furnace. Points 1-3 were adjacent to the tube wall at axial coordinates: $x = 0, 10$ and 14 mm. Point 4 was on the radial central line and adjacent to the platform. Points 5 and 6 were on the axial central line of the tube at axial coordinates: $x = 10$ and 14 mm. $\alpha = 2 \text{ K ms}^{-1}$, $T_i = 300 \text{ K}$, $T_f = 2870 \text{ K}$. The dimensions of the Perkin-Elmer pyrolytically-coated tube are given in Table 2. A platform having the dimensions given in Table 3 and thickness 0.35 mm (mass 60 mg) was used in computing its temperature. In computing the gas temperature, the platform was assumed to be a graphite rod having the same length and a radius of 0.79 mm .

Figure 32. Computed temperature distributions of Ar gas in the axial direction in the graphite platform furnace at radial coordinates as shown in the figure when the tube wall temperature at the furnace centre reached 2570 K. The computing parameters used were the same as given in Fig. 31.

Figure 33. Computed temperature distributions of Ar gas in the radial direction in the graphite platform furnace at axial coordinates: $x = 0, 10$ and 14 mm, and at selected times: (a) $0.135, 0.485$ and 0.835 s when the tube wall temperature at the furnace centre reached $870, 1270$ and 1970 K, respectively. (b) 1.285 s when it reached 2870 K, and 2.285 s after it had remained at 2870 K for 1 s. The same computing parameters as given in Fig. 31 were used. The dashed lines represent the platform temperatures.

every instant between curves 1 and 4, 2 and 5, 3 and 6 indicate the instantaneous temperature gradient of the gas in the radial direction at the corresponding axial positions. Figures 29-30, and 32-33 show the temperature distribution of the gas in the axial and the radial direction at selected times for the graphite tube furnace and the graphite platform furnace, respectively. These figures show the complexity of the time-dependent temperature distribution of the gas phase. The following generalizations can be made from these figures.

In both the graphite tube furnace and the graphite platform furnace, there are gas temperature shoulders corresponding to the tube wall temperature shoulders shown in Chapter 1 because of the dimensions of the contoured tube used in the computing.

In the graphite tube furnace, the gas temperature at the furnace central line (longitudinal axis) increases at a much lower rate than the corresponding tube wall temperature at the beginning of the heating cycle. Hence, the maximum gas temperature gradient in the radial direction at the central part of the furnace occurs near the beginning of the heating cycle (about 130 K at 0.1 s in this case). Thereafter, with increasing time, the gas temperature at the furnace central line (longitudinal axis) in the middle part of the furnace approaches the tube wall temperature and the temperature gradient in the radial direction decreases. Later on, because of thermal conduction in the axial direction from the high temperature in the gas temperature shoulder, the gas temperature at the middle part of the central line (longitudinal axis) of the furnace is even slightly higher than the corresponding tube wall temperature. In this case, for most of the heating cycle (i.e., from 0.235 s when the tube wall

temperature at the furnace center has reached 770 K to the time when it has remained at 2870 K for 1 s), there is always a 10 mm length in the middle part of the furnace where the temperature gradient of the gas is less than 50 K both in the axial and the radial direction.

In the graphite platform furnace, there is a much larger gradient in the gas phase in the radial direction, resulting from the delayed heating of the platform. Because the platform is shorter than the furnace tube and is located at the middle part of the tube, the platform temperature has little influence on the gas temperature at the furnace ends. The time-dependent temperature gradients in the radial direction at the furnace ends in the graphite tube furnace and in the graphite platform furnace are similar. After the tube wall temperature at the furnace centre has reached a steady state, the temperature gradient of the gas in the radial direction rapidly decreases with the platform temperature approaching the tube wall temperature. After the platform temperature becomes higher than that of the tube wall and of the gas near or at the furnace ends, the heat transfer between the tube wall and the platform and between the platform and the adjacent gas reduces the temperature gradient of the tube wall in the axial direction, and reduces the temperature gradients of the gas in the axial and the radial direction. As a result, after the tube wall temperature at the furnace centre has reached and remained at steady state, the weighted-average gas temperature is temporally more stable in the graphite platform furnace than in the graphite tube furnace, as shown in Fig. 34.

Figures 35-37 show the velocity distribution of the gas in the graphite tube furnace and in the graphite platform furnace.

Figure 34. Computed weighted-average temperature of Ar gas

($T_{g,w \text{ avg}}$) vs. time curves in the graphite tube furnace (curve 1), and in the graphite platform furnace (curve 2). The dashed and the dotted line are the temperature vs. time curves of the tube wall at the furnace centre and of the platform, respectively.

Figure 35 shows that the maximum gas velocities at the furnace ends occur near the beginning of the heating cycle. The maximum gas velocity near the tube wall occurs earlier than that near the centre because the initial heating of the gas near the centre is slower than that near the tube wall. After the gas velocity at the furnace ends has attained its maximum value, it decreases with time to a low value. When the tube wall temperature at the furnace centre has reached a steady state, gas velocity at the furnace end drops sharply to a negative value, indicating contraction of the gas phase. Thereafter, it rapidly approaches zero. At the ends of the graphite platform furnace, the gas velocity vs. time curve is similar to that in the graphite tube furnace.

Figure 36 shows that the instantaneous gas velocity (at a given radial position) increases nonlinearly with increasing axial distance from the furnace centre because of the temperature gradient of the gas in the axial direction. The large temperature gradient of the gas in the axial direction at the furnace ends even makes the gas velocity decrease with increasing axial coordinate near the furnace ends.

Figures 37(a) and 37(b) give the velocity distributions in the radial direction in the graphite tube furnace and in the graphite platform furnace. The boundary conditions used assumed that the velocities at the surfaces of the tube wall ($r = d_1/2$) and of the platform ($r = 0$) were zero. The velocity profiles near the above surfaces would be somehow modified if the effect of viscosity on the velocity were taken into account by solving the equation for conservation of momentum. Figure 37(a) shows that because of the limited tube length and the transient heating of the furnace tube, the

Figure 35. Computed velocity vs. time curves of Ar gas at the furnace ends at radial coordinates: $r = 0$ and 2.84 mm in the graphite furnace (—), and at $r = 0$, 1.26 and 2.84 mm in the graphite platform furnace (---); the computing parameters were the same as given in Figs. 28 and 31, respectively. The curve at $r = 2.84$ mm in the graphite platform furnace overlaps with that in the graphite tube furnace. Also shown is the temperature vs. time curve of the tube wall at the furnace centre.

Figure 36. Curves of computed velocity of Ar gas vs. axial coordinates at radial coordinates $r = 0$ and 2.84 mm and at selected times in the graphite tube furnace (—) and in the graphite platform furnace (---); the computing parameters were the same as given in Figs. 28 and 31, respectively.

Figure 37. Curves of computed velocity of Ar gas vs. radial coordinates at axial coordinates: $x = 0, 10$ and 14 mm and at selected times in the graphite tube furnace (a) and in the graphite platform furnace (b); the computing parameters used were the same as given in Figs. 28 and 31, respectively. The inset shows the scale for gas velocity: 2 cm s^{-1} .

parabolic velocity pattern of a laminar flow in the radial direction at steady state in the cylindrical tube is not developed. It is flat after the gas velocity has attained its maximum. Figure 37(b) shows the influence of the assumed geometry of the platform on the velocity distribution in the radial direction in the graphite platform furnace. Curves in Fig. 37(b) are probably approximations of those at the axial central plane which is normal to the flat platform.

3.4.5. Effects of the tube wall heating rates on the temperature and the velocity distribution of the gas phase in the graphite tube furnace and in the graphite platform furnace

Figures 38-41 show the above effects in the graphite tube furnace. The following observations are made from these figures.

For a given tube wall temperature, the temperature gradient of the gas in the radial direction increases with the tube wall heating rate. The temperature gradient in the radial direction develops in the central part of the furnace in the early heating stage (Fig. 38), but also develops in axial positions where the gas temperature shoulder is located in the late heating stage (Fig. 39). Also, the higher the tube wall heating rate, the higher is the gas temperature shoulder (Fig. 39), and the higher is the weighted-average gas temperature, $T_{g,w \text{ avg}}$ (Fig. 40). Table 12 gives the length of the middle part of the furnace in which the gas temperature is higher than a given value (which is 50 K lower than the given tube wall temperature at the furnace centre). It shows that this length increases with increasing heating rate. It nearly doubles at the high tube wall temperature of 2870 K if

Figure 38. The (computed) effect of the tube wall heating rate on Ar gas temperature at the furnace centre ($x = 0$, $r = 0$) (solid lines) vs. time curves in the graphite tube furnace. The dashed lines are the tube wall temperature (at the furnace centre) vs. time curves. For each set of curves from left to right: $\alpha = 6$, 2, and 1 K ms⁻¹. In all cases, $T_i = 300$ K, $T_f = 2870$ K. The tube dimensions of the Perkin-Elmer pyrolytically-coated graphite tube shown in Table 2 were used in the computing.

Figure 39. Curves of the (computed) effect of the tube wall heating rate on the temperature distributions vs. axial distance from the furnace centre in the Ar gas in the graphite tube furnace at the tube wall temperature 2270 K (at the furnace centre) and at radial coordinates: $r = 0$ mm (--- and empty symbols) and 3 mm (— and filled symbols). (Δ , $\triangle$) $\alpha = 1 \text{ K ms}^{-1}$, ($\circ$, $\bullet$) $\alpha = 2 \text{ K ms}^{-1}$, ($\square$, $\blacksquare$) $\alpha = 6 \text{ K ms}^{-1}$. The other computing parameters were the same as given in Fig. 38.

Table 12. Effects of heating rates and initial temperatures of the tube wall on the axial distance (in the middle part of the graphite tube furnace) over which the gas temperatures at given tube wall temperatures are higher than the given values^a

Temperature (K)	Axial distance in the middle part of the furnace (mm)				
	$\alpha=1 \text{ K ms}^{-1}$	$\alpha=6 \text{ K ms}^{-1}$	$\alpha=2 \text{ K ms}^{-1}$	$\alpha=2 \text{ K ms}^{-1}$	$\alpha=2 \text{ K ms}^{-1}$
	$T_1=300 \text{ K}$	$T_1=300 \text{ K}$	$T_1=300 \text{ K}$	$T_1=870 \text{ K}$	$T_1=1270 \text{ K}$
$T_w(0) = 1270$ and $T_g > 1220$	23	26	24	10	10
$T_w(0) = 2270$ and $T_g > 2220$	17	25	22	20	12
$T_w(0) = 2870$ and $T_g > 2820$	12	24	19	18	15
1 s after $T_w(0) = 2870$ and $T_g > 2820$	6	11	9	8	7

^a Dimensions of the pyrolytically-coated (Perkin-Elmer) graphite tube were as given in Table 2. $T_w(0)$ was the given tube wall temperature at the furnace centre.

the tube wall heating rate is increased from 1 to 6 K ms⁻¹. Figure 40 shows that the maximum $T_{g,w \text{ avg}}$ obtained at the given final tube wall temperature increases with increasing tube wall heating rate. This trend agrees well with that of $T_{g, \text{eff}}$, as shown in Fig. 26 in section 3.4.3, and results from the higher gas temperature shoulder and the reduced temperature gradient in the axial direction near the furnace ends. In Fig 40, the maximum $T_{g,w \text{ avg}}$ obtained at $\alpha = 6 \text{ K ms}^{-1}$ is nearly 300 K higher than that obtained at $\alpha = 1 \text{ K ms}^{-1}$. However, the above effects decrease with increasing time after the tube wall temperature at the furnace centre has reached a steady state.

Figure 41 shows that for any given tube wall temperature at the furnace centre, the gas velocity at the furnace ends is considerably higher at a high heating rate than at a low heating rate.

Similar trends are also observed in the graphite platform furnace, as seen from Figs. 42-44. However, since in the graphite platform furnace the sample is deposited on the platform surface, further studies should be made at a given platform temperature, instead of at a given tube wall temperature.

Generally speaking, at a given platform temperature, the higher the tube wall heating rate, the larger is the gas temperature gradient in the radial direction, the higher is the gas temperature shoulder, and the higher is the weighted-average gas temperature, $T_{g,w \text{ avg}}$. These effects stem not only from the heating rate effects on the temperature distribution of the tube wall, but also from the low platform temperature at the instant when the tube wall temperature reaches a steady state at high heating rates. As seen from dashed arrows in Fig. 43, these platform temperatures under the computing

Figure 40. The (computed) effect of the tube wall heating rate on the weighted-average temperature of Ar gas vs. time curves (solid lines) in the graphite tube furnace. The dashed lines are the tube wall temperature at the furnace centre vs. time curves. The other computing parameters were the same as given in Fig. 38.

Figure 41. Curves of the (computed) effect of the tube wall heating rate on Ar gas velocity (at the furnace ends) vs. the tube wall temperature (at the furnace centre) in the graphite tube furnace at radial coordinates: $r = 0$ mm (---) and 2.84 mm (—). In each set of curves from bottom to top: $\alpha = 1, 2$, and 6 K ms^{-1} . The other computing parameters were the same as given in Fig. 38.

Figure 42. The (computed) effect of the tube wall heating rate on the temperature distribution vs. axial distance from the furnace centre in the Ar gas in the graphite platform furnace at a platform temperature of 1400 K and at radial coordinates: $r = 0.95$ mm (--- and empty symbols) and 3 mm (— and filled symbols). (A, A) $\alpha = 1 \text{ K ms}^{-1}$, (o, o) $\alpha = 2 \text{ K ms}^{-1}$, (□, □) $\alpha = 6 \text{ K ms}^{-1}$. In all cases, $T_i = 300 \text{ K}$, $T_f = 2870 \text{ K}$. The other computing parameters were the same as given in Fig. 31.

Figure 43. The (computed) effect of the tube wall heating rate on the weighted-average temperature gas vs. time curves of Ar gas (solid lines) in the graphite platform furnace. The dashed and dotted lines are the temperature vs. time curves of the tube wall at the furnace centre and the corresponding temperature vs. time curves of the platform, respectively. In each set of curves from left to right: $\alpha = 6, 2$ and 1 K ms^{-1} . The other computing parameters were the same as given in Fig. 42. The solid arrows show the $T_{g,w \text{ avg}}$ at $T_p = 1400 \text{ K}$. The - - - - arrows show the T_p when the tube wall temperature reached the steady state.

parameters considered are 2200, 1700, and 750 K for the tube wall heating rates of 1, 2, and 6 K ms⁻¹, respectively. Therefore, starting from a low platform temperature, the temperature vs. time curve of the platform obtained at a high tube wall heating rate is located inside the isothermal region of the temperature vs. time curve of the tube wall (at the furnace centre). In this region, the gas temperature is relatively high and stable. At the platform temperature 1400 K, $T_{g,w \text{ avg}}$ obtained at $\alpha = 6 \text{ K ms}^{-1}$ is about 400 K higher than that obtained at $\alpha = 1 \text{ K ms}^{-1}$, as seen from solid arrows in Fig. 43.

Figure 44 shows that when the tube wall temperature is rising, for a given platform temperature the gas velocity at the furnace ends is higher at a high tube wall heating rate than at a low tube wall heating rate. However, as soon as the tube wall temperature at the furnace centre reaches a steady state, the gas velocity at the furnace ends rapidly drops to near zero.

3.4.6. Effects of the initial tube wall temperature on the temperature and the velocity distribution of the gas phase in the graphite tube furnace and the graphite platform furnace

In both the graphite tube furnace and the graphite platform furnace, a low initial tube wall temperature produces effects similar to those of a high tube wall heating rate, as will be seen below.

For a given tube wall temperature in the graphite tube furnace, a low initial tube wall temperature gives a relatively large temperature gradient of the gas in the radial direction. In the early stage of the heating cycle, a temperature gradient in the radial direction develops

Figure 44. Curves of the (computed) effect of the tube wall heating rate on Ar gas velocity (at the furnace ends) vs. platform temperature in the graphite platform furnace at radial coordinates $r = 2.84$ mm. The computing parameters were the same as given in Fig. 42. Also shown are the corresponding temperature vs. time curves of the tube wall at the furnace centre.

along the length (longitudinal axis) [Figs. 45 and 46(b)], but in the late stage of the heating cycle, the temperature gradient spreads to the axial region where the temperature shoulder is located [Fig. 46(c)]. Also, a low initial tube wall temperature gives a relatively high gas temperature shoulder, and therefore, high values of $T_{g,w \text{ avg}}$ and relatively long section in the middle part of the furnace over which the gas temperature is high. Table 12 shows that for a decrease in T_1 from $T_1 = 1270 \text{ K}$ to $T_1 = 300 \text{ K}$, the length of this section, under the parameters considered, nearly doubles at tube wall temperatures lower than 2270 K and increases $\sim 25\%$ at a tube wall temperature of 2870 K . Therefore, such an effect is more pronounced at a low tube wall temperature than at a high one. For a given tube wall temperature, $T_{g,w \text{ avg}}$ is about 100 K higher at a low initial tube wall temperature of 300 K than that at a high initial tube wall temperature of 1270 K when the tube wall temperature at the furnace centre is increasing with increasing time (Fig. 47). However, after the tube wall temperature at the furnace centre has attained a steady state, the effect of the initial tube wall temperature on the gas temperature distribution diminishes and the $T_{g,w \text{ avg}}$ at different initial tube wall temperatures is nearly the same.

The effects of the initial tube wall temperature on the ²⁸ gas temperature distribution are mainly due to the effects of the former on the tube wall temperature distribution. Because the furnace tube is preheated from a given initial tube wall temperature, the initial axial temperature gradient of the tube wall and of the gas is fully developed before the atomization cycle commences, being small at a low initial wall temperature [Figs. 46(a)-46(b)]. Also, at a low initial

Figure 45. Curves of the (computed) effect of the initial tube wall temperature on the temperature of Ar gas at the furnace centre ($x = 0$, $r = 0$) vs. time (solid lines) in the graphite tube furnace. The dashed lines are the tube wall temperatures (at the furnace centre) vs. time curves. For each set of curves from top to bottom: $T_1 = 1270$, 870, and 300 K. In each case, $T_f = 2870$ K, $\alpha = 2$ K ms⁻¹. The dimensions of the Perkin-Elmer pyrolytically-coated graphite tubes given in Table 2 were used in the computing.

Figure 46. Curves of the (computed) effect of the initial tube wall temperature on Ar gas temperature vs. the axial distance from the furnace centre in the graphite tube furnace, at radial coordinates: $r = 0$ mm (— and empty symbols) and 3 mm (--- and filled symbols), and at selected tube wall temperatures (at the furnace centre): (a) 300 and 870 K, (b) 1270 K, and (c) 2270 K. (o, e) $T_1 = 300$ K, (Δ , Δ) $T_1 = 870$ K, ($\square$, $\blacksquare$) $T_1 = 1270$ K. The other computing parameters were the same as given in Fig. 45.

Figure 47. The (computed) effect of the initial tube wall temperature on the weighted-average temperature vs. time curves (solid lines) in the Ar gas in the graphite tube furnace. The dashed lines are the tube wall temperature (at the furnace centre) vs. time curves. In each set of curves from left to right: $T_i = 1270, 870$ and 300 K. The other computing parameters were the same as given in Fig. 45.

tube wall temperature, the tube wall shows a relatively high temperature shoulder and a greater length in the middle part of the tube wall over which the temperature is relatively high (Chapter 1). Because of thermal conduction, the temperature distribution of the gas in the axial direction follows that of the tube wall. In addition, at a low initial tube wall temperature, the rate of heat dissipation from the gas at the furnace ends to the cool gas outside is small because of the small initial temperature difference between them.

For a given platform temperature in the ²³graphite platform furnace, the lower the initial tube wall temperature, the larger is the temperature gradient in the radial direction (Fig. 48), the higher is the gas temperature at the same axial and radial coordinates, and the higher is the weighted-average gas temperature (Fig. 49). For a platform temperature of 1400 K and under the computing parameters considered, $T_{g,w \text{ avg}}$ at $T_i = 300$ K is about 400 K higher than at $T_i = 1270$ K (solid arrows in Fig. 49). This value is considerably higher than what can be explained by the effects of the initial tube wall temperature on the temperature distribution of the tube wall and by the influence of the latter on the gas temperature distribution. Indeed, there is another contributing factor, which is the longer delay in the heating of the platform relative to the heating of the tube wall at a low initial tube wall temperature. In other words, at the time when the tube wall temperature at the furnace centre attains a steady state, the platform temperature is lower at a low initial tube wall temperature than at a high T_i . Figure 49 shows that the above platform temperatures are 1600, 1800 and 2000 K for the initial

Figure 48. Curves showing the (computed) effect of the initial tube wall temperature on the Ar gas temperature vs. the axial distance from the furnace centre at a platform temperature of 1400 K in the graphite platform furnace, at radial coordinates: $r = 0.95 \text{ mm}$ (--- and empty symbols) and 3 mm (— and filled symbols). (o, e) $T_1 = 300 \text{ K}$, (Δ , Δ) $T_1 = 870 \text{ K}$, ($\square$, $\blacksquare$) $T_1 = 1270 \text{ K}$. In all cases, $T_f = 2870 \text{ K}$, $\alpha = 2 \text{ K ms}^{-1}$. The other computing parameters were the same as given in Fig. 31.

Figure 49. The (computed) effect of the initial tube wall temperature on the weighted-average temperature vs. time curves (solid lines) of Ar gas in the graphite platform furnace. The dashed and dotted lines are the temperature vs. time curves of the tube wall at the furnace centre and of the platform, respectively. In each set of curves from left to right: $T_i = 1270, 870$ and 300 K. The other computing parameters were the same as given in Fig. 48. The solid arrows show the $T_{g, w \text{ avg}}$ at $T_p = 1400$ K. The - - - arrows show the T_p when the tube wall temperature at the furnace centre attained the steady state.

arrows). Therefore, the high gas temperature distribution or the high $T_{g,w \text{ avg}}$ at a given platform temperature and at a low initial tube wall temperature is primarily due to the delayed heating of the platform, and secondarily to the improved temperature gradient in the axial direction and to the enhanced gas temperature shoulder at a low initial tube wall temperature.

The effects of the initial tube wall temperature on the velocity distribution of the gas (Figs. 50-51) are quite different from those of the tube wall heating rate (Figs. 41 and 44). In the graphite tube furnace, the lowest initial tube wall temperature gives the highest gas velocity at the furnace ends. However, for a given tube wall temperature, the difference in the gas velocities at the furnace ends at different initial tube wall temperatures is negligible (Fig. 50). In the graphite platform furnace, a low initial tube wall temperature yields a low gas velocity at the furnace ends for any given platform temperature and is, therefore, always desirable (Fig. 51).

3.4.7. Effects of the final tube wall temperatures on the temperature and the velocity distribution of the gas phase in the graphite tube furnace and in the graphite platform furnace

For a given tube wall heating rate and a given initial tube wall temperature, the final tube wall temperature determines the time taken by the tube wall to attain the steady-state temperature. However, it has no effect on the temperature and the velocity distribution of the gas prior to this time. At a relatively high final tube wall temperature in the graphite tube furnace, the maximum average gas temperature is relatively high; and the time period for the gas velocities at the furnace end to decrease to near zero is relatively

Figure 50. The (computed) effect of the initial tube wall temperature on Ar gas velocity (at the furnace ends) vs. tube wall temperature (at the furnace centre) curves in the graphite tube furnace at radial coordinates: (a) $r = 0 \text{ mm}$, and (b) $r = 2.84 \text{ mm}$. In each set of curves from left to right: $T_1 = 300, 870 \text{ and } 1270 \text{ K}$. The other computing parameters were the same as given in Fig. 45.

Figure 51. The (computed) effect of the initial tube wall temperature on Ar gas velocity at the furnace ends and at $r = 2.84 \text{ mm}$ vs. the platform temperature curves in the graphite platform furnace. The other computing parameters were the same as given in Fig. 48. Also shown are the tube wall temperature (at the furnace centre) vs. time curves.

long which is undesirable. In the graphite platform furnace, a relatively high, final tube wall temperature results in a relatively short delay in the platform heating, a relatively large temperature gradient in the gas in the radial direction, a relatively fast heating of the platform, and a high maximum $T_{g,w \text{ avg}}$ (Fig. 52).

3.4.8. Effects of the thermal properties of the purge gas on its temperature distribution in the graphite tube furnace

Figure 53 shows that substitution of N_2 for Ar as the purge gas affects the temperature distribution of the gas phase because of differences in their thermal properties. Table 13 shows the thermal properties of N_2 gas; those of Ar gas have been given in Table 1. At high temperatures, the specific heat (at constant volume) and the thermal conductivity of N_2 gas are much higher than those of Ar gas, whereas the density of N_2 gas is much lower than that of Ar gas. As a result, the rate of heat transfer by thermal conduction in N_2 gas is much higher than that in Ar gas. When the tube wall temperature is rising with increasing time, the fast heat transfer from the hot region (the gas temperature shoulder) to the cold region results in a relatively small temperature gradient in N_2 gas in both the axial and radial directions. After the tube wall temperature has attained a steady state, the high rate of heat transfer from the hot gas inside the furnace towards the cold gas in the space between the ends of the graphite tube and the quartz end windows results in relatively large temperature gradients in N_2 gas in the axial and the radial direction.

Figure 52. The (computed) effect of the final tube wall temperature on the weighted-average temperature vs. time curves (solid lines) of Ar gas in the graphite platform furnace. The dashed and dotted lines are the temperature vs. time curves of the tube wall at the furnace centre and of the platform, respectively. In each set of curves from bottom to top: $T_f = 1970, 2270$ and 2870 K. In all cases, $T_i = 300$ K, $\alpha = 2 \text{ K ms}^{-1}$. The other computing parameters were the same as given in Fig. 31.

Figure 53. Curves of the computed temperature of N_2 and Ar gases vs. axial distance from the furnace centre in the graphite tube furnace at selected times. (—) is the N_2 and Ar gas temperature curve at $r = 3$ mm. (---) is the N_2 gas temperature curve at $r = 0$ mm. (- · - · -) is the Ar gas temperature curve at $r = 0$ mm. In all cases, $T_i = 300$ K, $T_f = 2870$ K, $u = 2$ K ms⁻¹. The dimensions of the Perkin-Elmer pyrolytically-coated graphite tube are given in Table 2.

3

Table 13. Temperature-dependent property values of nitrogen gas

Property	Values	Reference
Density, ρ (g cm ⁻³)	$\rho(T) = 1.250 \times 10^{-3} (273/T)$	[81]
Heat capacity, c_p (J g ⁻¹ K ⁻¹)	$c_p(T) = 1.09 - 3.52 \times 10^{-4}T$ $+ 7.20 \times 10^{-7}T^2 - 2.82 \times 10^{-10}T^3$ for $T \leq 775$ K $c_p(T) = 0.844 + 4.52 \times 10^{-4}T$ $+ 1.39 \times 10^{-7}T^2 - 1.03 \times 10^{-11}T^3$ for 3000 K $> T > 775$ K	[82]
Thermal conductivity, κ (W cm ⁻¹ K ⁻¹)	$\kappa(T) = 1.26 \times 10^{-4} + 5.18 \times 10^{-7}T$ $- 1.81 \times 10^{-11}T^2 + 4.63 \times 10^{-15}T^3$	[83]

3.4.9. Effects of the furnace geometry on the temperature distribution of the gas phase in the graphite tube furnace.

The above discussions are all based on the dimensions of the Perkin-Elmer pyrolytically-coated graphite tube, which is, in fact, a contoured tube. For a standard graphite tube with uniform thickness of the tube wall, the effects discussed above will be valid except that the gas temperature shoulder that occurs in a contoured tube will be absent. Figure 54 shows that when the tube wall temperature is rising with increasing time, substitution of a standard tube for a contoured tube will reduce the gas temperature gradient, specially in the axial direction. However, the length (longitudinal axis) in the middle part of the furnace over which the gas temperature is higher than a given value is relatively short, and the highest gas temperature achievable is relatively low. After the tube wall temperature has attained a steady state, the tube wall temperature gradient in the axial direction in the middle part of the furnace tube is smaller in the contoured tube than in the standard tube.

3.5. Summary

In the absence of a forced, convective flow of purge gas, the gas phase in the Massmann-type graphite tube furnace with or without a graphite platform is, strictly speaking, nonisothermal throughout the duration of the entire heating cycle. The extent of nonisothermality of the gas phase depends on the atomizer geometry, design features of the atomizer (which determine the boundary temperatures), thermal

Figure 54. Computed temperature distributions of Ar gas in the axial direction in the graphite tube furnace fitted with the standard graphite tube (shadowed zones) and with the Perkin-Elmer pyrolytically-coated graphite tube at selected times: (a) 0.285, 0.485 and 1.135 s; and (b) 2.285 s (1 s after the wall temperature at the furnace centre had remained at 2870 K). (—) is the gas temperature at $r = 3$ mm, (- - -) is the Ar gas temperature at $r = 0$ mm. In all cases, $T_1 = 300$ K, $T_f = 2870$ K, and $\alpha = 2 \text{ K ms}^{-1}$.

properties of the purge gas, and the temperature program of the furnace, including the initial and the final tube wall temperature, and the tube wall heating rate.

Generally speaking, in the graphite tube furnace, the maximum temperature gradient of the gas in the radial direction occurs in the early stage of the heating, being 100-200 K for a wall heating rate of $1-6 \text{ K ms}^{-1}$ at an initial tube wall temperature of 300 K. After that, in a standard tube (i.e., having uniform thickness), the temperature of the gas in the middle part of the furnace approaches that of the tube wall, whereas in a contoured tube, the gas temperature in the middle part of the furnace attains and surpasses the tube wall temperature. In a contoured tube, the temperature gradient of the gas in the axial direction is generally larger in the later stage than in the earlier stage of heating, is larger for a high tube wall temperature than for a low tube wall temperature, and is larger near the tube wall than near the central line (longitudinal axis) of the tube. The temperature gradient in the axial direction varies from about 100 to over 1500 K, depending on the heating and the geometric parameter. However, there is about a 10-mm length in the middle part of the 28-mm-long tube where the gas temperature gradient in both the axial and the radial direction is less than 50 K for a tube wall heating rate of 2 K ms^{-1} and an initial tube wall temperature of 300 K.

The time when the tube wall temperature attains a steady state is significant in terms of isothermality. Before this time, the gas temperature is non-isothermal both spatially and temporally. After this time, the gas temperature distribution is nonisothermal

spatially, but the gas temperature (and its distribution) varies slowly with increasing time, being high and approximately isothermal temporally. Also, the corresponding velocity field of the gas is low. Therefore, if the atomic absorption signal pulse of the analyte appears after this time, the loss of analyte vapour by expulsion will be negligible, and the analyte vapour will experience a stable, maximum temperature achieved in the whole heating cycle.

In the graphite platform furnace, the heating of the platform is delayed. It is mainly because of the delayed heating of the platform that atomization from the platform occurs at a relatively high temperature with a nearly-stable temperature distribution of the gas phase and a considerably lower gas velocity field. The non-isothermality of gas temperature in the radial direction in the graphite platform furnace is generally much larger than that in the graphite tube furnace. The non-isothermality of gas temperature in the axial direction in the graphite platform furnace is similar to that in the graphite tube furnace. However, at long heating times when the platform temperature is higher than the tube wall temperature and the gas temperature near the furnace ends, the gas temperature gradient in the axial direction in the graphite platform furnace is smaller and is more stable than in the graphite tube furnace (without a platform).

Among the tube wall heating parameters, a low initial tube wall temperature and a high tube wall heating rate have similar effects on the temperature distribution of the tube wall, of the platform and of the gas phase. They both result in a large radial temperature gradient in the gas, a small temperature gradient along the tube wall and throughout the gas in the axial direction in the middle part of the

furnace for a standard graphite tube (with a uniform wall thickness), and a high average temperature over the tube wall and throughout the gas for the contoured tube. They both delay the platform heating, shift the platform temperature vs. time curve towards the isothermal region of the temperature vs. time curve of the tube wall, and result in a high platform heating rate at a given platform temperature. However, a low initial tube wall temperature and a high tube wall heating rate have different effects on the velocity distribution in the gas. A high tube wall heating rate results in a high velocity distribution in the gas, especially at a relatively low temperature of the tube wall or of the platform; whereas the effect of the initial tube wall temperature is negligible. Because a low initial tube wall temperature has all the advantages of a high tube wall heating rate but without the disadvantage of a concomitant increase in the gas velocity, it is desirable to insert a cooling cycle between the charring cycle and the atomization cycle during atomization from the tube wall in the graphite tube furnace, or during atomization from the platform in the graphite platform furnace. A high tube wall heating rate combined with a high final tube wall temperature will result in attainment of a high gas temperature attainable. However, it will also result in a high gas velocity. For atomization from the tube wall in the graphite tube furnace, the analyte atomic absorption signal pulse will be located partly or wholly outside the isothermal region of the temperature vs. time curve of the tube wall under these conditions, and the effects of thermal expansion of the gas phase and expulsion of analyte vapour with the expanding gas phase will be important.

Chapter 4

TIME-DEPENDENT ATOM DISTRIBUTIONS AND ATOMIC ABSORPTION SIGNALS IN GRAPHITE PLATFORM FURNACE ATOMIC ABSORPTION SPECTROMETRY

4.1. Introduction

In atomic absorption spectrometry, the transient atomic absorption signal of a spectral line is the result of the time-dependent density distribution of the analyte atoms in the analysis volume. Following the references 64, 112 and 115, one can write:

$$A(t) = \frac{0.432 \sqrt{4\pi \ln 2} e^2 f g_1 \exp(-E_1/kT) H(a, \omega=0.725a)}{m_e c Z \Delta \nu_D q s} N(t) \quad 4.1$$

where e and m_e are the charge and the mass of the electron, c is the velocity of light in vacuum, f is the oscillator strength, g_1 and E_1 are the statistical weight and the energy of the lower level for the analytical line, Z is the partition function of the element, k is the Boltzmann constant, $\Delta \nu_D$ is the Doppler half-width of the atomic absorption line, $H(a, \omega=0.725a)$ is the Voigt integral, which is a convolution integral of the Doppler and the Lorentz broadened absorption line profile and is determined by the damping parameter, a [119], q is a correction factor which accounts for the hyperfine structure in the analytical line [112], s is the transverse cross-sectional area of the furnace, $N(t)$ is the total number of free

analyte atoms in the analysis volume at time t . In equation 4.1, Δv_D , $H(a, w=0.725a)$, Z , and q are all temperature-dependent [112-113, 116-117]. Equation 4.1 was derived under assumptions that distribution of free analyte atoms is uniform over the transverse cross-sectional area of the furnace, and that the furnace maintains a constant temperature during sample atomization and is isothermal over its length. The former assumption has been experimentally found to be valid for the later stage in the atomization cycle for some elements in the graphite tube furnace [118-121]. The latter assumption is, however, not valid for a commercial, pulse-heated graphite furnace in which both temporal and spatial nonisothermality occur. However, the $H(a, w=0.725a)/\Delta v_D$ ratio is less temperature-dependent [115] and the temperature dependence of the other terms for the analytical absorption line in the temperature range of the furnace is small. Under the assumption that in equation 4.1, the term before $N(t)$ is independent of variation of temperature in the furnace during sample atomization, the relation between the measured and the total number of atoms in the analysis volume can be approximated by equation 4.1 under nonisothermal conditions.

Because the measured absorbance reflects the integral of the number density of free analyte atoms along the length of the absorbing layer, knowledge of the time-dependent number density distribution of analyte atoms is extremely important in graphite furnace atomic absorption spectrometry. It is also extremely complex because it results from chemical and physical processes occurring in the condensed phase, in the graphite/metal interface, in the graphite (solid)/metal (solid, liquid)/gas interface, and in the gas phase.

Over the past years, several models have been proposed [5, 92, 109, 113, 115, 122-152] to simulate the time-dependent atom distribution and to interpret transient atomic absorbance signals in graphite furnace atomic absorption spectrometry. It is now well-accepted [109, 115, 140-141, 148, 153] that the measured atomic absorption signal in an electrothermal atomizer is determined by two concurrent processes: supply and transport or removal of analyte atom vapour. Using the supply function, $S(t)$ (the supply rate of the analyte atoms), and the transport or the removal function, $R(t)$ (the normalized response of the system upon the supply of an infinitely rapid pulse of atoms), the analytical expression for the time-dependent number of atoms present in the analysis volume, $N(t)$, can be expressed as a convolution integral of the following form [115, 140-141, 148]:

$$N(t) = \int_0^t S(t') R(t-t') dt' \quad 4.2$$

The integral of the time-dependent number of atoms is then given by [115]:

$$\int_0^\infty N(t) dt = \left[\int_0^\infty S(t) dt \right] \left[\int_0^\infty R(t) dt \right] = N_0 \tau_R \quad 4.3$$

where N_0 is the total number of analyte atoms introduced into the graphite furnace, and τ_R is the equivalent time constant of the removal function [115], or, more generally, the mean residence time of the analyte atoms [126].

There are generally two different approaches taken in these models. The first approach assumes that a reversible release process occurring at the interface between the condensed phase and the gas phase (where a pseudo-equilibrium of the analyte concentration is established), controls the overall atomization process. The supply function in this approach is mainly decided by an equilibrium vaporization and is influenced by the transport or the removal process. This approach has been applied to a laboratory-made graphite rod atomizer [140-147] and to a graphite platform furnace [151]. The second approach, which is the more widely applied, is based on the overall mass balance of the gaseous atoms in the analysis volume, and basically neglects the processes occurring at the interface of the condensed phase and the gas phase [5, 109, 113, 115, 126-128, 136-139, 152]. In this approach, the overall process at each instant can be treated as composed of two sequential and concurrent processes: supply process, and transport or removal process. The latter depends on the former but has no influence on the former. In this approach, most models assume that the supply function shows a simple first-order dependence on the mass of the analyte present on the graphite surface (in the condensed phase), i.e.,

$$S(t) = - \frac{dN_{\text{condensed phase}}(t)}{dt}$$

$$= B \exp [E_a/RT(t)] N_{\text{condensed phase}}(t), \quad 4.4$$

where $N_{\text{condensed phase}}(t)$ is the number of analyte atoms in the condensed phase at time t , R is the universal gas constant, B is the

frequency factor, E_a is the activation energy of the rate-determining step in the sequence of reactions in the atomization process, and T is the absolute temperature of the condensed phase. Recognizing that the total number of the analyte atoms introduced in the condensed phase is N_0 , i.e.,

$$N_0 = \int_0^{\infty} S(t) dt = N_{\text{condensed phase}}(0),$$

the supply function, $S(t)$, has the following form [115]:

$$S(t) = B \exp[-E_a/RT(t)] N_0 \exp \left\{ - \int_0^t B \exp[-E_a/RT(t')] dt' \right\}. \quad 4.5$$

In almost all the models considered, removal of the analyte atoms from the analysis volume by concentration diffusion has been considered as the major removal process. The other removal processes considered are losses of the analyte atoms by a forced, convective gas flow [115, 141, 145, 151], by expulsion with the concurrently-vaporized matrix [108], by expansion of the heated gas [108-109, 115], by thermal diffusion due to temperature gradients in the gas [109], by diffusion into the graphite tube wall [132], and by redeposition on the graphite surface [135]. When diffusion into or redeposition of analyte atoms onto the graphite surface is considered, diffusion out of or revaporization of the analyte atoms from the graphite surface is also considered at the same time [132, 135].

In spite of limitations (due to oversimplifications in the assumptions made), each model has its own merits and contributes to understanding of the atomization process in electrothermal atomic

absorption spectrometry. The common limitation of these models is lack of information on the time-dependent temperature distribution of the gas phase inside the furnace. Because of the lack of the above information, many of these models have assumed spatial isothermality and/or temporal isothermality of the analysis volume. When such models are applied to commercial, pulse-heated, semi-enclosed graphite tube atomizers which most likely do not have spatial and temporal isothermality, analytical formulations of the processes which are temperature-dependent (for example, the concentration diffusion process) become seriously flawed. The only exception is the recently-developed model by Gilmurdinov et al. [109], which has made a rigorous analytical treatment of transport processes involved in all pulse-heated, semi-enclosed, tube-type atomizers. It has also made allowances for spatial and temporal nonisothermalities of commercial atomizers which are described by non-dimensional parameters. However, spatial and temporal nonisothermalities of commercial atomizers have been considered by Gilmurdinov et al. [109] as independent of each other; and also non-dimensional parameters cannot vary with time, whereas spatial and temporal nonisothermalities of commercial atomizers are interrelated and vary with time, as has been discussed in Chapter 3.

Distribution of atoms in the analysis volume of real graphite furnaces is complex. Experimental studies of the temporal and spatial (radial) absorbance profiles by Holcombe et al. [118-121] have revealed that a radially-uniform, free-atom distribution in the analysis volume of a CRA-90 graphite tube furnace does not occur at

all times during atomization of a number of metals. These authors have reported that the degree of the above nonuniformity is element-dependent and is affected by the chemical nature of the graphite surface including specific, anisotropic reactivity of the graphite surface (carbon atoms in the ab plane versus carbon atoms in the c direction), and is dependent on transport processes of analyte atoms. Whereas gas phase reactions may influence spatial (radial) distribution of analyte atoms, these reactions cannot account for many of the observations. For many elements studied, desorption kinetics appear to govern absorbance vs. time curves including the falling edge of the absorbance signal profile [118-121].

A model describing the time-dependent analyte atom distribution in the graphite platform furnace which takes into account the time-dependent temperature distribution of the gas phase is proposed in this chapter. The predictions of the model have been tested quantitatively by comparing the computed curves of absorbance vs. time with the experimental curves using silver as the test analyte. Effects of some physical and chemical parameters of the analyte, experimental parameters, and sample matrices on absorbance vs. time curves, and on peak-height and integrated absorbances of analyte elements atomized from the graphite platform have been studied and discussed. This study has provided an understanding of the factors that influence absorbance signals profiles, which will allow optimization of experimental and operating parameters of commercial, pulse-heated graphite furnaces for best results.

4.2. Theoretical model

This model calculates the time-dependent distribution of the analyte atom density inside a graphite platform furnace without a forced convective flow of a purge gas. The graphite furnace considered is a commercial, pulse-heated, semi-enclosed, Massmann-type graphite tube furnace. The geometry of the graphite platform furnace considered is shown in Fig 1. The geometric configuration assumed in the model is the same as that in the model for temperature distribution of the gas phase (Fig. 23). The time-dependent temperature field of the graphite platform furnace, i.e., the temperature of the platform, the temperature distribution of the tube wall and of the gas phase, and the time-dependent velocity field of the gas are as calculated from the model described in the previous chapters. Therefore, all the assumptions made in Chapters 1-3 regarding the heat transfer processes involving temperature of the tube wall, platform and gas phase also apply to the model formulated in this chapter.

The following assumptions are made in the analytical model regarding the time-dependent distribution of the analyte atom density inside the graphite platform furnace.

(a) The platform is assumed to be a cylindrical rod located at the central line (longitudinal axis) of the furnace having the same mass and similar volume and surface area as the real, rectangular, flat platform has. The distribution of the analyte atom density in the graphite platform furnace is time- and space- dependent. For

simplicity, it is also assumed that distribution of the analyte atoms in the gas phase has no dependence on the azimuthal coordinate; it varies at each instant only along axial and radial coordinates.

Admittedly, the above assumption is oversimplified. However, under this assumption the same cylindrical coordinate system which has been applied to calculate the time-dependent temperature distribution of the gas phase can be applied to calculate the time-dependent distribution of the analyte atoms in the graphite platform furnace. This simplifies the mathematics for the analytical model considerably.

(b) Initially, atoms of the pre-atomization analyte species are dispersed uniformly on a small area on the surface at the central part of the platform. The release of the analyte atoms from the platform is governed by a first-order or a pseudo-first-order rate process.

(c) The process by which the analyte atoms are released from the graphite platform surface is irreversible, i.e., there is no re-deposition of the released atomic vapour on the platform. There is also no redeposition of the analyte atoms on the graphite furnace wall.

(d) Loss of the analyte atoms from the analysis volume is governed by concentration diffusion in the gas medium and by thermal expansion of the heated gas towards the ends of the graphite platform furnace. For the sake of simplicity, analyte atom loss by condensation on the cooler parts of the tube wall, or by diffusion into the tube wall, or by diffusion and expansion through the injection hole, or by thermal diffusion towards the ends of the furnace are not considered.

Also, chemical reactions involving analyte atoms in the gas phase (i.e., ionization, re-combination, dissociation, etc.) or in the

condensed phase are not considered.

(e) The concentration diffusion coefficient, D , of the analyte atoms in the gas phase is temperature-dependent and is therefore time- and space- dependent. However, temperature-dependence of other physicochemical properties of the analyte atom is not considered.

(f) The effective length of the absorbing layer of the analyte atoms is equal to the geometric length of the furnace tube. Also, re-entry of the analyte atoms through the furnace ends is not considered.

With the above assumptions and simplifications, the conservation of atoms of analyte Y in the infinitesimal ring of the gas phase located at (x, r) with length dx and width dr (Fig. 24) yields the following equation:

$$\frac{\partial n_{(Y)}(x, r, t)}{\partial t} + \text{div} [n_{(Y)}(x, r, t) \mathbf{u}_g(x, r, t) + \mathbf{J}_{(Y)}(x, r, t)] = f_{(Y)}(x, r, t), \quad 4.6$$

where $n_{(Y)}$ is the atom density of the analyte Y , $\mathbf{u}_g(x, r, t)$ is the velocity vector of the gas medium, $\mathbf{J}_{(Y)}(x, r, t)$ is the atom flux vector of the analyte Y relative to the velocity of the gas medium, $f_{(Y)}$ is the rate of atom formation of analyte Y per unit volume in the gas phase by presence of an atom source and/or by homogeneous chemical reactions and/or by elementary processes. These terms are defined as follows. The derivation of equation 4.6 is given in Appendix IV.

The atom flux vector $\mathbf{J}_{(Y)}$ is the combined effect of four separate contributing fluxes [154-155], i.e.,

$$\mathbf{J}_{(Y)} = \mathbf{J}_{(Y)}^c + \mathbf{J}_{(Y)}^p + \mathbf{J}_{(Y)}^f + \mathbf{J}_{(Y)}^T. \quad 4.7$$

The term $J_{(y)}^c$ is atom flux due to the concentration gradient of the analyte atoms, and is also called ordinary diffusion, which can be expressed by Fick's First Law of Diffusion as

$$J_{(y)}^c = - D \text{ grad } n_{(y)}(x, r, t) . \quad 4.8a$$

where $n_{(y)}$ is a function of (x, r, t) . In equation 4.8a, D is the diffusion coefficient of the analyte atoms Y in the gas phase, which, at constant pressure, is temperature-dependent [113,156], and is hence time- and space- dependent, as shown by equation 4.8b:

$$D(x, r, t) = D_0 \left[\frac{T_g(x, r, t)}{T_0} \right]^\gamma . \quad 4.8b$$

In equation 4.8b, D_0 is the diffusion coefficient of the gaseous analyte atom in the gas medium at one atmosphere pressure and at temperature $T_0 = 273 \text{ K}$. γ is the exponent of power in the temperature-dependence of the diffusion coefficient. Its value varies from 1.5-2.0 [113,156]. The term $J_{(y)}^p$ stands for atom flux vector due to pressure diffusion as a result of a pressure gradient. In the semi-enclosed furnace considered, the pressure in the atomizer can be considered invariant in time and space, and hence, this term is negligible. The term $J_{(y)}^f$ is atom flux vector due to forced diffusion, and results from an external force when it is acting upon different components of the gas phase differently. This term is of primary importance in ionic systems where the external force on an ion is given by the product of the ionic charge and the local electrical field strength [155]. When gravity is the only external force, as in the present system, this

term is zero. The term $J_{(y)}^T$ is atom flux vector due to thermal diffusion and is caused by a large temperature gradient. It can be expressed as [157-158]

$$J_{(y)}^T = -D \frac{K_T P}{k T_g^2} \text{grad } T_g, \quad 4.9a$$

where k is the Boltzmann constant, P is the gas pressure inside the furnace, K_T is the ratio of the thermal diffusion coefficient D_T and the concentration diffusion coefficient D (i.e., $K_T = D_T/D$). For analyte atoms Y of mass $m_{(y)}$ and density $n_{(y)}$ in a monatomic gas (e.g., Ar used as a purge gas) having atom mass $m_{(g)}$ and density $n_{(g)}$, the following expression for K_T can be used [109, 138].

$$K_T = \frac{n_{(y)} n_{(g)}}{n_{(y)} + n_{(g)}} \frac{m_{(y)} - m_{(g)}}{n_{(y)} m_{(y)} + n_{(g)} m_{(g)}} (1 - \gamma), \quad 4.9b$$

An estimate for the gas mixture containing trace amounts of silver in argon gas (as used in the experimental verification of the model) has shown that the thermal diffusion ratio K_T is very small. Since the temperature gradient is not very large, excepting near the furnace ends and near the platform, the mass flux by thermal diffusion is much less than that by concentration diffusion. Thus, thermal diffusion can be neglected as a first approximation. The analytical model has been later refined to include thermal diffusion, and the above estimate has been confirmed (see section 4.4.2 for the discussion).

With these considerations, equation 4.7 can be rewritten as

$$J_{(y)} = -D_0 \left[\frac{T_g(x, r, t)}{T_0} \right]^{\gamma} \text{grad } n_{(y)}(x, r, t) \quad 4.10$$

Since neither gas-phase reactions nor other elementary processes involving the analyte atoms are considered [assumptions (c) and (d)], the rate of production of analyte atoms Y per unit volume in the gas phase, $f_{(y)}$, can be expressed as

$$f_{(y)}(x, r, t) = \begin{cases} 0, & \text{for } \frac{l_p}{2} \geq x \geq 0, \quad \frac{d_i}{2} \geq r \geq r_p, \quad t > 0, \\ \text{and for } \frac{l_w}{2} \geq x > \frac{l_p}{2}, \quad \frac{d_i}{2} \geq r \geq 0, \quad t > 0, \\ S(t)/\Delta v(0, r_p), & \text{for } \delta' \geq x \geq 0, \quad r_p + \delta'' \geq r \geq r_p, \quad t > 0. \end{cases} \quad 4.11$$

In equation 4.11, $\Delta v(0, r_p)$ is the volume of an infinitesimal gas ring which contains the surface area of the platform centre where the analyte sample is deposited, and δ' and δ'' are the length and the width, respectively, of the gas ring. The supply function, $S(t)$, can be described by a first-order or a pseudo-first-order rate process [assumption (b)]. Its analytical form can be expressed as follows [115, 151].

$$S(t) = \beta N_0 B \exp[-E_a/RT_p(t)] \exp \left\{ -\int_0^t B \exp[-E_a/RT_p(t')] dt' \right\} \quad 4.12$$

where β is the fraction of analyte atoms which are actually atomized [131]. For $\beta=1$, equation 4.12 has the same form as equation 4.5.

Substituting equations 4.10-4.12 into equation 4.6 and rearranging it, the following equation is obtained:

$$\begin{aligned} \frac{\partial n_{(y)}(x, r, t)}{\partial t} + \frac{\partial}{\partial x} [n_{(y)}(x, r, t) u_{x, g}(x, r, t)] \\ - \frac{\partial}{\partial x} \left\{ D_0 \left[\frac{T_g(x, r, t)}{T_0} \right]^{\gamma} \frac{\partial n_{(y)}(x, r, t)}{\partial x} \right\} \\ - \frac{1}{r} \frac{\partial}{\partial r} \left\{ r D_0 \left[\frac{T_g(x, r, t)}{T_0} \right]^{\gamma} \frac{\partial n_{(y)}(x, r, t)}{\partial r} \right\} \end{aligned}$$

0,

for $\frac{l_p}{2} \geq x \geq 0$, $\frac{d_i}{2} \geq r \geq r_p$, $t > 0$,and for $\frac{l_w}{2} \geq x > \frac{l_p}{2}$, $\frac{d_i}{2} \geq r \geq 0$, $t > 0$.

4.13

$$\beta N_0 B \exp[-E_a/RT_p(t)] \exp\left\{-\int_0^t B \exp[-E_a/RT_p(t')] dt'\right\}$$

 $\Delta v(0, r_p)$ for $\delta' \geq x \geq 0$, $r_p + \delta'' \geq r \geq r_p$, $t > 0$.

Equation 4.13 is subject to the following boundary conditions:

$$\frac{\partial n(y)(x, r, t)}{\partial x} = 0,$$

$$\text{for } x = 0, \quad \frac{d_1}{2} \geq r \geq r_p, \quad t > 0; \quad 4.14a$$

$$n(y)(x, r, t) = 0,$$

$$\text{for } x = \frac{l_w}{2}, \quad \frac{d_1}{2} \geq r \geq 0, \quad t > 0; \quad 4.14b$$

$$\frac{\partial n(y)(x, r, t)}{\partial r} = 0,$$

$$\text{for } \frac{l_w}{2} \geq x > \frac{l_p}{2}, \quad r = 0, \quad t > 0; \quad 4.14c$$

$$n(y)(x, r, t) = 0,$$

$$\text{for } \frac{l_w}{2} \geq x \geq 0, \quad r = \frac{d_1}{2}, \quad t > 0,$$

$$\text{for } \frac{l_p}{2} \geq x > 0, \quad r = r_p, \quad t > 0; \quad 4.14d$$

and the initial condition

$$n(y)(x, r, 0) = 0,$$

$$\text{for } \frac{l_w}{2} \geq x > \frac{l_p}{2}, \quad \frac{d_1}{2} \geq r \geq 0,$$

$$\text{and for } \frac{l_p}{2} \geq x \geq 0, \quad \frac{d_1}{2} \geq r \geq r_p. \quad 4.15$$

The time-dependent number of the analyte atoms in the graphite platform furnace is obtained by integrating the time-dependent density distribution $n_{(y)}(x, r, t)$ over the furnace volume, which, for the cylindrical coordinates used in the model, is:

$$N(t) = \int \int_{(\text{furnace volume})} n_{(y)}(x, r, t) 2\pi r dr dx . \quad 4.16$$

If the analyte is completely atomized (i.e., $\beta=1$) and if all of the analyte atoms enter into the analysis volume, the mean residence time of the analyte atoms, τ_R , can be expressed as follows [115, 126]:

$$\tau_R = \frac{\int_0^\infty N(t) dt}{N_0} \quad 4.17$$

A computer program has been written using equations 4.13-4.17 to obtain the time-dependent atom distribution in the graphite platform furnace, $n_{(y)}(x, r, t)$, the number of the analyte atoms in the furnace, $N(t)$, and the mean residence time of the analyte atoms, τ_R . In the computer program, equation 4.13 has been approximated by a numerical method using the splitting technique [110-111]. Using this technique, the two-dimensional problem of equation 4.13 is reduced to two steps which involve a finite-difference approximation in only one dimension at a time, i.e., the distribution of analyte atoms due to their formation from the atom source and radial diffusion, and that due to axial diffusion and axial thermal expansion. In each step, the backward finite-difference approximations were used at a set of nodal

points. The Crout Reduction method for Tridiagonal Linear Systems was used for solving the above problem [76]. The numerical approximation of the distribution of the analyte atom density is similar to the numerical approximation of the temperature distribution of the gas phase described in Appendix 2. In each time step, the platform temperature, the temperature and the velocity distribution of the gas phase are obtained by calling the corresponding subroutine program which has been described in Chapter 3.

In the computer program, there are 15 nodes in the axial direction (including the central and the end node) and 10 nodes in the radial direction, which are the same as used in the calculation of the temperature and the velocity distribution of the gas (see Fig. 127 in Appendix IV). As discussed in Chapter 3 (section 3.2), the accuracy of the calculation by the implicit finite-difference approximation depends on the magnitude of the time step once the increments in the space coordinates have been decided. A mass balance of the analyte atoms is checked at each time step.

4.3. Experimental

4.3.1 Apparatus and measurement procedure

Several instruments were used as follows: a research instrument which is a modified Perkin-Elmer Heated Graphite Atomizer (HGA), model 400, equipped with the laboratory-made power supply described earlier; a Varian-Techtron atomic absorption spectrophotometer, model AA-6, fitted with a Hamamatsu R955 photomultiplier tube (Hamamatsu

Corporation, Middlessex, NJ., USA). A laboratory-made amplifier having a time constant of 8 ms was used for studying the atomic absorbance signal of silver. Another research instrument, which is a modified Perkin-Elmer Heated Graphite Atomizer (HGA), model 74, equipped with the laboratory-made power supply described earlier, and a modified Perkin-Elmer atomic absorption spectrometer, model 503, equipped with a Deuterium-Arc Background Corrector, were used for studying absorbance signals and matrix interferences. The Perkin-Elmer atomic absorption spectrometer, model 503, was modified so that the absorbance signal was obtained direct from the output of its logarithmic amplifier, which was provided with a variable time constant. A time constant of 20 ms was used. In some cases, another Perkin-Elmer spectrometer, model 5000, equipped with a Perkin-Elmer Heated Graphite Atomizer (HGA), model 500, was used. In all cases, commercial hollow-cathode lamps were used and operated at lamp currents well below the maximum lamp currents prescribed by the manufactures. The Perkin-Elmer pyrolytically-coated graphite tubes (part no. B0091-504, long-lasting), and pyrocoated graphite tubes (part No. 0290-1766) were used. Details of platforms made of anisotropic pyrolytic graphite were given in Chapter 1 (Fig. 1 and Table 3).

The tube wall temperatures reported were those of the inside graphite surface of the tube wall directly below the sample injection hole. The tube wall temperature was measured with two automatic optical pyrometers: one series 3G0 and the other series 1100 - both by Ircon Inc., Skokie, IL., USA. The details of measurement of the tube wall temperature, and of determination of the initial platform

temperature in the atomization cycle have been given in Chapters 1 and 2, respectively.

In the atomization cycle, the absorbance signal and the output voltage from the optical pyrometer were recorded simultaneously with a Nicolet model 2090-III, two-channel digital oscilloscope, fitted with a model 201 plug-in unit and a disk recorder, or with a Nicolet model 4094, 4-channel programmable digital oscilloscope, fitted with two model 4562 plug-in units and an XF-44 disk recorder. As described earlier, the output voltage of the optical pyrometer was converted into a temperature profile using the pyrometer calibration curve provided by the manufacturer. Most of the oscilloscope traces were recorded with a Hewlett-Packard plotter, model 7470A (Hewlett-Packard Company, San Diego, CA, USA). Oscilloscopic traces were photographed with a Polaroid camera (Tektronix Inc., Portland, Oregon, USA). Integrated absorbance signals were measured with the Nicolet programmable digital oscilloscope using a software package provided by Nicolet Instrument Corporation.

4.3.2. Reagents and sampling procedure

A stock solution containing $1000 \mu\text{g mL}^{-1}$ of Ag was prepared by dissolving an appropriate mass of AgNO_3 (99.999% pure) in ULTREX nitric acid (Baker Chemical Co.). Stock solutions containing $1000 \mu\text{g mL}^{-1}$ of Pb and Cd were prepared separately by dissolving appropriate masses of pure metal oxides (99.99% pure) in ULTREX nitric acid (Baker Chemical Co.). Stock solutions containing $1000 \mu\text{g mL}^{-1}$ of Ni and Co were prepared separately by dissolving appropriate masses of pure metals (99.999% pure) in ULTREX nitric acid (Baker Chemical Co.). The

above solutions were diluted with ultrapure water to make the stock solutions 1% (v/v) in nitric acid. Stock solutions containing 1000 $\mu\text{g mL}^{-1}$ of V and Mo were prepared separately by dissolving appropriate masses of the metal oxides in ammonium hydroxide (ACS reagent grade) and diluting the solutions with ultrapure water. Stock solutions of NaCl, MgCl_2 and CaCl_2 were prepared separately - each by dissolving an appropriate mass of the pure salt (ACS reagent grade) in ultrapure water containing 0.1% (v/v) HCl. These solutions were then diluted with ultrapure water to make the final solutions contain 5% (w/v) of these salts. A stock solution of CuCl_2 was prepared by dissolving an appropriate mass of cupric chloride (BDH laboratory reagent) in ultrapure water containing 0.1% (v/v) HCl and the solution was made up to 10% (w/v) with ultrapure water. 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 serial dilution of the above stock solutions with ultrapure water immediately prior to determination. In all cases, 5 μL volume of the sample solution was manually injected into the furnace with an Eppendorf microlitre pipette fitted with disposable plastic tips.

4.3.3. Instrumental parameters

The Instrumental parameters for measuring absorbance of Ag, Cd, Pb, Ni, Co, V, and Mo are presented in Table 14.

4.4. Results and discussion

The limitation of the present analytical model stems largely from its oversimplified assumptions in formulating the model and results in the computed density distribution, $n_{(y)}(x, r, t)$, deviating from the actual one. This deviation is primarily due to the oversimplified assumption of the geometry made in the analytical model. The model assumes a cylindrical rod geometry of the platform located at the central line (longitudinal axis) of the furnace, whereas the real platform is flat and rectangular, and its actual location is below the furnace central line. The model assumes cylindrical symmetry in atom distribution, whereas atoms are actually vaporized from the upper side of the platform. However, if the other assumptions are satisfied, this limitation should not seriously affect the number of analyte atoms in the furnace, $N(t)$, at any time, t , and the mean residence time of the analyte atoms, τ_R , computed from the model; nor should it seriously affect the predicting power and usefulness of the model. This has been confirmed experimentally. Figure 55 shows that the absorbance vs. time curve of silver deposited at the centre of the upper surface of the platform is almost the same as that generated by the same amount of silver but deposited half on each side of the platform at its centre.

The experimental results and discussions presented in the following sections will be mostly concerned with the $N(t)$ (or the relative atom population, $N(t)/N_0$) vs. time curve, the maximum amount of analyte atoms, N_{max} , (or the maximum relative atom population,

Figure 55. Absorbance signal of 0.1 ng silver (taken as the nitrate in an aqueous solution) deposited at the centre of the upper surface of the platform (curve A) and deposited half on each side of the platform at its centre (curve B). Perkin-Elmer-HGA-500. Maximum power heating mode. $T_i = 300$ K. $T_f = 2300$ K. The deposition of the sample on the platform was done outside the furnace. The drying of the sample was done with an infrared lamp.

$N_{\max}/N_0$), and the mean residence time, τ_p . The first of the above three determines the shape and the relative position of the absorbance vs. time curve on the time axis. The other two are characteristics of the absorbance signals, and determine the magnitude of the peak-height and the integrated absorbance. By equating $N(t)$ with the absorbance value at time t , the predictions of the analytical model can be compared with the experimental results.

4.4.1. The experimental and the computed absorbance vs. time curve for silver

Silver was selected as the test analyte for experimental verification of the model since it was most likely to satisfy the non-geometrical assumptions made in formulating the model, as shown below.

Silver is relatively inert towards oxygen and graphite. Its oxides are unstable at elevated temperatures [159]. Experimental studies of silver in graphite furnace atomic absorption spectrometry have indicated absence of influence of the amount of oxygen gas on the atomic absorbance signal of silver in the furnace [160-161], and absence of any interaction between Ag(g) and the graphite tube wall [121, 131, 132]. A strong interaction between the gaseous analyte atoms and the furnace wall may result in multiple condensation and re-evaporation of the analyte atoms, which has not been provided for in the model. The activation energy for silver obtained from the absorbance signal of silver atomized from a graphite tube wall in the graphite furnace correlates well with the vaporization enthalpy of pure silver metal [131, 134, 162]. Hence, it is generally accepted that gaseous silver atoms are formed by direct vaporization of the

metal. Also, changes in the amount of silver introduced into the atomizer do not give a different value for the rate constant for formation of $\text{Ag}_{(g)}$ atoms [131]; this validates the assumption of first-order kinetics for $\text{Ag}_{(g)}$ atom formation. The fraction of silver atomized, β , may be taken as 1, as done by Smets [131].

The computed absorbance vs. time curves of silver have been obtained from the theoretical $N(t)$ vs. time curves, assuming that the analysis volume is equal to the volume of the furnace and that the absorbance value at any instant t is proportional to the number of analyte atoms in the analysis volume according to equation 4.1, i.e.,

$$A(t) = Q N(t) \quad 4.18$$

where Q is a proportionality constant. The value of Q was evaluated experimentally by equating one of the measured peak absorbance values with the maximum amount of the analyte atoms computed using the other parameters given in Table 15 as inputs. The parameters shown in Table 15 were used as inputs for all the theoretical absorbance vs. time curves and the relative atom population vs. time curves for silver.

In Table 15, the fraction of the silver atomized, β , was taken as 1. The concentration diffusion coefficient, D_0 , for $\text{Ag}_{(g)}$ in argon gas at a pressure of 1 atmosphere and $T_0 = 273 \text{ K}$, was taken from that for the Ar-Ar system [163] as an estimation of the unknown D_0 . The exponent power of the temperature-dependent diffusion coefficient, γ , was selected by curve-fitting the computed results with the experimental results. The vaporization enthalpy of pure silver metal, 276 kJ mol^{-1} [164], was taken as the activation energy value. The frequency factor, B , was selected by applying the model to atomization

Table 15. Input parameter values for computing the
absorbance vs. time curves for silver

Description	Input values
Proportionality constant, Q (absorbance per atom)	1.31×10^{-12} for $B = 1.0 \times 10^{12} \text{ s}^{-1}$ 1.28×10^{-12} for $B = 5.0 \times 10^{12} \text{ s}^{-1}$
Fraction of atoms atomized, β	1
Activation energy, E_a (kJ mol^{-1})	276*
Frequency factor, B (s^{-1})	1.0×10^{12} and 5.0×10^{12}
Diffusion coefficient, D_0 ($\text{cm}^2 \text{ s}^{-1}$) (in argon gas at 273 K and 1 atm)	0.157
Exponent power of temperature- dependent diffusion coefficient, γ	1.65
Length of the absorbing layer (mm) (= length of the furnace tube)	28
Total number of Ag introduced, N_0	5.58×10^{11} (the same as in the experiments)
Heating parameters of the tube wall at the furnace centre	Measured tube wall temperature at the furnace centre as a function of time
Dimensions of the graphite tube	Dimension of pyrolytically- coated graphite tubes (which were used in experiments) were as given in Table 2
Dimensions of the graphite platform used in calculating its temperature	Dimensions of pyrolytic graphite platform given in Table 3 with thickness (and mass) used in experiments
Dimensions of the graphite platform used in calculating the gas temperature	Graphite rod having length 18 mm and diameter 0.79 mm

* Value of vaporization enthalpy of pure silver metal was used [164].

from the tube wall and by curve-fitting the rising part of the computed results with the experimental ones for atomization from the tube wall. Figure 56 shows that both B values of $1.0 \times 10^{12} \text{ s}^{-1}$ and $5.0 \times 10^{12} \text{ s}^{-1}$ fit reasonably well with the experimental curves for atomization from the tube wall. Therefore, these two B values were used for the computation for atomization from the platform.

Using equations 4.17 and 4.18, the integrated absorbance was calculated as follows:

$$\int_0^{\infty} A(t) dt = Q N_0 \tau_R \quad 4.19$$

Figures 57-60 show the measured and the computed absorbance vs. time curves for silver at various tube wall heating rates (Fig. 57), initial tube wall (atomization) temperatures (Fig. 58), final tube wall (atomization) temperatures (Fig. 59), and at various platform thicknesses (masses) (Fig. 60).

Table 16 shows that with the parameters given in Table 15, ratios of the computed peak-height absorbance values vs. the experimental ones are 97-120% for a B value of $1.0 \times 10^{12} \text{ s}^{-1}$, and 86-118% for a B value of $5.0 \times 10^{12} \text{ s}^{-1}$, whereas those of the integrated absorbance are 81-104% for a B value of $1.0 \times 10^{12} \text{ s}^{-1}$, and 77-101% for a B value of $5.0 \times 10^{12} \text{ s}^{-1}$. If the peak position of the computed curve is shifted to coincide with the peak position of the experimental curve, one finds a good agreement between the falling parts of these curves. However, most of the computed curves appear later than the experimental ones, and the rise times (i.e., the time intervals from the appearance to the peak of the absorbance) are shorter for the computed curves than for the experimental ones.

Figure 56. The measured (solid lines) and the computed (dashed lines) absorbance vs. time curves for 0.1 ng silver (taken as the nitrate in an aqueous solution) with atomization from the tube wall and the corresponding tube wall temperature (at the furnace centre) vs. time curves. $\alpha \approx 2.3 \text{ K m s}^{-1}$. Curve A: $T_1 = 920 \text{ K}$. Curve B: $T_1 = 700 \text{ K}$. Curve C: $T_1 = 470 \text{ K}$. The other computing parameters were: $Q = 1.05 \times 10^{-12} \text{ abs. per atom}$, $E_a = 276 \text{ kJ mol}^{-1}$, $D_0 = 0.157 \text{ cm}^2 \text{ s}^{-1}$, $\gamma = 1.95$. (a) $B = 1.0 \times 10^{12} \text{ s}^{-1}$. (b) $B = 5.0 \times 10^{12} \text{ s}^{-1}$.

Figure 57. The measured (solid lines) and the computed (dashed lines) absorbance vs. time curves for 0.1 ng silver (taken as the nitrate in an aqueous solution) with atomization from the platform at various tube wall heating rates, and the corresponding tube wall temperature (at the furnace centre) vs. time curves. For all the curves, $b = 0.30$ mm (mass 50 mg).

(a) $B = 1.0 \times 10^{12} \text{ s}^{-1}$. (b) $B = 5.0 \times 10^{12} \text{ s}^{-1}$. The other computing parameters were the same as given in Table 15. For each set of curves from left to right,

- curve A: $\alpha \approx 5.3 \text{ K ms}^{-1}$, $T_1 = 520 \text{ K}$;
- curve B: $\alpha \approx 4.3 \text{ K ms}^{-1}$, $T_1 = 540 \text{ K}$;
- curve C: $\alpha \approx 2.3 \text{ K ms}^{-1}$, $T_1 = 510 \text{ K}$;
- curve D: $\alpha \approx 1.0 \text{ K ms}^{-1}$, $T_1 = 520 \text{ K}$.

Figure 58. The measured (solid lines) and the computed (dashed lines) absorbance vs. time curves for 0.1 ng silver (taken as the nitrate in an aqueous solution) with atomization from the platform at various initial tube wall (atomization) temperatures, and the corresponding tube wall temperature (at the furnace centre) vs. time curves. For all the curves, $a \approx 2 \text{ K ms}^{-1}$, $b = 0.30 \text{ mm}$ (mass 50 ng). (a) $B = 1.0 \times 10^{12} \text{ s}^{-1}$. (b) $B = 5.0 \times 10^{12} \text{ s}^{-1}$. The other computing parameters were the same as given in Table 15. For each set of curves from left to right, curve A: $T_i = 920 \text{ K}$; curve B: $T_i = 700 \text{ K}$; curve C: $T_i = 470 \text{ K}$.

Figure 59. The measured (solid lines) and the computed (dashed lines) absorbance vs. time curves for 0.1 ng silver (taken as the nitrate in an aqueous solution) with atomization from the platform at various final tube wall temperatures, and the corresponding tube wall temperature (at the furnace centre) vs. time curves. For all the curves, $\alpha \approx 2 \text{ K ms}^{-1}$, $T_i = 530 \text{ K}$, $b = 0.30 \text{ mm}$ (mass 50 ng). (a) $B = 1.0 \times 10^{12} \text{ s}^{-1}$. (b) $B = 5.0 \times 10^{12} \text{ s}^{-1}$. The other computing parameters were the same as given in Table 15. For each set of curves from left to right, curve A: $T_f = 3070 \text{ K}$; curve B: $T_f = 2570 \text{ K}$; curve C: $T_f = 2070 \text{ K}$.

Figure 60. The measured (solid lines) and the computed (dashed lines) absorbance vs. time curves for 0.1 ng silver (taken as the nitrate in an aqueous solution) with atomization from the platform with thickness as a parameter, and the corresponding tube wall temperature, T_w , (at the furnace centre) vs. time curve. T_p is the (computed) platform temperature. For all the curves, $\alpha \approx 2 \text{ K ms}^{-1}$, $T_i = 470 \text{ K}$, $T_f = 2280 \text{ K}$. (a) $B = 1.0 \times 10^{12} \text{ s}^{-1}$. (b) $B = 5.0 \times 10^{12} \text{ s}^{-1}$. The other computing parameters were the same as given in Table 15. For each set of curves from left to right, curve A: $b = 0.24 \text{ mm}$ (mass of 35 mg); curve B: $b = 0.30 \text{ mm}$ (mass 50 mg); curve C: $b = 0.44 \text{ mm}$ (mass 60 mg).

Table 17 shows that with a B value of $1.0 \times 10^{12} \text{ s}^{-1}$, the ratios of appearance times of the computed and the experimental curve are 100-125%, and the ratios of the rise times of the computed and the measured absorbance vs. time curves are 56-75%. With a B value of $5.0 \times 10^{12} \text{ s}^{-1}$, the former ratios become 92-118%, but there is no improvement in the latter ratios.

Compared to the much better agreement between the rising parts of the computed and the experimental curve for atomization from the tube wall (Fig. 56), the disagreements between the rising parts of the computed and the experimental curves for atomization from the platform are most likely due to the deviation of the computed platform temperatures from the actual ones. In calculating the platform temperature, electrical resistive heating of the platform was neglected as a first approximation. This neglect results in an overprediction of the delay in the platform heating (i.e., an underprediction of the platform temperature at a given time), and also results in an overprediction of the heating rate of the platform after the initial heating stage. Also, in calculating the platform temperature, a homogeneous surface temperature of the platform was assumed; whereas the temperature of the central areas of the platform which are near the tube wall is probably slightly higher than that of the centre, resulting in an earlier (relative to the computed time) release of the analyte atoms from these areas.

The computed curves of silver are obtained under the assumption that the length of the absorbing layer of the silver atoms equals the length of the furnace tube. However, since the atomic absorbance signal generated during atomization from the platform appears at a

Table 17. The measured and the computed appearance and rise time. of the absorbance signal for silver

Figure No.	Curve	Appearance time				Rise time					
		$B = 1.0 \times 10^{12} \text{ s}^{-1}$		$B = 5.0 \times 10^{12} \text{ s}^{-1}$		$B = 1.0 \times 10^{12} \text{ s}^{-1}$		$B = 5.0 \times 10^{12} \text{ s}^{-1}$			
		$t_{\text{exp}} \left\{ \frac{t_{\text{cal}}}{t_{\text{exp}}} \right\} \%$	$t_{\text{cal}} \left\{ \frac{t_{\text{cal}}}{t_{\text{exp}}} \right\} \%$	$t_{\text{cal}} \left(\frac{t_{\text{cal}}}{t_{\text{exp}}} \right)$	$t_{\text{exp}} \left(\frac{t_{\text{cal}}}{t_{\text{exp}}} \right) \%$	$t_{\text{exp}} \left(\frac{t_{\text{cal}}}{t_{\text{exp}}} \right) \%$	$t_{\text{cal}} \left(\frac{t_{\text{cal}}}{t_{\text{exp}}} \right) \%$	$t_{\text{cal}} \left(\frac{t_{\text{cal}}}{t_{\text{exp}}} \right) \%$	$t_{\text{cal}} \left(\frac{t_{\text{cal}}}{t_{\text{exp}}} \right) \%$		
57	A	0.45	0.45	100	0.42	93	0.20	0.13	65	0.12	60
57	B	0.50	0.53	106	0.46	92	0.24	0.16	66	0.19	79
57	C	0.80	0.85	106	0.81	101	0.25	0.15	60	0.13	52
57	D	1.37	1.58	115	1.50	109	0.38	0.24	63	0.25	66
58	A	0.65	0.70	106	0.66	102	0.32	0.24	75	0.21	66
58	B	0.77	0.88	114	0.80	104	0.32	0.21	66	0.23	72
58	C	0.92	1.05	114	0.98	109	0.36	0.23	64	0.24	67
59	A	0.80	0.85	106	0.80	100	0.23	0.16	70	0.16	69
59	B	0.86	0.94	109	0.90	105	0.26	0.16	62	0.16	61
59	C	0.97	1.10	108	1.00	103	0.39	0.31	79	0.31	79
60	A	0.76	0.93	122	0.90	118	0.39	0.22	56	0.21	54
60	B	0.92	1.05	114	0.98	109	0.36	0.23	64	0.24	67
60	C	0.95	1.10	125	1.02	107	0.43	0.27	63	0.20	47

longer time than that atomized from the tube wall, the gas temperature outside the furnace ends is probably higher at longer heating times. Because of the higher vapour pressure of the analyte atoms at the higher temperature at the ends of the graphite platform furnace, the actual length of the absorbing layer of the analyte atoms in the graphite platform furnace is probably greater than the geometrical tube length. Hence, the zero density of the analyte atoms may occur at a position which is a few millimeters outside of and further away from the furnace ends, and this position may be a function of time. Figure 61 shows that the computed absorbance vs. time curve (symbols) obtained using $D_0 = 0.157 \text{ cm}^2 \text{ s}^{-1}$ and $\gamma = 1.95$ and assuming a constant zero atom density at a transverse cross section 3 mm outside of and further away from the furnace ends agrees well with the one computed using $D_0 = 0.157 \text{ cm}^2 \text{ s}^{-1}$ and $\gamma = 1.65$, and assuming a constant zero atom density at the transverse cross section exactly at the furnace ends (dashed line). Therefore, without knowing the actual length of the absorbing layer of analyte atoms, the temperature dependence of the concentration diffusion coefficient obtained by curve-fitting of the computed results with the experimental results may not represent the actual one.

It should be pointed out that the difference between the ratios of computed and measured peak-height absorbances (i.e., 97-120%) and the ratios of computed and measured integrated absorbances (i.e., 81-104%) may be partly due to the difference in the temperature distributions between the peak-height and the integrated absorbance measurement, resulting in the proportionality constant being different for the peak-height absorbance and the integrated absorbance. Also, when

Figure 61. The measured (solid line) and the computed (dashed lines and the symbols) absorbance vs. time curves for 0.1 ng silver (taken as the nitrate in an aqueous solution) with atomization from the platform, and the corresponding tube wall temperature, T_w , (at the furnace centre) vs. time curve. $T_i = 470$ K, $T_f = 2280$ K,

$\alpha \approx 2.3$ K ms⁻¹. T_p is the (computed) platform temperature vs. time curves for platform thickness 0.30 mm (mass 50 mg).

Dashed line: $\gamma = 1.65$, Atom densities were taken to be zero at the cross section just at the furnace ends, $B = 1.0 \times 10^{12}$ s⁻¹.

Symbols: $\gamma = 1.95$. Atom densities were taken to be zero at the cross section, 3 mm further away from the furnace ends, $B = 1.0 \times 10^{12}$ s⁻¹.

The other computing parameters were the same as given in Table 15.

different heating parameters of the tube wall are used, the proportionality constant, Q , will be different because of different temperature distributions under different heating parameters.

Based on the results and discussions presented above, it is concluded that the measured and computed absorbance vs. time curves for silver agree reasonably well.

4.4.2. Formation of silver atoms in and their removal from the graphite platform furnace

Figures 62-63 show the relative atom density distribution at various times. The relative atom density considered here is the computed atom density $n_{(y)}(x, r, t)$ over the average atom density assuming all the atoms introduced have been distributed homogeneously in the furnace. Because of the oversimplified assumptions made for the platform geometry, Figs. 62-63 show only qualitative trends in the density distribution of the analyte atoms, and cannot be relied on for quantitative predictions.

The computed results show that for the computing parameters used in Figs. 62-63, more than 90% of the analyte atoms have been released from the platform at the time, t_p , corresponding to the maximum amount of the analyte atoms being present in the furnace. At time $t < t_p$, the release of the analyte atoms into the analysis volume predominates over the atom removal processes. The atom density gradient both in the radial and the axial direction increases rapidly with increasing time, with the highest atom density occurring around the atom source at the furnace centre [Fig. 62(a), 62(c), 63(a)]. Such a highly inhomogeneous atom distribution originates from the limited sampling area and the

Figure 62. The computed distributions of relative atom density of silver in the axial direction at selected times and radial coordinates: (a) $r = r_p$, $t < t_p$ (b) $r = r_p$, $t > t_p$ (c) $r = 2.84$ mm. For all the curves, $b = 0.35$ mm (mass 60 mg), $B = 5.0 \times 10^{12} \text{ s}^{-1}$, $T_i = 470 \text{ K}$, $T_f = 2280 \text{ K}$, $\alpha \approx 2.3 \text{ K ms}^{-1}$. The other computing parameters were the same as given in Table 15.

Figure 63. The computed distributions of relative atom density of silver in the radial direction at selected times and axial coordinates: (a) $x = 0$ mm, $t < t_p$; (b) $x = 0$ mm, $t > t_p$; (c) $x = 10$ mm. The computing parameters were the same as given in Fig. 62.

exponential term in the supply function (equation 4.12). The value of this term increases rapidly with increasing platform temperature, which increases with time. This is similar to atomization from the tube wall in which in the initial stage of the atomization cycle, the analyte atom density near the centre of the tube has been experimentally found to be higher than that at the furnace ends [165]. The analyte atoms released from the central area require a certain time to reach the furnace ends and to be removed from the analysis volume by condensation. In the present case, τ_p , the time interval from the time when the amount of $Ag(g)$ in the furnace gives 1% absorption to the time when the same amount of $Ag(g)$ is removed from the analysis volume, is about 110 ms. During this time the $N(t)$ vs. time curve (or the absorbance vs. time curve) is completely determined by the supply function. At $t > \tau_p$ the atom removal processes are predominant since most of analyte atoms are then in the gas phase. The atom density gradient in the radial direction rapidly decreases [Fig. 63(b) and 63(c)], and the gradient in the axial direction decreases gradually with time [Fig. 62(b) and 62(c)]. The mean residence time, τ_R , of the analyte atoms in the case considered is about 300 ms.

The model has been refined to also include other atom loss mechanisms as follows: thermal diffusion and atom loss through the sample injection hole. Thermal diffusion was taken into account in the axial direction by equations 4.7 and 4.9. Atom loss through the sample injection hole was taken into account (approximately) by including in the calculation an extra loss of analyte atoms from the infinitesimal gas ring where the sample injection hole was located. The amount of this extra loss of analyte atoms was assumed to be equal to the product

of the amount of analyte atom loss by diffusion in the axial direction from this ring and the ratio of the hole area to the cross-sectional area of the gas ring. The effects of the analyte atom loss by concentration diffusion, thermal diffusion, loss through the sample injection hole, and loss through the furnace ends by thermal expansion were estimated. The results are shown in Figs. 64-65, from which the following general conclusions are drawn.

Under the assumptions made in the model, the predominant atom loss process in the graphite platform furnace is by concentration diffusion. Therefore, the time-dependent temperature field involved in the diffusion process must be known for the particular graphite furnace. Loss of analyte atoms by thermal diffusion and through the sample injection hole plays a secondary role. However, loss of analyte atoms through the sample injection hole has a relatively large role at $t < t_p$ when the analyte atoms are rapidly released. In the present case, of the total loss of analyte atoms, the analyte atom loss through the sample injection hole is less than 5%. This probably gives the minimum estimation since near the sample injection hole, concentration gradient is smaller in the axial direction than in the radial direction towards the outside of the hole (where the analyte concentration can be taken as zero). Of the total loss, the analyte loss by thermal diffusion is less than 5%. Analyte atom loss through the furnace ends by thermal expansion is not important because the absorbance signal appears at a time when the temperature of tube wall (at the furnace centre) has almost attained a steady state, and the corresponding gas velocities are very low, as discussed in Chapter 3.

Figure 64. The effect of various loss processes on the computed relative atom population vs. time curves. The computing parameters were the same as given in Fig. 62.

Curve 1 - concentration diffusion alone.

Curve 2 - concentration diffusion and atom loss by thermal expansion of heated gas through the furnace ends.

Curve 3 - processes considered in curve 2 plus atom loss through the sample injection hole.

Curve 4 - processes considered in curve 3 plus thermal diffusion in the axial direction.

Figure 65. Time-dependent relative amounts of the analyte atoms remaining in the furnace and those lost by various processes. The computing parameters were the same as given in Fig. 62.

Curve 1 - relative amounts remaining in the furnace.

Curve 2 - relative amounts lost by concentration diffusion.

Curve 3 - relative amounts lost through the sample injection hole.

Curve 4 - relative amounts lost by thermal diffusion in the axial direction.

Curve 5 - relative amounts lost by thermal expansion of the heated gas through the furnace ends.

4.4.3. Relative atom population vs. time curves of analyte atoms in the graphite platform furnace

Effects of the activation energy, E_a , and the frequency factor, B

Figures 66 and 67 show the effect of the activation energy, E_a , and Fig. 68 shows the effect of the frequency factor B , on the relative atom population vs. time curves. A high activation energy means that the energy barrier to the chemical reaction is relatively difficult to overcome. Hence, the rate of atom supply is low at relatively low temperatures, and a high platform temperature is required for a relatively high rate of atom supply. As a result, with increasing activation energy, the relative atom population curve is shifted more towards the constant temperature region of the tube wall (at the furnace centre), and the maximum relative atom population decreases mainly because of the decreased supply rate of analyte atoms. A decrease in the frequency factor, B , has a similar (but much less) effect as an increase in the activation energy (Fig. 68).

Tables 18 and 19 show that both E_a and B values have much less effect on the mean residence time of the analyte atoms, τ_R , than on the maximum relative atom population, N_{max}/N_0 . The insensitivity of τ_R to variations in E_a and B is attributed to the factor that atomization from the platform is temporally isothermal, as explained below. For each analyte atom in the gas phase of a graphite platform furnace, its duration time inside the furnace depends mainly on the diffusion coefficient and the atom density gradient, since concentration diffusion is the main removal process for atomization from the platform. Although variations in E_a and B shift the position of the

Figure 66. The (computed) effect of activation energy, E_a , on the relative atom population vs. time curves at a final tube wall (atomization) temperature of 3170 K. For all the curves, $b = 0.35$ mm (mass 60 mg), $B = 5.0 \times 10^{12} \text{ s}^{-1}$, $T_i = 300 \text{ K}$, $\alpha = 2.0 \text{ K ms}^{-1}$. The other computing parameters were the same as given in Table 15.

Figure 67. The (computed) effect of activation energy, E_a , on the relative atom population vs. time curves at a final tube wall temperature of 2280 K. The other computing parameters were the same as given in Fig. 62.

Figure 68. The (computed) effect of frequency factor, B , on the relative atom population vs. time curves at a final tube wall temperature of 2280 K. The other computing parameters were the same as given in Fig. 62.

Table 18. Effect of activation energy, E_a ,
on the relative atom population

Tube wall heating parameters	E_a (kJ mol ⁻¹)	t_{app} (s)	t_p (s)	τ_p (s)	τ_R (s)	N_{max}/N_0 (%)
$\alpha = 2 \text{ K ms}^{-1}$	220	1.019	1.127	0.072	0.198	97.9
$T_i = 300 \text{ K}$	331	1.203	1.307	0.064	0.174	95.6
$T_f = 3170 \text{ K}^*$	430	1.321	1.423	0.042	0.169	93.5
	530	1.413	1.516	0.056	0.170	88.2
	630	1.687	1.695	0.100	0.172	66.8
$\alpha = 2.3 \text{ K ms}^{-1}$	220	0.880	1.058	0.100	0.298	93.2
$T_i = 470 \text{ K}$	248	0.966	1.170	0.106	0.301	90.5
$T_f = 2300 \text{ K}^\dagger$	276	1.058	1.286	0.110	0.303	87.8
	304	1.150	1.408	0.116	0.307	84.5
	331	1.244	1.550	0.112	0.308	81.2

* The other computing parameters were the same as in Fig. 66.

† The other computing parameters were the same as in Fig. 67.

Table 19. Effect of frequency factor, B ,
on the relative atom population*

B (s^{-1})	t_{app} (s)	t_p (s)	τ_p (s)	τ_R (s)	N_{max}/N_0 (%)
5.0×10^{10}	1.214	1.548	0.128	0.308	76.7
5.0×10^{11}	1.130	1.402	0.118	0.305	82.7
5.0×10^{12}	1.058	1.286	0.110	0.303	87.8
5.0×10^{13}	0.996	1.192	0.104	0.301	91.4
5.0×10^{14}	0.942	1.112	0.098	0.299	94.2

* The other computing parameters were the same as in Fig. 68.

relative atom population vs. time curve on the time axis, the diffusion coefficients at each space coordinate remain nearly the same because of the nearly constant gas temperature distribution in isothermal (temporal) atomization. Variations in E_a and B affect the time-dependent density gradient of analyte atoms. However, the effect is much less at $t > t_p$ when most of analyte atoms have been formed, and at $t < \tau_p$ when the initially formed free analyte atoms at the furnace centre are moving inside the furnace before being removed from the analysis volume. Therefore, variation in the atom density gradient caused by variation in E_a and B values does not significantly affect τ_R values.

In isothermal (temporal) atomization, the slight increase in τ_R value with increasing E_a value is attributable to slow development of

the atom density gradient in the axial direction, which hinders removal by concentration diffusion. In nonisothermal (temporal) atomization (Fig. 66 - the two curves on the left-hand side), analyte atoms with a low E_a value experience a relatively low gas temperature, which results in a relatively low diffusion coefficient; hence, the τ_R value is relatively high although fast development of the atom density gradient in the axial direction speeds the removal of the analyte atoms. The effect of variation in E_a on τ_R is much larger in nonisothermal atomization than in isothermal (temporal) atomization.

Effects of the diffusion coefficient, D_0 , and the exponent power of the temperature-dependent diffusion coefficient, γ

Figures 69 and 70 show that an increase in the diffusion coefficient, D_0 , and the exponent power, γ , reduce the relative atom population because of an increased removal rate of analyte atoms by concentration diffusion. However, the initial rising part of the atomization efficiency curve is hardly affected by D_0 or γ since it requires a certain time, τ_p , for analyte atoms initially formed at the furnace centre to reach the furnace ends and to be removed by condensation. Because D_0 and γ determine the removal rate of the analyte atoms by concentration diffusion (which is the predominant removal process), their effect on the mean residence time, τ_R , is much greater than on the maximum relative atom population.

Figure 69. The (computed) effect of concentration diffusion coefficient, D_o , at 273 K and at 1 atm, on the relative atom population vs. time curves. The other computing parameters were the same as given in Fig. 62.

Figure 70. The (computed) effect of exponent power, γ , of the temperature dependence of the concentration diffusion coefficient on the relative atom population vs. time curves. The other computing parameters were the same as given in Fig. 62.

Effects of the tube wall heating parameters

Heating parameters of the tube wall (at the furnace centre) affect both the platform temperature (Chapter 2) and the temperature distribution of the gas phase in the graphite platform furnace (Chapter 3). Platform temperature affects the supply function of analyte atoms. The temperature distribution of the gas phase affects the diffusion coefficient and thus the removal rate of analyte atoms. Therefore, the tube wall heating parameters affect the atomization efficiency vs. time curve.

Figure 71 shows the computed effect of the tube wall heating rate on the relative atom population vs. time curve. A quantitative comparison of the absorbance vs. time curves for silver predicted by the model with the experimental ones has been given earlier in Fig. 57. Generally speaking, the heating rate of the platform increases with increasing heating rate of the tube wall, resulting in an increased supply rate of analyte atoms. Also, with an increasing heating rate of the tube wall, heating of the platform is delayed, and the atomization efficiency vs. time curve is shifted towards the isothermal region of the tube wall temperature vs. time curve. This results in an increased removal rate of atoms because of the relatively high gas temperature that the analyte atoms experience. However, if the relative atom population curve is located within the isothermal region of the tube wall temperature vs. time curve, a further increase in the heating rate of the tube wall will not significantly increase the heating rate of the platform in the platform temperature range of about 1600-2600 K, nor will it significantly change the temperature distribution of the gas phase. As a result, with an increasing heating rate of the tube

• Figure 71. The (computed) effect of tube wall heating rate (at the furnace centre) on the relative atom population vs. time curves. The dashed and the dotted lines represent the tube wall temperature (at the furnace centre) vs. time curves and the platform temperature vs. time curves, respectively. For each set of curves from left to right: $\alpha = 6.0, 2.0$ and 1.0 K ms^{-1} . For all the curves, $T_i = 300 \text{ K}$, $T_f = 2870 \text{ K}$, $b = 0.35 \text{ mm}$ (mass 60 mg), $E_a = 430 \text{ kJ mol}^{-1}$, $B = 5.0 \times 10^{12} \text{ s}^{-1}$, $D_0 = 0.157 \text{ cm}^2 \text{ s}^{-1}$, $\gamma = 1.65$.

wall, the maximum relative atom population increases and the mean residence time of the analyte atoms decreases; both of them approach constant values at a relatively high heating rate of the tube wall in the case of isothermal (temporal) atomization.

Figures 72 and 73 show the effect of the heating rate of the tube wall on the experimentally observed peak-height and the integrated absorbance for Cd, Pb, Ni, Co, V and Mo. These figures agree with the general predictions of the theoretical model. At low tube wall heating rates (Fig. 73), the observed increase in the integrated absorbance of Ni, Co, V and Mo with increasing tube wall heating rate is however, not predicted by the theoretical model. This aspect will be further discussed later.

Figure 74 shows the effect of the initial tube wall (atomization) temperature on the computed relative atom population vs. time curve. Figure 75 shows the oscillographic traces of Pb and Co atomized from the platform at different initial (atomization) temperatures of the tube wall. A quantitative comparison of the computed absorbance vs. time curves for silver with the experimental ones at different initial tube wall temperatures has been given earlier in Fig. 58. Generally speaking, a low initial temperature of the tube wall shifts the relative atom population (or absorbance) vs. time curves for atomization from the platform more towards or into the constant-temperature region of the tube wall temperature vs. time curve and increases the heating rate of the platform, especially at low platform temperatures. However, if the relative atom population (or the absorbance) vs. time curve is located inside the constant-temperature region of the tube wall temperature vs. time curve, a still lower

Figure 72. The (measured) effect of tube wall heating rate (at the furnace centre) on the peak-height absorbance with atomization from the platform. $T_1 = 470$ K. T_f was 1870 K for Cd (○), 2270 K for Pb (Δ), 2970 K for Co (□) and Ni (○), 3170 K for V (●) and Mo (■).

Figure 73. The (measured) effect of tube wall heating rates (at the furnace centre) on the integrated absorbance with atomization from the platform. $T_i = 470$ K. T_f was 1870 K for Cd (○), 2270 K for Pb (△), 2970 K for Co (□) and Ni (○), 3170 K for V (●) and Mo (■).

Figure 74. The (computed) effect of initial tube wall (atomization) temperature (at the furnace centre) on the relative atom population vs. time curves. The dashed and the dotted line represent the tube wall temperature (at the furnace centre) vs. time curves and the platform temperature vs. time curves, respectively. For each set of curves from left to right: $T_1 = 300, 870$ and 1270 K. For all the curves, $\alpha = 2 \text{ K ms}^{-1}$, $T_f = 2870$ K. $b = 0.35$ mm (mass 60 mg), $E_a = 430 \text{ kJ mol}^{-1}$, $B = 5.0 \times 10^{12} \text{ s}^{-1}$, $D_0 = 0.157 \text{ cm}^2 \text{ s}^{-1}$, $\gamma = 1.65$.

initial tube wall temperature will not alter the removal rate of the analyte atoms; the result is that a similar mean residence time of the analyte atoms or a similar integrated absorbance is observed. The maximum relative atom population or the peak-height absorbance of relatively volatile elements increases slightly with decreasing initial tube wall temperature because of the increasing heating rate of the platform at low platform temperatures. But this will not be so for relatively involatile elements. In the case of a shift of the absorbance vs. time curve from the nonisothermal region towards the isothermal region by use of a lower initial tube wall temperature, the

Figure 75. The (measured) effect of initial tube wall (atomization) temperature (at the furnace centre) on the atomization of Pb and Co (both taken as the nitrate in aqueous solutions) from the platform.

For each set of curves from left to right: $T_i = 970$ and 570 K.

Left frame: oscilloscopic traces of absorbance profiles of

Pb 6.0×10^{-13} kg. $\alpha = 3.0$ K ms $^{-1}$, $T_f = 2220$ K.

Right frame: oscilloscopic traces of absorbance profiles of

Co 1.0×10^{-12} kg. $\alpha = 3.0$ K ms $^{-1}$, $T_f = 2870$ K.

peak-height and the integrated absorbance may increase or decrease slightly, depending on the combined result of the following effects: the increased removal rate of analyte atoms by diffusion at the higher gas temperature, the reduced/removal rate of the analyte atoms by thermal expansion, and the increased supply rate of analyte atoms.

In our previous papers [15, 42], we suggested the use of a cooling cycle before the atomization cycle in order to obtain a low initial tube wall (atomization) temperature. Since that time, a 10-15% increase in peak-height absorbance signal has been reported for certain elements [39], which agrees with the predictions from the theoretical model. Although the cooling cycle has a limited effect on the peak-height and the integrated absorbance, it produces a greater shift of the absorbance pulse towards or into the isothermal region of the tube wall temperature at the furnace centre vs. time curve. This is important for reduction or elimination of matrix interferences, as will be discussed in section 4.4.4.

Figure 76 shows the effect of the final tube wall (atomization) temperature on the computed relative atom population vs. time curves. Figures 77 and 78 show the measured peak-height and integrated absorbances, respectively, of Cd, Pb, Ni, Co, V and Mo as a function of the final tube wall temperature. Quantitative comparison of the computed absorbance vs. time curves of silver with the experimental ones has been made in Fig. 59. These curves confirm our intuitive feeling that a high final tube wall (atomization) temperature is beneficial for atomization of analyte elements from the platform which have a relatively high activation energy from the platform. This is because a relatively high final tube wall (atomization) temperature

Figure 76. The (computed) effect of the final tube wall (atomization) temperature (at the furnace centre) on the relative atom population vs. time curves. The dashed and the dotted line represent the tube wall temperature (at the furnace centre) vs. time curves and the platform temperature vs. time curves, respectively. For each set of curves from left to right: $T_f = 3170, 2870$ and 2570 K. For all the curves $\alpha = 2 \text{ K ms}^{-1}$, $T_i = 300 \text{ K}$, $b = 0.35 \text{ mm}$ (mass 60 mg), $E_a = 430 \text{ kJ mol}^{-1}$, $B = 5.0 \times 10^{12} \text{ s}^{-1}$, $D_0 = 0.157 \text{ cm}^2 \text{ s}^{-1}$, $\gamma = 1.65$.

Figure 77. The (measured) effect of the final tube wall (atomization) temperatures on the peak-height absorbance for atomization from the platform. $T_i = 470$ K. The tube wall heating rate α was 3.0 K ms^{-1} for Cd (○), Pb (△), Co (□) Ni (○), and was 7.0 K ms^{-1} for V (●) and Mo (■).

Figure 78. The (measured) effect of final tube wall (atomization) temperatures on the integrated absorbance for atomization from the platform. $T_i = 470$ K. The tube wall heating rate α was 3.0 K ms^{-1} for Cd (o), Pb (Δ), Co ($\square$) Ni ($\circ$), and was 7.0 K ms^{-1} for V ($\bullet$) and Mo ($\blacksquare$).

results in a relatively high platform heating rate as well as in the highest attainable platform temperature. Therefore, the supply rate of analyte atoms is high at high final tube wall (atomization) temperatures. The corresponding gas temperature is also high, which results in relatively high removal rates of analyte atoms by diffusion. However, the removal rate of analyte atoms by diffusion is not as sensitive to temperature change as the supply rate of analyte atoms is. Hence, with increasing final tube wall (atomization) temperature, the model predicts an increase in the maximum relative atom population and in the peak-height absorbance, and a decrease in the mean residence time of analyte atoms and in the integrated absorbance.

The measured integrated absorbances of Ag, Cd and Pb, shown in Figs. 59 and 78, agree with the above theoretical predictions, but their peak-height absorbances do not (Fig. 77). The measured peak-height absorbances of Ni, Co, V and Mo agree with the above theoretical predictions (Fig. 77), but their integrated absorbances (Fig. 78) do not. These disagreements may be partly due to the fact that the present theoretical model is based on oversimplified assumptions: neither does it take into account chemical reactions involving analyte atoms in the vapour phase or in the condensed phase, nor does it take into account adsorption, desorption, recondensation, revolatilization, recombination and other processes that change the fraction of analyte atomized. For example, it is known that Mo and V form interstitial compounds with graphite [159] and/or form carbides [166-171], which are relatively involatile. The fraction of Mo or V atomized, therefore, increases with the highest platform temperature

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achieved, i.e., the total amount of analyte atomized increases with increasing final tube wall (atomization) temperature. Therefore, both the peak-height and the integrated absorbance increase with increasing final tube wall (atomization) temperature. The measured peak-height absorbance of silver decreased with increasing tube wall temperature, which is not predicted by the model. This decrease may be explained by the over-estimated platform heating rate used in the model, as discussed earlier.

Effect of the platform thickness

For a given type of graphite (having constant density) the thickness of the platform has a larger effect on the heating rate of the platform than its width or length (Chapter 2). Figure 60 shows that a thicker platform delays the appearance of the absorbance signal longer than a thinner platform because of delayed heating of the platform; it also results in a decreased peak-height absorbance because of a low rate of analyte atom formation from a slowly heated platform. However, the mean residence times of the analyte atoms are nearly the same for platforms of different thicknesses as long as the absorbance vs. time curves are located inside the isothermal region of the tube wall temperature vs. time curve.

4.4.4. Chloride matrix interferences

Chloride matrices interfere severely with determination of some metals by graphite furnace atomic absorption spectrometry.

Modification of the existing atomizers and development of new atomizers by several workers [5, 34, 47-52, 98, 172-174] were attempted to eliminate or to reduce chloride matrix interferences.

This section presents the results of our studies on chloride matrix interferences during the determination of Cd and Pb. The chloride matrices studied were: (1) CuCl_2 , (2) a mixture of $\text{NaCl} + \text{MgCl}_2 + \text{CaCl}_2$, both in aqueous solutions. Cadmium or lead in an aqueous solution was added as the analyte to each matrix. The $\text{NaCl} + \text{MgCl}_2 + \text{CaCl}_2$ matrix represents the major salt components of seawater. These salts were added in the ratio of their occurrence in seawater [175]. Direct determination of trace amounts of Cd and Pb in seawater presents a challenge in eliminating matrix interferences by these salts which are present in an overwhelming excess. The reason for selecting these two matrices is to assess the ability of the platform technique to eliminate or to reduce interferences by these matrices.

Figure 79 and 80 show the absorbance vs. time curves of Cd and Pb with or without the matrices, and the background absorbance vs. time curves for atomization from the tube wall and the platform, respectively. Relative to the tube wall, atomization from the platform shifts all absorbance signals towards the isothermal region of the temperature vs. time curve of the tube wall. The background absorbance signal due to a matrix is also shifted towards the isothermal region, not only relative to its position during atomization from the tube wall, but also relative to the analyte absorbance signal.

The relative position in time of the analyte absorbance signal and the background absorbance signal may be different for atomization from the platform and from the tube wall, as can be seen from Figs. 79 and 80. This information is important for the purpose of setting experimental parameters in order to eliminate or to reduce matrix interferences when using the platform.

The background absorbance signal due to the CuCl_2 matrix appears earlier than the Pb absorbance signal from the same matrix for both atomization from the platform and the tube wall (Fig. 79, bottom frame). Therefore, the bulk of the CuCl_2 matrix can be driven off from the analysis volume during the pre-atomization heating cycle using an optimum charring temperature of 870 K. With atomization from the platform, the background absorption signal due to the CuCl_2 matrix appears almost at the same time as the Cd atomic absorption signal from the same matrix (Fig. 79, upper frame). Therefore, in the latter case, determination of Cd in the CuCl_2 matrix is limited by the capability of the D_2 -arc background corrector to correct for the background absorbance.

The background absorbance signal due to the matrix of $\text{NaCl} + \text{MgCl}_2 + \text{CaCl}_2$ appears later than the absorbance signal of both Cd and Pb in the same matrix (Fig. 80). This means that in the vapour phase, only a part of the matrix molecular species exist simultaneously with the analyte species, and hence the effect of the chlorine gas from the matrix molecular species recombining with the analyte element to form lead or cadmium chloride species in the gas phase is relatively small. Also, the over- or under-correction of the high background signal only affects the decay part of the analyte absorption signal, not the rising part and the peak of the analyte absorbance signal, as can be seen from Fig. 81. Consequently, the peak absorbance of Pb and Cd from the $\text{NaCl} + \text{MgCl}_2 + \text{CaCl}_2$ matrix can be accurately measured from the oscilloscopic trace of the analyte absorption signal. The recoveries of Cd and Pb from the salt matrix reported later in this section were obtained by such measurements.

Figure 79. Oscilloscopic traces of Cd and Pb (both taken as the nitrate in an aqueous solution) in CuCl_2 matrix in an aqueous solution. Upper frame: Cd 8.0×10^{-14} kg plus CuCl_2 2.5×10^{-8} kg. Charring $T = T_i = 570$ K, $T_f = 1870$ K. Lower frame: Pb 6.0×10^{-13} kg plus CuCl_2 1.5×10^{-7} kg. Charring $T = 870$ K, $T_i = 570$ K, $T_f = 2220$ K. Curve A: absorbance signal (background-corrected) of Cd or Pb. Curve B: absorbance signal (background-corrected) of Cd or Pb in the matrix. Curve C: background absorbance signal due to the CuCl_2 matrix. Curve D: tube wall temperature at the furnace centre. $\alpha = 0.7$ K ms^{-1} for atomization from the tube wall. $\alpha = 3.0$ K ms^{-1} for atomization from the platform.

Figure 80. Oscilloscopic traces of Cd and Pb (both taken as the nitrate) in the $\text{NaCl} + \text{MgCl}_2 + \text{CaCl}_2$ matrix in an aqueous solution.

Upper frame: Cd 4.0×10^{-14} kg + NaCl 5.0×10^{-9} kg + MgCl_2 6.0×10^{-10} kg + CaCl_2 2.0×10^{-10} kg, Charring $T = T_1 = 570$ K, $T_f = 1870$ K.

Lower frame: Pb 6.0×10^{-13} kg + NaCl 2.0×10^{-8} kg + MgCl_2 2.4×10^{-9} kg + CaCl_2 8.0×10^{-10} kg, Charring $T = T_1 = 570$ K, $T_f = 2220$ K.

Curves A to D were the same as in Fig. 79.

Figure 81. Oscilloscopic traces of Cd (taken as nitrate) in the NaCl + MgCl_2 + CaCl_2 matrix in an aqueous solution. All absorbances were background-corrected.

Curve A: Cd 4.0×10^{-14} kg.

Curve B: Cd 4.0×10^{-14} kg + NaCl 5.0×10^{-8} kg + MgCl_2 6.0×10^{-9} kg + CaCl_2 2.0×10^{-9} kg.

Curve C: tube wall temperature at the furnace centre. Charring T

- $T_1 = 570$ K. $T_f = 1870$ K.

Upper frame: atomization from the tube wall, $s = 0.7$ K ms^{-1} .

Lower frame: atomization from the platform, $a = 2.6$ K ms^{-1} .

Figures 82 and 83 show the absorbance signals of Cd and Pb with and without the CuCl_2 matrix, atomized from the tube wall and from the platform, respectively. Using the experimental conditions given in Figs. 82 and 83, recoveries (%) of Cd and Pb as a function of the mass of CuCl_2 are presented in Figs. 84 and 85, respectively. Figure 86 shows the Pb absorbance signal with and without the $\text{NaCl} + \text{MgCl}_2 + \text{CaCl}_2$ matrix, atomized from the platform using different heating rates and atomization temperatures. Using the experimental conditions of Figs. 81 and 86, recoveries (%) of Cd and Pb as a function of the mass of the above matrix are presented in Fig. 87 and 88, respectively.

Figures 84 and 85, and 87 and 88 show that both Pb and Cd absorbance signals from these matrices were severely depressed when Cd and Pb were atomized from the tube wall, whereas with atomization from the platform, the chloride interferences with both Cd and Pb were greatly reduced or entirely eliminated. A 100% recovery of the Pb absorbance signal from the matrix of 1.0×10^{-7} kg CuCl_2 (2% w/v) was obtained using the platform at a tube wall heating rate of 3.0 K ms^{-1} and a final tube wall temperature of 2220 K. Also, when Cd and Pb were atomized from the platform, the peak-height absorbance method gave 100% recoveries of Cd and Pb from a matrix of 1.0×10^{-7} kg $\text{NaCl} + 1.2 \times 10^{-8}$ kg $\text{MgCl}_2 + 4.0 \times 10^{-9}$ kg CaCl_2 , and from a matrix of 2.0×10^{-7} kg $\text{NaCl} + 2.4 \times 10^{-8}$ kg $\text{MgCl}_2 + 8.0 \times 10^{-9}$ kg CaCl_2 , respectively.

Figure 82. Oscilloscopic traces of Cd (taken as the nitrate) in the CuCl_2 matrix in an aqueous solution. All absorbances were background-corrected.

Curve A: $\text{Cd } 8.0 \times 10^{-14} \text{ kg}$.

Curve B: $\text{Cd } 8.0 \times 10^{-14} \text{ kg} + \text{CuCl}_2 \text{ } 1.0 \times 10^{-8} \text{ kg}$.

Curve C: tube wall temperature at the furnace centre. Charring T
 $= T_i = 670 \text{ K}$, $T_f = 1870 \text{ K}$.

Top frame: atomization from the tube wall, $\alpha = 0.7 \text{ K ms}^{-1}$.

Middle frame: atomization from the platform, $\alpha = 0.7 \text{ K ms}^{-1}$.

Bottom frame: atomization from the platform, $\alpha = 2.6 \text{ K ms}^{-1}$.

Figure 83. Oscilloscopic traces of Pb (taken as the nitrate) in the CuCl_2 matrix in an aqueous solution. All absorbances were background-corrected.

Curve A: Pb 6.0×10^{-13} kg.

Curve B: Pb 6.0×10^{-13} kg plus CuCl_2 1.0×10^{-7} kg.

Curve C: tube wall temperature at the furnace centre.

Charring $T = 870$ K. $T_i = 570$ K. $T_f = 2220$ K.

Top frame: atomization from the tube wall, $\alpha = 0.7$ K ms^{-1} .

Middle frame: atomization from the platform, $\alpha = 0.7$ K ms^{-1} .

Bottom frame: atomization from the platform, $\alpha = 3.0$ K ms^{-1} .

Figure 84. Recovery (%) of $\text{Cd } 4.0 \times 10^{-14} \text{ kg}$ (taken as the nitrate in an aqueous solution) as a function of the mass of CuCl_2 . All absorbances were background-corrected. Charring $T = T_i = 620 \text{ K}$. $T_f = 1870 \text{ K}$. (Δ) Atomization from the tube wall, $\alpha = 0.7 \text{ K ms}^{-1}$. (□) Atomization from the platform, $S = 0.7 \text{ K ms}^{-1}$. (o) Atomization from the platform, $S = 2.6 \text{ K ms}^{-1}$.

Figure 85. Recovery (%) of $\text{Pb } 6.0 \times 10^{-13} \text{ kg}$ (taken as the nitrate in an aqueous solution) as a function of the mass of CuCl_2 . All absorbances were background-corrected. Charring $T_f = 870 \text{ K}$. $T_i = 570 \text{ K}$. $T_f = 2220 \text{ K}$. (Δ) Atomization from the tube wall, $\alpha = 0.7 \text{ K ms}^{-1}$. (□) Atomization from the platform, $S = 0.7 \text{ K ms}^{-1}$. (o) Atomization from the platform, $S = 3.0 \text{ K ms}^{-1}$.

Figure 86. Oscilloscopic traces of Pb (taken as the nitrate) in the $\text{NaCl} + \text{MgCl}_2 + \text{CaCl}_2$ matrix in an aqueous solution with atomization from the platform. All absorbances were background-corrected.

Curve A: Pb 6.0×10^{-13} kg

Curve B: Pb 6.0×10^{-13} kg + NaCl 5.0×10^{-8} kg + MgCl_2 6.0×10^{-9} kg
+ CaCl_2 2.0×10^{-9} kg

Curve C: tube wall temperature at the furnace centre. Charring T
= T_1 = 570 K.

Top frame: $\alpha = 3.4 \text{ K ms}^{-1}$, $T_f = 2700 \text{ K}$.

Bottom frame: $\alpha = 2.4 \text{ K ms}^{-1}$, $T_f = 2300 \text{ K}$.

Figure 88. Recovery (%) of Pb 6.0×10^{-13} kg (taken as the nitrate) as a function of the mass of the NaCl + MgCl₂ + CaCl₂ matrix in an aqueous solution. All absorbances were background-corrected. Charring $T = T_i = 570$ K.

(A) Atomization from the tube wall, $\alpha = 1.0 \text{ K ms}^{-1}$, $T_f = 2300 \text{ K}$.

(B) Atomization from the platform, $\alpha = 3.4 \text{ K ms}^{-1}$, $T_f = 2700 \text{ K}$.

(C) Atomization from the platform, $\alpha = 2.4 \text{ K ms}^{-1}$, $T_f = 2300 \text{ K}$.

It has been reported in the literature [5, 174, 176-177] that the chloride interference is primarily a vapour phase interference effect. The chloride interference with atomization from the tube wall can be explained by using Pb as an example (a similar explanation is also valid for Cd since Cd and its chlorides have volatilities similar to those of Pb). With atomization from the tube wall, partial loss of volatile lead chlorides apparently occurs at the instant of vaporization of the bulk of the matrix ($\text{NaCl} + \text{MgCl}_2 + \text{CaCl}_2$) i.e., when the tube wall surface temperature is 1100-1200 K. This effect can be explained by the 'carrier effect', as called in emission spectroscopy [178]; this effect is also known as co-volatilization. It is reasonable to expect that the vaporization of the salt matrix would cause simultaneous introduction of lead as chlorides into the gas phase. At the temperature (1100-1200K) of their co-volatilization, the extent of dissociation of the lead chlorides is less than that at a higher gas phase temperature; also, a part of the gas phase lead chlorides is lost by expulsion with the rapidly expanding gas phase and by diffusion. The lower the temperature of co-volatilization of the analyte chlorides, i.e., the earlier the analyte chlorides are vaporized, the longer is the time available for the loss process to deplete the analyte chlorides before the analyte peak-height absorbance signal is recorded. The above is a fairly qualitative picture of the chloride matrix interferences with Cd and Pb determination. The quantitative difference between the Cd and the Pb system arises from the difference in the volatilities of their chlorides vis-a-vis the volatilities of the matrices, the difference in the dissociation energies of the chlorides and the matrix species.

and the difference in the appearance temperatures of Cd and Pb in the above matrix.

The reduction or elimination of the chloride matrix interference by atomization from the platform can be attributed to isothermal (temporal) atomization at a higher gas phase temperature. It has been explained earlier that with atomization from the platform, almost the entire (Cd and Pb) absorbance signals appear at a time when the tube wall (at the furnace centre) has attained a nearly constant temperature (temporal), and the corresponding gas temperature is higher, resulting in a greater extent of dissociation of the analyte molecular species; hence, the chloride matrix interferences are reduced or eliminated. Furthermore, the delayed vaporization of the $\text{NaCl} + \text{MgCl}_2 + \text{CaCl}_2$ matrix relative to that of the analyte (Cd or Pb) eliminates their potential loss by co-volatilization with the above matrix and by expulsion caused by co-volatilization of a very large amount of the salt matrix. It is interesting to note the difference in the time of occurrence of the analyte absorbance signal of the same element from different matrices, which may be partly due to formation of analyte species of different thermal stability. For example, the Pb absorbance signal from the CuCl_2 matrix appears later in time than that of Pb without the CuCl_2 matrix, whereas the Pb absorbance signal from the $\text{NaCl} + \text{MgCl}_2 + \text{CaCl}_2$ matrix appears at almost the same time as that of Pb without the matrix. However, both peak-height and integrated absorbances are roughly the same if almost the entire analyte absorbance signal is shifted into the isothermal (temporal) region of the temperature vs. time curve of the tube wall (Figs. 79 and 80). This is consistent with the above atomization mechanism which

postulates that the chloride interference is due to gas-phase reactions.

It is also seen from Figs. 82-88 that there is a close correlation between an increasing fraction of the analyte absorbance signal profile being within the isothermal (temporal) region of the tube wall temperature vs. time curve and a greater extent of freedom from the chloride matrix interference. Complete freedom from the matrix interference is achieved only when about 90% or more of the analyte absorbance signal profile is shifted into the isothermal (temporal) region of the tube wall temperature vs. time curve. This freedom is expected since the greater the fraction of the analyte absorbance signal profile inside the isothermal (temporal) region, the smaller is the loss of the analyte by expulsion with the vaporized matrix; also the greater the fraction of the analyte absorption signal profile in the isothermal (temporal) region, which is higher in temperature, the higher is the gas phase temperature, and the greater is the extent of dissociation of the analyte species, resulting in a greater freedom from matrix interferences.

4.5. Conclusions

The present study has revealed relative insensitivity of the mean residence time of the analyte atoms, τ_p , to variations in some physical and chemical properties of the analyte species and to some experimental parameters in graphite platform furnace atomic absorption spectrometry. The physical and chemical properties of the analyte include the activation energy, E_a , and the frequency factor, A , for the rate-determining step. The experimental conditions include tube

wall heating rate, initial (atomization) temperature of the tube wall, and thickness (mass) of the platform. The above-mentioned relative insensitivity is due to the heating of the platform being mainly by radiation heat transfer, and the resulting isothermal (temporal) atomization in which the concentration diffusion is the main removal process.

The assumption of isothermal (temporal) atomization in graphite platform furnace atomic absorption spectrometry is correct only to a first approximation. With atomization from the platform, throughout the duration of the analyte absorbance signal, the gas temperature in most regions inside the furnace varies slowly with time and can therefore be approximated as nearly constant. However, this is not so for the gas temperature in the region near the platform, which changes relatively fast with time. Fortunately, the region in which the gas temperature is temporally nonisothermal is much smaller than the region in which the gas temperature can be considered as temporally isothermal. Also, after the analyte atoms are completely atomized, density gradient of the analyte atoms in the region near the platform is relatively small. Variations in gas temperature distribution, activation energy, E_a , frequency factor, B , tube wall heating rate, α , initial tube wall (atomization) temperature, T_1 , and platform thickness (mass), do not significantly affect the mean residence time of analyte atoms, τ_R .

With atomization from the platform, the analyte atomic absorption signal is usually located inside the isothermal (temporal) region of the tube wall temperature vs. time curve. Hence, integrated absorbance is nearly proportional to the amount of the analyte introduced.

regardless of variations in the analyte atom supply rate due to variations in the nature of analyte species formed in different matrices and in their atomization mechanisms, provided that the analyte is completely atomized and introduced into the analysis volume during the time the absorbance signal is recorded and that concentration diffusion is the main process for removal of analyte atoms.

In order to ensure that concentration diffusion is the main process for removal of the analyte atoms, it is sometimes necessary to use matrix modifiers to eliminate or to convert the matrix at the charring cycle (pre-atomization heating cycle) into a relatively involatile compound, and thus, to avoid analyte expulsion due to the co-volatilization of the analyte with the matrix during the atomization cycle.

In order to ensure complete atomization of analyte, it is desirable to apply a relatively high final tube wall (atomization) temperature so that volatilization and atomization of analyte species from the condensed phase occur from the resulting high temperature of the platform, and that dissociation of the analyte molecular species occurs in the resulting high-temperature gaseous environment. However, the final tube wall (atomization) temperature should not be higher than what is necessary for the above purpose. If it is too high, the mean residence time of the analyte atoms will be shortened because of increased loss of analyte atoms due to temporal nonisothermality of the gas phase near the platform. In addition, the integrated absorbance signal will decrease because of the increased removal rate of the analyte atoms by diffusion at the higher gas temperature.

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To ensure isothermal (temporal) atomization, adoption of a cooling cycle before the atomization cycle is recommended in order to obtain a low initial tube wall (atomization) temperature. Also recommended is a relatively high tube wall heating rate as it increases the heating rate of the platform (to a limited extent), delays the heating of the platform (to a relatively large extent), and enables isothermal (temporal) atomization at a relatively high temperature of the tube wall and of the gas phase.

In order to ensure isothermal (temporal) atomization, thickness (mass) of the platform should be optimized for different elements. Generally, a thin platform should be used for an element having a high activation energy for the rate-determining step, whereas a relatively thick platform should be used for an analyte element having a low activation energy for the rate-determining step.

An increase in the effective length of the absorbing layer of analyte atoms is important, since it will not only increase the mean residence time of analyte atoms and thus the integrated absorbance signal, but will also increase the insensitivity of the mean residence time and hence, of the integrated absorbance to variations in experimental parameters and in physical and chemical forms of the analyte species. The effective length of absorbing layer of analyte atoms can be increased by using a relatively long tube (which, however, will require increased electrical power for heating), or by increasing the boundary temperature of the tube wall at the furnace ends (such as, by using a contoured tube).

In general, integrated absorbance obtained using atomization from the platform is relatively free from matrix effects, and is therefore

generally recommended for quantitative determination by graphite platform furnace atomic absorption spectrometry. However, use of peak absorbance may be more advantageous in certain cases.

Among limitations of graphite platform furnace atomic absorption spectrometry are spatial nonisothermality and limited heating rate of the platform. Spatial nonisothermality may result in redeposition, recombination, and re-volatilization of analytes, especially for analyte elements having low volatility. By using the platform technique in conjunction with the 'side-heated graphite cuvette with integrated contact', Frech et al. [52] recently reported achieving both temporal and spatial (axial) isothermal atomization. For elements which form refractory carbides with the graphite substrate and which are therefore not completely atomized in graphite furnaces, metal furnaces are more suitable [179].

The predictions of the theoretical model presented above are strictly valid for the particular graphite furnace used in this study. However, the principle can be applied to other similar graphite furnaces. As long as the boundary temperature of the furnace (the tube wall and the gas phase), and the geometry of the furnace are known, the temperature field and the gas velocity field in the furnace can be calculated. The concentration distribution of the analyte atoms can then be calculated by the model using the calculated temperature and the gas velocity fields. Knowing the temperature distribution of the gas phase, a more sophisticated model can be developed to include the rate constants for condensation, redeposition and re-volatilization processes of the analyte atoms occurring at the interface of the gas phase and the condensed phase (at surfaces of the platform and/or of the tube wall).

Chapter 5

ATOMIC ABSORPTION SPECTROMETRY WITH A LABORATORY-MADE GRAPHITE PROBE FURNACE

5.1. Introduction

Graphite furnace atomic absorption spectrometry with sample atomization from a probe surface (the probe technique) is an approach proposed by L'vov et al. [10] to establish conditions for isothermal (temporal) atomization using commercial, pulse-heated atomizers. Several authors [6, 16-23, 180-181] have further developed the probe furnace and reported on its high sensitivity and on its reduction or elimination of vapour-phase interferences. Basically, two types of probe have been developed: 1) the metal wire probe [6, 10, 16-17, 19, 181], and 2) the graphite probe [18, 20-23, 182-183]. The metal wire probe is easily operated by mounting it on the arm of the Perkin-Elmer auto-sampler without the need for any further modification of the furnace. However, the metal wire probe suffers from its relatively short lifetime at high atomization temperatures. Probes made of tungsten, tantalum, rhenium and molybdenum were reported to be destroyed at atomization temperatures higher than 2970 K [18]. Also, only a very small amount of sample can be deposited on a metal wire probe, which limits its applicability. Graphite probes have proved to be more satisfactory in both respects. However, some modifications of the furnace and some engineering re-designing are required for adapting commercial, pulse-heated graphite furnaces for use with a graphite probe.

The graphite probe furnace and the graphite platform furnace are similar in the mechanism of their heating in that both the probe and the platform are heated primarily by radiation heat transfer from the heated tube wall and both attempt to establish temporally isothermal atomization using commercial, pulse-heated atomizers. Yet, they are different in one important respect. The platform is heated by radiation while it is inside the atomizer which is pulse-heated from the initial tube wall temperature (usually, room temperature) to a final, steady-state tube wall temperature. The probe, however, is inserted into the atomizer only after it has attained a final, steady-state temperature. Therefore, a graphite probe furnace is much closer to the original graphite furnace designed by L'vov [1-2] into which the sample was inserted after the latter had attained a final, steady-state temperature. However, in order to be commercially successful, a graphite probe furnace would require more sophisticated engineering re-designing than the 'converted' graphite probe furnace used in this study. The cost-benefit ratio of such re-designing of a commercial graphite probe furnace may not compare favourably with that of the graphite platform furnace. In other words, only if the performance of a graphite probe furnace is significantly better than a well-designed graphite platform furnace will a probe furnace be commercially viable. However, important considerations in the above comparison will be their temperature fields (the surface temperature of the the probe and the platform, and the gas temperature with each inside the graphite furnace), and most importantly, their analytical performance.

Presented in this chapter are the theoretical model of the probe surface temperature based on heat transfer theory, the measured probe

surface temperature, the experimentally determined effective gas temperature inside the graphite probe furnace, the optimized working conditions of the graphite probe furnace, comparison of the sensitivity and selectivity of the graphite probe furnace with those of the graphite platform furnace, and the results of direct analysis of solid samples of airborne particulates by graphite probe furnace atomic absorption spectrometry using the same graphite probe as a filter for collection of airborne particulate matter.

5.2. Theoretical model for the surface temperature of the graphite probe

This model calculates the time-dependent surface temperature of the graphite probe in the absence of a forced, convective flow of a purge gas. Figure 89 shows the schematic diagram of the graphite probe furnace. Fig. 90 shows the geometric configuration assumed in the theoretical model. Analysis of the time-dependent surface temperature of the graphite probe is based on the following assumptions.

(a) The graphite probe is initially outside the furnace and its temperature is that of its surroundings. The probe is inserted very rapidly into the furnace and no heat transfer during the insertion is considered. This is justified by the fact that it takes only 5 ms for the probe to be inserted fully into the furnace, which is of the order of the time step used in the model and is sufficiently rapid compared to the rate of heat transfer from the donor to the receiver.

(b) Radiation heat transfer is the only mechanism of heat

Figure 89. Schematic diagram of the graphite probe furnace.

Figure 90. The geometry assumed in the theoretical modelling of the temperature of the graphite probe and the infinitesimal graphite strip located at position z with length dz , width w , and thickness b .

transfer from the furnace tube wall to the graphite probe. Previous analysis (Chapters 1-3) has shown that heat transfer by convection and conduction through the argon gas in the furnace is insignificant compared to heat transfer by radiation.

(c) The steady-state tube wall temperature at the furnace centre is responsible for heating of the probe by radiation. This is a reasonable assumption because the probe is actually inserted into the central part of the furnace where the tube wall has no appreciable temperature gradient in the axial direction (Chapter 1) and the furnace heating control keeps the tube wall temperature at the furnace centre invariant with time. Also, the rapid insertion of the cold probe does not have a very significant effect in reducing momentarily the temperature of the furnace wall near the probe.

(d) Heat flow in the graphite probe by thermal conduction is one-dimensional along its length, i.e., temperature gradient across the thickness and the width of the probe is ignored. The small thickness and width of the probe justify this assumption.

(e) The part of the probe lying outside the furnace is cooled by radiation and natural convection to the constant-temperature surroundings, with the surroundings treated as a blackbody in the radiation analysis because of their large area compared to that of the part of the probe lying outside the furnace.

(f) The probe-holder (Fig. 90) is assumed to be at a fixed, uniform temperature equal to that of the surroundings throughout the temperature transient. The mass and the thermal capacity of the probe-holder are much greater than those of the head of the probe, and the probe-holder is at the room temperature. Therefore, the model assumes

that there will be no significant heating of the probe-holder during the temperature transient.

(g) The surface of the tube wall and the probe act as gray bodies which emit and reflect radiation diffusely. These assumptions are discussed and shown as justified in Chapters 1-3.

(h) The argon gas in the furnace does not emit nor absorb radiation, as explained in Chapters 1-3. Any analyte atoms vaporized into the gas would have a negligible effect on radiation heat transfer between the surfaces because of their low concentration and because of the very short radiation beam length between the surfaces.

With the above considerations and assumptions, an energy balance between the rate of heat storage in and the rate of heat transfer from an infinitesimal strip of the probe, located at position x with length dx , width w , and thickness b , as shown in Fig. 90, gives

$$\dot{Q}_{s, pr} = - \dot{Q}_{t, pr} \quad 5.1$$

The rate of heat storage in the graphite strip of the probe is given by

$$\dot{Q}_{s, pr} = \rho_{pr} w(x) b(x) dx c_{p, pr}(x, t) \frac{\partial T_{pr}(x, t)}{\partial t} \quad 5.2$$

where ρ_{pr} , $c_{p, pr}$ and T_{pr} are the density, the heat capacity, and the temperature of the infinitesimal strip of the probe, respectively.

The rate of heat transfer from the graphite strip of the probe is given by

$$\begin{aligned} \dot{Q}_{t, pr} = & \dot{Q}_{cond, pr-pr}(z, t) + \dot{Q}_{conv}(z, t) \\ & + \dot{Q}_{rad, pr-w}(z, t) + \dot{Q}_{rad, pr-s}(z, t) \end{aligned} \quad 5.3$$

The terms at the right side of equation 5.3 are defined as follows.

The rate of heat transfer by thermal conduction along the probe length (z direction), $\dot{Q}_{cond}$, is expressed by

$$\dot{Q}_{cond, pr-pr} = - \frac{\partial}{\partial z} \left[w(z) b(z) \kappa_{pr}(z, t) \frac{\partial T_{pr}(z, t)}{\partial z} \right] dz \quad 5.4$$

where κ_{pr} is thermal conductivity of the graphite probe in the z direction.

The rate of heat transfer by natural convection is only considered for that part of the probe which is located outside the furnace. It is given by

$$\dot{Q}_{conv} = 2[w(z) + b(z)]dz h [T_{pr}(z, t) - T_s] \quad 5.5a$$

where T_s is the surrounding temperature outside the furnace, h is the convection heat transfer coefficient. The convection heat transfer coefficient, h , may be expressed as [184]

$$h = 1.32 \left[\frac{T_{pr}(z, t) - T_s}{b(z)} \right]^{0.25} \quad 5.5b$$

This is applicable to laminar condition for natural convection heat transfer from a horizontal body in air, considered to act as a cylinder with a diameter b (in SI units) as far as natural convection flow patterns are considered.

The rate of heat transfer by radiation from the infinitesimal

strip of the probe to the furnace tube wall is only considered for the probe strips located inside the furnace, and is expressed as

$$\dot{Q}_{\text{rad, pr-w}} = 2[w(z) + b(z)]dz \sigma \mathcal{F}_{\text{pr-w}} [T_{\text{pr}}^4(z, t) - T_w^4(t)], \quad 5.6a$$

where σ is the Stefan-Boltzmann constant, $\mathcal{F}_{\text{pr-w}}$ is the total radiation interchange factor [75] for the radiation heat transfer from the surface of the probe strip to the inner surface of the tube wall.

Similar to the mathematical treatment of the graphite platform furnace (Chapter 2), $\mathcal{F}_{\text{pr-w}}$ may be expressed approximately as

$$\mathcal{F}_{\text{pr-w}} = \frac{1}{2} \left[\frac{1}{\frac{1}{\epsilon_{\text{pr}}} + \frac{\Lambda_{1\text{pr}}}{\Lambda_{1\text{w}}} \left(\frac{1}{\epsilon_{\text{w}}} - 1 \right)} + \frac{1}{\frac{1}{\epsilon_{\text{pr}}} + \frac{\Lambda_{2\text{pr}}}{\Lambda_{2\text{w}}} \left(\frac{1}{\epsilon_{\text{w}}} - 1 \right)} \right], \quad 5.6b$$

where ϵ_{pr} and ϵ_{w} are the emissivities of the probe strip and the tube wall, respectively, $\Lambda_{1\text{w}}$ and $\Lambda_{2\text{w}}$ are the surface area of the tube wall above and below the probe over the probe width, respectively, $\Lambda_{1\text{pr}}$ and $\Lambda_{2\text{pr}}$ are the top and the bottom surface area of the probe strip, respectively.

The rate of heat transfer by radiation from the probe strip to the surrounding environment outside the furnace, $\dot{Q}_{\text{rad, pr-s}}$ is only considered for the probe strips located outside the furnace and is given by

$$\dot{Q}_{\text{rad, pr-s}} = 2[w(z) + b(z)]dz \sigma \mathcal{F}_{\text{pr-s}} [T_{\text{pr}}^4(z, t) - T_s^4(t)], \quad 5.7a$$

where $\mathcal{F}_{\text{pr-s}}$ is the total radiation interchange factor for radiation heat transfer from the surface of the probe strips to the surroundings

outside the furnace. Since the area of the surroundings are much larger than the surface area of the probe strip, we have

$$\mathcal{F}_{pr-s} = \epsilon_{pr} \quad 5.7b$$

Substituting equations 5.2-5.7 into equation 5.1 and rearranging the latter, the following equations are obtained.

$$\begin{aligned} \rho_{pr} w(z) b(z) dz c_{p, pr}(z, t) \frac{\partial T_{pr}(z, t)}{\partial t} = \\ \frac{\partial}{\partial z} \left[w(z) b(z) \kappa_{pr}(z, t) \frac{\partial T_{pr}(z, t)}{\partial z} \right] dz \\ - 2[w(z) + b(z)] dz \left\{ \mathcal{F}_{pr-w} [T_{pr}^4(z, t) - T_w^4(t)] \right\}, \end{aligned} \quad 5.8a$$

for the probe strips located inside the furnace; and

$$\begin{aligned} \rho_{pr} w(z) b(z) dz c_{p, pr}(z, t) \frac{\partial T_{pr}(z, t)}{\partial t} = \\ \frac{\partial}{\partial z} \left[w(z) b(z) \kappa_{pr}(z, t) \frac{\partial T_{pr}(z, t)}{\partial z} \right] dz \\ - 2[w(z) + b(z)] dz h [T_{pr}(z, t) - T_s] \\ - 2[w(z) + b(z)] dz \epsilon_{pr} [T_{pr}^4(z, t) - T_s^4(t)], \end{aligned} \quad 5.8b$$

for the probe strips located outside the furnace.

Equations 5.8a and 5.8b are subject to the following boundary and initial conditions:

$$T_{pr}(z, t) = T_s, \quad \text{for } z = l_{pr}, \quad t \geq 0, \quad 5.9$$

$$T_{pr}(z, t) = T_s, \quad \text{for } l_{pr} \geq z \geq 0, \quad t = 0. \quad 5.10$$

In the above equations, $c_{p, pr}$, ϵ_w , ϵ_{pr} and κ_{pr} are temperature-dependent property values, and are therefore functions of space

coordinates and time.

A computer program was written to solve equations 5.8a and 5.8b (subject to the initial and boundary conditions). In the computer program, equations 5.8a and 5.8b have been approximated by a numerical method of analysis using forward finite-difference approximations. Using this approach, the temperature distribution of the probe at any time step has been expressed explicitly in terms of the temperature distribution of the probe, the temperature of the tube wall and of the surroundings at the previous time step. In the program, the number of equally-spaced longitudinal nodes along the probe can be specified by the user. For each node the width and the thickness of the probe were considered as constant. The time step used in the forward finite-difference approximation is an input value in the computer program. At each time step for each node a check is made to ensure that a numerical stability requirement of the explicit finite-difference method is satisfied. The temperature-dependent property values of the graphite probe have been shown in Table 1. However, these property values at any node are considered to be constant over the control volume and over each time step. For the adjacent nodes, the arithmetic mean temperature of these two nodes is used to calculate the temperature-dependent property values.

5.3. Experimental

5.3.1. The atomic absorption spectrometer

The following two instruments were used.

A research instrument which was a modified Perkin-Elmer spectrometer, model 503, equipped with the Perkin-Elmer Heated Graphite Atomizer (HGA), model 2100, a laboratory-made power supply described earlier, and a probe insertion device described below, was used in this study for comparison of the probe technique with the platform technique and for measuring the probe temperature.

The Perkin-Elmer spectrometer, model 5000, equipped with the Perkin-Elmer Heated Graphite Atomizer (HGA), model 500, and a probe device described below, was later used for some experiments and also for determination of the metal contents in airborne particulates. The Perkin-Elmer professional computer, model 7500, and the Perkin-Elmer HGA Graphics II version 2.0 program (part No. m065-0038) were used for data processing.

To allow insertion of the graphite probe, the contact cylinders of the HGA-500 and HGA-2100 were rotated and a slot was cut along one of the ports on the contact cylinders. For the research instrument (described above), the absorbance and temperature profiles were recorded with the digital oscilloscope described earlier.

In all cases, commercial hollow-cathode lamps were used and operated at lamp currents well below the maximum lamp currents prescribed by the manufacturers.

5.3.2. The graphite probe and the probe insertion device

Figure 91 shows the configurations of the graphite probe used. The graphite probe was made of anisotropic pyrolytic graphite, and was 25 mm long, 4 mm wide at the head, and about 4.8 mm long at the head. The thickness of the probe head varied from 0.18 mm to 0.48 mm from probe to probe. A maximum of 20 μ L of the test solution was deposited on the sampling head of the graphite probe. For direct determination of metal contents associated with airborne particulates, a rectangular graphite probe made of porous electrographite, 25 mm long, 5 mm wide and 0.5 mm thick, with a circular depression of 3 mm diameter and 0.2-0.3 mm depth at its head (probe D in Fig. 91) was used.

Figure 92 shows a block diagram of the graphite probe insertion device. The probe was mounted on a ceramic holder which was fixed on the shaft of a 2-way air cylinder with a maximum 3-inch moving distance. The displacement of the 2-way air cylinder was controlled by a 4-way, solenoid-operated, pneumatic direction-control valve. The switching on and off of the power supply (110 V A.C.) made the shaft of the 2-way air cylinder move forward and backward, respectively. These movements resulted from pressurizing one inlet side and opening the other inlet side to the ambient atmosphere. Adjustment of the air flow control valves allowed variation of the speed of the probe into and out of the graphite tube. It normally took 5 ms for the entire probe head (about 4.8 mm long) to be fully inserted into the graphite tube.

The pneumatic insertion of the probe into the heated graphite tube was controlled by a laboratory-made solenoid actuated power supply controller. The solenoid power supply controller contained a

Figure 91. Configuration of the graphite probe.

Figure 92. Schematic diagram of the graphite probe insertion device.

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

programmable delay timer which had a maximum delay time of 130 s and an on-time 120 s. The delay time was triggered simultaneously with the triggering of the heating cycle of the atomizer by pushing the program button of the atomizer power supply controller. The total delay time registered on the timer was 3-10 s more than the sum of the drying and charring times which were set on the programmer. This resulted in a 3-10 s delay of the probe in its automatic insertion into the heated furnace tube to ensure attainment of a preset atomization temperature by the furnace. The probe remained inside the furnace tube during the entire preset on-time of the delay timer and was automatically withdrawn at the end of the on-time cycle. The on-time cycle included a cooling period of 30 s. The internal purge gas (Ar) was interrupted during the entire atomization cycle but was turned on immediately at the termination of the atomization cycle in order to provide an Ar gas atmosphere in which the probe cooled to room temperature inside the graphite tube before it was automatically withdrawn at the end of the on-time. Operation of the probe could also be controlled manually.

5.3.3. The graphite tubes and platforms

Both Perkin-Elmer pyrocoated and pyrolytically-coated graphite tubes were used. The sample injection hole of the graphite tube was enlarged so as to produce a rectangular slot 1.8 mm in height and 4.5 or 5.5 mm in length. The two ends of the slot being equidistant from the two ends of the graphite tube. The graphite tube was positioned in the atomizer so that the inserted probe was located in the lower, central part of the tube. The same graphite tube was used with the platform technique for comparison of the probe technique with the platform technique; the graphite platform used was the same as that

reported earlier.

5.3.4. Measurement of the tube wall temperature, the effective gas temperature and the probe temperature

The temperature of the outside surface of the tube wall (at the furnace centre) was measured with an automatic optical pyrometer, Ircon series 1100, which monitored the temperature continuously throughout the run. The measured temperature of the outside surface was then corrected to read the inside temperature of the graphite tube.

The effective gas temperature inside the graphite probe furnace was determined by the two-line atomic absorption method, as reported previously in Chapter 3. The line pair of Sn 286.3/284.0 nm was used for the determination.

The surface temperature of the probe was measured in the same way as the surface temperature of the platform was measured (described in Chapter 2), using a similar experimental set-up, as shown in Fig. 13; the only difference was that the platform furnace in Fig. 13 was replaced by the probe furnace. A laser beam was passed through a small hole (having diameter of 1.5 mm) on the top of the tube and was focussed on the probe head. An oscilloscopic trace of the change in reflected intensity of the laser beam by the silver metal powder is shown in Fig. 93. At the instant the probe was inserted a high signal was recorded because of high reflection by the silver metal powder. At the melting point of silver, the silver metal melted into a small bead and rolled away from the laser beam, resulting in a sharp fall in the signal back to the base line. Similar to the measurement

Figure 93. An oscilloscopic trace of the change in reflected intensity of the laser beam from the silver metal powder (deposited on the surface of the probe head) as a function of time. t_{ins} is the time of insertion of the probe. t_m is the time corresponding to the melting of the metal.

of the surface temperature of the platform, the measurement of the surface temperature of the probe was limited by the emission signal of the tube wall when the temperature of the tube wall exceeded 2300 K. Pure metals of Ag, Cu, Ni, Pd, and Pt (99.99%-99.999% pure) were used for the measurement.

5.3.5. The graphite probe filter device for collecting airborne particulates

Figure 94 shows the graphite probe filter device for collecting airborne particulates. The probe filter was made of porous electrographite. The circular depression in the probe head was used for filtration of air and collection of airborne particulates.

5.3.6. Reagents and sampling procedures

Stock solutions containing 1000 $\mu\text{g/mL}$ of the following were prepared - each containing only one metal or compound: Sn, Pb, Cd, Ni, Co, V, Mo, NaCl, MgCl_2 , and CaCl_2 , as reported in Chapter 3 (section 3.3), and in Chapter 4 (section 4.3), respectively. Stock solutions containing 1000 $\mu\text{g/mL}$ of Cu and Mn were prepared - each separately - by dissolving appropriate masses of pure metals in Ultrex nitric acid and the solutions were diluted with ultrapure water of resistivity 18.3 megohm-cm. All test solutions were prepared by serial dilution of the above stock solutions with ultrapure water immediately prior to determination. In all cases, 5 μL of the test solution was deposited on the probe head, or on the platform centre with an Eppendorf microlitre pipette fitted with disposable plastic tips when the probe or the platform was outside the furnace. The sample was dried with an infrared lamp, and then the probe or the platform was inserted into

the furnace. Charring was not done.

Since no aerosol was available as a standard reference material, the performance of the total analytical system consisting of the air-particulate collection device and the quantitative determination device, acting as a single unit, could not be evaluated. The performance of these devices were therefore studied as follows. This study however could not therefore be considered as an evaluation of the total analytical system because it lacked rigorous evaluation of

Figure 94. Graphite probe filter device (single filter).

the performance and characterization of the air-particulate collection device (graphite filter), and of the quantitative recovery of the collected elements from the graphite filter in the quantitative determination step. The National Bureau of Standards (NBS), Standard Reference Material (SRM) 1648, Urban Particulate Matter, was used for study of recovery of its metals content. The SRM was wet-digested by heating it with a mixture of HClO_4 , HF and HNO_3 . The digested solution was then appropriately diluted with ultrapure water for determination of the elements. The results are presented in a later section.

5.3.7. Procedure for determination of metals content in airborne particulates

For determination of metal contents in airborne particulates, the porous electrographite probe, whose head had been decontaminated prior to use by repeated firings at a high temperature (2870 K) in the furnace, was installed in the filtering device (Fig. 94) for filtering air for a pre-determined length of time. After the filtering was complete, the probe was attached to the probe insertion device and the probe head was subjected to the atomization cycle at a pre-determined atomization temperature. The metals collected by the probe head were determined by the Bracketing method [185], using aqueous standard solution of the analyte element. The concentration of the metal content in airborne particulates was then calculated from the volume of the air filtered. The results are presented at a later section.

5.4. Results and discussion

5.4.1. Comparison of the measured and the computed temperature of the graphite probe head

Figure 95 shows the measured (symbols) and the computed (solid lines) temperature vs. time curves of the probe head at a tube wall temperature (at the furnace centre) of 2270 K. As in the measurement of the platform temperature, the main source of error in the measured temperature of the probe head was the variable physical contact between the metal powder and the probe, resulting in possible systematic errors and scatter in the experimental data points. The relative standard deviation of a single measurement of the time corresponding to the melting points of various pure metals was $\leq \pm 14\%$, and corresponded to a $\leq \pm 10\%$ relative standard deviation of a single value of the various measured temperature of the probe head. However, Fig. 95 shows that the computed temperature agrees well with the measured temperature, which suggests that the simplifying assumptions made in deriving the above model are reasonable and have resulted in a simple theory having good predictive ability.

5.4.2. Characteristics of time-dependent temperature distribution of the graphite probe

Figure 96 presents the computed temperature distribution along the probe length at selected times and shows development of a temperature gradient along the probe head with increasing time, and a rapid drop in the probe temperature from the part inside the furnace

Figure 95. The measured (symbols) and the computed (solid lines) surface temperature of the probe head as a function of time.

$T_f = 2300$ K. The thickness of the probe head was 0.18 mm for curve A and empty circles, and 0.30 mm for curve B and filled circles. The error bars represent one standard deviation.

Figure 96. The computed temperature distribution of the probe along the probe length at selected times. A probe of trapezoidal shape (probe A in Fig. 5.3) and of uniform thickness 0.18 mm was used in the computing. $T_f = 2970$ K.

to the part outside the furnace. However, there was always a 3 mm-long section in the probe head where the temperature at any instant was spatially invariant.

Figures 97 and 98 show non-linear temperature vs. time curves of the probe head, and the effect of the probe thickness and the tube wall temperature on the curves. The upper line of the shaded zone shows the temperature of tip of the probe head; the bottom line shows the temperature of the probe head which is just inside the furnace. The heating rate of the probe head decreased monotonically with increasing time. For a given probe temperature, the thinner the probe (Fig. 97), the faster its heating rate and the smaller the temperature gradient on the probe head along its length. For a given temperature (of the tip) of the probe head, the higher the tube wall temperature, the higher the heating rate of the probe head (Fig. 98). The model predicts that the most important geometric factor affecting the heating of the probe head is the thickness of the probe head (actually, the mass per unit area of the probe head). For probes with the same thickness (over the entire probe head), different probe configurations shown in Fig. 91 have a negligible effect on the heating of the probe head. Variations in thickness of the probe outside the furnace have little effect on the heating of the probe head. For example, when the thickness of the probe head was 0.18 mm and the thickness of the probe outside the furnace changed from 0.15 mm to 0.30 mm, the corresponding maximum difference in the temperature at any given position along the length of the probe head and at any instant was within 20 K for a tube wall temperature of 2270 K, and was within 5 K for a tube wall temperature of 2970 K. In the

Figure 97. The computed temperature vs. time curves of the probe head (having different thickness) at the tube wall temperature (at the furnace centre) 2970 K (dashed line). Zone A: 0.18 mm. Zone B: 0.36 mm. The upper line of each shaded zone represents the temperature of the tip of the probe head; the bottom line represents the temperature of the transverse cross-section of the probe head which is just inside the furnace.

Figure 98. The computed temperature vs. time curves of the probe head (shaded zones) at various tube wall temperatures at the furnace centre (dashed lines). Zone A: $T_f = 2970$ K. Zone B: $T_f = 2770$ K. Zone C: $T_f = 2270$ K. The upper line of each shaded zone represents the temperature of the tip of the probe head; the bottom line represents the temperature of the transverse cross-section of the probe head which is just inside the furnace.

latter case, radiation heat transfer to the probe head at a high tube wall temperature was much larger than heat transfer by thermal conduction along the length of the probe; the result was that the thickness of the probe outside the furnace had a very little effect on the heating of the probe head.

Figure 99 presents the comparison of the surface temperature of the platform (solid lines) and the probe head (shaded zone) having the same thickness and the same final tube wall temperature. Curve A is the platform temperature vs. time curve obtained using an extremely high (3000 K ms^{-1}) tube wall heating rate. Curve B is the platform temperature vs. time curve obtained using a tube wall heating rate of 2 K ms^{-1} and an initial tube wall temperature of 470 K . At an extremely high tube wall heating rate (at constant tube wall temperature), the heating rate of both the platform and the probe decreases monotonically with increasing time. The slower heating of the probe compared to that of the platform (curve A in Fig. 99) is due to dissipation of heat to the part of probe outside the furnace. When the heating of the probe (shaded zone) is compared with the heating of the platform at normal heating rate of the platform (curve B in Fig. 99), the heating rate of the platform is higher than that of the probe at surface temperatures of platform and of probe higher than 1100 K . However, a probe head thinner than a platform can be used without the problem of lack of stability that a thin platform suffers from during its heating. With a thin probe head, the heating rate of the probe head at a high surface temperature of the probe will be similar to or higher than that of the platform, depending on the actual thickness of the probe and the tube wall temperature.

Figure 99. The computed temperature vs. time curves of the probe head (shaded zone) and of the platform (solid lines). Curve A: platform temperature at $\alpha = 3000 \text{ K ms}^{-1}$. Curve B: platform temperature at $\alpha = 2 \text{ K ms}^{-1}$. The thickness of the platform or the probe was 0.30 mm. $T_f = 2970 \text{ K}$. The dashed line is the constant tube wall temperature curve.

5.4.3. Temperature distribution of the gas phase inside the graphite probe furnace

No theoretical model of the temperature distribution of the gas phase inside the graphite probe furnace has been attempted in this study. Discussions presented here are based on the experimental results and the knowledge of the temperature distributions of the gas phase in the graphite tube furnace and in the graphite platform furnace.

The probe is inserted into the furnace after the tube wall temperature has attained a steady state. The gas temperature distribution in the furnace before the insertion of the probe is similar to that of the graphite tube furnace (without platform or probe), as described in Chapter 3, i.e., there is a temperature gradient in the gas phase in the axial direction, but the temperature is relatively stable with increasing time. After the insertion of the initially cold graphite probe (at room temperature), the temperature distribution over the tube wall and in the gas at the furnace centre is disturbed because the graphite probe acts as a heat sink.

Figure 100 shows the perturbation of the tube wall temperature (at the furnace centre) due to the insertion of the probe having different thickness at its head. The thicker the probe head, the greater is the drop in the steady-state temperature of the tube wall, and the slower is the relaxation of the temperature to its pre-perturbation, steady-state value. This will be so regardless of whether the probe is inserted into the furnace: from the front of the tube as in this study and as in [18, 20-23], or from one end of the tube as in [183].

Figure 100. Absorbance vs. time curves of Sn atomized from probe heads of different thickness, and the corresponding temperature (at the furnace centre) of the outside surface of the tube wall vs. time curves. The thicknesses of the probe heads were: curve A: 0.18 mm; curve B: 0.30 mm; curve C: 0.48 mm.

Figure 101 shows the effective gas temperature, $T_{g, \text{eff}}$, as a function of time for probes (of different thickness) measured by the two-line atomic absorption method using Sn as the thermometric species. The initial part of each $T_{g, \text{eff}}$ curve corresponds to the initial part of the absorbance signal when relatively large amounts of atoms which have the low temperature of the probe surface just enter the thin layer of gas in the immediate vicinity of the probe surface and impart to it the relatively low temperature of the probe surface. The initial increase in $T_{g, \text{eff}}$ with increasing time is, therefore, caused by the increasing probe surface temperature with increasing time. The shift of the $T_{g, \text{eff}}$ curve towards longer time for the thicker probe is due to the slower heating of the thicker probe, resulting in longer time to attain a given surface temperature of the probe and thus a given effective gas temperature. The initial differences between the tube wall temperature and the effective gas temperature reflect the temperature gradient (over the width of the probe head) of the gas phase both in the axial and the radial direction. With increasing time, the probe temperature approaches the tube wall temperature. The temperature gradient (over the width of the probe head) in the radial direction therefore decreases and the effective gas temperature attains a steady state. The nearly constant difference between the tube wall temperature and the effective gas temperature during this period is mainly due to the nearly constant temperature gradient of the gas phase in the axial direction, similar to the case of the graphite platform furnace.

Figure 101. Effective gas temperature in the graphite probe furnace as a function of time for probes of different thickness, determined by the two-line atomic absorption method using Sn 286.3/284.0 nm line pair. The thicknesses of the probe heads were: (o) 0.18 mm, (●) 0.30 mm, (Δ) 0.48 mm.

Figure 102 shows a comparison of the probe and the platform furnace with respect to their effective, steady-state gas temperatures. Measurement of these effective, steady-state gas temperatures was repeated over a period of one month and the results showed satisfactory day-to-day reproducibility ($< \pm 10\%$ RSD, for both the probe and the platform furnace). The relatively lower effective, steady-state gas temperature in the graphite probe furnace may be attributed to the relatively large gas temperature gradient in the axial direction at longer heating times (Chapter 3).

5.4.4. Optimization of the working conditions of a graphite probe furnace

The following points are made based on the temperature field and the atomization process in the graphite probe furnace.

It is preferable to use a probe that holds the sample in the front part of the probe head and almost fills the slot in the tube without actually touching the tube. The former prevents spread of sample solutions to the lower temperature region of the probe head and assures that a high fraction of the analyte species is volatilized or atomized from the probe; the latter minimizes loss of the analyte atoms through the slot. A thin probe is usually preferred to a thick probe since it produces fast heating of the probe at a given tube wall temperature. However, a very thin probe will have a short life time because of oxidation, particularly of that portion just outside the furnace. Among the configurations shown in Fig. 91, probe C is most satisfactory in these respects. It has a thin head and a thick neck and stem. Spread of the sample solutions is prevented by the neck and the thick stem. However, probe C is relatively difficult to make.

Figure 102. Effective steady-state gas temperature in the graphite probe furnace (●) and in the graphite platform furnace (o) as a function of the final tube wall (atomization) temperature determined by the two-line atomic absorption method using Sn 286.3/284.0 nm line pair. The thickness of the platform was 0.30 mm, and of the probe head 0.36 mm. (▲) are the data points of the effective steady-state gas temperature in the graphite probe furnace taken from [186]. The error bars represent one standard deviation.

Probe D, in Fig. 91 having a thickness of 0.2-0.3 mm in the sampling circle, is relatively easy to make and is satisfactory for most analyte. Probe A and B are easy to make but give relatively poor precision because of spread of sample solutions and the relatively large gap between the probe stem and the slot on the tube. However, there is no significant difference in the sensitivities attainable with these configurations if the thickness of the probe heads is similar.

The tube wall (atomization) temperature should not be too high. However, the heating rate of the probe head should be fast enough to yield high atomization efficiency; and the gas temperature should be high enough for efficient dissociation of any analyte molecular species. A very high tube wall (atomization) temperature results in a lower integrated absorbance because of the faster atom dissipation rate by diffusion at higher gas temperature. Generally speaking, for low-volatility elements, a thin probe and a relatively high tube wall (atomization) temperature are preferred. The graphite probe should be inserted as soon as the temperature of the tube wall at the furnace centre attains a steady state. The insertion of the probe at a later time is inadvisable because the temperature gradient in the axial direction increases with longer heating times.

The slot cut in the graphite tube should be as small as practicable to prevent loss of the analyte vapour through it. It is also preferable to make the slot include the sample injection hole of the graphite tube. Figure 103 shows the additional loss of Cd and Ni atoms if a graphite tube having both a slot and a sample injection hole is used. Table 20 shows that with the sample injection hole on

Figure 103. Superimposed absorbance vs. time curves obtained using slotted, pyrolytically-coated graphite tube with or without the sample injection hole (of diameter 0.18 mm). The Perkin-Elmer HGA-500.

(a) Cd 7.5×10^{-14} kg (taken as the nitrate in an aqueous solution).

$T_f = 2390$ K. without the hole (curve A) and with the hole (curve B).

$T_f = 1970$ K. without the hole (curve C) and with the hole (curve D).

(b) Ni 2.0×10^{-12} kg (taken as the nitrate in an aqueous solution).

$T_f = 3070$ K. without the hole (curve A) and with the hole (curve B).

Table 20. Effect of the sample injection hole on the absorbance in the graphite probe furnace atomic absorption spectrometry*

Elements†	Amount added (ng)	Tube wall temperature (K)	Peak-height absorbance			Integrated absorbance (abs.s)		
			With a hole A_1	Without a hole A_2	A_1/A_2 ratio (%)	With a hole A_3	Without a hole A_4	A_3/A_4 ratio (%)
Cd	0.075	1970	0.181	0.220	82	0.547	0.676	81
Cd	0.075	2390	0.478	0.668	72	0.403	0.420	96
Pb	0.150	2870	0.665	0.790	84	0.288	0.310	93
Ni	2.00	3070	0.345	0.371	93	0.540	0.590	92
Co	1.00	3070	0.295	0.325	91	0.326	0.372	88
V	5.00	3270	0.441	0.446	99	0.612	0.688	89

* HGA-500 (Perkin-Elmer) with a slotted, pyrolytically-coated (Perkin-Elmer) graphite tube and a pyrolytic graphite probe (probe D in Fig. 91 having thickness 0.5 mm, sampling circle thickness 0.2-0.3 mm and diameter 3 mm). The other experimental conditions were the same as given in Table 21.

† Used aqueous solutions of the metals singly. See the section on Reagents and Sampling Procedure (section 5.3.5) for details.

the top of the slotted tube, the peak-height and the integrated absorbance are reduced by 10-20% for the elements studied.

Finally, because of similarities in the temperature field of the graphite probe furnace and the graphite platform furnace, it is reasonable to conclude that, similar to the platform technique, other developments in electrothermal atomic absorption spectrometry should be integrated with the probe technique, to provide a remarkably interference-free performance. These include the use of the integrated absorbance signal, matrix modifier and Zeeman-effect background correction. The importance of using signal integration in analytical determinations has been discussed in Chapter 4.

5.4.5. Comparison of the analytical performance of the graphite probe furnace and the graphite platform furnace in atomic absorption spectrometry

Figures 104-109 show a comparison of the atomic absorbance signal of selected elements, Cd, Pb, Co, Ni, V and Mo, atomized from the graphite probe furnace and from the graphite platform furnace. These figures were obtained using the research instrument described earlier in the experimental section. The experimental conditions are given in Table 21. Both the probe and the platform used were made of the same anisotropic pyrolytic graphite material and had comparable thickness. The same slotted Perkin-Elmer pyrolytically-coated graphite tube described earlier and the same final tube wall (atomization) temperature were used for both techniques. The absorbance vs. time curves were superimposed in each figure for ready comparison.

Table 21. Instrumental parameters for absorbance measurements
with the graphite platform and the graphite probe furnace*

Parameters	Elements				
	Cd	Pb	Co	Ni	Mo
Wavelength (nm)	228.8	283.3	240.7	232.0	318.4 313.3
Spectral bandpass (nm)	0.2	0.2	0.2	0.2	0.2 0.2
Integration time (s)	4	4	10	10	10 10
Mass of analyte added (ng)	0.05	0.75	1.0	2.0	7.5 2.0
Initial tube wall atomization temperature, T_i (K)	470	470	470	470	470 470
Final tube wall atomization temperature, T_f (K)	various	various	various	various	various various
Tube wall heating rate, ($K\ ms^{-1}$)	various	various	various	various	various various
Purge gas	Ar in the interrupt mode				
Thickness of probe head (mm)	0.30	0.30	0.18	0.18	0.18 0.18
Thickness of platform (mm)	0.30	0.30	0.24	0.24	0.24 0.24

* Slotted pyrocoated (Perkin-Elmer) graphite tubes (part No. 0290-1766) were used.

Figure 104. Superimposed peak-height absorbance vs. time curves of Cd (taken as the nitrate in an aqueous solution) obtained with the graphite platform furnace (curve A) and with the graphite probe furnace (curve B). Curve C is the temperature vs. time curve of the tube wall at the furnace centre. (a) $T_f = 2170$ K. (b) $T_f = 2970$ K. The Perkin-Elmer BGA-2100 was used.

Figure 105. Superimposed peak-height absorbance vs. time curves of Pb (taken as the nitrate in an aqueous solution) obtained with the graphite platform furnace (curve A) and with the graphite probe furnace (curve B). Curve C is the temperature vs. time curve of the tube wall at the furnace centre. (a) $T_f = 2270$ K. (b) $T_f = 2970$ K. The Perkin-Elmer HGA-2100 was used.

Figure 106. Superimposed peak-height absorbance vs. time curves of Ni (taken as the nitrate in an aqueous solution) obtained with the graphite platform furnace (curve A) and with the graphite probe furnace (curve B). Curve C was the temperature vs. time curve of the tube wall at the furnace centre. $T_f = 2970 \text{ K}$. The Perkin-Elmer HGA-2100.

Figure 107. Superimposed peak-height absorbance vs. time curves of Co (taken as the nitrate in an aqueous solution) obtained with the graphite platform furnace (curve A) and with the graphite probe furnace (curve B). Curve C was the temperature vs. time curve of the tube wall at the furnace centre. $T_f = 2970$ K. The Perkin-Elmer IGA-2100.

Figure 108. Superimposed peak-height absorbance vs. time curves of V obtained with the graphite platform furnace (curve A) and with the graphite probe furnace (curve B). Curve C was the temperature vs. time curve of the tube wall at the furnace centre. $T_f = 2970$ K. The Perkin-Elmer HGA-2100. An ammonium vanadate aqueous solution was used.

Figure 109. Superimposed peak-height absorbance vs. time curves of Mo obtained with the graphite platform furnace (curve A) and with the graphite probe furnace (curve B). Curve C was the temperature vs. time curve of the tube wall at the furnace centre. $T_f = 2970$ K. The Perkin-Elmer HGA-2100. An ammonium molybdate solution was used.

Table 22 shows the values of the peak-height and the integrated absorbance - the values are arithmetic means of 3-5 replicate determinations done on the same day.

Table 22 and Figs. 104-108 show that when isothermal (temporal) atomization is achieved with the platform technique, i.e., when the absorbance vs. time curve is located inside the isothermal region of the tube wall temperature (at the furnace centre) vs. time curve, the peak-height and the integrated absorbance of Cd, Pb, Co, Ni and V obtained using the platform technique are similar to that obtained using the probe technique. The similarity in integrated absorbances given by the two techniques reflects similar mean residence times of the analyte atoms, resulting from the similar gas temperature distribution. The similarity in peak-height absorbances given by the two techniques reflect similar heating rates of the probe and the platform under the experimental conditions used, resulting in similar rates of supply and loss of the analyte atoms.

When isothermal (temporal) atomization of Cd and Pb was not fully achieved because of a too-high tube wall (atomization) temperature (2970 K) in the platform technique [Figs. 104(b) and 105(b)], both the peak-height and the integrated absorbance of Cd and Pb were lower than those obtained in the probe technique. This was due to the fact that Cd and Pb were vaporized earlier from the platform at a time when the tube wall temperatures, and hence the temperatures of the gas phase, were rapidly increasing, causing loss of the analyte atoms by thermal expansion and by expulsion with the rapidly expanding gas phase through the slot and the furnace ends. In this respect, the probe technique has one important advantage over the platform technique -

Table 22. Comparison of peak-height and integrated absorbance of the graphite platform and the probe furnace*

Elements†	Tube wall temperature (K)	Peak-height absorbance		Integrated absorbance (abs.s)	
		Platform	Probe	Platform	Probe
Cd	2170	0.310	0.306	0.229	0.239
Cd	2970	0.272	0.333	0.118	0.151
Pb	2270	0.320	0.310	0.189	0.181
Pb	2970	0.198	0.316	0.080	0.144
Co	2970	0.313	0.351	0.266	0.262
Ni	2970	0.318	0.320	0.289	0.310
V	2970	0.334	0.318	0.420	0.404
Mo	2970	0.380	0.268	0.448	0.580

* HGA-2100 (Perkin-Elmer) with probe A (Fig. 91). Other experimental conditions are the same as given in Table 21.

† Aqueous solutions of the metals were used singly. See the section on Reagents and Sampling Procedure (section 5.3.6) for details.

with probe atomization a high atomization temperature can be used for atomization of volatile elements without the risk of analyte loss by thermal expansion of the gas and by expulsion with the rapidly expanding gas. However, it has been pointed out in earlier chapters that use of a relatively thick platform combined with a fast tube wall heating rate and a low initial tube wall (atomization) temperature will achieve isothermal (temporal) atomization for a volatile element at a relatively high final tube wall (atomization) temperature.

Figure 109 shows a significant difference in the absorbance vs. time curves of Mo obtained with the platform technique and with the probe technique. The peak-height absorbance of Mo by the platform technique is about 42% greater than that by the probe technique, whereas the integrated absorbance by the probe technique is about 30% greater than by the platform technique. This reversal in the sensitivity may be due to formation of various intermediate compounds of molybdenum in various stages of the heating cycle, as described in Chapter 6, and their effects on the peak-height and the integrated absorbance. The former is sensitive to heating rate (which determines the time when the atomization temperature is attained) whereas the latter is insensitive to these parameters and should give better sensitivity for refractory compounds. However, different extents of formation and dissociation of refractory compounds of molybdenum in the two techniques (because of the difference in their operation) may also be partly responsible for above difference in the sensitivity. In light of the various reaction pathways possible for molybdenum atomization from a pyrolytic graphite surface, as shown in Chapter 6, further study is required to determine the factors involved in the

above reversal in sensitivity by the peak-height and the integrated absorbance mode of measurement and the relative importance of these factors in reversing the sensitivity. Such a study, by throwing light on the unexpected observation of higher peak-height sensitivity for refractory compounds, should also be of practical interest.

For a given probe, the tube wall temperature is the most important factor affecting the absorbance signal of the analyte elements. Figures 110 and 111 show the effect of tube wall temperature on the peak-height and the integrated absorbance with the probe technique obtained with HGA-500. With increasing tube wall (atomization) temperatures the trends of most curves are similar to those observed with the platform technique (Figs. 78 and 79), and have similar explanations. The increasing peak-height absorbance of Cd and Pb with increasing (atomization) temperature of the tube wall (at the furnace centre) with the probe technique (Fig. 110) is opposite to that observed with the platform technique (Fig. 78). This is explained as follows. In both the graphite platform furnace and the graphite probe furnace, a higher tube wall temperature results in a higher gas temperature, and thus a higher removal rate of the analyte atoms by diffusion. A higher tube wall temperature also increases the heating rate of a probe at any given probe temperature (Fig. 98), but only increases the heating rate of a platform at relatively high platform temperatures (Fig. 21). The appearance temperatures of volatile elements, Cd and Pb, are relatively low. However, the heating rate of the platform, and thus the supply rate of Cd or Pb atoms at platform temperatures corresponding to the rising part of the absorbance signal do not appreciably increase with increasing tube

Figure 110. Effect of the final tube wall (atomization) temperature on the peak-height absorbance with atomization from the probe. The pyrolytic graphite probe (probe D in Fig. 5.3) was used. The thickness of the probe head was 0.5 mm and of the sampling circle was 0.2-0.3 mm. (○) Cd, (△) Pb, (○) Ni, (□) Co, (●) V and (■) Mo. The Perkin-Elmer BBA-500 was used. Aqueous solution of the metals were prepared as described earlier.

Figure 111. Effect of the final tube wall (atomization) temperature on the integrated absorbance with atomization from the probe. The pyrolytic graphite probe (probe D in Fig. 5.3) was used. The thickness of the probe head was 0.5 mm and of the sampling circle was 0.2-0.3 mm. (○) Cd, (△) Pb, (○) Ni, (□) Co, (●) V and (■) Mo. The Perkin-Elmer HGA-500 was used. Aqueous solution of the metals were prepared as described earlier.

wall temperatures, whereas the removal rate of the analyte atoms increases. As a result, peak-height absorbances of Cd and Pb decrease with increasing tube wall temperatures. The heating rate of the probe, and hence the supply rate of the Cd and Pb atoms at the probe temperatures corresponding to the rising part of the absorbance signal increase appreciably with increasing tube wall temperature. The supply rate of Cd and Pb is more sensitive to increase in the probe temperature than their removal rate by diffusion is to increase in the gas temperature. As a result, the peak-height absorbance of Cd and Pb obtained with the probe technique increases with increasing tube wall temperature.

Elimination of matrix interferences with the probe technique and the platform technique is illustrated in Fig. 112, which shows recovery of Pb from a synthetic seawater matrix consisting of an aqueous solution of $\text{NaCl} + \text{MgCl}_2 + \text{CaCl}_2$. The synthetic seawater was prepared by dissolving proportionate amounts of these salts in ultrapure water, i.e., in the proportion they exist in seawater [175]. The highest concentration of the matrix used in Fig. 112 corresponds to undiluted seawater. Figure 112 shows that both the probe and the platform technique gave 100% recovery from undiluted seawater matrix (the highest concentration used). However, the precision (% RSD) of the probe technique and the platform technique were 20 and 10, respectively. The much poorer precision of the probe technique with the concentrated seawater matrix was due to the relatively large mass of the dry salt matrix remaining on the probe head after drying and charring, and some of the salt matrix flying loose from the probe head during its rapid insertion into the graphite furnace by the automatic

Figure 112. Recovery of Pb from the NaCl + MgCl₂ + CaCl₂ matrix in an aqueous solution. Pb 6.0×10^{-13} kg (taken as the nitrate). All absorbances were background-corrected. The Perkin-Elmer HGA-2100.

(A) Atomization from the tube wall. $\alpha = 1 \text{ K ms}^{-1}$, $T_f = 2300 \text{ K}$.

charring $T = T_i = 570 \text{ K}$.

(o) Atomization from the platform. $\alpha = 3 \text{ K ms}^{-1}$, $T_f = 2300 \text{ K}$.

charring $T = T_i = 570 \text{ K}$.

(□) Atomization from the probe. $T_f = 2300 \text{ K}$, no charring step.

insertion device. This problem could not occur in the platform technique. The precision of the probe technique for synthetic seawater was later on improved to the level of the platform technique (~ 10% R.S.D.) by using manual insertion. However, in view of the much lower level of lead concentration in uncontaminated seawater, direct determination of lead by the probe (or the platform) technique is not possible.

In contrast to the 100% recovery given by both the probe and the platform technique, atomization of Pb from the tube wall showed severe depression in the absorbance signal even at low concentrations of the salt matrix. The freedom of lead determination from matrix interference in the platform technique and the severe matrix interference in the tube wall atomization technique (Fig. 112) has been fully explained in Chapter 4. A similar explanation applies also to atomization of lead from the probe, which produce temporally isothermal atomization of lead into a gas phase which has attained a higher and steady-state temperature (isothermal-temporal), in contrast to atomization of lead from the tube wall. Also, oscillographic traces of the absorption pulses (not shown) revealed the following additional factor which favoured 100% recovery of the lead signal in atomization from both the probe and the platform. Unlike atomization of lead from the tube wall, the probe and the platform caused the lead absorbance signal profile to appear earlier than and temporally separated from the seawater matrix molecular absorption spectrum. Oscillographic traces of the absorbance signal profile for atomization of lead from the synthetic seawater matrix using the platform technique (Fig. 84) demonstrate the importance of the above factor. Seawater matrix

presents a problem of severe chloride interference with the determination of lead using atomization from the tube wall. Its elimination using the probe and the platform technique indicates their remarkable freedom from chloride interference, and is of considerable practical importance.

Table 23 gives the characteristic mass of the six elements measured using the probe technique with the HGA-500 and the characteristic mass reported for the platform technique in the Operation Manual of the Perkin-Elmer HGA-500 (1985). The characteristic masses of these elements with the probe technique are similar to those with the platform technique.

5.4.6, Direct determination of metals content associated with airborne particulates

Atmospheric pollution is a problem of increasing world-wide concern. Scientists have made considerable advances in developing new sampling and analytical methods for qualitative and quantitative determination of metals in airborne particulates. In turn, these advances have stimulated studies of biological effects of airborne metals and their compounds and in the use of aerosol composition as a tracer for the pollution source. Generally speaking, among the techniques currently used for the direct determination of metals in airborne particulates, graphite furnace atomic absorption spectrometry has the advantage in terms of speed, sensitivity, range of elements, precision, accuracy, possible automation and cost [187-191]. Presented here is a new analytical system which uses the graphite probe furnace atomic absorption spectrometric technique for direct determination of metal contents of airborne particulates. In this system, a porous

Table 23. Characteristic mass for Cd, Pb, Co, Ni, V and Mo in graphite probe furnace and in graphite platform furnace atomic absorption spectrometry

Elements*	Graphite probe furnace†		Graphite platform furnace‡	
	Tube wall temperature (K)	Characteristic mass (pg/0.0044 abs.s)	Tube wall temperature (K)	Characteristic mass (pg/0.0044 abs.s)
Cd	1970	0.49	1870	0.35
Pb	2070	11.4	2070	10.0
Ni	2870	13.7	2770	13.0
Co	3070	9.8	2770	6.0
V	3120	32.0	2920	30.0 [‡]
Mo	3270	9.2	2920	9.0 [‡]

* Aqueous solutions of the metals used singly. See the section on Reagents and Sampling Procedure (section 5.3.6) for details.

† Perkin-Elmer HGA-500 with the slotted pyrolytically-coated (Perkin-Elmer) graphite tube (part No. B0091-504) and the pyrolytic graphite probe (probe D in Fig. 91 with head thickness 0.5 mm, sampling circle thickness 0.2-0.3 mm and diameter 3 mm).

‡ The Perkin-Elmer Operation Manual of HGA-500 (1985).

‡ Atomization from the tube wall and characteristic mass (pg/0.0044 abs.).

Fig. 94 for the probe filter device). It has a high collection efficiency that is suitable for filtration of super-micron- and sub-micron-sized airborne particulates [192]. After filtration, the metals are atomized in the graphite probe furnace, one metal per probe, in a rapid, sequential mode.

Table 24 presents the characteristic mass and the detection limits of probe (porous electrographite) furnace atomic absorption spectrometry. Table 25 presents the results of determination of metals present in our laboratory environment (uncontrolled). The measurements were usually repeated many times over a period of a few weeks. The determination of Pb was done over a period of several months at different times of the day.

Table 25 shows that the fluctuation in the amounts found for the analytes are large, especially for Pb, which probably reflects large variations in the laboratory environment at the different times of the sample collection (air filtration). The filtration time depends on the concentration level of the metals in the airborne particulates, the concentration of particulates in the air samples collected, the filtration rate and the limits of detection. For our laboratory environment, the filtration time was about 5-25 min for the determination of Pb, Cd and Mn, and 2-5 hours for Cu and Ni - all at a filtration rate of 50-100 mL min⁻¹.

The limits of detection shown in Table 25 are low. This can be attributed to two factors: one is the extremely high sensitivity of graphite furnace atomic absorption spectrometry, especially for temporally isothermal atomization with the probe technique; the other is the freedom from contamination, which produces very low and

reproducible blanks. The head of the probe (a small part of the probe) which was used to filter air (and for atomization) being only 5 mm in length allowed more effective control of contamination from the ambient environment and in the handling of the probe. Also, the head of the probe could be easily decontaminated by firing it in the

Table 24. Characteristic mass and limits of detection for determination of Cd, Pb, Ni, Cu and Mn using a porous electrographite probe for atomization*

Elements†	Wavelength (nm)	Atomization temperature T_f (K)	Characteristic mass (pg/0.0044 abs)	Limits of detection 2σ (pg)
Cd	228.8	2100	0.43	1.2
Pb	283.3	2470	13.0	29.5
Ni	232.0	2920	30.0	109
Cu	324.5	2920	14.2	38.7
Mn	279.5	2920	3.7	6.7

* Perkin-Elmer HGA-500. Porous electrographite probe D in Fig. 19 having width 5 mm, thickness of head 0.5 mm, sampling circle thickness 0.2-0.3 mm and diameter 3 mm). Slotted Perkin-Elmer pyrolytically-coated graphite tubes (part No. B0091-504) were used.

† Aqueous solutions of the metals were used singly. See the section on Reagents and Sampling Procedure (section 5.3.6) for details.

Table 25. Results of determination of Cd, Pb, Ni, Cu and Mn
in airborne particulates in our chemical laboratory
at Carleton University

Elements	Amount found (ng m^{-3})	Limits of detection [†] (ng m^{-3})	Filtration time [‡] (min)
Cd	0.5-1.0	0.4	12
Pb	20-200	9.8	1.4
Ni	0.7-8.7	36.3	125
Cu	1.0-8.3	12.9	47
Mn	6.2-6.4	2.2	10

* Experimental conditions used were the same as given in Table 24.

† Based on limits of detection 2σ for graphite probe furnace atomic absorption spectrometry given in Table 24, filtration time of 30 min and filtration flow rate of 100 mL min^{-1} .

‡ Based on limits of detection 2σ for graphite probe furnace atomic absorption spectrometry given in Table 24, the maximum amount found (shown in this Table), and filtration flow rate of 100 mL min^{-1} .

atomizer before filtration with no risk of contamination while it is inside the furnace. Additionally, there is even less risk of contamination during the sampling procedure.

The filtration efficiency of the filter was tested using the dual-probe device shown in Fig. 113, in which two probes were connected in series. A 100% collection efficiency for the second probe (filter) (which was new and had a relatively low flow rate) was assumed. The amount of analyte found in the first probe over the total amount found in the two probes was taken as the filtration efficiency of the first probe. Figure 114 shows that with increasing number of firings (atomization), the filtration efficiency of the first probe (filter) for Pb decreases gradually, whereas the flow rate of the first probe (filter) increases almost linearly. This can be explained by an increase in the pore size of the graphite probe with increasing number of firings due to oxidation of the graphite at high temperatures. For the configuration of the probe used, the filtration efficiency of the first probe (filter) for Pb was greater than 90% for the first 200 firings and greater than 80% for the first 300 firings.

Since no standard aerosol sample was available, the accuracy of the quantitation determination step only was estimated by determining Pb, Cd, Ni, Mn and Cu in the Urban Particulate Matter, Standard Reference Material (SRM) No. 1648 of the National Bureau of Standards. Table 26 shows that the recoveries obtained for this SRM using both the peak-height and the integrated absorbance are satisfactory.

Figure 113. A dual-probe filter used for determining the filtration efficiency of the graphite probe filter.

Figure 114. Filtration efficiency for Pb determination (o) and the flow rate of the graphite probe filter used for the above determination (Δ) as a function of the number of firings. The final tube wall (atomization) temperature (at the furnace centre) was 2470 K. The atomization time was 4 s. The initial thickness of the sampling circle on the probe head was 0.3 mm.

Table 26. Results of analysis of trace metals in the National Bureau of Standards, Urban Particulate Matter, SRM 1648^a, by the graphite probe furnace atomic absorption spectrometry

Elements	Certified values ($\mu\text{g g}^{-1}$)	Values found in this study					
		Using peak-height absorbance			Using integrated absorbance		
		Mean ($\mu\text{g g}^{-1}$)	R.S.D. (%)	Recovery [*] (%)	Mean ($\mu\text{g g}^{-1}$)	R.S.D. (%)	Recovery [*] (%)
Cd	75 $\pm$ 7	72 $\pm$ 4	5.6	96	76 $\pm$ 4	3.6	101
Pb	6650 $\pm$ 80	6260 $\pm$ 200	3.2	96	6910 $\pm$ 210	3.1	105
Ni	82 $\pm$ 3	76 $\pm$ 5	6.6	93	75 $\pm$ 7	9.3	91
Cu	609 $\pm$ 27	578 $\pm$ 27	4.7	95	603 $\pm$ 18	3.0	99
Mn	860 [†]	904 $\pm$ 47	5.2	105	918 $\pm$ 49	5.3	107

^{*} Used aqueous solutions of SRM 1648 and determined the % recoveries against aqueous solutions of the metals used singly as reference solutions.

[†] Uncertified value.

5.5. Some further observations

This study has shown considerable promise for the probe technique as a competitive analytical technique, comparable with the platform technique in sensitivity and selectivity. However, the main limitations of both techniques stem from the fact that there is a spatial gradient in the gas temperature in both the probe furnace and the platform furnace and that both the probe and the platform are heated by radiational heat transfer from the tube wall. Because of the spatial gradient in gas temperature, truly isothermal (spatial) atomization is not achieved. Since the maximum temperature of the tube wall is limited and the minimum thickness (and hence, the lowest mass per unit area of both probe and platform) is limited, both the heating rate of probe and platform, and their maximum surface temperatures, are limited. These limitations are inherent in a pulse-heated graphite furnace and cannot be eliminated without changing the furnace design and replacing graphite with other suitable materials (capable of being used at much higher temperature than graphite while retaining its desirable chemical and physical properties) for constructing the furnace.

One way to achieve isothermal (both temporal and spatial) atomization is to apply the probe and the platform techniques to the recently developed 'side-heated graphite cuvette with integrated contacts' [52], in which the temperature gradient in the axial direction is nearly eliminated. One way to heat the probe or the platform more rapidly would be to employ additional heating such as

electrical resistive heating. This should reduce or eliminate the problem of condensation and re-evaporation of refractory elements reported by other workers [18]. However, the technical problem of supplying the additional resistive heating can be more readily solved for the probe than for the platform, the former can be resistively heated with a power supply both before and after its insertion into the graphite tube and throughout the duration of the atomization cycle. This additional heating of the probe should increase its heating rate, thereby tending to increase the peak-height absorbance. However, such additional heating of the probe is not expected to increase the integrated absorbance under the condition that the fraction of the analyte atomized is the same. The integrated absorbance is determined by the total number of analyte atoms in the analysis volume and their mean residence time, both of which should remain unchanged once the analyte absorbance signal is located fully inside the constant temperature region of the temperature vs. time curve of the gas phase. Finally, the cost of additional instrumentation for the additional heating of the probe, added to the extra cost of the probe furnace would detract from its competitiveness as an analytical technique for routine analysis, especially when its competitor (the platform technique) has almost all of its advantages and has the additional important advantage of being a much simpler and more elegant technique. Added to this is the significant cost advantage of not requiring any additional instrumentation and of lower operating cost.

The graphite probe furnace atomic absorption spectrometric technique for determination of metals content in atmospheric

particulates has the potential of direct analysis of solid samples of airborne particulates. Important advantages include much greater relative sensitivity and shorter analysis time. It is relatively free from contamination from sampling, reagents, and the environment, and from matrix interferences. The technique is simple, sensitive, rapid and inexpensive. Additionally, this analytical technique, by combining a highly efficient filtering system with the extremely high relative sensitivity of the solid sampling technique, offers the potential of monitoring sources of airborne particulate emission with sufficient temporal and spatial resolution for unequivocal identification of the pollution source. In principle, a porous electrographite platform can also be used for the direct determination of the metal content of airborne particulates. However, since the entire platform is heated (in the probe technique, only the probe head is heated), a platform filter would be much less free from contamination, which is a major consideration in trace and ultratrace element analysis.

Finally, the graphite probe insertion device described here can be easily attached to other atomizers with little modification to the atomizer and at modest cost.

Chapter 6

MECHANISMS OF ATOMIZATION OF MOLYBDENUM IN GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY

6.1. Introduction

Since Bodrov and Nikolaev [193] determined molybdenum by graphite furnace atomic absorption spectrometry in 1969, other workers [96, 166-169, 194-207] have reported on various aspects of molybdenum atomization in graphite furnaces. The reports include determination of trace amounts of molybdenum in plant samples [196-198], rocks [199-201], sea water [202-203], and high-purity silver [204]. Some of the analytical methods reported have separation steps [199-200, 203-204] preceding the atomic-absorption-spectrometric finish. Among different atomization techniques, that from the tube wall has been reported to be superior to atomization from the platform [42, 205]. Another paper [206], based on comparison of coated and uncoated graphite tubes, laboratory-made and commercially-produced carbon-rod atomizers and graphite-platform atomizers, concluded that the best results for molybdenum are obtained by use of commercially-produced pyrolytically-coated graphite tubes. A more recent paper [207] investigated not only the effect of pyrocoated graphite and uncoated graphite, but also that of metal carbide and of metal surfaces (for atomization) on quantitation of molybdenum in a sodium chloride matrix (or without the matrix) by atomic absorption spectrometry. The

authors [207] reported that the sensitivities and limits of detection are similar for all the above atomization surfaces except for the uncoated graphite surface, which gives poorer results for molybdenum. However, it has also been reported that an uncoated graphite tube is better for quantitative determination of molybdenum in a sodium chloride matrix because an ashing temperature higher than the boiling point of sodium chloride can be used without loss of molybdenum. However, the authors [207] have not given any explanation for their observations.

Using a combined thermodynamic-kinetic model for atom formation in a graphite furnace, Sturgeon et al. [96] obtained an activation energy value for atomization of Mo from a graphite tube wall and proposed that $\text{Mo}_{(g)}$ atoms are formed by the process:

From X-ray diffraction analysis, Runnels et al. [166] reported formation of molybdenum carbide in a graphite furnace. Also based on X-ray diffraction analysis, Sneddon et al. [167] confirmed formation of two molybdenum carbides, $\text{Mo}_2\text{C}_{(s)}$ and $\text{MoC}_{(s)}$, in a Perkin-Elmer HGA 72 furnace and proposed the reaction route to $\text{Mo}_{(g)}$ as follows:

Müller-Vogt et al. [168-169] used X-ray diffraction analysis and electron micrography to identify molybdenum species and their location in a graphite tube. Like Sneddon et al. [167], they found that $\text{Mo}_2\text{C}_{(s)}$ was formed below 1900 K and then the $\text{Mo}_2\text{C}_{(s)}$ was slowly converted into $\text{MoC}_{(s)}$ at higher temperatures. Since the charring curve of molybdenum obtained by them [168-169] showed a decrease in the molybdenum absorbance at 1900 K, they concluded that during the atomization step, $\text{Mo}_2\text{C}_{(s)}$ decomposed into $\text{MoC}_{(s)}$ and $\text{Mo}_{(s)}$, and the $\text{MoC}_{(s)}$ subsequently decomposed into $\text{Mo}_{(s)}$. They suggested that formation of $\text{MoC}_{(s)}$ at temperatures $>1900 \text{ K}$ and its incomplete decomposition were the reason for the observed decrease in the molybdenum absorbance when temperatures $>1900 \text{ K}$ were used in the charring cycle. In all these X-ray diffraction studies [166-169], a large amount of molybdenum (as an aqueous solution of its salt) was dosed into the graphite furnace, and after the usual heating cycles, the graphite tubes were broken open and small residues were scraped from the area on which the molybdenum solution had been earlier deposited.

The objective of the present study was to investigate some unusual features observed in the charring curve of molybdenum atomized

from pyrolytic graphite surfaces and to elucidate the mechanisms of molybdenum atomization in graphite furnace atomic absorption spectrometry.

In the present study, graphite platforms were used along with X-ray diffraction analysis, scanning electron micrography (SEM), energy dispersive X-ray (EDX), and Auger electron spectrometry (AES) to study the physical and chemical processes occurring in the condensed phase. Atomization from graphite platforms rather than from graphite tube walls had the advantage of the platforms being easily removed from the graphite tubes and subjected to analysis by the above-mentioned techniques without any further treatment. Use of graphite platforms (of the same dimensions and mass) also allowed the use of the same graphite tube, and hence the same heating program to be reproduced from one experiment to another. The result was that better reproducibility was achieved using graphite platforms than what would have been achieved using graphite tubes alone. Also, graphite platforms are inexpensive, easy to make, are easily detachable and usable for the above-mentioned analytical techniques; they also save expensive graphite tubes. The observations from the above techniques were used to elucidate the mechanisms of molybdenum atomization in graphite furnace atomic absorption spectrometry.

6.2. Experimental

6.2.1. Apparatus

The apparatus used was the modified Perkin-Elmer model 993 atomic absorption spectrophotometer equipped with a deuterium-arc background corrector and the Perkin-Elmer BGA 74 graphite furnace fitted with a laboratory-made power supply and controller described in Chapter 4. The molybdenum 312.3 nm line was used for atomic absorption spectrometry. Argon was used as purge gas in the interrupt-mode, and also as the sheath gas.

X-ray diffraction analysis was done with a Philips automated powder diffractometer, PW 1050/81, equipped with a PW 1710 microprocessor. Monochromatic Cu radiation at a voltage of 40 kV and a current of 40 mA was used.

The scanning electron micrographs (SEM) were taken with a scanning electron microscope, AMR model 1000, fitted with an energy dispersive X-ray (EDX) system, Kevex 7000.

The Auger electron spectrometer (AES) used was a Physical Electronics Industries 590 System, which employed a cylindrical mirror analyzer with a concentric electron gun operated at 5 keV. For the sputtering experiments, an ion gun was operated with xenon at voltages of 4 keV. The sputtering rate was estimated to be $\sim 30 \text{ \AA min}^{-1}$.

6.2.2. Graphite tubes and platforms

The Perkin-Elmer pyrolytically-coated graphite tubes (part No. B0091-504), pyrocoated tubes (part No. 0290-1766), and electrographite

tubes (uncoated, partNo. 0290-1633) were used. In all cases, laboratory-made graphite platforms were used. They were made either from electrographite (isotropic) or from anisotropic pyrolytic graphite (Super-Temp, Santa Fe Spings, California). The pyrolytic graphite platforms were cut with a safety razor from blocks of anisotropic pyrolytic graphite along an axis parallel to its plane of deposition. The electrographite platforms were machine-cut from blocks of electrographite. All platforms used were 18 mm long, 0.3 mm thick, 5.2 mm wide with cuts 0.5 mm deep along their lateral edges to prevent physical contact between the sides and the tube wall except at the four pointed corners of the platform.

6.2.3. Measurement of temperature

The temperatures reported were that of the graphite surface of either the tube wall or the platform located directly below the sample injection hole. Measurement of the tube wall temperature and the platform temperature have been described in Chapters 1 and 2, respectively.

6.2.4. Procedure

Atomic absorption spectrometric measurement. Atomic absorption spectrometric measurements were made using atomization from the tube wall and the platform. 5 μ L of an aqueous solution of $(\text{NH}_4)_2\text{MoO}_4$ containing 1-3 ng molybdenum was injected with an Eppendorf microlitre pipette. The solution was dried at a wall temperature of 370-470 K for 30 s. The charring temperature was set between 670-2670 K; charring time was 30 s except where otherwise stated. Atomization was done at 2970 K for 10 s except where otherwise stated.

Investigations into the molybdenum reaction products. All the results of X-ray diffraction analysis, SEM, EDX, and AES were obtained using graphite platforms. Except where otherwise stated, 10 μL of a 5% (w/v) aqueous solution of $(\text{NH}_4)_2\text{MoO}_4$ containing 240 μg molybdenum was injected onto the platform with an Eppendorf microlitre pipette. The solution was dried and then heated at a preset temperature for 30 s. After the graphite tube had been cooled to room temperature, the platform was taken out and placed directly on the sample holder of the X-ray diffractometer for X-ray diffraction analysis. The X-ray diffraction spectrum obtained was compared with standard X-ray diffraction data [208] to identify the species in the condensed phase. The same platform was then studied under the scanning electron microscope. Some of the platforms were also studied by energy dispersive X-ray spectrometry. Auger electron spectrometry was used with or without ion sputtering to analyze only a few of the platforms. The species present on the platforms were identified using a combination of a Chart of Principal Auger Electron Energies and the standard spectra given in Ref. [209]. Some platforms were subjected to the entire atomization step; some were subjected to a partial atomization step (which was interrupted just before the temperature of the platform reached the appearance temperature of molybdenum), and then studied with the X-ray diffractometer.

6.3. Results and discussion

6.3.1. Characteristics of the charring and the atomization curve of molybdenum

Figure 115 presents the charring curve and the atomization curve of molybdenum; the charring curve is a plot of molybdenum absorbance at a constant atomization temperature as a function of charring temperature; the atomization curve is a plot of molybdenum absorbance at a constant charring temperature as a function of atomization temperature. Figure 115 shows that in the charring curve of molybdenum there is a marked dip in the absorbance of molybdenum if it is atomized from a pyrolytically-coated or a pyrocoated graphite tube or from a platform made of pyrolytic graphite. However, there is no dip in the absorbance of molybdenum if it is atomized from a electrographite tube, or from a platform made of electrographite. It has also been found that the shape of the dip is independent of the tube wall heating rate and the atomization temperature of the tube wall. It seems that the dip in the charring curve of molybdenum is related to chemical reactions of molybdenum with the graphite material. The dip occurs with pyrolytic graphite, but not with electrographite, regardless of whether the molybdenum solution is atomized from a tube wall or from a platform.

The atomization curves of molybdenum at two charring temperatures were obtained from a pyrolytically-coated graphite tube. The curves show that the integrated absorbance of molybdenum increases rapidly with increasing atomization temperature. However, for the same amount

Figure 115. Charring curves (left) and atomization curves (right) of Mo (taken as an aqueous solution of $(\text{NH}_4)_2\text{MoO}_4$). Charring curves: (●) 3 ng of Mo atomized from a electrographite platform inside a pyrolytically-coated graphite tube. (Δ) 3 ng of Mo atomized from a electrographite tube. (○) 1 ng of Mo atomized from a pyrolytic graphite platform inside a pyrolytically-coated graphite tube. (□) 1 ng of Mo atomized from a pyrolytically-coated graphite tube. For all charring curves a tube wall heating rate of 2 K ms^{-1} and an atomization temperature of 2970 K were used. Atomization curves: 1 ng of molybdenum atomized from a pyrolytically-coated graphite tube at a tube wall heating rate of 2 K ms^{-1} and at charring temperatures of 670 K (○) and 1470 K (□) for 30 s.

of molybdenum, the atomization curve obtained using a charring temperature of 1470 K [which is the temperature corresponding to the minimum absorbance of the dip in the charring curve (Fig. 115)] shows an appearance temperature higher than that obtained using a charring temperature of 670 K. Also, the molybdenum absorbance obtained at the former charring temperature is much lower than that obtained using the latter charring temperature even using an atomization temperature as high as 3400 K. Further experiments showed that if a charring temperature corresponding to the minimum of the dip in the charring curve (Fig. 115) was employed with a pyrolytically-coated graphite tube, the absorbances were much lower than those obtained using the latter charring temperature regardless of any subsequent temperature program to which the molybdenum was subjected.

Figure 116 shows the morphology of the graphite tubes and the platforms studied by SEM. It shows a close similarity between the tubes and the platforms made of or coated with the same graphite material. Because of the similarities in the morphology of graphite tubes and graphite platforms, and in the molybdenum atomization characteristics from graphite platforms and from tube walls, it was decided to use graphite platforms instead of graphite tubes to investigate the dip in the charring curve of molybdenum (Fig. 115).

6.3.2. X-ray diffraction analysis

Table 27 shows the standard X-ray diffraction data [208] used for identifying the molybdenum species formed on heating an aqueous solution of $(\text{NH}_4)_2\text{MoO}_4$ on graphite platforms in the graphite furnace. Figure 117 shows normalized X-ray diffraction intensities of all

Figure 116. Scanning electron micrographs of the surfaces:

- (a) pyrolytic graphite platform, (b) pyrocoated graphite tube,
- (c) pyrolytically coated graphite tube, (d) electrographite platform,
- (e) electrographite tube. Magnification: $\times 1000$.

Table 27. Standard X-ray diffraction data used for identifying molybdenum species formed on heating the molybdenum solution on the platform in the graphite furnace

Species identified	JCPD [208] Card Index No.	d-spacings identified (Å) and their relative intensities		

Mo	4-809	2.225(100)	1.285(39),	
		1.574(21)	1.1127(11)	
MoO ₂	32-671	2.442(28)	1.6033(1)	1.3033(5)
		2.437(32)	1.5443(7)	1.2912(5)
		2.426(69)	1.5360(13)	1.2219(7)
		2.403(34)	1.5272(9)	1.2175(10)
		2.156(5)	1.4057(4)	1.2146(6)
		1.841(11)	1.4019(21)	1.2076(7)
		1.6976(22) [†]	1.3845(5)	
MoO ₃	21-569	9.12(80)	2.097(10)	1.392(10)
		4.56(20)	1.993(20)	1.362(15)
		3.04(40)	1.947(15)	
		2.53(30)	1.860(15)	
Mo ₄ O ₁₁	5-0337	4.25(45)	2.700(45)	1.877(40)
	5-0338	4.00(100)	2.663(70)	1.852(35)
		3.95(65)	2.593(30)	1.810(30)
		3.75(95) [†]	2.146(35)	1.784(35) [†]
		2.787(50)	1.975(30)	1.726(50) [†]
		2.722(60)	1.941(45)	1.648(70)
β-Mo ₂ C	11-680	2.60(20)	1.75(16) [†]	1.269(16)
		2.37(30)	1.503(12)	1.255(8)
		2.28(100)	1.349(18)	
α-MoC	8-384	2.56(50)	1.631(30)	1.275(40)
		2.442(100)	1.506(80)	1.261(50)
		2.292(100)	1.479(40)	1.228(40)
		2.122(80)	1.379(40)	
		1.941(40)	1.281(80)	

* d-spacing were covered by the diffraction pattern of electrographite.

† d-spacing were covered by the diffraction pattern of pyrolytic graphite.

species identified on the surface of platforms made of pyrolytic graphite or electrographite as a function of temperature at which the heating was continued for a given time. Figure 118 shows normalized X-ray diffraction intensities of the species identified on the surface of a platform made of pyrolytic graphite as a function of heating time at a given temperature. For each species identified in Figs. 117 and 118, one diffraction line which was sensitive and free of interferences was chosen. The integrated diffraction intensity of the line was calculated and normalized to the strongest intensity of that line obtained at all temperatures tested using platforms made of electrographite. Since the x-ray diffractometer had not been calibrated for these species, the normalized diffraction intensity does not represent the relative concentration of the species present, but represents the amount of a given molybdenum-species present or formed as a function of the experimental variables (temperature and heating time).

Molybdenum-oxide. It is seen from Fig. 117 that in the temperature range used, the same Mo-species were identified on both pyrolytic graphite and electrographite surface. Three Mo-oxides: $\text{MoO}_{3(s)}$, $\text{Mo}_4\text{O}_{11(s)}$, and $\text{MoO}_{2(s)}$, were formed, all at relatively low temperatures (<1500 K). Since the injected molybdenum solution was made of $(\text{NH}_4)_2\text{MoO}_4$, it is reasonable to conclude that the $(\text{NH}_4)_2\text{MoO}_4$ was converted into $\text{MoO}_{3(s)}$ below 700 K. At higher temperatures, the $\text{MoO}_{3(s)}$ was converted into $\text{Mo}_4\text{O}_{11(s)}$, and the latter was converted into $\text{MoO}_{2(s)}$ below 1200 K.

Figure 117. Normalized X-ray diffraction intensities of the reaction products obtained from surfaces of pyrolytic graphite platforms (filled symbols) and electrographite platforms (open symbols), as a function of the temperature at which the heating was done:
 ($\diamond, \blacklozenge$) MoO_3 , ($\circ, \bullet$) Mo_4O_{11} , ($\Delta, \blacktriangle$) MoO_2 , ($\circ, \bullet$) Mo,
 ($\square, \blacksquare$) Mo_2C , ($\nabla, \blacktriangledown$) MoC. The heating time was 30 s.

Figure 118. Normalized X-ray diffraction intensities of the reaction products identified on the surface of pyrolytic graphite platforms at preset temperatures as a function of heating time. Preset temperatures: (a) 1170 K. (b) 1870 K. (c) 2270 K.

Molybdenum species identified in the charring temperature range where the dip in the charring curve occurs. In the temperature range corresponding to the occurrence of the dip in the charring curve (Fig. 113), i.e., 1200-1800 K, there are three species of Mo present: $\text{MoO}_{2(s)}$, $\text{Mo}_{(s)}$ and $\text{Mo}_2\text{C}_{(s)}$; among them only $\text{Mo}_{(s)}$ appears over the entire temperature range spanned by the dip. Also, the temperature corresponding to the maximum normalized diffraction intensity of $\text{Mo}_{(s)}$ coincides with the temperature corresponding to the minimum absorbance point in the dip. At this temperature (~1470 K), the normalized diffraction intensity of $\text{Mo}_{(s)}$ obtained using pyrolytic graphite was much less than that obtained using electrographite. This agrees with the observation that the dip in the molybdenum charring curve occurred when pyrolytic graphite was used, but not when electrographite was used. Furthermore, when a platform made of pyrolytic graphite was treated with 10 μL of 5% (w/v) $(\text{NH}_4)_2\text{MoO}_4$ solution and heated for 1 s from any charring temperature in the range 470-1500 K to the atomization temperature of 2970 K, both $\text{Mo}_2\text{C}_{(s)}$ and $\text{MoC}_{(s)}$ were formed on the surface, as identified by X-ray diffraction analysis. However, the X-ray diffraction intensity of $\text{Mo}_2\text{C}_{(s)}$ and $\text{MoC}_{(s)}$ formed at the charring temperature of 1470 K corresponding to the minimum of the dip in the charring curve (Fig. 115) was much less than that formed at the charring temperature of 670 K.

All these experimental results indicate that lesser amounts of Mo were present in various species in the condensed phase on a pyrolytic graphite surface if a charring temperature corresponding to the minimum of the dip in the charring curve (Fig. 115) was used. Since in this case there are also fewer Mo atoms in the gas phase, as indicated

by a decrease in the atomic absorption signal (Fig. 115), it is reasonable to conclude that some molybdenum is lost in the charring cycle if the charring is done from a pyrolytic graphite surface at a charring temperature corresponding to the minimum of the dip in the charring curve (Fig. 115). This phenomenon is likely to be related to the Mo species which are formed in the condensed phase at the above-mentioned charring temperature, viz. $\text{MoO}_{2(s)}$, $\text{Mo}_{(s)}$ and $\text{Mo}_2\text{C}_{(s)}$, as have been identified by various physico-chemical techniques used in this study. The results of studies by SEM and AES are presented in the following section.

$\text{Mo}_{(s)} - \text{Mo}_2\text{C}_{(s)} - \text{MoC}_{(s)}$ system. It has been reported [171] that the reduction of $\text{MoO}_{2(s)}$ by carbon leads to the formation of $\text{Mo}_2\text{C}_{(s)}$ in two steps: above 820 K $\text{Mo}_{(s)}$ begins to form; the carbide is formed only after the oxide is exhausted. We have found that $\text{MoO}_{2(s)}$ is mainly converted into $\text{Mo}_{(s)}$, as can be seen from Figs. 117 and 118(a), in which with increasing heating time at 1170 K, the intensity of $\text{MoO}_{2(s)}$ decreases rapidly to zero, whereas that of $\text{Mo}_{(s)}$ increases to a plateau, and that of $\text{Mo}_2\text{C}_{(s)}$ remains constant. It has also been reported [171] that $\text{Mo}_{(s)}$ can be converted into $\text{Mo}_2\text{C}_{(s)}$ by reaction with $\text{CO}_{(g)}$. Direct reaction of $\text{Mo}_{(s)}$ with graphite forms both $\text{Mo}_2\text{C}_{(s)}$ and $\text{MoC}_{(s)}$, starting at about 1270 K and forming the $\text{Mo}_2\text{C}_{(s)}$ phase first; the $\text{MoC}_{(s)}$ phase starts to form at about 1930 K [27]. In our system, $\text{Mo}_2\text{C}_{(s)}$ and $\text{MoC}_{(s)}$ phases also start to form at 1300 and 1900 K, respectively (Fig. 117). Figure 118(b) shows that with increasing heating time at 1870 K, the normalized X-ray diffraction intensity of $\text{MoC}_{(s)}$ increases, whereas that of $\text{Mo}_2\text{C}_{(s)}$ decreases gradually. This is consistent with the fact that the conversion of $\text{Mo}_2\text{C}_{(s)}$ into $\text{MoC}_{(s)}$ is

a slow reaction, as suggested by Müller-Vogt et al. [168]. It can be seen from Fig. 117 that at temperatures higher than 2100 K, a small amount of free $\text{Mo}_{(s)}$ co-exists with $\text{MoC}_{(s)}$. However, Fig. 118(c) shows that at 2270 K and with increasing heating time, the normalized X-ray diffraction intensity of $\text{MoC}_{(s)}$ decreases and that of $\text{Mo}_{(s)}$ and $\text{Mo}_2\text{C}_{(s)}$ are reduced to zero. When a platform made of pyrolytic graphite was heated from 670 K to 2300–2500 K (platform temperature) at a wall heating rate of 2 K ms^{-1} (total atomization time 1.3 s), the reaction products were $\text{MoC}_{(s)}$, $\text{Mo}_2\text{C}_{(s)}$ and $\text{Mo}_{(s)}$. Furthermore, the formation of free $\text{Mo}_{(s)}$ was critically dependent on the platform temperature; only $\text{MoC}_{(s)}$ and $\text{Mo}_2\text{C}_{(s)}$ were formed when the platform temperature was higher than 2500 K.

6.3.3. Scanning electron micrography and Auger electron spectrometry of molybdenum reaction products

Scanning electron micrographs of platforms heated at temperatures ranging from 670–2570 K were taken. Auger electron spectrometry of both pyrolytic graphite and electrographite was performed at only two temperatures, 1170 and 1470 K, in order to determine the cause for the dip in the charring curve of molybdenum (Fig. 115) when it was atomized from pyrolytic graphite. It is seen from Figs. 115 and 117 that at 1170 K, the dip in the charring curve is about to start and the reaction product is $\text{MoO}_{2(s)}$ only; at 1470 K, the temperature corresponding to the minimum of the dip (Fig. 115), the reaction products in the condensed phase are $\text{MoO}_{2(s)}$, $\text{Mo}_{(s)}$ and $\text{Mo}_2\text{C}_{(s)}$.

Figure 119 is a scanning electron micrograph of the reaction products at 1170 K. It is seen that large, well-formed crystals are randomly distributed on the pyrolytic graphite platform [Fig. 119(a)].

whereas the reaction site of the electrographite platform is mostly covered with needle-like crystallites with small plates on the top [Fig. 119(b)]. Whether large crystals or small crystallites are formed is probably related to the orientation and the size of the crystallites of the graphite material: large well-formed crystals are formed on the surface of the highly-oriented, anisotropic pyrolytic graphite, and small crystallites are formed on the surface of isotropic electrographite. Figure 120 shows an Auger electron spectrum of the substrate (pyrolytic graphite platform) and of a crystal on the platform - the electron micrograph is shown in Fig. 119(a). Figure 120(a) shows a large Auger peak of C and small Auger peaks of O which originated from the pyrolytic graphite platform. Figure 120(b) shows large Auger peaks of Mo and O, small peaks of C and N which originated from the surface of the crystal. Figure 120(c) shows Mo and O Auger peaks which originated from the inside of the crystal after one minute of ion sputtering. These results, together with the results obtained from X-ray diffraction analysis, suggest that there was no $\text{MoO}_{2(s)}$ on the pyrolytic graphite platform; the crystals consisted of $\text{MoO}_{2(s)}$, C (probably as CO species adsorbed on the surface of the crystals) and N, which might have originated from the $(\text{NH}_4)_2\text{MoO}_4$ used as the Mo sample and had been adsorbed on the surface of the crystals as N_2 species. Because the atomization characteristics and the X-ray intensity of species identified from the pyrolytic graphite and electrographite platforms were similar at 1170 K, no Auger electron spectrum of the electrographite platform was taken at this temperature. The needle-like crystallites shown in Fig. 119(b) probably consisted mainly of $\text{MoO}_{2(s)}$.

Figure 119. Scanning electron micrographs of platform surface on which 10 μL of 5% (w/v) aqueous solution of $(\text{NH}_4)_2\text{MoO}_4$ was deposited and the platform heated at 1170 K for 30 s: (a) pyrolytic graphite, $\times 1000$. (b) electrographite, $\times 1000$.

Figure 120. Auger electron spectrum of the reaction product (crystal) obtained from the surface of the pyrolytic graphite platform [as shown in Fig. 5(a)]:

- (a) substrate (pyrolytic graphite platform),
- (b) surface of the crystal,
- (c) inside of the crystal after 1 min of ion sputtering.

The scanning electron micrographs obtained at 1470 K from the pyrolytic graphite and electrographite platforms and the corresponding Auger depth profiles are shown in Figs. 121 and 122, respectively. Figure 122(a) shows that Mo and C were on the substrate (pyrolytic graphite) within a certain depth (ion sputtering time was about 12 min), for which a mixed spectrum of molybdenum carbide and carbon was observed, as shown in Fig. 123. Figure 122(b) is the Auger depth profile of the particle on the pyrolytic graphite platform and shows variable, high concentrations of Mo and O along the depth, but no C until after 24 min of ion sputtering, when the O concentration decreased to zero and the C concentration increased rapidly. It was found that at this instant the substrate was stripped of the particle and became exposed. Figure 122(c) is the Auger depth profile for electrographite and shows a thick layer of $\text{Mo}_{(s)}$ with a little O, covering the surface, with no Auger peak of carbide being detected until at greater depths. Thus, it is seen that although $\text{MoO}_{2(s)}$, $\text{Mo}_{(s)}$, and $\text{Mo}_2\text{C}_{(s)}$ were identified by X-ray diffraction analysis at 1470 K from both the pyrolytic graphite and the electrographite platform, their distribution on the surface was different. The reaction site of the electrographite platform was covered mainly with a relatively thick layer of $\text{Mo}_{(s)}$, which was loose and rough in appearance and contained a little $\text{MoO}_{2(s)}$. Near the surface of the electrographite substrate, $\text{Mo}_{(s)}$ was mixed with $\text{Mo}_2\text{C}_{(s)}$. However, for the pyrolytic graphite platform, large particles having rough surfaces were distributed on the rough surface of the pyrolytic graphite. Inside the large particles $\text{Mo}_{(s)}$ and $\text{MoO}_{2(s)}$ were detected, as indicated by the O component in Fig. 122(b), and by Fig. 117. Only

Figure 121. Scanning electron micrographs of the surface of the platform on which 10 μL of 5% (w/v) aqueous solution of $(\text{NH}_4)_2\text{MoO}_4$ was deposited and the platform heated at 1470 K for 30 s: (a) pyrolytic graphite, $\times 5000$, (b) electrographite, $\times 5000$.

Figure 122. Auger depth profiles of reaction products as shown in Fig. 121: (a) substrate (pyrolytic graphite platform), (b) particle on the substrate of pyrolytic graphite platform, (c) surface of electrographite platform.

Figure 123. Auger electron spectrum of Mo carbide and C (graphite) obtained from the substrate (pyrolytic graphite platform) after two min of ion sputtering. The first two (from the left) C peaks are the characteristic C peaks of the carbide formed.

$\text{Mo}_{(s)}$ and some $\text{Mo}_2\text{C}_{(s)}$ were found on the pyrolytic graphite substrate.

6.3.4. Mechanisms of molybdenum atomization.

Based on the results of AAS, X-ray diffraction analysis, SEM, and AES, the following reaction mechanisms are proposed. In the temperature range 1170–1470 K (corresponding to the decrease in the normalized X-ray diffraction intensity of $\text{MoO}_{2(s)}$ shown in Fig. 117) there were solid-solid or solid-gas reactions (reactions 6.1–6.3) at the substrate (pyrolytic graphite or electrographite) and at the surface of the crystallites.

Since most $\text{MoO}_{2(s)}$ crystallites formed on electrographite at 1170 K had a needle-like shape, they had a large total surface area available to react with $\text{C}_{(s)}$ and $\text{CO}_{(g)}$. Thus, reactions 6.1 and 6.2 may be kinetically favourable when Mo is atomized from an electrographite surface. However, at 1170 K, large, well-developed crystallites of $\text{MoO}_{2(s)}$ were formed on the pyrolytic graphite surface [Fig. 119(a)]. These large $\text{MoO}_{2(s)}$ crystallites offered much less surface area where reduction by $\text{C}_{(s)}$ and $\text{CO}_{(g)}$ could occur. Since the surface reaction took longer for the entire mass of the particle to be reduced through reactions 6.1 and 6.2, some $\text{MoO}_{2(s)}$ was left unreduced and was detected by AES. It is known that $\text{MoO}_{2(s)}$ is unstable at temperatures above 1270 K, some of it sublimes without decomposition, but the bulk of it disproportionates into $\text{Mo}_{(s)}$ and $\text{MoO}_{3(g)}$ [210]:

The gaseous products of reactions 6.4 and 6.5 flowed out of the graphite tube and were carried away by the Ar sheath gas flow. Therefore, less $\text{Mo}_{(s)}$ or Mo-species were available to be converted into $\text{Mo}_{(g)}$, which resulted in a dip in the charring curve of molybdenum obtained using the pyrolytic graphite platform.

the condensed phase at 2300–2500 K were $\text{MoC}_{(s)}$, $\text{Mo}_2\text{C}_{(s)}$ and $\text{Mo}_{(s)}$, and at 2600 K are $\text{MoC}_{(s)}$ and $\text{Mo}_2\text{C}_{(s)}$. Since no $\text{MoO}_{2(s)}$ was found at temperatures above 1600 K, the possibility that the $\text{Mo}_{(g)}$ formed in the temperature range 2100–2500 K originated from the reduction of $\text{MoO}_{2(s)}$ can be ruled out. However, the following three reactions are possible sources for $\text{Mo}_{(g)}$ formation, and are therefore assessed as to the thermodynamic feasibility of the reactions at the temperatures involved.

The standard free energy changes (ΔG^θ) at 2400 K calculated according to the data available [211–212] are all positive (10.8, 54.1, and 65.0 kJ mol⁻¹ for reactions 6.6–6.8, respectively), although reaction 6.6 has the lowest value. However, if the activities of the solid phases are much less than unity (which would be the case when the reaction surface is not completely covered with the solids at least one monolayer thick because of progressive stripping of the graphite surface on vaporization), reaction 6.6 should be spontaneous (i.e., $\Delta G < 0$).

Since MoC , Mo_2C and Mo are all found in the condensed phase prior to atomization, the following mechanisms for $\text{Mo}_{(g)}$ formation are considered.

5 of /de 5

Micro

Table 28. Maximum tolerable partial pressures of molybdenum for reactions 6.9 - 6.11

Temperature (K)	Reaction 6.9	Reaction 6.10	Reaction 6.11	Vapour pressure of 0.05 ng of Mo(s) converted into Mo(g) in the graphite furnace (atm)
	$\text{Mo(s)} \rightarrow \text{Mo(g)}$ P_{Mo} (atm)	$\text{MoC(s)} \rightarrow \text{Mo(g)} + \text{C(s)}$ P_{Mo} (atm)	$\text{Mo}_2\text{C(s)} \rightarrow 2\text{Mo(g)} + \text{C(s)}$ P_{Mo} (atm)	
2400	1.6×10^{-7}	6.8×10^{-8}	3.1×10^{-8}	1.3×10^{-7}
2500	5.6×10^{-7}	1.4×10^{-7}	6.4×10^{-8}	1.3×10^{-7}
2600	1.8×10^{-6}	8.4×10^{-7}	7.0×10^{-7}	1.4×10^{-7}
2700	5.4×10^{-6}	1.6×10^{-6}	1.3×10^{-6}	1.4×10^{-7}
2800	1.5×10^{-5}	7.1×10^{-6}	3.6×10^{-6}	1.5×10^{-7}
2900	3.5×10^{-5}	1.7×10^{-5}	9.2×10^{-6}	1.5×10^{-7}

thermodynamic data given by Gupta et al. [213] indicate that reaction 6.10b is spontaneous at temperatures >2670 K.

Figure 115 shows that for atomization from the tube wall, the charring curve of molybdenum starts to descend at about 2100 K; however, atomization of molybdenum starts at much higher temperatures: 2550 and 2900 K for charring temperatures of 670 and 1470 K, respectively. Figures 117 and 118 indicate that mainly $\text{MoC}_{(g)}$ was formed in the condensed phase at temperatures above 2170 K, and that the amount of $\text{MoC}_{(g)}$ formed decreased with increasing heating time. These experimental observations suggest that a part of the molybdenum was lost as $\text{MoC}_{(g)}$ at temperatures above 2170 K, which was supported by the observation of MoC^+ and MoC_2^+ species in the gas phase by mass spectrometry [213]. Hence, reaction 6.10a is possible. A congruently vaporizing composition of $\text{MoC}_{0.49}$ has been reported at temperatures from 2525 to 2575 K [214], whereas the appearance temperature of $\text{Mo}_{(g)}$ in our system is 2500 ± 80 K. However, no Mo_2C species has been found in the gas phase by mass-spectrometric studies [214]. Therefore, it is reasonable to conclude that reactions 6.11a and 6.11b do not occur. The activation energy values have been also calculated from the initial part of the atomic absorption signal profile using the method proposed by Sturgeon et al. [96]. A value of 610 ± 40 kJ mol $^{-1}$ was obtained using the pyrolytically coated graphite tube. This value is in good agreement with that of 625 kJ mol $^{-1}$ reported by Sneddon et al. [167], 695 kJ mol $^{-1}$ reported by Sturgeon et al. [96], and the value of 657 kJ mol $^{-1}$ [215] for reaction 6.9.

The scanning electron micrographs of the platform surface inside and outside the reaction site after molybdenum atomization at 2970 K

for 10 s are shown in Fig. 124. No molybdenum carbide was identified outside the reaction site by EDX from either the pyrolytic graphite or the electrographite surface. This suggests that the main reactions of molybdenum occur in the condensed phase.

On the basis of the evidence presented in this paper, we propose the mechanisms of molybdenum atomization shown in Fig. 125.

The activation energy obtained using analytical amounts of molybdenum or 10^5 -fold larger amounts of Mo [taken as aqueous solutions of $(\text{NH}_4)_2\text{MoO}_4$] by the method of Sturgeon et al. [167] was the same within experimental uncertainty. Also, charring curves obtained using analytical amounts (nanograms) of molybdenum had the same features as those obtained with larger amounts of molybdenum. However, since the amounts of molybdenum taken for the above charring curves are lower by orders of magnitude than the amounts used for study by X-ray diffraction, SEM, AES, and EDX, it cannot be said with complete certainty that the proposed reaction mechanisms (based on the results obtained by the above techniques) apply also to the usual analytical amounts of molybdenum.

6.4. Conclusions

In graphite furnace atomic absorption spectrometry, molybdenum atomized from a pyrolytic graphite surface shows a pronounced decrease in absorbance in the charring curve. The decrease spans a temperature range of 1200 K to 1800 K, whereas molybdenum atomized from an electrographite surface does not show any such decrease in the

Figure 124. Scanning electron micrographs of the surface of the graphite platforms heated at 670 K for 30 s and then atomized at 2970 K for 10 s:

(a) inside the reaction site of the pyrolytic graphite platform on which 10 μL of 0.2% (w/v)

aqueous solution of $(\text{NH}_4)_2\text{MoO}_4$ was deposited ($\text{Mo}_{(s)}$ was identified by EDX), x1000;

(b) the same as (a) but outside the reaction site (no $\text{Mo}_{(s)}$ could be identified by EDX), x1000;

(c) the same as (a) but from an electrographite platform on which 10 μL of 5% (w/v) aqueous

solution of $(\text{NH}_4)_2\text{MoO}_4$ was deposited, x5000;

(d) the same as (b) but from an electrographite platform on which 10 μL of 5% (w/v) aqueous

solution of $(\text{NH}_4)_2\text{MoO}_4$ was deposited, x5000.

Figure 125. Mechanisms of Mo atomization (Mo taken as an aqueous solution of $(\text{NH}_4)_2\text{MoO}_4$) in graphite furnace atomic absorption spectrometry. Dashed lines are for the reactions that are less favourable.

charring curve. The above decrease means that a part of the atomizable molybdenum is lost at the charring stage if charring is done from a pyrolytic graphite surface at a charring temperature within the above temperature range. Hence, a charring temperature < 1200 K should be used for determination of molybdenum from a pyrolytic graphite surface (i.e., pyrolytic graphite tube or pyrolytic graphite platform). However, a charring temperature as high as 2100 K can be used without risking any loss of molybdenum by volatilization if molybdenum is atomized from an electrographite surface.

Atomization curves of molybdenum atomized from the above-mentioned surfaces are similar except that the sensitivity of molybdenum is much greater when molybdenum is atomized from a pyrolytic graphite surface than from an electrographite surface.

The available experimental evidence (which is not conclusive) suggests that atomization of molybdenum from a graphite surface involves a final step: sublimation of $\text{Mo}_{(s)}$ to $\text{Mo}_{(g)}$ which is spontaneous at the appearance temperature of 2500 ± 80 K. and/or dissociation of $\text{MoC}_{(g)}$ which is spontaneous at temperatures > 2600 K.

The above experimental evidence for atomization of molybdenum was collected (and the mechanisms deduced from the evidence) using molybdenum taken as an aqueous solution of $(\text{NH}_4)_2\text{MoO}_4$ without any matrix. In real samples, the matrix may alter charring and atomization characteristics and atomization mechanisms of molybdenum in unpredictable ways.

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Appendices

Appendix I. Glossary of symbols

δ	- damping parameter, dimensionless
$A(t)$	- absorbance of analyte Y at time t, dimensionless
$A_{c,g}$	- cross-sectional area of of the gas ring, m^2
$A_{c,pr}$	- cross-sectional area of the graphite probe strip, m^2
$A_{c,w}$	- cross-sectional area of the graphite ring, m^2
$A_{i,g}$	- lateral inner surface area of the gas ring, m^2
$A_{i,w}$	- lateral inner surface area of the graphite ring, m^2
$A_{o,g}$	- lateral outer surface area of the gas ring, m^2
$A_{o,w}$	- lateral outer surface area of the graphite ring, m^2
A_p	- surface area of the platform segment of length dx , m^2
$A_{p,total}$	- total surface area of the platform, m^2
A_{1p}	- top surface area of the platform, m^2
A_{1pr}	- top surface area of the probe strip, m^2
A_{2p}	- bottom surface area of the platform, m^2
A_{2pr}	- bottom surface area of the probe strip, m^2
A_{1w}	- surface area of the furnace wall above the platform, m^2
A_{2w}	- surface area of the furnace wall below the platform, m^2
b	- thickness of the platform or the probe, m
b_0, b_1, b_2	- constants used in boundary temperatures at the furnace ends, $K\ m\ s^{-1}$
b_3	- constant used in boundary temperatures at the furnace ends, K

- B** - frequency factor, s^{-1}
B_g - boundary temperature of the gas phase at the furnace ends, K
B_{1w} - boundary temperature of the tube wall at the furnace centre, K
B_{2w} - boundary temperatures of the tube wall at the furnace ends, K
c - velocity of light in vacuum, $2.9979 \times 10^8 \text{ m s}^{-1}$
c₂ - Planck's second radiation constant, $1.4387 \times 10^{-2} \text{ m K}$
c_p - specific heat at constant pressure, $J \text{ kg}^{-1} \text{ K}^{-1}$
c_v - specific heat at constant volume, $J \text{ kg}^{-1} \text{ K}^{-1}$
C₁, C₂ - parameters used in equations describing the boundary temperatures of the tube wall at the furnace ends, $K \text{ m s}^{-1}$
div - the divergence of a vector field
d_i - inner diameter of the furnace tube, m
d_o - outer diameter of the furnace tube, m
D - concentration diffusion coefficient of the analyte atoms Y in the gas medium, $\text{m}^2 \text{ s}^{-1}$
D₀ - concentration diffusion coefficient of the analyte Y in the gas phase at 273 K and at one atmosphere, $\text{cm}^2 \text{ s}^{-1}$
D_T - thermal diffusion coefficient, $\text{cm}^2 \text{ s}^{-1}$
e - electronic charge, $1.6021 \times 10^{-19} \text{ C}$
E_a - activation energy, $J \text{ mol}^{-1}$
E_{h,j} - blackbody emissive power of surface j, $E_{h,j} = \sigma T_j^4$, W m^{-2}
ΔE - difference in energy of the line pair in the lower level, J

- f - oscillator strength of the line considered, dimensionless
 $f_{(y)}$ - rate of generation of analyte atoms per unit volume in the gas phase, number of atoms $m^{-3} s^{-1}$
 F_{i-j} - view factor of surface j from surface i , dimensionless
 $\mathcal{F}_{i-j}$ - total radiation interchange factor from surface i to surface j , dimensionless
 g - statistical weight of the lower level for the analysis line, dimensionless
 $grad$ - the gradient of a scalar field
 h - heat transfer coefficient, $W m^{-2} K^{-1}$
 $H(a, \omega=0.725a)$ - Voigt integral as a function of the line damping parameter, a , and of the distance of any part of an absorption line from the centre of the line, ω .
 I - electrical current, A
 I_g - initial temperature distribution of the gas phase, K
 I_p - initial temperature of the platform, K
 I_w - initial temperature distribution of the tube wall, K
 $J_{(y)}$ - atom flux vector of the analyte atom Y with respect to the velocity of the gas phase, number of atoms $m^{-2} s^{-1}$
 k - Boltzmann constant, $1.3803 \times 10^{-23} J K^{-1}$
 l_p - length of the platform, m
 l_{pr} - length of the probe, m
 l_w - length of the furnace tube wall, m
 m_e - electron mass, $9.1091 \times 10^{-31} kg$
 m_p - mass of the platform, kg
 $m(g)$ - atomic mass of Ar gas, kg
 $m(y)$ - atomic mass of analyte Y , kg

- M_g - molar mass of gas, kg mol^{-1}
 $M_{(Y)}$ - molar mass of analyte Y, kg mol^{-1}
 $n(g)$ - atomic density of gas, number of atoms m^{-3}
 $n_{(Y)}$ - number density of analyte atom, Y, number of atoms m^{-3}
 $N(t)$ - total number of free analyte atoms in the analysis volume at time t
 $N_{\text{condensed phase}}(t)$ - number of analyte atoms in the condensed phase at time t
 N_{max} - maximum number of free analyte atoms in the analysis volume
 N_0 - initial number of analyte atoms introduced into the furnace
 P - gas pressure, Pa
 P_{in} - input electrical power, W
 q - correction factor which accounts for hyperfine structure in the analysis line, dimensionless
 Q - proportionality constant linking absorbance and number of free atoms in the analysis volume, absorbance per atom
 $\dot{Q}_{\text{cond}, i-j}$ - rate of heat transfer by thermal conduction from i to j, W
 $\dot{Q}_{\text{conv}}$ - rate of heat transfer by convection, W
 $\dot{Q}_{\text{rad}, i-j}$ - rate of heat transfer by radiation from i to j, W
 $\dot{Q}_s$ - rate of heat storage, W
 $\dot{Q}_t$ - rate of heat transfer, W
 r - radial coordinate in the cylindrical system
 dr - infinitesimal increment in the radial direction, m
 r' - specific position in the radial coordinate

- r_p - radius of the graphite rod assumed in the theoretical model of the gas temperature in the graphite platform furnace, m
- Δr - radial distance from the platform, m
- R - universal gas constant, $8.3144 \text{ J K}^{-1} \text{ mol}^{-1}$
- $R(t)$ - normalized response of the system upon supply of an infinitely rapid pulse of atoms, dimensionless
- R_w - electrical resistance of the graphite furnace tube wall, ohm
- s - transverse cross-sectional area of the furnace tube, m^2
- S - Boundary temperature function of the tube wall at the furnace ends at steady state, K
- Δs - distance between the graphite furnace tube and the graphite shield, m
- t - time, s
- t_{app} - appearance time of the analyte atoms, s
- t_p - time corresponding to the maximum number of free analyte atoms in the analysis volume or to the peak absorbance, s
- Δt - size of time step, s
- dt - infinitesimal time increment, s
- T - temperature, K
- T_b - brightness temperature, K
- T_i - initial tube wall temperature at the furnace centre, K
- T_f - final tube wall temperature at the furnace centre, K
- T_g - gas temperature, K
- $T_{g, avg}$ - average gas temperature over the length of the platform at radial distance, Δr , from the platform, K

- $T_{g, eff}$ - effective gas temperature determined by the two-line atomic absorption method, K
 $T_{g, w \text{ avg}}$ - weighted-average gas temperature of the furnace, K
 T_p - platform temperature, K
 T_s - temperature of the graphite shield in Chapter 1 and of the surrounding gas in Chapter 5, K
 T_w - temperature of the furnace tube wall, K
 $T_{w, avg}$ - average temperature of the tube wall over the length of the platform, K
 $T_{w, plateau}$ - plateau temperature of the tube wall at the furnace ends at steady state, K
 T_0 - temperature of 273 K
 u_g - velocity vector of the gas medium, $m \text{ s}^{-1}$
 $u_{x, g}$ - x component of the gas velocity vector, $m \text{ s}^{-1}$
 w - width of the platform or the probe, m
 Δw - additional width of the platform at its ends, m
 x - axial coordinate in the cylindrical system
 dx - infinitesimal increment in the x direction, m
 Y - analyte
 z - z coordinate used in Chapter 5
 dz - infinitesimal increment in the z direction
 Z - partition function

Greek letters

- α - heating rate of the tube wall at the furnace centre, $K \text{ ms}^{-1}$
 β - fraction of analyte atomized

- γ - exponential power of the temperature-dependent diffusion coefficient, dimensionless
- γ_w - electrical resistivity of the graphite furnace tube, ohm-cm
- $\gamma(\lambda_2/\lambda_1)$ - dimensionless function related to Doppler half-widths and Voigt integrals of the line pair
- δ', δ'' - length and width of the infinitesimal gas ring which contains the surface area of the platform centre where the analyte sample is deposited
- ϵ_i - total normal emissivity of surface i , dimensionless
- κ_i - thermal conductivity of i , $\text{W m}^{-1} \text{K}^{-1}$
- λ_c - operational wavelength of an optical pyrometer, m
- $\Delta\nu_D$ - Doppler half-width of the atomic line, s^{-1}
- ρ_g - density of gas inside the furnace, kg m^{-3}
- ρ_i - density of graphite in i , kg m^{-3}
- σ - Stefan-Boltzmann constant, $5.6703 \times 10^{-8} \text{ W m}^{-2} \text{K}^{-4}$
- τ_p - time interval from the time when the amount of free analyte atoms in furnace gives 1% absorption to the time when the same amount of above atoms is removed from the analysis volume, s
- τ_R - mean residence time of analyte atoms, s

Subscripts

Unless otherwise defined in the above list of symbols, subscripts are defined below:

- g - gas or gas ring
- g, s - sheath gas

- p - graphite platform
- pr - graphite probe or graphite probe strip
- s - graphite shield in Chapter 1 or the surrounding gas in Chapter 5
- w - furnace tube wall or the graphite ring of the tube wall

Appendix II. Numerical approximation of equations 1.10-1.13

In the numerical approximation, two integers m and j and step sizes Δx and Δt are chosen with the stipulation that $l_w/\Delta x$ is an integer. The m integer indicates the x increment and the j integer indicates the t increment, i.e.,

$$x_m = m\Delta x, \quad \text{for } m = 0, 1, \dots, mm, \quad mm = l_w/2\Delta x; \quad 1.14a$$

$$t_j = j\Delta t, \quad \text{for } j = 0, 1, \dots, jj. \quad 1.14b$$

Figure 126 shows the nodal geometry for the platform furnace and the control volume.

Figure 126. The nodal geometry and the control volume for the numerical approximation of the temperature distribution of the furnace wall in the graphite platform furnace.

The finite-difference approximations of the first and the second derivative for the nodal points (x_m, t_j) for $m = 1, 2, \dots, m-1$, $j = 1, 2, \dots, j$ are [76-77]

$$\frac{\partial T_w(x, t)}{\partial t} = \frac{T_w(x_m, t_{j+1}) - T_w(x_m, t_j)}{\Delta t} \quad 1.15a$$

$$\frac{\partial^2 T_w(x, t)}{\partial x^2} = \frac{T_w(x_{m+1}, t_j) - 2T_w(x_m, t_j) + T_w(x_{m-1}, t_j)}{\Delta x^2} \quad 1.15b$$

Substituting equations 1.15a and 1.15b into equation 1.10, and denoting the nodal points (x_m, t_j) as (m, j) , and omitting, for simplicity, the dependence of the property values on the space and time coordinates, and rearranging, equation 1.10 can be approximated as

$$\begin{aligned} T_w(m, j+1) = & \frac{\Delta t}{c_{p, w} \rho_w A_{c, w}(m) \Delta x} \left[\frac{A_{c, w}(0) \gamma_w(m, j)}{A_{c, w}(m) \gamma_w(0, j)} P_{in}(0, j) \right. \\ & + \frac{A_{o, w}(m) \kappa_{g, s}}{\Delta s} T_s + \sigma \mathcal{F}_{w-s} A_{o, w}(m) T_s^4 + \sigma \mathcal{F}_{w-p} A_{i, w} T_p^4(j) \left. \right] \\ & + Fo_w [T_w(m+1, j) + T_w(m-1, j)] \\ & + [1 - 2Fo_w \frac{\Delta t}{c_{p, w} \rho_w A_{c, w}(m) \Delta x} \left[\frac{A_{o, w}(m) \kappa_{g, s}}{\Delta s} \right. \\ & \left. + \sigma (\mathcal{F}_{w-s} A_{o, w}(m) + \mathcal{F}_{w-p} A_{i, w}) T_w^3(m, j) \right]] T_w(m, j) \quad 1.16 \end{aligned}$$

for both the graphite tube furnace and the graphite platform

furnace and for

$$m = 1, 2, \dots, mm-1, \quad j = 1, 2, \dots, jj.$$

Equation 1.16 is subject to the following boundary conditions for both the graphite tube furnace and the graphite platform furnace:

$$T_w(m, j) = B_{1w}(j), \quad \text{for } m = 0, \quad j = 0, 1, \dots, jj; \quad 1.17a$$

$$T_w(m, j) = B_{2w}(j), \quad \text{for } m = mm, \quad j = 0, 1, \dots, jj; \quad 1.17b$$

and the initial condition for both furnaces

$$T_w(m, j) = I_w(m), \quad \text{for } m = 0, 1, \dots, mm, \quad j = 0. \quad 1.18a$$

The additional initial condition for the graphite platform furnace is:

$$T_p(j) = I_p, \quad m = 0, 1, \dots, mp, \quad j = 0. \quad 1.18b$$

In the above equations, mp is the integer of $l_p/2\Delta x$; Fo_w is the Fourier modulus for the furnace tube wall and is defined as

$$Fo_w = \frac{\Delta t \cdot \kappa_w}{c_{p,w} \rho_w \Delta x^2}. \quad 1.19$$

$P_{in}(0, j)$ is the input power applied at the central node, and is discretized from equation 1.13 as

$$\begin{aligned}
P_{in}(0,j) = & c_{p,w} \rho_w A_{c,w}(0) \Delta x \frac{T_w(0,j+1) - T_w(0,j)}{\Delta t} \\
& - \frac{2 \kappa_w A_{c,w}(0)}{\Delta x} [T_w(1,j) - T_w(0,j)] + \kappa_{g,s} A_{o,w}(0) \frac{[T_w(0,j) - T_g]}{\Delta s} \\
& + \sigma \mathcal{F}_{w-s} A_{o,w}(0) [T_w^4(0,j) + T_g^4] - \sigma \mathcal{F}_{w-p} A_{i,w} [T_w^4(0,j) - T_p^4(j)]. \quad 1.20
\end{aligned}$$

Thus, the temperature of the tube wall at any node m , at time step $j+1$ is explicitly expressed in terms of the temperature distribution at time step j . Knowing the initial and the boundary condition, the temperature distribution of the tube wall at any time can be calculated, provided that numerical stability of the discretized algebraic equation 1.16 is maintained. The stability criterion for equation 1.16 is that in the last term in equation 1.16, the coefficient for $T_w(i,j)$ must be equal to or larger than zero, i.e.,

$$\begin{aligned}
1 - 2 Fo_w - \frac{\Delta t}{c_{p,w} \rho_w A_{c,w}(m) \Delta x} \left[\frac{A_{o,w}(m) \kappa_{g,s}}{\Delta s} \right. \\
\left. + \sigma (\mathcal{F}_{w-s} A_{o,w}(m) + \mathcal{F}_{w-p} A_{i,w}) T_w^3(m,j) \right] \geq 0. \quad 1.21
\end{aligned}$$

This criterion ensures that the solution of equation 1.16 (discretized from equation 1.10) by forward finite-difference approximation will converge to the solution of equation 1.10. If this criterion is not satisfied, then the error produced by the forward finite-difference approximation will grow without limits as time integer j increases, and a situation will be created in which the second law of thermodynamics will be violated [75-76]. Equation 1.21 shows that the stability criterion automatically limits the choice of Δt , once Δx has been decided.

Appendix III. Numerical approximation of equations 3.7-3.10

In the approximation, equation 3.8 has been split into two steps using the method of fractional steps [110-111] which involves implicit finite-difference approximation in only one dimension: thermal conduction in the radial direction, and thermal expansion and conduction in the axial direction.

The expression for thermal conduction in the radial direction is

$$\begin{aligned} \Delta v_g(r) \rho_g(x, r, t) c_{p, g} \frac{T'_g(x, r, t+\Delta t) - T_g(x, r, t)}{\Delta t} \\ = 2\pi r \Delta x \Delta r \kappa_g(x, r, t) \frac{\partial^2 T'_g(x, r, t+\Delta t)}{\partial r^2} \end{aligned} \quad 3.15$$

The expression for thermal expansion and conduction in the axial direction is:

$$\begin{aligned} \rho_g(x, r, t) c_{p, g} \left[\frac{T_g(x, r, t+\Delta t) - T'_g(x, r, t+\Delta t)}{\Delta t} + u_{x, g}(x, r, t) \frac{\partial T_g(x, r, t+\Delta t)}{\partial x} \right] \\ = \kappa_g(x, r, t) \frac{\partial^2 T_g(x, r, t+\Delta t)}{\partial x^2} \end{aligned} \quad 3.16$$

In the above equations, $T'_g(x, r, t+\Delta t)$ denotes the intermediate value due to radial thermal conduction alone, in which heat is considered to be transferred radially through the area of the radial interface of the infinitesimal gas ring, $2\pi r \Delta x$ (i.e., $A_{o, g}$ and $A_{i, g}$ shown in Fig. 127), into the control volume Δv_g to avoid the singularity at the tube centre in the first term of the right side of equation 3.8.

Figure 127. The nodal geometry (a) and the control volume (b) for the numerical approximation of the temperature distribution of the gas phase.

$T_g(x, r, t + \Delta t)$ is the complete approximation made at the end of a whole step, i.e., after the axial thermal expansion and conduction has been taken into account.

The velocity and the temperature of the gas were calculated according to the following steps.

Step 1. Use equation 3.15 to calculate $T'_g(x, r, t + \Delta t)$.

Step 2. Assuming $\partial T_g(x, r, t) / \partial x = 0$, calculate u_{xg} using equation 3.7, in which $T'_g(x, r, t + \Delta t)$ calculated in step 1 is used as the temperature at $t + \Delta t$.

Step 3. u_{xg} obtained in step 2 is used in equation 3.16 to calculate the gas temperature $T_g(x, r, t + \Delta t)$.

Step 4. $T_g(x, r, t + \Delta t)$ obtained in the above step is used in equation 3.7 to recalculate u_{xg} which is then used to recalculate $T_g(x, r, t + \Delta t)$ using equation 3.16.

Step 5. Repeat step 4 several times until the velocity and the temperature of the gas are stabilized within 0.1%.

In the numerical approximation, three integers m , n , and j and three step sizes Δx , Δr and Δt are chosen with the stipulation that $l_w / \Delta x$ and $d_i / \Delta r$ are integers. The m integer indicates the x increment, the n integer indicates the r increment and the j integer indicates the t increment, i.e.,

$$x_m = m \Delta x, \quad \text{for } m = 0, 1, \dots, m_m, \quad m_m = l_w / (2\Delta x); \quad 3.17a$$

$$r_n = n \Delta r, \quad \text{for } n = 0, 1, \dots, n_n, \quad n_n = d_i / (2\Delta r); \quad 3.17b$$

$$t_j = j \Delta t, \quad \text{for } j = 0, 1, \dots, j_j. \quad 3.17c$$

The nodal geometry used for the temperature distribution of the gas

phase in the graphite tube furnace and in the graphite platform furnace as well as the control volume are shown in Fig. 127. In the graphite platform furnace, the platform occupies the axial nodes $m = 0, 1, \dots, m_p$ and the radial nodes $n = 0, 1, \dots, n_p$. In Fig. 127, the control volume Δv_g and the outer and inner areas of the radial interface of the control volume of the gas ring, $A_{o,g}$ and $A_{i,g}$, are only functions of the radial coordinate since the step size Δx is a constant, and are expressed as follows:

$$\Delta v_g(r_n) = \pi [(r_n + \Delta r/2)^2 - (r_n - \Delta r/2)^2] \Delta x; \quad 3.18a$$

$$A_{o,g}(r_n) = 2\pi (r_n + \Delta r/2) \Delta x; \quad 3.18b$$

$$A_{i,g}(r_n) = 2\pi (r_n - \Delta r/2) \Delta x. \quad 3.18c$$

The one-dimensional finite-difference approximations of the first and the second derivative for the nodal points (x_m, r_n, t_j) for $m = 1, \dots, m-1$, $n = 1, 2, \dots, n-1$ and $j = 1, 2, \dots, j_j$ are [76-77]

$$\frac{\partial^2 T_g(x_m, r_n, t_j)}{\partial r^2} = \frac{T_g(x_m, r_{n+1}, t_j) - 2T_g(x_m, r_n, t_j) + T_g(x_m, r_{n-1}, t_j)}{\Delta r^2}; \quad 3.19a$$

$$\frac{\partial T_g(x_m, r_n, t_j)}{\partial x} = \frac{T_g(x_{m+1}, r_n, t_j) - T_g(x_{m-1}, r_n, t_j)}{2\Delta x}; \quad 3.19b$$

$$\frac{\partial^2 T_g(x_m, r_n, t_j)}{\partial x^2} = \frac{T_g(x_{m+1}, r_n, t_j) - 2T_g(x_m, r_n, t_j) + T_g(x_{m-1}, r_n, t_j)}{\Delta x^2}. \quad 3.19c$$

Applying equation 3.19a to equation 3.15, denoting the nodal points (x_m, r_n, t_j) as (m, n, j) and omitting, for simplicity, the dependence of the property values on the space and time coordinates,

and noting the boundary conditions given in equation 3.9 and rearranging equation 3.9, the following equations are obtained.

$$T_g(m, n, j) = (1 + 4Fo_{n+1}) T'_g(m, n, j+1) - 4Fo_{n+1} T'_g(m, n+1, j+1), \quad 3.20a$$

for the graphite tube furnace, $m = 0, 1, \dots, mm$, $n = 0, j = 0, \dots, jj$;

for the graphite platform furnace, $m = mp+1, \dots, mm$, $n = 0, j = 0, \dots, jj$.

$$\begin{aligned} T_g(m, n, j) = & -Fo_{np} \frac{\Delta r A_{i, g}(n)}{\Delta v_g(n)} T_p(j+1) \\ & + [1 + Fo_{np} \frac{\Delta r A_{i, g}(n)}{\Delta v_g(n)} + Fo_{n+1} \frac{\Delta r A_{o, g}(n)}{\Delta v_g(n)}] T'_g(m, n, j+1) \\ & - Fo_{n+1} \frac{\Delta r A_{o, g}(n)}{\Delta v_g(n)} T'_g(m, n+1, j+1), \end{aligned} \quad 3.20b$$

for the graphite platform furnace, $m = 0, 1, \dots, mp$, $n = np+1$,

$j = 0, \dots, jj$.

$$\begin{aligned} T_g(m, n, j) = & -Fo_{n-1} \frac{\Delta r A_{i, g}(n)}{\Delta v_g(n)} T'_g(m, n-1, j+1) \\ & + [1 + Fo_{n-1} \frac{\Delta r A_{i, g}(n)}{\Delta v_g(n)} + Fo_{nn} \frac{\Delta r A_{o, g}(n)}{\Delta v_g(n)}] T'_g(m, n, j+1) \\ & - Fo_{nn} \frac{\Delta r A_{o, g}(n)}{\Delta v_g(n)} T'_g(m, j+1), \end{aligned} \quad 3.20c$$

for both graphite tube furnace and graphite platform furnace and

for $m = 0, \dots, mm$, $n = nn$, $j = 0, \dots, jj$.

$$\begin{aligned}
T_g(m, n, j) = & - Fo_{n-1} \frac{\Delta r \lambda_{1,g}(n)}{\Delta v_g(n)} T'_g(m, n-1, j+1) \\
& + [1 + Fo_{n-1} \frac{\Delta r \lambda_{1,g}(n)}{\Delta v_g(n)} + Fo_{n+1} \frac{\Delta r \lambda_{0,g}(n)}{\Delta v_g(n)}] T'_g(m, n, j+1) \\
& - Fo_{n+1} \frac{\Delta r \lambda_{0,g}(n)}{\Delta v_g(n)} T'_g(m, n, j+1), \quad 3.20d
\end{aligned}$$

for the graphite tube furnace, $m = 0, \dots, mm,$

$n = 1, \dots, nn-1, \quad j = 0, \dots, jj;$

for the graphite platform furnace, $m = 0, \dots, mp,$

$n = np+2, \dots, nn-1, \quad j = 0, \dots, jj;$

and $m = mp+1, \dots, mm, \quad n = 1, \dots, nn-1, \quad j = 0, \dots, jj.$

$$T_p(j+1) = T'_g(m, n, j+1), \quad 3.20e$$

for the graphite platform furnace, $m = 0, \dots, mp,$

$n = 0, \dots, np, \quad j = 0, \dots, jj.$

In the above equations, $\Delta v_g(n)$, $\lambda_{1,g}(n)$ and $\lambda_{0,g}(n)$ are as expressed in equation 3.18. Fo is the Fourier modulus for the gas phase and is expressed as follows

$$Fo = \frac{\Delta t \kappa_g}{c_{p,g} \rho_g \Delta r^2}.$$

Fo_{n-1} , Fo_{n+1} , Fo_{np} and Fo_{nn} in above equations are the Fourier moduli in which thermal conductivities are for the arithmetic mean temperature of the node (m, n) and the node $(m, n-1)$, of the node (m, n) and the node $(m, n+1)$, of the node $(m, np+1)$ and the node (m, np) and of the node (m, n) and the tube wall, respectively.

Similarly, using equations 3.19b-3.19c, equation 3.16 can be

expressed as follows:

$$T'_g(m, n, j+1) = (1 + 2Fo_{m+1}) T_g(m, n, j+1) - 2Fo_{m+1} T_g(m+1, n, j+1), \quad 3.21a$$

for the graphite tube furnace, $m = 0, n = 0, \dots, nn, j = 0, \dots, jj$;

for the graphite platform furnace, $m = 0, n = np+1, \dots, nn, j = 0, \dots, jj$.

$$\begin{aligned} T'_g(m, n, j+1) = & - [Fo_{m-1} + u_{x,g}(m, n, j) \frac{\Delta t}{2\Delta x}] T_g(m-1, n, j+1) \\ & + [1 + Fo_{m-1} + \frac{Fo_{mm}}{2} + \frac{u_{x,g}(m, n, j) \Delta t}{4\Delta x}] T_g(m, n, j+1) \\ & - [\frac{Fo_{mm}}{2} - \frac{u_{x,g}(m, n, j) \Delta t}{4\Delta x}] T_{g,e}. \end{aligned} \quad 3.21b$$

for both graphite tube furnace and graphite platform furnace and for

$$m = mm, \quad n = 0, \dots, nn, \quad j = 0, \dots, jj.$$

$$\begin{aligned} T'_g(m, n, j+1) = & - [Fo_{m-1} + u_{x,g}(m, n, j) \frac{\Delta t}{2\Delta x}] T_g(m-1, n, j+1) \\ & + (1 + Fo_{m-1} + Fo_{m+1}) T_g(m, n, j+1) \\ & - [Fo_{m+1} - u_{x,g}(m, n, j) \frac{\Delta t}{2\Delta x}] T_g(m+1, n, j+1). \end{aligned} \quad 3.21c$$

for the graphite tube furnace, $m = 1, \dots, mm-1$.

$$n = 0, \dots, nn, \quad j = 0, \dots, jj;$$

for the graphite platform furnace, $m = 1, \dots, mm-1$.

$$n = np+1, \dots, nn, \quad j = 0, \dots, jj;$$

and

$$m = np+1, \dots, mm-1, \quad n = 0, \dots, nn, \quad j = 0, \dots, jj.$$

In the above equations, Fo is the Fourier modulus for the gas phase which is expressed as

$$Fo = \frac{\Delta t \kappa_g}{c_{p,g} \rho_g \Delta x^2}.$$

Fo_{m-1} , Fo_{m+1} and Fo_{mm} represent the Fourier moduli in which the thermal conductivities are for the arithmetic mean temperature of the node (m, n) and node $(m-1, n)$, of the node (m, n) and the node $(m+1, n)$, and of the node (m, n) and the gas outside the furnace tube, respectively.

Equation 3.7 is simulated as follows.

$$u_{x,g}(m, n, t) = 0, \quad 3.22a$$

for the graphite tube furnace in all steps,

$$m = 0, \quad n = 0, \dots, nn, \quad j = 0, \dots, jj;$$

for the graphite platform furnace in all steps,

$$m = 0, \quad n = np+1, \dots, nn, \quad j = 0, \dots, jj,$$

$$\text{and} \quad m = 0, \dots, mp, \quad n = 0, \dots, np, \quad j = 0, \dots, jj.$$

$$u_{x,g}(m+1, n, j) = u_{x,g}(m, n, j) + \frac{u_{x,g}(m, n, j) \Delta t}{\Delta x} \frac{T'_g(m, n, j+1) - T_g(m, n, j)}{T_g(m, n, j)}, \quad 3.22b$$

for the graphite tube furnace in step 2 and for

$$m = 0, \dots, mm-1, \quad n = 0, \dots, nn, \quad j = 0, \dots, jj;$$

for the graphite platform furnace in step 2 and for

$$m = 0, \dots, mm-1, \quad n = np+1, \dots, nn, \quad j = 0, \dots, jj,$$

$$\text{and} \quad m = mp, \dots, mm-1, \quad n = 0, \dots, nn, \quad j = 0, \dots, jj.$$

$$u_{x,g}(m+1, n, j) = u_{x,g}(m, n, j) \frac{T_g(m+1, n, j)}{T_g(m, n, j)} + \frac{u_{x,g}(m, n, j) \Delta t}{\Delta x} \frac{T_g(m, n, j+1) - T_g(m, n, j)}{T_g(m, n, j)} \quad 3.22c$$

for the graphite tube furnace in steps 4-5 and for

$$m = 0, \dots, mm-1, \quad n = 0, \dots, nn, \quad j = 0, \dots, jj;$$

for the graphite platform furnace in steps 4-5 and for

$$m = 0, \dots, mm-1, \quad n = np+1, \dots, nn, \quad j = 0, \dots, jj,$$

$$\text{and} \quad m = mp, \dots, mm-1, \quad n = 0, \dots, nn, \quad j = 0, \dots, jj.$$

Thus, by solving equations 3.20-3.22 with the steps outlined above, the temperature distribution of the gas at any space node (m, n) at any time step $j+1$ can be obtained using the temperature distribution of the gas at time step j .

Appendix IV. Derivation of equation 4.6

Applying a mass balance for analyte atoms Y, we have in general [155].

$$\frac{d}{dt} \int_{v(y)} n(y) dv = \int_{v(y)} f(y) dv, \quad 4.20$$

where $v(y)$ denotes that the integration is to be performed over the region of space occupied by the body of analyte atoms Y in its current configuration and $v(y)$ is a function of time; $n(y)$ represents the atom density of analyte Y (number of atoms per unit volume); $f(y)$ denotes the rate of production of analyte atoms Y per unit volume by homogeneous chemical reactions or by the presence of an atom source.

Interchanging the differentiation and integration in the above operation using the transport theorem [155], i.e.,

$$\frac{d}{dt} \int_{v(y)} n(y) dv = \int_{v(y)} \left[\frac{d(y)n(y)}{dt} + n(y) \operatorname{div} u(y) \right] dv, \quad 4.21$$

where $u(y)$ is the velocity vector of analyte atoms Y with respect to the fixed frame of reference, we have

$$\int_{v(y)} \left[\frac{d(y)n(y)}{dt} + n(y) \operatorname{div} u(y) \right] dv = \int_{v(y)} f(y) dv. \quad 4.22$$

Since this applies to an arbitrary body of analyte atoms Y, it is concluded that at every point of the body

$$\frac{d_{(y)}n_{(y)}}{dt} + n_{(y)} \operatorname{div} u_{(y)} = f_{(y)}. \quad 4.23a$$

This is usually referred to as equation of continuity [155]. Equation 4.23a can also be rearranged as

$$\frac{\partial n_{(y)}}{\partial t} + \operatorname{div} [n_{(y)} u_{(y)}] = f_{(y)}, \quad 4.23b$$

where $n_{(y)}u_{(y)}$ is the atom flux of analyte Y with respect to the fixed frame of reference. $n_{(y)}u_{(y)}$ can also be expressed [155] as

$$n_{(y)} u_{(y)} = n_{(y)} u + J_{(y)}, \quad 4.24a$$

where u is the mass-averaged gas velocity; $J_{(y)}$ is the atom flux of analyte Y with respect to the mass-averaged velocity. Since the system considered consists of an extremely small amount of analyte atoms within the medium gas (the internal gas), the velocity of the medium gas, u_g , can be taken as the mass-averaged velocity. So, we have

$$n_{(y)} u_{(y)} = n_{(y)} u_g + J_{(y)}. \quad 4.24b$$

Substituting equation 4.24b into equation 4.23b, the form of equation 4.6 is obtained, i.e.,

$$\frac{\partial n_{(y)}}{\partial t} + \operatorname{div} [n_{(y)} u_g + J_{(y)}] = f_{(y)}.$$

END

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