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FACTORS AFFECTING ATOMIZATION IN GRAPHITE FURNACE
ATOMIC ABSORPTION SPECTROMETRY

by

© Shye-Bin Chang, B.Sc., M.Sc.

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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ABSTRACT - A theoretical model, based on a pseudo-first-order consecutive rate process, has been established which describes transient characteristics of an atomic absorption pulse generated in a pulse-heated graphite furnace. The effects of change in the parameters on the shape and height of the atom population-time curves have been studied using a numerical integration method. The effect of heating rate and furnace-tube length are presented and discussed. The experimental results agree with the predictions of the simple theoretical model that peak-height absorbance will increase with increasing heating rates up to a limiting heating rate. Beyond this limiting heating rate, peak-height absorbance will either remain constant or decrease depending on the role of expulsion loss in the analyte vapour loss mechanism.

Thermodynamically, the conversion of the metal oxide into metal in the condensed phase at the appearance temperature by carbon reduction or by thermal decomposition is determined by the instantaneous partial pressures of oxygen and carbon monoxide inside the furnace. A theoretical estimation of the partial pressures of oxygen and carbon monoxide inside the furnace has been made. The instantaneous partial pressure of oxygen inside the furnace depends strongly on the heating rate of the furnace and the surface reactivity of the graphite. Theoretical studies show that in graphite furnaces the role of carbon is not limited to reduction of metal oxide to metal, but also extends to reducing the partial pressure of oxygen in the furnace to the value required for thermal decomposition of metal

oxide to be thermodynamically favourable at the appearance temperature of the metal.

For the capacitive discharge technique, three tubular furnaces made of anisotropic pyrolytic graphite and having different configurations of lamellar planes relative to the optical axis of the furnace, were studied. These furnaces were very rapidly heated ($6-60 \text{ K ms}^{-1}$) by discharge of a large bank of electrolytic capacitors. The requirements for the detection system for recording the transient signal generated by fast heating of the furnace were also studied.

Temperature distribution in the graphite tube surface and the gas-filled space inside the furnace were theoretically and experimentally studied. The results indicate that the distribution of the surface temperature and the gas phase temperature are very different for different orientations (perpendicular or parallel) of lamellar planes of the anisotropic pyrolytic graphite tube relative to the optical axis. These differences result in a large difference in the atomic absorption signals. Variations in the results from different configurations have been attributed to change in the spatial temperature distribution of the graphite surface, in the gas phase temperature, in the expulsion of analyte atoms from the analysis cell during heating, and in the reactivity of the graphite surface.

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CHAPTER 1
THEORETICAL STUDY OF TRANSIENT SIGNAL IN
GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY

At any instant, t , the relationship between the measured absorbance, $A(t)$, and the number of the analyte atoms, $N(t)$, at a characteristic spectral line in atomic absorption spectrometry is given by the following equation [1-3]:

$$A(t) = \frac{0.434 \sqrt{4\pi \ln 2} e^2 g_i \exp(-E_i/kT) f H(a, \omega=0.725a)}{m c \Delta\nu_D Q S q} N(t) \quad 1.1$$

where e and m are the charge and the mass of the electron, c is the velocity of light, f is the oscillator strength of the resonance line considered, g_i and Q are the statistical weight of the lower level of the transition and the partition function of the analyte element, E_i is the energy of the lower level, S is the cross-sectional area of the furnace, q is a correction factor which accounts for the hyperfine structure in the analytical line [1], $\Delta\nu_D$ is the Doppler width at half-intensity of the atomic absorption line inside the furnace, $H(a, \omega=0.725a)$ is the Voigt integral determined by the damping parameter a [4] and $N(t)$ is the time dependent total number of free analyte atoms in the observation zone of the furnace.

The measured absorbance reflects the integral of the number density of analyte atoms along the length of observation. As an approximation it is assumed that $\Delta\nu_D$ and $H(a, \omega=0.725a)$ are independent

of both the position of the absorbing vapour within the furnace as well as the vapour temperature. Temperature gradients in the vapour are neglected. Under these assumptions, the measured absorbance is proportional to the number of free analyte atoms inside the furnace.

The transient atomic absorption signal generated by rapid atomization of an analyte in a pulse-heated electrothermal atomizer provides a temporal history of the atom population. Several dynamic models for interpretation of this temporal signal generated by various types of electrothermal atomizers have been proposed [2,4-23].

Recent experimental studies by HOLCOMBE et al. [24-27] on the atomization process and the spatial distribution of gaseous analyte atoms within a CRA-90 graphite furnace have revealed the complexity of the processes involved in atom formation and loss. The authors [24-27] have concluded as follows. A uniform, free atom distribution within a furnace atomizer does not exist at all times during atomization of a number of metals, and the degree of nonuniformity appears to be 1) element-dependent, 2) affected by the chemical nature of the surface, and 3) dependent on mass transport processes. Diffusional processes alone cannot account for the concentration gradients observed in all cases and, whereas gas phase reactions may influence the spatial distribution, these reactions cannot justify many of the observed signals. For many elements studied, the desorption kinetics appear to govern the absorbance-time profiles, including the falling edge of the signal.

An alternative, simplified model of the atomization based on assumptions specified in the following section is proposed. The

proposed model describes the characteristics of a transient atomic absorption pulse under linear thermal perturbation in an electrothermal graphite tube furnace. The effect of the major parameters on the shape, position, and height of the atomic absorption pulse under the postulated conditions has been theoretically investigated using a numerical integration method.

MATHEMATICAL FORMULATION OF THE MODEL

In the simplified model considered here, the following assumptions have been made. (a) The atoms are dispersed on an extremely small area at the middle part of the graphite tube surface with a monolayer distribution. (b) The atomic release from the graphite surface-gas interface is irreversible, i.e. no re-deposition of the released atomic vapour is allowed. (c) Atom distribution in the gas phase over each transverse cross-sectional plane is uniform. (d) The loss of atoms from the analysis volume is diffusion-controlled (Fick's first law) with the density gradient falling linearly from a maximum at the middle part of the graphite tube to zero at the ends, i.e. the loss of atoms by convection and expulsion is not considered in the present study. (e) There is no temperature gradient along the length of the graphite tube and no temperature difference between the tube-surface and the gas-phase. (f) The effective path length is equal to the geometric length of the graphite tube. (g) Temperature-dependence of the atomic partition function is ignored. (h) Absorbance is proportional to the number of analyte atoms in the analysis volume (the latter is equal to the cross-sectional area of the incident beam of radiation times the

effective path length).

The major species inside the graphite tube furnace during the atomization cycle include carbon (graphite), inert purge gas (usually argon), and analyte species (usually in the form of metal oxides or metal halides). The large quantities of carbon (graphite) and argon present relative to the analyte atoms are essentially unchanged by the atomization process. Therefore, it is reasonable to assume that the atom formation reaction is a first-order or a pseudo-first-order rate process for atom formation. Furthermore, if it is assumed that the rate of atom loss is diffusion-controlled (assumption (d) above), the atom loss is also a first-order rate process provided that the distribution of the gaseous atoms along the length of the graphite tube furnace results in a linearly-decreased concentration from the middle part of the graphite tube furnace to the ends. The atom loss process will be treated as a first-order rate process.

With the above simplifying assumptions, the time-dependence of the atom population in a graphite tube furnace can be described by a first-order or a pseudo-first-order consecutive rate process as follows:

where X is the pre-atomization analyte species, Y is the absorbing analyte atomic vapour formed, Z is the analyte species that is lost from the analysis volume, $k_1(T)$ and $k_2(T)$ are respectively the first-order rate constants for the formation and the loss of the observable atomic species, Y, as a function of temperature, T. Since the

temperature of a pulse-heated graphite furnace is a function of time, t , the expressions $k_1(T)$ and $k_2(T)$, may be described as $k_1(T(t))$ and $k_2(T(t))$, respectively. One uses the $k_1(t)$ and $k_2(t)$ instead of $k_1(T(t))$ and $k_2(T(t))$ in the following text to simplify notation for the rate constants.

Since the process involved in Eqn 1.2 takes place in a constant-volume graphite tube furnace, the amount of change for each species can be described by a set of differential equations as follows:

$$\frac{dX_t}{dt} = -k_1(t) X_t \quad 1.3$$

$$\frac{dY_t}{dt} = k_1(t) X_t - k_2(t) Y_t \quad 1.4$$

$$\frac{dZ_t}{dt} = k_2(t) Y_t \quad 1.5$$

where $k_1(t)$ and $k_2(t)$ have units of s^{-1} , and X_t , Y_t , and Z_t have units of number of atoms. Since the volume of the graphite tube furnace is constant, the unit of Y_t in terms of number of atoms allows its number density at any time to be readily determined. When the absorbing analyte species, Y , is the only observable species, the first and the second terms on the right-hand side of Eqn 1.4 are the rate of atom formation and the rate of atom loss, respectively.

Rate of the gaseous atom formation - For a first-order (or a pseudo-first-order) atom formation reaction, the rate of formation of the gaseous atomic analyte species, Y , is equal to the product of the rate constant, $k_1(t)$, and the amount of the preatomization species, X_t , at

time t . The Arrhenius equation, when applied to this case, results in the equality given by Eqn 1.6

$$\text{Rate of atom formation} = k_1(t) X_t = A \exp(-E_a/RT(t)) X_t \quad 1.6$$

where E_a , A , R , and T are the activation energy of the rate-determining step, frequency factor, gas constant, and absolute temperature, respectively.

Rate of the gaseous atom loss - For a first-order loss process, the rate of atom loss can be expressed as the product of the rate constant, $k_2(t)$, and the amount of the gaseous analyte atomic species, Y_t , in the analysis volume at time t .

$$\text{Rate of atom loss} = -k_2(t) Y_t \quad 1.7$$

Although the loss of atoms from the analysis volume can be attributed to five different processes [28], only the diffusion process will be considered for the sake of simplicity.

The rate of atom loss by diffusion is given by the following equation [4,29]:

$$\text{Rate of atom loss} = -D \frac{d\rho_t}{dx} S \quad 1.8$$

where D is the diffusion coefficient; $d\rho_t/dx$ is the analyte atom density gradient in the direction of diffusion at time t along the length of the graphite tube which is aligned parallel to the x -axis; S is the transverse cross-sectional area of a plane perpendicular to the

x-axis in the graphite tube furnace across which diffusion occurs.

Assuming that the atomic vapour is lost by diffusion symmetrically from the middle part of the graphite tube towards its ends, and that the density of atomic vapour falls linearly from $\rho_t^{x=0}$ at the middle part of the graphite tube (where the sample is deposited and atomized) to zero at a distance $x=l/2$ away (where l is the length of graphite tube), one can derive Eqn 1.9.

$$\frac{d\rho_t}{dx} = \frac{\rho_t^{x=0} - \rho_t^{x=l/2}}{l/2} = \frac{\rho_t^{x=0}}{l/2} \quad 1.9$$

Since the density falls linearly, the average density, $\bar{\rho}_t$ inside the graphite tube furnace at time t is

$$\bar{\rho}_t = \frac{Y_t}{V} = \frac{\rho_t^{x=0}}{2} \quad 1.10$$

Thus,

$$\frac{d\rho_t}{dx} = \frac{2\bar{\rho}_t}{l/2} = \frac{2(Y_t/V)}{l/2} = \frac{4Y_t}{l \cdot V} = \frac{4Y_t}{S \cdot l^2} \quad 1.11$$

where $V=S \cdot l$ is the volume of the graphite tube furnace. Since the diffusion of atomic vapour is from the middle part of the graphite tube to both ends, substitution of $2(d\rho_t/dx)$ into Eqn 1.8 gives

$$\text{Rate of atom loss} = -\frac{8D}{l^2} Y_t \quad 1.12$$

The relationship between the diffusion coefficient, D , of the diffusing gas, and the temperature has been empirically established [4, p. 287; 29] as follows:

$$D = D_0 \left(\frac{T}{T_0} \right)^n \quad 1.13$$

where D_0 is the diffusion coefficient at S.T.P. ($T_0 = 273$ K), and the value of n (to be called gas combination factor) varies from 1.5 to 2.0 for various combinations of gases [4, p. 204].

Substituting Eqn 1.13 into 1.12, one gets

$$\text{Rate of atom loss} = - \frac{8D_0}{\ell^2} \left(\frac{T(t)}{T_0} \right)^n Y_t \quad 1.14$$

From Eqns 1.7 and 1.14, one gets the rate constant for atom loss, $k_2(t)$:

$$k_2(t) = \frac{8D_0}{\ell^2} \left(\frac{T(t)}{T_0} \right)^n \quad 1.15$$

Finally, the kinetic expressions of Eqns 1.3-1.4 be written respectively as:

$$\frac{dX_t}{dt} = - A \exp(-E_a/RT(t)) X_t \quad 1.16$$

$$\frac{dY_t}{dt} = A \exp(-E_a/RT(t)) X_t - \frac{8D_0}{\ell^2} \left(\frac{T(t)}{T_0} \right)^n Y_t \quad 1.17$$

$$\frac{dZ_t}{dt} = - \frac{8D_o}{\ell^2} \left(\frac{T(t)}{T_o} \right)^n Y_t \quad 1.18$$

As mentioned earlier, the temperature of a pulse-heated graphite furnace is a function of time. When the temperature of the furnace is increased at a certain heating rate, α , (from the charring temperature, T_c , to a preset final atomization temperature, T_f) and then held constant at T_f , the relationship between the temperature and the time can be expressed as follows:

$$t < \frac{T_f - T_c}{\alpha} \quad T(t) = T_c + \alpha t \quad 1.19$$

$$t \geq \frac{T_f - T_c}{\alpha} \quad T(t) = T_f \quad 1.20$$

Since the rate constants are temperature-dependent and the temperature is a function of time, the above differential Eqns 1.16-1.18 are too complicated to be solved analytically. A numerical integration method has therefore been used to study the change in the number of atoms inside the graphite tube furnace as a function of time.

CALCULATION

Various methods are available for numerical iterative integration of a first-order differential equation [30,31], such as the consecutive process of atom formation in and loss from graphite tube furnace, e.g. see Eqns 1.16-1.18. In the present studies, a multi-step integration method - the Adams-Bashforth method - has been applied to the numerical

solution of differential equations such as

$$\frac{dX_t}{dt} = -A \exp(-E_a/RT(t)) X_t = f(t, X_t) \quad 1.21$$

The algorithm of the Adams-Bashforth method is commonly expressed as

$$\begin{aligned} X_{t+\Delta t} = X_t + \frac{\Delta t}{24} [55f(t, X_t) - 59f(t-\Delta t, X_{t-\Delta t}) \\ + 37f(t-2\Delta t, X_{t-2\Delta t}) - 9f(t-3\Delta t, X_{t-3\Delta t})] \end{aligned} \quad 1.22$$

If the solution X has been computed for the four points, t , $t-\Delta t$, $t-2\Delta t$ and $t-3\Delta t$, then Eqn 1.22 can be used to compute $X_{t+\Delta t}$ for different temperatures, since the temperature is a function of time. The initial amount of X is known at $t=0$, i.e. $X_{t=0} = X_0$. In order to obtain enough values to initiate the multi-step iterative integration, a single-step, fourth-order, Runge-Kutta method has been employed to evaluate the first three values according to the following equation:

$$X_{t+\Delta t} = X_t + \frac{\Delta t}{6} (S_0 + 2S_1 + 2S_2 + S_3) \quad 1.23$$

where

$$S_0 = f(t, X_t)$$

$$S_1 = f\left(t + \frac{\Delta t}{2}, X_t + \frac{\Delta t \cdot S_0}{2}\right)$$

$$S_2 = f\left(t + \frac{\Delta t}{2}, X_t + \frac{\Delta t \cdot S_1}{2}\right)$$

$$S_3 = f(t + \Delta t, X_t + \Delta t \cdot S_2)$$

After that, the solution of X is done systematically by the Adams-Bashforth method.

In practice, Eqn 1.22 is not used by itself. Instead, it is used as a predictor and then another equation is used as a corrector. The corrector usually employed with Eqn 1.22 uses the Adams-Moulton method as follows:

$$X_{t+\Delta t} = X_t + \frac{\Delta t}{24} [9f(t+\Delta t, X_{t+\Delta t}^p) + 19f(t, X_t) - 5f(t-\Delta t, X_{t-\Delta t}) + f(t-2\Delta t, X_{t-2\Delta t})] \quad 1.24$$

Here $X_{t+\Delta t}^p$ is the tentative value of $X_{t+\Delta t}$, computed from Eqn 1.22. Thus, Eqn 1.22 predicts a tentative value of $X_{t+\Delta t}$, and Eqn 1.24 computes this X value more accurately. The combination of the two equations results in a predictor-corrector scheme which has been used for the present studies.

RESULTS AND DISCUSSION

The shape of atom population-time curves can be characterized by the atom-population maximum (peak height), the position of the maximum (time at the peak height), and the half-width (the pulse width at half of the peak height). However, it should be noted that the simulated results of the present studies serve only as a model, the validity of which must be established by experimental verification.

Effect of the Temperature on the Atom Population-Time Curves

In pulse-heated graphite furnace atomic absorption spectrometry, the temperature of the furnace at a given instant during the atomization cycle is described by Eqns 1.19 and 1.20. It is well known (also, Eqns 1.6 and 1.15 show) that the rate constants for atom formation and loss are temperature-dependent. Therefore, the maximum rate constants for atom formation and loss, are determined by the final (highest) atomization temperature. However, the role of the heating rate in determining the maximum atom population will be clearly seen if the degree of change in the rate constant for atom formation and loss with temperature is compared.

Figure 1 shows the effect of the heating rate on the shape of atom population-time curves. The atom population-time curves A, B, C, D and E are simulated under the temperature-time profiles a, b, c, d and e, respectively. As can be seen from Fig. 1, an increase in the heating rate increases the maximum atom population and the area of the atom population-time curve which lies in the constant temperature region of the final atomization temperature.

Figure 2 shows the effect of the final atomization temperature on the atom population-time curves at a constant heating rate (5 K ms^{-1}). The atom population curves A, B, C, D and E are simulated under the temperature-time profiles a, b, c, d and e, respectively. No significant increase in the maximum atom population is observed at a final temperature exceeding 2600 K if one uses the present numerical values for the parameters in Eqns 1.16-1.18. However, the more rapid fall in the decay part of the atom population-time curve at higher

Figure 1. Effect of the heating rate, α , on the shape of atom population-time curves.

General parameters: $E_a = 480 \text{ kJ mol}^{-1}$, $A = 1.0 \times 10^{12} \text{ s}^{-1}$, $T_c = 700 \text{ K}$,
 $T_f = 2500 \text{ K}$, $\ell = 2.0 \text{ cm}$, $D_0 = 0.10 \text{ cm}^2 \text{ s}^{-1}$, $n = 1.8$.
 Heating rate: a 100 K ms^{-1} ; b 10 K ms^{-1} ; c 5 K ms^{-1} ;
 d 2.5 K ms^{-1} ; e 1.5 K ms^{-1} .

Figure 2. Effect of the final atomization temperature, T_f , on the shape of atom population-time curves.

General parameters: $E_a = 480 \text{ kJ mol}^{-1}$, $A = 1.0 \times 10^{12} \text{ s}^{-1}$, $T_c = 700 \text{ K}$, $\alpha = 5.0 \text{ K ms}^{-1}$, $r = 2.0 \text{ cm}$, $D_0 = 0.10 \text{ cm}^2 \text{ s}^{-1}$, $n = 1.8$.

Final atomization temperatures: a 2700 K; b 2500 K; c 2400 K; d 2300 K; e 2200 K.

final atomization temperatures reflects the effect of the greater rate of loss of the atoms at higher temperatures on the shape and the area of the atom population-time curves.

Effect of the Tube Length on the Atom Population-Time Curves

Figure 3 shows the effect of the tube length on the atom population-time curves when the other parameters are the same as in Fig. 2 but $T_f = 2500$ K. As can be seen from Eqn 1.15, the rate constant for the loss of the atoms depends on the tube length. Increase in the tube length slows down the rate of atom loss because an increase in the tube length increases the residence time of the atoms, i.e. decreases the rate constant for atom loss, in the analysis volume, which results in a higher maximum atom population as well as a longer tail in the decay part of the atom population-time curves.

Effect of Diffusion Coefficient, D_0 , Gas Combination Factor, n , Frequency Factor, A , and Activation Energy, E_a , on Atom Population-Time Curves

Figures 4-6 present the effect of the diffusion coefficient, the gas combination factor, and the frequency factor, respectively, on atom population-time curves at the same heating conditions. An increase in the diffusion coefficient and the gas combination factor reduces the maximum atom population because of the faster rate of loss of the atoms. On the other hand, a high value for the frequency factor increases the rate of atom formation by increasing the rate constant for atom formation thereby increasing the maximum atom population.

Figure 7 shows the effect of the activation energy on the atom

Figure 3. Effect of the tube length, ℓ , on the shape of atom population-time curves.

General parameters: $E_a = 480 \text{ kJ mol}^{-1}$, $A = 1.0 \times 10^{12} \text{ s}^{-1}$, $T_c = 700 \text{ K}$,
 $T_f = 2500 \text{ K}$, $\alpha = 5.0 \text{ K ms}^{-1}$, $D_0 = 0.10 \text{ cm}^2 \text{ s}^{-1}$, $n = 1.8$.
 Tube length: A 5.0 cm; B 4.0 cm; C 3.0 cm; D 2.0 cm;
 E 1.0 cm.

Figure 4. Effect of the diffusion coefficient, D_0 , on the shape of atom population-time curves.

General parameters: $E_a = 480 \text{ kJ mol}^{-1}$, $A = 1.0 \times 10^{12} \text{ s}^{-1}$, $T_c = 700 \text{ K}$,
 $T_f = 2500 \text{ K}$, $\alpha = 5.0 \text{ K ms}^{-1}$, $\ell = 2.0 \text{ cm}$, $n = 1.8$.
 Diffusion coefficient: A $0.05 \text{ cm}^2 \text{ s}^{-1}$; B $0.10 \text{ cm}^2 \text{ s}^{-1}$;
 C $0.20 \text{ cm}^2 \text{ s}^{-1}$; D $0.40 \text{ cm}^2 \text{ s}^{-1}$.

Figure 5. Effect of the gas combination factor, n , on the shape of atom population-time curves.

General parameters: $E_a = 480 \text{ kJ mol}^{-1}$, $A = 1.0 \times 10^{12} \text{ s}^{-1}$,
 $T_c = 700 \text{ K}$, $T_f = 2500 \text{ K}$, $\alpha = 5.0 \text{ K ms}^{-1}$, $\ell = 2.0 \text{ cm}$,
 $D_0 = 0.10 \text{ cm}^2 \text{ s}^{-1}$.

Gas combination factor: A 1.5; B 1.8; C 2.0.

Figure 6. Effect of the frequency factor, A , on the shape of atom population-time curves.

General parameters: $E_a = 480 \text{ kJ mol}^{-1}$, $T_a = 700 \text{ K}$, $T_f = 2500 \text{ K}$,

$\alpha = 5.0 \text{ K ms}^{-1}$, $\ell = 2.0 \text{ cm}$, $D_0 = 0.10 \text{ cm}^2 \text{ s}^{-1}$, $n = 1.8$.

Frequency factor: A $1.0 \times 10^{13} \text{ s}^{-1}$; B $1.0 \times 10^{12} \text{ s}^{-1}$;

C $1.0 \times 10^{11} \text{ s}^{-1}$; D $5.0 \times 10^{10} \text{ s}^{-1}$.

Figure 7. Effect of the activation energy, E_a , on the shape of atom population-time curves.

General parameters: $A = 1.0 \times 10^{12} \text{ s}^{-1}$, $T_c = 700 \text{ K}$, $T_f = 2500 \text{ K}$,
 $\alpha = 5.0 \text{ K ms}^{-1}$, $D_0 = 0.10 \text{ cm}^2 \text{ s}^{-1}$, $\ell = 2.0 \text{ cm}$, $n = 1.8$.
 Activation energy: A 300 kJ mol^{-1} ; B 400 kJ mol^{-1} ;
 C 480 kJ mol^{-1} ; D 500 kJ mol^{-1} ; E 530 kJ mol^{-1} .

population-time curves. Equation 1.6 shows that for a given temperature, the rate constant for atom formation, $k_1(t)$, is governed by both the frequency factor and the activation energy. A very high activation energy means a difficult-to-overcome energy barrier to a chemical reaction. The decrease in the height of the atom population-time curve in Fig. 7 indicates that for the given temperature, the higher the activation energy barrier the slower the rate of atom formation, and hence the lower the maximum atom population. Also, a higher activation energy results in atom population-time curves which are shallower and broader.

The Effect of the Heating Rate and the Tube Length on the Maximum Atom Population, $Y_{\max}$, with the Activation Energy as a Parameter

In Eqns 1.16-1.18, the parameters: diffusion coefficient, gas combination factor, frequency factor, and activation energy, are all natural properties of an analyte species under given experimental conditions. As can be seen from Eqns 1.16-1.18, only two parameters, the heating rate and the tube length, can be varied by changing the instrumental setting. The effect of the heating rate and the tube length on the maximum atom population can be simulated by assuming that all the other natural properties except the activation energy remain the same.

Figure 8 shows the effect of the heating rate on the maximum atom population. Figure 8 indicates that with the increasing heating rate, the smaller the activation energy, the greater the increase in the maximum atom population. Because of the relatively low atomization temperatures used in Fig. 8, no significant increase is observed for

Figure 8. Effect of the heating rate on the maximum atom population, $Y_{\max}$, with activation energy as a parameter.

General parameter: $A = 1.0 \times 10^{12} \text{ s}^{-1}$, $T_c = 700 \text{ K}$, $T_f = 2500 \text{ K}$,
 $\ell = 2.0 \text{ cm}$, $D_0 = 0.10 \text{ cm}^2 \text{ s}^{-1}$, $n = 1.8$.

Activation energy: ● 400 kJ mol^{-1} ; ▲ 450 kJ mol^{-1} ; ◐ 480 kJ mol^{-1} ;
 ▼ 500 kJ mol^{-1} ; ■ 530 kJ mol^{-1} .

the high activation energy systems.

Figure 9 presents the effect of heating rates on a system having a high activation energy (630 kJ mol^{-1}), with the final atomization temperature as a parameter. A comparison of the curves in groups A and B in Fig. 9 indicates the following. As expected, a higher heating rate shifts the atom population-time curve to an earlier time. Figure 9 shows that the maximum in atom population is sensitive to the heating rate only for the highest final atomization temperature (3300 K); it is not sensitive to the heating rate for lower final atomization temperatures. Since the rate constant for atom loss (by diffusion alone) is not as sensitive to the temperature change as the rate constant for atom formation, the effect of the final atomization temperature (and the heating rate) on a high activation energy system can be predicted from the Arrhenius-type equation (Eqn 1.6), which states that the rate constant for atom formation is proportional to $\exp(-E_a/T(t))$. For a given (high) activation energy, only a high enough temperature (especially when such a high temperature is attained at a high heating rate) can maximize the rate of atom formation and minimize atom loss (by diffusion alone), thereby giving the highest ratio of Y_t/X_0 . A faster heating rate results in a shorter time required to reach a high atomization temperature and also a shorter time during which atom loss can occur by diffusion alone. Therefore, a system having a high value of E_a will be sensitive to both a high heating rate and a high final atomization temperature only when these two parameters are coupled, i.e. only when a high heating rate is used to yield a high atomization temperature. Also, the highest value for

Figure 9. Effect of the heating rate and the final atomization temperature on a high activation energy system.

General parameters: $E_a = 630 \text{ kJ mol}^{-1}$, $A = 1.0 \times 10^{12} \text{ s}^{-1}$, $T_c = 700 \text{ K}$
 $l = 2.0 \text{ cm}$, $D_o = 0.10 \text{ cm}^2 \text{ s}^{-1}$, $n = 1.8$.

A: $\alpha = 50 \text{ K ms}^{-1}$; $T_f = 3300 \text{ K}$ (for A-1), 3000 K (for A-2), 2800 K (for A-3).
 B: $\alpha = 5.0 \text{ K ms}^{-1}$; $T_f = 3300 \text{ K}$ (for B-1), 3000 K (for B-2), 2800 K (for B-3).

the atom-population maximum for such a system is attainable only when a high heating rate is used to yield a high atomization temperature. In Fig. 9, curves A, the coupling of the atomization temperature of 3300 K with the heating rate of 50 K ms^{-1} yields a value of $Y_t/X_0 \sim 70\%$ against a maximum possible value of 100% that is theoretically possible. Absence of coupling of high heating rates with high atomization temperatures will make such a system not very sensitive to changes in these two parameters.

Because of the upper temperature constraints of the pyrolytic graphite used for the construction of the furnace, an atomization temperature higher than 3300 K was not practical and was therefore not used. As has been mentioned earlier, an alternative method of increasing the maximum atom population is to reduce the rate of atom loss by increasing the tube length.

Figure 10 shows the effect of variation in the tube length on the maximum atom population with the activation energy as a parameter. A considerable enhancement in the maximum atom population for the high activation energy systems is observed.

SUMMARY

This simple model has some limitations which stem largely from its simplifying assumptions and oversimplified treatment of the atom loss processes. However, such limitations do not seriously impair its usefulness, which lies not so much in its predictive power (which is considerable), as in its ability to offer a theoretical framework for understanding the effect of various experimental parameters on the

Figure 10. Effect of the tube length on the maximum atom population, $Y_{\max}$, with activation energy as a parameter.

General parameters: $A = 1.0 \times 10^{12} \text{ s}^{-1}$, $T_c = 700 \text{ K}$, $T_f = 2500 \text{ K}$,
 $\alpha = 5.0 \text{ K ms}^{-1}$, $D_0 = 0.10 \text{ cm}^2 \text{ s}^{-1}$, $n = 1.8$.

Activation energy: ● 400 kJ mol⁻¹; ▲ 450 kJ mol⁻¹;
 ⬢ 480 kJ mol⁻¹; ▼ 500 kJ mol⁻¹; ■ 530 kJ mol⁻¹.

analytical sensitivity

High heating rates enhance the maximum atom population inside the furnace and result in shifting the atom population-time curves towards the constant temperature region. The enhancement of the maximum atom population inside the furnace with increase in heating rates is highly dependent on the characteristics of the chemical and physical parameters. In all cases studied here, the maximum atom population inside the furnace tends to reach a limiting value with increase in the heating rates. The heating rate required to achieve this limiting value is determined by the final temperature and the kinetics of atom formation and loss.

The importance of furnace length to the maximum atom population has been demonstrated. The results indicate that atom loss occurs by the time maximum atom population is achieved. Long tubes as well as high heating rates, which maximize the $k_1(t)/k_2(t)$ ratio, result in the highest peak-height absorbance.

CHAPTER 2

THE ROLE OF CARBON IN ATOMIZATION IN GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY

Several workers [7,15,19,28,32-41] have studied mechanisms of gaseous atom formation in graphite furnace atomizers using the following approaches: thermodynamic [32,33], kinetic [7,15,34], combined thermodynamic-kinetic [28,35], and an empirical approach based on atomization/decomposition curves [36,37]. L'VOV [42] and SMETS [19] have discussed atomization processes in graphite furnace atomic absorption spectrometry (GFAAS).

STURGEON et al. [28,35] proposed a model in which the logarithm of the absorbance value from the initial rising edge of the atomic absorption pulse was plotted against the reciprocal of the absolute temperature to yield an "activation energy" for the rate-determining step in the sequence of reactions leading to atomization of the analyte. The "activation energy" was correlated for best agreement with one of the following values: (a) dissociation energy of the metal oxide; (b) dissociation energy of the metal halide; (c) the heat of atomization of the analyte metal; (d) dissociation energy of the metal dimer; or (e) the metal-carbon bond dissociation energy.

The vaporization or sublimation of the analyte from its elemental form in the condensed phase has been reported to be one of the mechanisms of atom formation in GFAAS [20,28,35]. This mechanism has also been supported by independent data from x-ray structure analysis of the products left on the surface of the graphite furnace after the

analyte has been atomized at a high temperature. The results from x-ray structure analysis indicate that the free metal is formed in the case of Cu, Fe, Co, Pb and Ni [43,44].

In pulse-heated graphite furnace atomic absorption spectrometry, the metal, usually as a nitrate or sulphate in aqueous solution, is injected into the furnace. The metal oxide usually results on heating even when the analyte was taken as a halide, since hydrolysis to oxygen-containing species frequently occurs. Additionally, results of thermal analysis indicate that when oxygen is present in the reaction system, a metal halide may be converted into a metal oxide during pyrolysis prior to the atomization stage [45]. Recently, the experimental results of a multiple probe method combining atomic absorption spectrometry and mass spectrometry show that the atomization of vanadium [46] and lead [47] samples in an ultra-high vacuum produces VO_2^+ and VO^+ at a temperature of about 1500 K, and PbO^+ at a temperature of about 700 K, respectively. The majority of precursors to gas phase atoms are either the free metal, metal oxides (usually monoxides [4, p. 129]), halides or carbides.

When a metal oxide is a precursor, conversion to the metal in the condensed phase at low temperatures (even below its appearance temperature) may occur by thermal decomposition or by carbon reduction [43,44].

CAMPBELL and OTTAWAY [32] assumed that reduction of metal oxides by carbon is rapid, and correlated the appearance temperature of the absorption pulse with the temperature at which reduction of the metal oxides by solid carbon at the surface of the graphite atomizer becomes

thermodynamically favourable using the temperature at which $\Delta G^\ominus < 0$ as the appearance temperature. The work of CAMPBELL and OTTAWAY [32] suggests that a large number of analyte species produce gaseous analyte atoms by carbon reduction. STURGEON et al. [48,49] have defined the appearance temperature as the lowest temperature at which the analyte absorbance signal becomes detectable above the baseline signal. They have calculated the standard free energy change for the conversion of the metal oxide to metal in the condensed phase at the temperature nearest to the experimental appearance temperature and concluded that for some elements, gaseous atoms are formed by carbon reduction of the metal oxide to the metal in the condensed phase, followed by vaporization or sublimation of the metal into the gas phase.

BYRNE [50] has commented that the role of carbon in the atomization process has, in the past, been overemphasized. Basing his reasonings on a simple thermodynamic model, BYRNE [50] proposed direct thermal decomposition of metal oxides as the mechanism for atomization of the 15 elements reported by him.

L'VOV and RYABCHUK [51] have theoretically predicted and experimentally measured the partial pressure of oxygen inside a graphite tube furnace. The measured partial pressure of oxygen is many orders of magnitude higher than that estimated from a consideration of the thermodynamic equilibrium: $O_2 + 2C \rightleftharpoons 2CO$. They concluded that atomization of metal oxides proceeds by their condensed phase thermal dissociation without direct participation of carbon, i.e., without carbon reduction. STURGEON et al. [52] directly measured the oxygen content inside the graphite furnace as a function of temperature using

a chemiluminescence method with phosphorus as a probe. Reported results were in good agreement with those given by L'VOV and RYABCHUK [51]. They have also suggested that thermal decomposition of many metal oxides to free metal in the condensed phase occurs despite the feasibility of their carbon reduction. CEDERGREN et al. [53] reported experimental values of the partial pressure of oxygen in a graphite furnace as a function of temperature in agreement with those thermodynamically predicted by the $C-O_2$ reaction. Their results show that, contrary to the results reported by L'VOV et al. [51] and STURGEON et al. [52], the partial pressure of oxygen inside the graphite furnace drops steeply as the temperature of the furnace increases.

The objective of the present work is to re-examine the role of carbon in the atomization process of some elements in the Perkin-Elmer graphite tube furnace.

THEORY

In developing the following theory, partial chemical equilibrium inside the graphite furnace has been assumed. ALKEMADE et al. [54] have defined partial chemical equilibrium as follows. Suppose a certain reaction $A + B \rightleftharpoons C + D$ is balanced, i.e., it proceeds in both directions at equal, high rates, whereas another reaction $A + C \rightarrow E$, also involving A and C, is not balanced because of slow relaxation. The mass-action law will then hold for the concentration A, B, C and D relative to each other, but not for the concentration A, C and E. Then

it is said that a partial chemical equilibrium exists for the first mentioned reaction.

There are a number of potential pathways by which gaseous analyte atoms may be formed. Only the following two atomization mechanisms will be considered, since the point raised by BYRNE [50] concerns only the metal oxides.

Mechanism I. Reduction of the metal oxide by carbon, followed by sublimation or vaporization of the metal.

Mechanism II. Thermal decomposition of the metal oxide, followed by sublimation or vaporization of the metal.

It is assumed that in mechanisms I and II, a partial chemical equilibrium between the intermediate, $M_{(s/l)}$, and its precursor, $M_x O_y(s/l)$, is established because of the rapid balancing of the forward and reverse reactions. Mechanisms for metal atom formation involving gas phase-condensed phase equilibria (written with a double-arrow) should more properly be labelled as quasi-equilibria since equilibrium exists only as long as a part of the analyte exists as a condensed phase on the graphite furnace surface. The condensed-phase transition

processes which may be precursors to the gaseous oxides can be evaluated by assuming localized thermodynamic equilibrium at the location of the sample, i.e., this localized region can be considered isothermal. It is assumed that partial chemical equilibrium and localized thermodynamic equilibrium exist for the reactions considered in this chapter.

For any given reaction shown as Eqn 2.5, the relationship between the free energy change (ΔG) and the standard free energy change ($\Delta G^\ominus$) for the reaction is expressed by Eqn 2.6.

$$\Delta G = \Delta G^\ominus + RT \ln \frac{\prod_{i=1}^k a_{T_i}^{t_i}}{\prod_{i=1}^m a_{R_i}^{r_i}} \quad 2.6$$

where a is the activity of the substance shown as a subscript. The value of the standard free energy change, $\Delta G^\ominus$, determines the position of equilibrium, i.e., the relative number of moles of reactants and products that will be present when the chemical system achieves equilibrium and serves as a useful guide to feasibility of the reaction. However, the value of the free energy change, ΔG , not $\Delta G^\ominus$, determines spontaneity of a given chemical reaction. Equation 2.6 shows that the spontaneity of a chemical reaction is dependent on both the standard free energy change of the reaction and the ratio of the activities of products and reactants. It should be noted that the

above term - spontaneity of a chemical reaction - has been used in the present context only to mean that the chemical equilibrium will favour the products over the reactants - it says nothing about the rate of attainment of the chemical equilibrium. The equilibrium composition of a reaction system, i.e., the relative number of moles of reactants and products in the defined chemical system at $\Delta G=0$, can be applied as a limit to examine the driving force of a chemical reaction in a given reaction system at any instant of time when the actual composition of reaction system is known.

Consider reactions 2.1 and 2.3. The extent of occurrence of these reactions is given by their respective equilibrium constant values, K , at the temperature, T . For reaction 2.1:

$$K_p = \frac{y/x}{P_{CO}(\text{equilibrium}, T)} \quad 2.7$$

and for reaction 2.3:

$$K_p = \frac{y/2x}{P_{O_2}(\text{equilibrium}, T)} \quad 2.8$$

Equations 2.5-2.8 indicate that the spontaneity and the extent of reactions 2.1 and 2.3 are dependent on the activity of the gaseous species: $CO_{(g)}$ for reaction 2.1, and $O_{2(g)}$ for reaction 2.3. Since the partial pressures of $CO_{(g)}$ and $O_{2(g)}$ present in the systems considered are low, partial pressures in units of atmosphere will be substituted for the unitless activities in Eqn 2.6. The substances in the solid phase are assumed to have unit activity.

RESULTS AND DISCUSSION

Maximum Tolerable Partial Pressures of CO, CO₂, O₂ and O in the Reaction System: M_xO_y(s/l)-M(s/l)-C

The equilibrium partial pressures of CO_(g) and O_{2(g)} in a reaction system containing M_xO_y(s/l), M(s/l) and C(s) determine the maximum tolerable partial pressures of those gases in the system for the forward reactions 2.1 and 2.3 to be spontaneous. The equilibrium constants of the reactions have been calculated using thermodynamic values published in the literature [55-57]. The semi-enclosed cylindrical graphite tube furnace (manufactured by The Perkin-Elmer Corporation) considered in the present studies has the following dimensions: 0.6 cm i.d., 2.8 cm long; hence its volume is 0.8 cm³. The graphite tube furnace has an injection hole of 1.5 mm diameter and the furnace is open to the ambient atmosphere through the injection hole.

To obtain accuracy in thermodynamic calculations of the equilibrium state it is important to consider all reactants and products which are present in amounts large enough to influence the mass balance constraints. As can be seen from reactions 2.1 and 2.3, formation of intermediate species, M(s/l), via carbon reduction or thermal decomposition depends on the partial pressures of CO_(g) and O_{2(g)}, respectively.

Thermodynamic calculations can be made for the formation of M(s/l) from M_xO_y(s/l) in a graphite furnace, for which the reaction system considered is M_xO_y(s/l)-M(s/l)-C(s)-CO_{2(g)}-CO_(g)-O_{2(g)}-O_(g). From Gibbs' phase rule: $F = C - P + 2$, where F is the number of degrees of freedom, C the number of components, and P the number of phases in the

system at equilibrium. The number of degrees of freedom for this system is one since there are three components and four phases (three condensed and one gaseous). This means that if one chooses a certain temperature, then the one degree of freedom is used up, and therefore the maximum partial pressures of O_2 , CO_2 , CO and O which can be tolerated in the reaction system are fixed and invariant, and can be calculated. For example, the appearance temperature of Ni (from $NiO_{(s/l)}$) is 1590 K [28]. If Ni atoms are considered to be formed by thermal decomposition of $NiO_{(s/l)}$ (reaction 2.3) at 1600 K (nearest to 1590 K):

then the equilibrium partial pressure of O_2 (p_{O_2}) at 1600 K is calculated from reaction 2.6, i.e.,

$$p_{O_2} = 3.2 \times 10^{-7} \text{ atm.}$$

Thus, in order that the thermal decomposition of $NiO_{(s/l)}$ proceed spontaneously at 1600 K, the partial pressure of O_2 in the system must be less than 3.2×10^{-7} atm.

The O_2 gives rise to an atomic oxygen pressure via the following reaction

At 1600 K, the equilibrium partial pressure of $O_{(g)}$ is calculated to be

$$p_O = 8.1 \times 10^{-9} \text{ atm}$$

If it is considered that $C_{(s)}$ is reducing $NiO_{(s/l)}$ to form $Ni_{(s/l)}$ and $CO_{(g)}$, then the pertinent reaction is

for which the equilibrium partial pressure of CO (p_{CO}) at 1600 K is calculated to be

$$p_{CO} = 9.7 \times 10^4 \text{ atm.}$$

Thus, in order that the reduction of $NiO_{(s/l)}$ by $C_{(s)}$ proceed spontaneously at 1600 K, the partial pressure of $CO_{(g)}$ in the system must be less than 9.7×10^4 atm.

If the CO is in equilibrium with the solid carbon present, then a CO_2 pressure is exerted via the equilibrium

which will give the same equilibrium partial pressure of CO_2 as will be given by the reaction:

At 1600 K, the equilibrium partial pressure of CO_2 (p_{CO_2}) is calculated to be

$$p_{CO_2} = 2.8 \times 10^6 \text{ atm.}$$

Thus, at 1600 K, for $NiO_{(s/l)}$, $Ni_{(s/l)}$ and C to be in equilibrium with a gaseous atmosphere, the atmosphere must be of composition:

$$p_{O_2} = 3.2 \times 10^{-7} \text{ atm}$$

$$p_O = 8.1 \times 10^{-9} \text{ atm}$$

$$p_{CO} = 9.7 \times 10^{-4} \text{ atm}$$

$$p_{CO_2} = 2.8 \times 10^{-6} \text{ atm}$$

and if the total pressure of the gaseous components in such a reaction system is less than 2.8×10^6 atm, then conversion of $NiO_{(s/l)}$ into $Ni_{(s/l)}$ will occur spontaneously. Since the graphite furnace is open to the ambient atmosphere, the equilibrium pressure inside the graphite furnace cannot exceed one atmosphere. Therefore, the conversion of $NiO_{(s/l)}$ into $Ni_{(s/l)}$ in the condensed phase at the appearance temperature is a spontaneous chemical reaction. However, the feasibility of the conversion reaction via the carbon reduction and/or thermal decomposition is determined by the partial pressures of oxygen and carbon monoxide inside the reaction system.

The above calculated composition of gaseous species of the $NiO_{(s/l)}-Ni_{(s/l)}-C_{(s)}-CO_{2(g)}-CO_{(g)}-O_{2(g)}-O_{(g)}$ reaction system at equilibrium at 1600 K suggests that $NiO_{(s/l)}$ has been completely exhausted by conversion into $Ni_{(s/l)}$, i.e., the equilibrium of reactions 2.1 and 2.3 no longer exists at this temperature. For nickel, the x-ray structure analysis indicates that only nickel metal is present on the graphite surface after the furnace has been heated to a temperature above 1570 K [43].

The results of similar calculations of the equilibrium composition

of gaseous species for other elements at temperatures nearest to their appearance temperatures are presented in Table 1. The spontaneity of the conversion reaction in the condensed phase via thermal decomposition or carbon reduction is determined by the partial pressure of oxygen inside the furnace.

Estimation of the Partial Pressures of CO and O₂ in the Graphite Furnace

i) Under chemical equilibrium conditions

In commercial, semi-enclosed graphite tube furnaces, attainment of complete thermodynamic equilibrium may be questionable. High thermal gradients, rapid rise in temperature, and transient signals generated by these furnaces may not allow adequate time for physical and chemical processes to attain an equilibrium state before the gaseous analyte atoms are lost. Despite this possibility attempts have been made to gain insight into the dominant processes of atom production based on the assumption that partial chemical equilibrium and localized thermodynamic equilibrium exist.

At equilibrium, the partial pressures of O_{2(g)} and CO_(g) are related through chemical equilibria to the concentration of all species present in the system. However, as an approximation, the partial pressure of oxygen inside the furnace can be estimated by ignoring the extremely small amount of the metal oxide usually present in actual analytical situations. The equilibrium partial pressure of oxygen in a carbon-rich environment (graphite furnace) is determined primarily by the equilibria of reactions 2.9, 2.10 and 2.11.

Table 1. Maximum tolerable partial pressures of CO, CO₂, O₂, and O in the reaction system,
 $M_xO_y(s/l) - M(s/l) - C^*$.

Metal, M	Metal oxide, M _x O _y	Appearance temperatures, K	Temperature used in the calculation, K	Partial pressures of gaseous species at equilibrium, atm			
				CO	CO ₂	O ₂	O
Pb	PbO	1040	1000	2.0×10^4	2.4×10^8	5.0×10^{-13}	1.1×10^{-16}
Cu	CuO	1270	1300	2.5×10^7	3.4×10^{12}	4.0×10^{-4}	3.5×10^{-9}
Co	CoO	1430	1400	5.0×10^3	4.4×10^4	7.2×10^{-11}	7.9×10^{-12}
Fe	FeO	1500	1500	2.4×10^2	3.8×10^1	6.0×10^{-13}	3.1×10^{-12}
Sn	SnO ₂	1560	1600	1.1×10^4	3.7×10^4	4.2×10^{-9}	9.4×10^{-10}
Ni	NiO	1590	1600	9.7×10^4	2.8×10^6	3.2×10^{-7}	8.1×10^{-9}
Cr	Cr ₂ O ₃	1660	1700	9.3×10^0	1.2×10^{-2}	8.2×10^{-15}	4.0×10^{-12}
Al	Al ₂ O ₃	2080	2100	9.9×10^{-2}	1.6×10^{-7}	2.2×10^{-17}	6.5×10^{-12}
V	V ₂ O ₃	2200	2200	4.8×10^1	2.5×10^{-2}	9.8×10^{-12}	8.4×10^{-9}
Cd	CdO	720	700	1.3×10^{-1}	7.0×10^1	2.2×10^{-28}	5.2×10^{-30}
Zn	ZnO	1140	1100	5.7×10^{-2}	2.8×10^{-4}	4.4×10^{-23}	1.6×10^{-20}
Mn	MnO	1480	1500	8.6×10^{-2}	4.9×10^{-6}	7.8×10^{-20}	1.1×10^{-15}
Mg	MgO	1510	1500	2.2×10^{-7}	3.3×10^{-17}	5.2×10^{-31}	2.9×10^{-21}
Ca	CaO	1850	1900	4.0×10^{-5}	5.8×10^{-14}	8.5×10^{-25}	2.7×10^{-16}

*Partial pressure of O₂ is calculated from reaction 2.3 at the given temperature. Partial pressures of CO₂, CO and O in the reaction system are then evaluated via the equilibria of reactions 2.9, 2.10 and 2.11, respectively.

§Ref. [28].

where K values are equilibrium constants for the reactions indicated by the subscripts. It is assumed that C remains a solid throughout the temperature range 300-3300 K used.

When the internal purge gas (Ar) is interrupted prior to atomization, the total initial amount of oxygen present in the constant-volume furnace is assumed to be contributed only by the oxygen in the internal purge gas (Ar) as an impurity. The contribution of oxygen by the ambient air entering through the injection hole is assumed to be negligible - a reasonable assumption during the atomization cycle when the temperature of the graphite furnace is rising rapidly, resulting in rapid expansion of the vapour with consequent partial expulsion of the vapour through the injection hole. It will be also shown later in this chapter that even if any air enters through the injection hole, its oxygen content will be rapidly reduced to effectively zero concentration. If the reactions 2.9, 2.10 and 2.11 are balanced, then by mass balance, one obtains

$$n_{O_2,I} = n_{O_2,E} + n_{CO_2,E} + \frac{1}{2} n_{CO,E} + \frac{1}{2} n_{O,E} \quad 2.12$$

where n_{O_2} , n_{CO_2} , n_{CO} , and n_O represent the number of moles of O_2 , CO_2 , CO and O, respectively. The subscripts I and E stand for the amount of the specified species at the initial and the equilibrium state,

respectively.

From Gibbs' phase rule, the C-CO₂-CO-O₂-O equilibrium system is composed of two components (carbon and oxygen), and two phases (solid C and a gas). Therefore, the number of degrees of freedom for this reaction system is two. Thus, if the initial amount of oxygen and the temperature are specified, then the equilibrium partial pressures of CO₂, CO, O₂, and O are fixed and invariant, and can be calculated.

When argon gas of 99.995% (v/v) purity is employed as the internal purge gas, O₂ is assumed to be the only impurity; thus, the pressure of O₂ contributed by the maximum O₂ impurity in the argon gas, at 1 atm, is 5.0×10^{-5} atm. At low temperature, e.g., during the charring stage, continuous flow of the internal purge gas will provide a maximum of 5.0×10^{-5} atm as the O₂ partial pressure (assuming no reaction between C_(s) and O_{2(g)} -- a reasonable assumption at low temperatures). During the atomization stage, the flow of internal purge gas is interrupted. The estimated maximum amount of O₂ present in the graphite furnace of volume of 0.8 cm³ at 500 K is 9.7×10^{-10} moles.

Although some of the oxygen and the oxygen-containing species in the furnace may be lost by expansion in the heating cycles, the maximum pressure of oxygen which can be tolerated in the reaction system can be calculated by assuming that no oxygen and oxygen-containing species are lost. Therefore, using the ideal gas law, $pV=nRT$, Eqn 2.12 can be transformed into Eqn 2.13.

$$n_{O_2, I} = \frac{V}{R T} (p_{O_2, E} + p_{CO_2, E} + \frac{1}{2} p_{CO, E} + \frac{1}{2} p_{O, E}) \quad 2.13$$

where V , R , T and p represent the volume of the graphite furnace, the universal gas constant, the absolute temperature, and the partial pressure, respectively. By substituting the equilibrium constants of Eqns 2.9-2.11 into 2.13, one obtains Eqn 2.14 as follows

$$(K_9+1)^2 p_{O_2,E}^2 - [2Q(K_9+1) + \frac{1}{4}(K_{10}+K_{11})^2] p_{O_2,E} + Q^2 = 0 \quad 2.14$$

where $Q = \frac{n_{O_2,I} \times R \times T}{V}$

By solving Eqn 2.14 one gets Eqn 2.15

$$p_{O_2,E} = \frac{2Q(K_9+1) + \frac{1}{4}(K_{10}+K_{11})^2 \pm \sqrt{[2Q(K_9+1) + \frac{1}{4}(K_{10}+K_{11})^2]^2 - 4(K_9+1)^2 Q^2}}{2(K_9+1)^2} \quad 2.15$$

Similarly, the partial pressures of CO , CO_2 and O at equilibrium can be calculated from Eqns 2.9-2.11.

Table 2 presents the equilibrium partial pressures of CO , CO_2 , O_2 and O in the graphite furnace calculated for different temperatures with the initial amount of oxygen 9.7×10^{-10} moles. Table 2 shows that the equilibrium partial pressures of oxygen inside the graphite furnace are extremely low; indeed, they are lower than the maximum tolerable partial pressures (equilibrium pressures) of oxygen given in Table 1 by many orders of magnitude. Note that a pressure on the order of 10^{-19} atm corresponds to about one molecule inside the furnace volume at a

Table 2. Estimated partial pressure of gases in the graphite furnace during atomization (gas-stop mode) as a function of temperature.

Temperature, K	Partial pressures of gaseous species, atm			
	CO	CO ₂	O ₂	O
1000	2.0×10^{-4}	2.3×10^{-8}	4.8×10^{-29}	1.1×10^{-24}
1100	2.2×10^{-4}	4.4×10^{-9}	6.8×10^{-28}	6.5×10^{-23}
1200	2.4×10^{-4}	1.1×10^{-9}	6.3×10^{-27}	2.0×10^{-21}
1300	2.6×10^{-4}	3.6×10^{-10}	4.3×10^{-26}	3.6×10^{-20}
1400	2.8×10^{-4}	1.8×10^{-10}	3.0×10^{-25}	5.1×10^{-19}
1500	3.0×10^{-4}	6.1×10^{-11}	9.6×10^{-25}	4.0×10^{-18}
1600	3.2×10^{-4}	3.0×10^{-11}	3.5×10^{-24}	2.7×10^{-17}
1700	3.4×10^{-4}	1.7×10^{-11}	1.1×10^{-23}	1.5×10^{-16}
1800	3.6×10^{-4}	9.9×10^{-12}	3.1×10^{-23}	6.7×10^{-16}
1900	3.8×10^{-4}	6.2×10^{-12}	7.9×10^{-23}	2.6×10^{-15}
2000	4.0×10^{-4}	4.2×10^{-12}	1.8×10^{-22}	9.0×10^{-15}
2100	4.2×10^{-4}	2.9×10^{-12}	4.0×10^{-22}	2.8×10^{-14}
2200	4.4×10^{-4}	2.1×10^{-12}	8.3×10^{-22}	7.7×10^{-14}
2300	4.6×10^{-4}	1.6×10^{-12}	1.6×10^{-21}	2.0×10^{-13}
2400	4.8×10^{-4}	1.2×10^{-12}	3.0×10^{-21}	4.7×10^{-13}
2500	5.0×10^{-4}	1.0×10^{-12}	5.2×10^{-21}	1.0×10^{-12}

Parameters used in the calculation of the partial pressures of gases: graphite tube length = 2.8 cm, internal diameter = 0.6 cm; and estimated initial amount of oxygen inside the graphite tube = 9.7×10^{-10} moles.

temperature of 1000 K. Such a low partial pressure of O_2 ($< 10^{-19}$ atm) has little physical significance. What it means is that if tiny amounts of oxygen were to effuse in from the outside through the injection hole during a determination, they would be rapidly reduced to effectively zero concentration.

ii) Under chemical non-equilibrium conditions

The rate of reaction between oxygen and graphite is slow at a temperature below 800 K [58]. The partial pressure of all forms of carbon, i.e., C, C_2 , C_3 , etc., are less than 2.5×10^{-6} atm at temperatures as high as 2400 K [59], and are less than that of oxygen present as an impurity in the purge gas (Ar) of high purity. The rate of oxygen disappearance in the graphite furnace may therefore be considered not to be determined by the interaction between oxygen and carbon in the gas phase. The rate of the heterogeneous solid-gas reaction, $2C(s) + O_{2(g)} \rightarrow 2CO(g)$, has been used to determine the oxygen partial pressure inside the graphite furnace under the conditions of diffusion-limited reaction rates [51].

Carbon and oxygen reactions involving the chemisorption of molecular and/or atomic oxygen onto the graphite surface and then their desorption as $CO_{2(g)}$ and/or $CO(g)$ have been reported [60,61]. Kinetic studies on the rate of reaction between graphite and oxygen indicate that the reaction order lies between zero and first and seems to be dependent on the temperature and the oxygen partial pressure. The change in reaction order with temperature has been attributed to two types of reaction sites on the graphite basal plane which differ in reactivity and vary fractionally with temperature. However, EYRING and

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LIN [62] have derived an expression for the rate of disappearance of oxygen with their postulated mechanism of reaction between oxygen and graphite, and concluded that only one type of reaction site on the graphite surface is responsible for the oxidation reaction and the change of the reaction order mainly results from the change in experimental conditions. Irrespective of the argument over the type of activated site on graphite surfaces, the instantaneous partial pressure of oxygen inside the pulse-heated graphite furnace has been estimated in this study using the postulated mechanism, rate expressions, and rate constants given by STRICKLAND-CONSTABLE [63-65]. These are given in Table 3.

In the simulation model considered here, the following assumptions have been made for the sake of simplicity. a) There is no temperature gradient along the length of graphite tube and no temperature difference between the tube surface and gas phase. b) Temperature-rise results in a proportional amount of gaseous species expanding and leaving the graphite furnace to maintain constant pressure. c) Pressure changes due to changes in the total number of atoms and/or molecules via chemical reactions inside the furnace are not taken into account. d) The products and the reactants have the same diffusion coefficients. e) Initially, the oxygen is uniformly distributed throughout the furnace volume. f) The direction of diffusion is perpendicular to the graphite tube surface. Length-wise (graphite tube) diffusion and gas phase expansion are not considered. g) The diffusion process is symmetrical about the graphite tube cross-section. h) The system is closed with respect to O_2 .

Table 3. Summary of the carbon-oxygen reactions, rate equations, and rate constants [63-65].

Reaction	Rate equation*
I) A site + O ₂ → A site + 2 CO	Rate = $\frac{k_A P_{O_2}}{1 + k_Z P_{O_2}} x$
II) B site + O ₂ → A site + 2 CO	Rate = $(1 - x) k_B P_{O_2}$
III) A site → B site	Rate = $k_T x$

Overall carbon oxidation rate (mol cm ⁻² s ⁻¹)	
= (rate of reaction I) + (rate of reaction II) =	$\frac{k_A P_{O_2}}{1 + k_Z P_{O_2}} x + (1 - x) k_B P_{O_2}$

Rate constants:	
$k_A = 20 \times \exp(-30000/RT)$	$k_B = 4.46 \times 10^{-3} \times \exp(-15200/RT)$
$k_Z = 21.3 \times \exp(4100/RT)$	$k_T = 1.51 \times 10^5 \times \exp(-97000/RT)$

*x is the fraction of the total number of reactive sites as A site.

As can be seen from Table 3, the overall rate expression is described as the rate of carbon depletion. If it is assumed that carbon monoxide is the only product of the reaction between the graphite and the oxygen, then,

$$\frac{1}{2} \frac{dn_C}{dt} = - \frac{dn_{O_2}}{dt} \quad 2.16$$

where n_C and n_{O_2} represent the number of moles of carbon and oxygen, respectively. Hence, the rate of oxygen disappearance can be expressed as follows.

$$\frac{dp_{O_2}}{dt} = - \frac{R T A}{2 V} \left[\frac{k_A p_{O_2}}{1 + k_2 p_{O_2}} x + (1-x) k_B p_{O_2} \right] \quad 2.17$$

where A is the interior surface area of the graphite tube, and x is the fraction of the total number of reactive sites as A site.

As can be seen from Table 3, it is assumed in the mechanism of the heterogeneous carbon-oxygen reaction that there are two types of carbon sites on the graphite surface, namely A , a more reactive, and B a less reactive type. Initially, the fraction of A sites, x , is estimated under a steady-state condition, i.e., $k_T x = (1-x) k_B p_{O_2}$. However, simulation of the progressive change in the fractional value of x with the overall rate expression of reactions I and II in Table 3 requires the total number of reactive sites on the graphite surface, N_{total} . The estimated total number of reactive sites on the ab-plane surface of pyrolytic graphite is 10% of the total number of carbon atoms in a unit surface area [66]. According to the crystal structure of ab-plane of

anisotropic pyrolytic graphite [58], a value of N_{total} of 6.4×10^{-10} mol cm^{-2} is estimated and used as a standard input value. Furthermore, it is assumed that the value of N_{total} does not vary with time. The change in the fractional value x with time can be expressed as follows.

$$\frac{dx}{dt} = \frac{k_B P_{O_2} (1-x) - k_T x}{N_{\text{total}}}$$

2.18

If the rate of radial diffusion of oxygen towards the graphite surface is much faster than that of the heterogeneous solid-gas reaction, the partial pressure of the surface oxygen remains the same as the oxygen partial pressure inside the furnace, i.e., the oxygen is uniformly distributed. However, the exponential increase in the reaction rate with increase in the temperature may result in a lower oxygen partial pressure on the graphite surface because of the relatively slow rate of diffusion. The occurrence of the carbon-oxygen reaction in the interface between the solid and the gas phase results in a decrease in the oxygen concentration on the graphite surface; hence, a concentration gradient induces diffusion of oxygen from the center of the transverse cross-section towards the graphite surface. According to Fick's second law [67], the diffusion of oxygen in a cylindrical tube along the radius with cylindrical coordinates can be expressed as

$$\frac{\partial C}{\partial t} = D \left(\frac{1}{r} \frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial r^2} \right) \quad 2.19$$

where D is the diffusion coefficient and r is the internal radius of

the graphite tube. The diffusion coefficient as a function of temperature for the argon-oxygen mixture is expressed as follows [68].

$$D = 9.21 \times 10^{-6} T^{1.75} \text{ cm}^2 \text{ s}^{-1} \quad 2.20$$

Since the rate of chemical reactions and the diffusional mass transport are temperature-dependent, and the temperature changes with time during pulse-heating of the furnace, the instantaneous oxygen partial pressure inside the graphite furnace cannot be readily expressed analytically. A numerical iteration with the single-step, fourth-order, Runge-Kutta integration method for the heterogeneous solid-gas reaction and with the explicit finite difference approximation for the diffusion process was used to simulate the instantaneous oxygen partial pressure inside the graphite furnace.

Figure 11 shows the geometry of a cross-sectional plane of the cylindrical graphite tube used for the finite difference approximation. The outermost zone, n , is specified as the kinetic zone where the partial pressure of oxygen is determined by the number of oxygen molecules inside this zone. Zones are numbered 1 to $n-1$ for iteration of the diffusion process. The concentration gradient produced by a decrease in the oxygen concentration in the kinetic zone, n , in each finite step, via chemical reactions I and II in Table 3, is the driving force for the diffusion and re-distribution of oxygen inside the graphite furnace. Decrease in total number of oxygen molecules in the diffusion zones 1 to $n-1$ after re-distribution by diffusion equals the amount of oxygen which enters the kinetic zone. The altered concentrations of oxygen in each zone, i.e., after the increase of

Figure 11. Nodal geometry of the cross-sectional plane of the graphite tube.

r_0 - internal radius of the graphite tube.

oxygen in the kinetic zone, were used in the calculation for the next finite time increment.

Furthermore, the terms of the first-order and the second-order derivatives in Eqn 2.19 can be expressed as their finite difference forms:

$$\frac{\partial C}{\partial t} \approx \frac{C_i^{p+1} - C_i^p}{\Delta t} \quad 2.21$$

$$\frac{\partial C}{\partial r} \approx \frac{C_{i+1}^p - C_{i-1}^p}{2 \Delta r} \quad 2.22$$

$$\frac{\partial^2 C}{\partial r^2} \approx \frac{C_{i+1}^p + C_{i-1}^p - 2 C_i^p}{(\Delta r)^2} \quad 2.23$$

where $\Delta r = \frac{r_o}{n}$ and $2 \leq i \leq n-1$.

C is the concentration of oxygen at the specified zone described by the subscript, i; the superscript p+1 denotes the time explicitly in terms of the previous time p plus a finite increment of time, Δt .

Substituting Eqns 2.21-2.23 into Eqn 2.19 and rearranging, the concentration in zone i after finite time increment can be described as follows:

$$C_i^{p+1} = \beta \left[\left(1 + \frac{\Delta r}{2r} \right) C_{i+1}^p + \left(1 - \frac{\Delta r}{2r} \right) C_{i-1}^p \right] + C_i^p (1 - 2\beta) \quad 2.24$$

where $\beta = D \cdot \Delta t / (\Delta r)^2$. The stability requirement of Eqn 2.24 is that the coupling of the two independent variables, Δt and Δr , must give a

positive coefficient of the C_1^P term. In other words, β must not be greater than 0.5. Furthermore, the problem of approximating the concentration at the central zone, $C_{i=1}$, with the cylindrical coordinate finite difference equation (Eqn 2.24) should be noted. This equation cannot be used to solve for the centre node because the radius, r , equals zero. In the model considered here, $C_{i=1}$ is assumed to be the same as $C_{i=2}$. In order to minimize the propagated error, Δr should be small so that the total number of molecules involved in the central zone does not significantly alter the result of the simulation model.

If it is assumed that the rate of oxygen disappearance inside the furnace is kinetically controlled by the heterogeneous solid-gas reaction, i.e., the rate of the radial diffusion of oxygen towards the graphite surface is assumed to be much faster than the rate of the heterogeneous solid-gas reaction, then the instantaneous partial pressure of oxygen inside the furnace as a function of temperature is shown by curve A in Fig. 12. Figure 12 has been drawn using a heating rate of 2 K ms^{-1} and an initial oxygen partial pressure of $5 \times 10^{-5} \text{ atm}$. Curve B in Fig. 12 shows the instantaneous partial pressure of oxygen inside the furnace as a function of temperature for which both the rate of the heterogeneous solid-gas reaction and the rate of oxygen diffusion towards the graphite surface have been taken into account. The heating rate and the initial partial pressure used for the iteration of curve B are the same as those used for the iteration of curve A. Comparison of the two curves suggests that the rate of oxygen disappearance is kinetically controlled by the heterogeneous solid-gas

Figure 12. Instantaneous partial pressures of oxygen inside the graphite furnace as a function of temperature.

Curves A and B are simulated using the model. Curve A - kinetically controlled heterogeneous reaction; curve B - the same as curve A with the rate of diffusion being also taken into account. Heating rate = 2.0 K ms^{-1} , initial temperature = 500 K , initial partial pressure of oxygen = $5.0 \times 10^{-5} \text{ atm}$, and total number of reactive site = $6.34 \times 10^{-10} \text{ mol cm}^{-2}$. Curve C is the partial pressure of one atom or molecule.

chemical reaction at temperatures below 1200 K. However, it becomes controlled by the rate of oxygen diffusion at higher temperatures.

Curve C in Fig. 12 shows the pressure which is attributable to one single molecule or atom, as a function of the temperature. The pressure below the line has no physical significance.

The value of the total number of reactive sites on the ab-plane of the graphite surface depends strongly on the type of graphite considered. Figure 13 shows the effect of total number of reactive sites, N_{total} , on the ab-plane of the graphite surface on the instantaneous partial pressure of oxygen inside the furnace. As can be seen from Fig. 13, the instantaneous partial pressure of oxygen inside the furnace increases as the total number of reactive sites decreases. The results in Fig. 13 indicate that the instantaneous partial pressure of oxygen inside the furnace depends strongly on the surface of the graphite used as well as on the variation of the surface condition resulting from the use of the furnace. However, the estimated value of 10% of the total number of atoms exposed on the ab-plane of the graphite surface [66] was used for the following studies.

Figure 14 shows the effect of furnace heating rate, coupled with the various final temperatures, on the calculated instantaneous partial pressure of oxygen inside the furnace. As can be seen from Fig. 14-I, the instantaneous partial pressure of oxygen at the time when the furnace reaches 2300 K with the heating rate of 2.5 K ms^{-1} , is below the point which has physical significance. However, the instantaneous partial pressure of oxygen at the time of attainment of 2300 K with the heating rate of 20 K ms^{-1} is about $5.0 \times 10^{-8} \text{ atm}$ (Fig. 14-IV). Since

Figure 13. Effect of the total number of the reactive sites, N_{total} , at the surface of the pyrolytically coated graphite tube on the instantaneous partial pressure of oxygen inside the graphite furnace as a function of temperature.

Heating rate = 2.0 K ms^{-1} , initial oxygen partial pressure = $5.0 \times 10^{-5} \text{ atm}$, and initial temperature = 500 K .

$N_{\text{total}} (\text{mol cm}^{-2})$: a 6.34×10^{-9} ; b 6.34×10^{-10} ;
c 6.34×10^{-11} ; d 6.34×10^{-12} .

Figure 14 (I-IV). Effect of the heating rate of the graphite furnace on the instantaneous partial pressure of oxygen inside the furnace.

Dashed lines a, b and c are the temperature-time curves. Solid lines A, B and C are the curves for partial pressure of oxygen as a function of time. A, B and C are simulated curves for which the temperature-time curves are a, b and c, respectively.

Fig. 14 (I-II)

Fig. 14 (III-IV).

the rate of diffusion of oxygen towards the graphite surface is not as sensitive to the change in temperature as that of the heterogeneous solid-gas reaction, the amount of oxygen left inside the furnace in the stop-flow mode of the purge gas (Ar) is therefore determined by the total reaction time and the instantaneous rate of the heterogeneous carbon-oxygen reaction. The high instantaneous partial pressure of oxygen at a given temperature with increasing heating rate, as shown in Fig. 14, may be attributable to decreasing reaction time between the carbon and the oxygen with increasing heating rate.

Essentially, the partial pressure of carbon monoxide inside the furnace is increased by the product of the carbon-oxygen reaction. Thus, the partial pressure of CO increases as the partial pressure of oxygen decreases. The amount of CO that can be formed is limited by the initial amount of O_2 in the furnace.

Instantaneous Partial Pressures of O_2 and CO inside the Graphite Furnace

As shown in Fig. 12, the instantaneous partial pressure of oxygen inside the furnace decreases as the furnace temperature increases. However, at 1900 K, the partial pressure of O_2 estimated under non-equilibrium conditions is about the same as that estimated under chemical equilibrium conditions, as shown in Table 2. Therefore, for temperatures > 1900 K, the partial pressure of O_2 inside the furnace may tend to reach the equilibrium composition instead of dropping steeply along curve B in Fig. 12.

The instantaneous partial pressure of oxygen inside the furnace also depends on the initial amount of the oxygen in the purge gas (Ar).

Figure 15. Effect of the initial pressure of oxygen on its instantaneous partial pressure inside the graphite furnace as a function of temperature.

A, B, C and D are simulated curves. Heating rate = 1.5 K ms^{-1} ; $N_{\text{total}} = 6.34 \times 10^{-10} \text{ mol cm}^{-2}$; initial temperature = 500 K. Curves a, b, c and d show the equilibrium partial pressures of oxygen as a function of temperature. Curve E is the partial pressure of one atom or molecule.

Initial oxygen partial pressure (atm): A, a 5.0×10^{-2} ; B, b 5.0×10^{-3} ; C, c 5.0×10^{-4} ; D, d 5.0×10^{-5} .

Curves A, B, C and D in Fig. 15 show the instantaneous partial pressure of oxygen as a function of temperature which is simulated at a heating rate of 1.5 K ms^{-1} with the initial partial pressures of oxygen 5.0×10^{-2} , 5.0×10^{-3} , 5.0×10^{-4} and 5.0×10^{-5} atm, respectively. Curves a, b, c and d in Fig. 15 are the equilibrium partial pressures of oxygen as a function of temperature calculated using Eqn 2.15 with initial amounts of O_2 9.7×10^{-7} , 9.7×10^{-8} , 9.7×10^{-9} and 9.7×10^{-10} moles, respectively. Thus, as discussed above, the instantaneous partial pressure of oxygen inside the furnace with increasing temperature at a heating rate of 1.5 K ms^{-1} may be described by the solid lines.

If it is assumed that carbon monoxide is the predominant product of oxygen-carbon reaction inside the graphite furnace, the increase in partial pressure of carbon monoxide is related to the rate of the oxygen-carbon reaction. At low temperatures ($< 1400 \text{ K}$), the partial pressure of carbon monoxide inside the graphite furnace is lower than that at chemical equilibrium. Based on a similar argument as for O_2 , the instantaneous partial pressure of carbon monoxide increases with increasing temperature up to the point of intersection where the reaction attains chemical equilibrium, and then increases as shown in Table 2.

As discussed earlier, the driving force for the conversion of metal oxide into metal in the condensed phase via carbon reduction (Eqn 2.1) and thermal decomposition (Eqn 2.3) is the instantaneous partial pressure of oxygen and carbon monoxide inside the graphite furnace. If the instantaneous partial pressures of oxygen and carbon monoxide are lower than the maximum tolerable partial pressures in

Table 1, both carbon reduction and thermal decomposition are spontaneous reactions. On the other hand, if the instantaneous partial pressures of these two gaseous species in the system are higher than those in Table 1, the above reactions are not spontaneous, but the reverse reactions are.

If high-purity argon is used as the purge gas, the partial pressure of oxygen inside the furnace decreases with increasing temperature as shown by curve D in Fig 15, whereas, as mentioned earlier, the partial pressure of carbon monoxide increases rapidly up to 10^{-4} atm at temperature > 1500 K. By comparing the instantaneous partial pressures of oxygen and carbon monoxide inside the furnace with the maximum tolerable partial pressures of oxygen and carbon monoxide in Table 1, spontaneity of conversion of metal oxide into metal in the condensed phase by carbon reduction (Eqn 2.1) or by thermal decomposition (Eqn 2.3) has been determined, as shown in Table 4. Table 4 also lists the mechanism for atom formation as reported in the literature. The conversion of metal oxide into metal in the condensed phase via carbon reduction or thermal decomposition are both spontaneous reactions in the graphite furnace for Cu, Ni, Sn, Cr, Al and V. Only carbon reduction is spontaneous for Pb, Co, Fe, Cd, Zn, and Mn. Neither reaction is spontaneous for Mg and Ca.

For Zn, Cd and Mn, conversion of metal oxide into metal, as shown in Table 4, by carbon reduction should occur spontaneously at a temperature nearest to the appearance temperature. However, the postulated mechanism for atom formation, based on experimental results, indicates that the precursor of gaseous atoms is the gaseous metal

Table 4. Spontaneity of the conversion of metal oxide into metal in the condensed phase at the appearance temperature.

Metal, M	Metal oxide, M_xO_y	Appearance temperature*, K	Spontaneity of the conversion of metal oxide into metal in the condensed phase [†]			Reported mechanism*
			$\frac{1}{x} M_xO_y(s/l) + \frac{y}{x} C$	$\frac{1}{x} M_xO_y(s/l)$	$\frac{1}{x} M_xO_y(s/l) + \frac{y}{2x} O_2(g)$	
			$\rightleftharpoons M(s/l) + \frac{y}{x} CO(g)$	$\rightleftharpoons M(s/l)$	$\rightleftharpoons M(s/l) + \frac{y}{2x} O_2(g)$	
Cu	CuO	1270	+	+	+	$Cu(s) \rightarrow Cu(g)$
Sn	SnO ₂	1560	+	+	+	$Sn(l) \rightarrow Sn(g)$
Ni	NiO	1590	+		+	$Ni(s) \rightarrow Ni(g)$
Cr	Cr ₂ O ₃	1660	+		+	$Cr(s) \rightarrow Cr(g)$
Al	Al ₂ O ₃	2080	+		+	
V	V ₂ O ₅	2200	+		+	$V(l) \rightarrow V(g)$
Pb	PbO	1040	+		-	$Pb(l) \rightarrow Pb(g)$
Co	CoO	1430	+		-	$Co(s) \rightarrow Co(g)$
Fe	FeO	1500	+		-	$Fe(s) \rightarrow Fe(g)$
Cd	CdO	720	+		-	$CdO(g) \rightarrow Cd(g)$
Zn	ZnO	1140	+		-	$ZnO(g) \rightarrow Zn(g)$
Mn	MnO	1480	+		-	$MnO(g) \rightarrow Mn(g)$
Mg	MgO	1510	-		-	$MgO(g) \rightarrow Mg(g)$
Ca	CaO	1850	-		-	$CaO(g) \rightarrow Ca(g)$

*Ref. [28].

†+ sign - the reaction from the left-hand side to the right-hand side is spontaneous. - sign - the reaction from the right-hand side to the left-hand side is spontaneous.

oxide, which arises from rapid vaporization of the metal oxide in the furnace.

The high partial pressures of the carbon monoxide as well as oxygen in the gas phase tend to stabilize Ca and Mg in the oxide form. This is consistent with the results of x-ray structure analysis [43,44]: only CaO and MgO have been detected on the surface of the graphite furnace after the furnace has been heated to the appearance temperatures of these elements.

SUMMARY

The results of theoretical studies of instantaneous partial pressures of oxygen inside the pulse-heated graphite furnace as a function of temperature show that, up to a relatively high furnace temperature, partial pressures of oxygen are very much greater than those at chemical equilibrium, and are controlled by the rate of heterogeneous solid-gas reaction between carbon and oxygen. Above 1200 K, the rate of the carbon-oxygen reaction rate increases rapidly with the temperature of the furnace; hence, the partial pressure of oxygen drops rapidly and approaches the low value present at chemical equilibrium. However, the instantaneous partial pressure of oxygen inside the furnace depends strongly on the surface reactivity of the graphite and the heating rate of the furnace.

It should be noted that the metal oxide present in the furnace is another source of oxygen and is not considered in this model. The increase in the oxygen content due to the dissociation of the metal

oxide depends on the temperature and the thermal stability of the metal oxide at the instantaneous partial pressures of the gases in the furnace. Hence, the estimated partial pressure of oxygen presented here should be considered to be a lower limit.

When a metal oxide is considered to be the precursor to free metal atoms, the instantaneous partial pressures of O_2 and CO at the appearance temperature determine the thermodynamic feasibility of the conversion of the metal oxide into metal in the condensed phase by thermal decomposition or carbon reduction. Thus, the role of carbon is not limited to reduction of metal oxide to metal, but also extends to reducing the partial pressure of oxygen in the furnace to the value required for thermal decomposition of metal oxide to be thermodynamically favourable at the appearance temperature of the metal.

CHAPTER 3
INSTRUMENTATION FOR
CAPACITIVE-DISCHARGE-HEATED GRAPHITE FURNACE
ATOMIC ABSORPTION SPECTROMETRY

MASSMANN [69] introduced the technique of pulse-heated, electrothermal graphite furnace atomic absorption spectrometry (GFAAS). Commercial electrothermal atomizers for AAS almost exclusively employ pulse-heated graphite furnaces with relatively slow heating rates (up to a maximum of about 2 K ms^{-1}). This technique will be called conventional GFAAS to differentiate it from the capacitive discharge technique (CDT) in which relatively high heating rates (up to a maximum of about 100 K ms^{-1}) are used.

The effect of heating rate on pulse-heated atomization in GFAAS has been reported [70-74]. Great increase in the heating rate of the atomizer at the atomization stage enables the final (constant) atomization temperature to be attained extremely rapidly, resulting in the analyte absorption pulse appearing wholly or partly in the constant-temperature region of the temperature-time curve (to be henceforth called "isothermal atomization"). Such isothermal atomization has been reported [72] to improve analytical recoveries significantly.

In general, the rate of change in temperature of the graphite furnace wall is nearly proportional to the input power level. When a step-down transformer is used in the power supply unit, the difficulties of increasing the heating rate above 5 K ms^{-1} for a

commercial graphite furnace are as follows.

- a) Low resistance of regular graphite - the low resistance of regular graphite limits the maximum output voltage of the transformer to a low value because high voltages would produce correspondingly high currents. Also, the large contact resistance and the low resistance of the regular graphite furnace result in a great loss of power at the contact points.
- b) Power limitation - the maximum power output of the transformer is limited by the current-carrying capability of the electrical supply line. Although a supply current of 300 A at voltage of 208 V a.c. can be obtained, a current of 40 A is in practice used for this voltage in most laboratories. Using an input power of 8 kW for the HGA-2100 which has a resistance of $22 \text{ m}\Omega$ a heating rate $< 4 \text{ K ms}^{-1}$ has been reported [28].

In order to increase the heating rate, an alternative technique is required to overcome the limitation of supplying power with the transformer to low-resistance, regular graphite. Such an alternative technique is to construct the furnace with highly oriented anisotropic pyrolytic graphite having high resistance in a certain direction, and to heat the furnace with a high output-level power supply unit.

GRESSER and MULLINS [75] have suggested the use of a large electrolytic capacitor for rapid heating of metal filament atomizers and discussed the feasibility of using this system for rod atomizers. A practical device for capacitive-discharge heating for GFAAS was patented in 1974 [76]. L'VOV [42] demonstrated the use of a high-voltage capacitor bank as a source of electrothermal energy for

heating a highly oriented anisotropic pyrolytic graphite tube furnace and reported a heating rate of 40 K ms^{-1} .

In this chapter, a capacitive-discharge-heated furnace made of anisotropic pyrolytic graphite and an atomic absorption spectrometer used for this furnace, are described.

APPARATUS

A block diagram of the capacitive-discharge-heated graphite furnace (CDT) AAS is shown in Fig. 16. It consists of three major components: a single-beam spectrometer with a detection system, an atomizer with a power supply unit, and temperature measuring devices.

I) Spectrometer with Detection System

Single-element hollow cathode lamps, manufactured by Perkin-Elmer, Varian Techtron, or Westinghouse were used. The lamps were operated at the recommended current using a modulation frequency of 843 Hz. The radiation from the lamp was collimated and focussed by quartz plano-convex lenses, L-1 and L-2, with focal length of 20 and 10 cm, respectively. A light baffle, B, with an aperture diameter slightly smaller than the internal diameter of the graphite tube was placed in the optical path between the atomizer and L-2 in order to prevent the intense continuum emitted by the incandescent graphite wall from entering the monochromator.

Atomic absorption measurements were made with a Varian-Techtron 0.5 m Ebert-mount monochromator ($50 \times 50 \text{ mm}^2$ grating ruled with 638 lines/nm) fitted with a Hamamatsu R955 photomultiplier tube (Hamamatsu

Figure 16. A block diagram of the capacitive-discharge-heated graphite furnace atomic absorption spectrometer.

Corporation, Middlesex, N.J., USA), which was enclosed within a magnetically and electrostatically shielded housing to reduce interferences. The signal from the photomultiplier tube was passed through a pre-amplifier into a lock-in amplifier. The reference signal of the lock-in amplifier was of the same frequency 843 Hz as used to modulate the hollow cathode lamp emission source. This high modulation frequency of the hollow cathode lamp permitted fast response time required by the CDT. The amplified signal was passed through a logarithmic converter and an active low-pass RC filter. This laboratory-made amplifier assembly has a variable time constant from 4 to 104 ms. A Nicolet model 2090-III, dual-channel digital oscilloscope fitted with a model 201 plug-in unit and a disk recorder (all from Nicolet Instrument Co., Madison, Wisconsin, USA) was used to record the output signal from the amplifier.

II) Atomizer and Power Supply Unit

The main difference between the CDT and the conventional (commercial) graphite furnace is that the former uses high heating rates (up to 60 K ms^{-1}) by capacitive discharge heating of an anisotropic pyrolytic graphite furnace; whereas, the latter uses much lower heating rates ($< 2 \text{ K ms}^{-1}$) of a furnace made of regular graphite, and is constructed as follows. A thin layer of anisotropic pyrolytic graphite is thermally deposited on the substrate of a regular graphite tube - the product is usually referred to as pyrolytic graphite coated graphite tube (PGCGT). The graphite tube used for the capacitive-discharge technique is quite different from PGCGT, the former being

entirely made (machined) from a block of anisotropic pyrolytic graphite. Some important properties of anisotropic pyrolytic graphite are summarized and discussed below.

i) Properties of anisotropic pyrolytic graphite

Structurally, the atomic arrangement of a perfect crystal of graphite has an orderly stacking of the hexagonal planes as shown in Fig. 17 [77]. The spacing between sheets of the graphite is 3.35 Å. Each sheet of graphite consists essentially of carbon atoms in the trigonal, sp^2 state. The interatomic bonding has $1\frac{1}{3}$ bond order, and the atoms are 1.42 Å apart. The crystallographic axes are a, b and c as shown in this figure.

Anisotropic pyrolytic graphite is a vapour-deposited form of carbon having a high degree of preferred crystalline orientation as shown in Fig. 17. This material is produced by the decomposition of a hydrocarbon gas, e.g. methane, on a hot surface and deposits in such a way that the lamellar planes (ab-plane) of graphite in bulk material are oriented parallel to the plane of deposition. The resulting material has physical and electrical properties that differ greatly if they are measured in a direction parallel (ab-direction), or perpendicular (c-direction) to the plane of deposition.

Table 5 lists some properties of anisotropic pyrolytic graphite at room temperature; these properties have been summarized from Table 1 given by Moore [78]. Differences in the physical and electrical properties between the ab-plane and the c-direction show a great anisotropy in the graphite crystal of the raw material. Variations in the literature values of properties of anisotropic pyrolytic graphite

Figure 17. The atomic arrangement of a perfect crystal of graphite.

Table 5. Properties of anisotropic pyrolytic graphite at room temperature [78].

Property	Units	Literature values [78]
Density	g cm^{-3}	2.18 - 2.22
Interlayer spacing	$\text{\AA}$	3.42 - 3.44
Electrical resistivity	ohm-cm	
ab-plane		5×10^{-4}
*c-direction		0.3 - 1.0
Thermal conductivity	$\text{W cm}^{-1} \text{K}^{-1}$	
ab-plane		3 - 6
*c-direction		0.02 - 0.03

*c-direction is perpendicular to the ab-plane.

are due to their strong dependence on the deposition conditions [66,79].

As can be seen from Table 5, pyrolytic graphite deposited at 2400-2500 K in a constant temperature enclosure has an interlayer spacing of 3.42 to 3.44 Å. The spread in interlayer spacing of anisotropic pyrolytic graphite relative to that of the single-crystal graphite is due to disorder in the stacking of the layers during deposition [79].

The thermal conductivity of anisotropic pyrolytic graphite in ab-planes at room temperature is higher than that along the c-direction by a factor of 100-300 depending on the deposition conditions. Also, thermal conductivity in the ab-plane is approximately 10-fold greater than that of regular (isotropic) graphite [77,78]. It has been reported that thermal conductivities in the ab-plane and along the c-direction are temperature-dependent. Upon heating from room temperature to 1400 K, thermal conductivity in the ab-plane decreases to about 15% of its original room temperature value [77]. Contrary to the value reported in Ref. 77, the thermal conductivity along the c-direction decreases with increasing temperature [58,80-82]. In the ab-plane, anisotropic pyrolytic graphite is one of the best thermal conductors among elementary materials, whereas it acts as a thermal insulator in the c-direction.

Table 5 also shows that the electrical resistivity in the c-direction at room temperature is greater than that in the ab-plane by a factor of 600 to 2000, depending on the deposition conditions. Typical electrical resistivities parallel and perpendicular to the

deposition plane of pyrolytic graphite at room temperature are 5×10^{-4} and 0.5 ohm-cm, respectively [78], compared with the resistivity of 3×10^{-3} ohm-cm for isotropic pitch-coke carbon baked to 2300 K [83]. Thus, in the ab-plane pyrolytic graphite is a good electrical conductor; whereas in c-direction it is a poor electrical conductor. The electrical resistivity in the ab-plane decreases from room temperature to 1300 K and then increases at higher temperatures [77]. The electrical resistivity in the c-direction shows no such minimum, decreasing steadily with temperature [80,84].

ii) Construction of furnace with anisotropic pyrolytic graphite

The raw material (anisotropic pyrolytic graphite manufactured by Super-Temp Co., Santa Fe Springs, California, USA) was obtained in rectangular blocks 4×10 cm in the ab-plane and 1 to 2.5 cm in the c-direction. Two ways of boring graphite tubes from a block of anisotropic pyrolytic graphite are illustrated in Fig. 18, i.e. parallel or perpendicular to the c-direction. Unless otherwise noted, the graphite tubes have the dimension of 3.0 mm i.d., 6.0 mm o.d., and 15.0 mm in length. A sample injection hole of 1.4 mm diameter was drilled at the middle of the tube.

Figure 19 demonstrates three arrangements of mounting the graphite tube on the contact electrodes using the two tubes shown in Fig. 18. The position of the sample injection hole drilled in tube A with respect to the deposition plane results in different configurations shown as the type 1 and the type 2 furnace in Fig. 19. Tube B in Fig. 18 was used only for the type 3 furnace. In all three cases, electric current

Figure 18. Two different configurations of the lamellar plane of the anisotropic pyrolytic graphite tube bored from an anisotropic pyrolytic graphite block. The narrow solid line show the lamellar plane (*ab*-plane) of the anisotropic pyrolytic graphite.

Figure 19. Three configurations for anisotropic pyrolytic graphite tube furnace.

E: contact electrodes.

is introduced perpendicular to the ab-plane in order to utilize the high electrical resistance in the c-direction.

The type 1 furnace was constructed with the lamellae of the graphite tube stacked parallel to the optical axis, and two contact electrodes in the horizontal positions across the tube diameter. The type 2 furnace was formed by rotating the type 1 furnace 90 degrees along the optical axis and placing the contact electrodes in vertical positions above and below the graphite tube. The type 3 furnace is made with the lamellae stacked perpendicular to the optical axis of the tube, and end-contacted electrodes similar to the Perkin-Elmer Heated Graphite Atomizer were used.

Both the type 1 and the type 2 furnace were operated as open (to the atmosphere) systems. For both furnaces, the internal purge gas was supplied by two ceramic-tipped copper capillary tubes positioned at the side of each end of the graphite tube. To prevent air oxidation, the graphite tube was continuously swept with a laminar flow of an inert gas (usually argon) via a series of rectangular slots cut into the furnace housing. The flow of the inert gas was directed from above and below the graphite tube for the type 1 furnace and from both sides of the graphite tube for the type 2 furnace to ensure its complete containment in a chemically inert atmosphere. In the type 3 furnace, quartz windows were placed at each end of the graphite tube, and the furnace was open to the atmosphere only through the sample injection hole; thus, it was operated as a semi-enclosed system. The internal purge gas flowed through both ends of the graphite tube and escaped, through the sample injection hole. Similar to the type 1 furnace, an

external sheath gas (usually argon) was directed from above and below the graphite tube furnace into the furnace housing.

The measured resistances of the anisotropic pyrolytic graphite furnaces, having the dimensions 3.0 mm i.d., 6.0 mm o.d. and 15.0 mm long, are 0.56, 0.50 and 4.10 ohms for the type 1, type 2 and type 3 furnaces, respectively. The resistance is higher than that of the commercial, graphite furnace (made of regular graphite) by a factor of 10 to 200. As the result of high resistance, the anisotropic pyrolytic graphite furnace has the following advantages over the commercial graphite furnace (made of regular graphite): 1) it allows use of a high output-voltage power supply unit, e.g., a high-voltage capacitive discharge power supply; 2) it permits a decrease in the contact area between the electrode and the furnace without a significant change in the overall resistance of the load; and, 3) the great decrease in the ratio of the contact resistance and the overall resistance of the anisotropic pyrolytic graphite furnace from that of the graphite furnace made of regular graphite, results in more efficient use of electrical energy to heat the furnace.

iii) Power supply controller

Figure 20 presents a basic circuit diagram of the power supply unit for the capacitive-discharge-heated graphite furnace fabricated in this laboratory.

The power supply controller is similar to the controller for a commercial, pulse-heated graphite furnace in that it provides a sequence of drying, charring and atomization stages. For only a very short period of time, at the beginning of the atomization stage, the

2

Figure 20. Basic circuit diagram of the power supply unit for the capacitive-discharge heated graphite furnace.

furnace is rapidly heated from the charring temperature to a preset atomization temperature by discharging the capacitor bank across it. The sequence and duration of each of the four steps, i.e. drying, charring, discharging and atomization, are controlled by a series of timing circuits. Since the time required for the furnace to reach the preset atomization temperature can be as short as 10 to 15 ms with a heating rate of 60 K ms^{-1} , timing control with a reproducibility of $\pm 10 \text{ } \mu\text{s}$ is required. With commercial, resistively-heated graphite furnaces having much lower heating rates ($< 2 \text{ Kms}^{-1}$), timing control with a reproducibility of only a fraction of a millisecond is adequate.

Two capacitor banks, referred to as banks A and B, were constructed using "Computamite" aluminum electrolytic capacitors (Cornell-Dubilier Electric Corporation, Newark, N.J., USA), which were connected in parallel. Bank A consisted of a total of 46 capacitors, consisting of 21 capacitors each having $6000 \text{ } \mu\text{F}$ capacitance and rated at 300 V d.c., and 25 capacitors each having $7000 \text{ } \mu\text{F}$ capacitance and rated at 250 V d.c. Bank A provided a total capacitance of 0.30 F and had a maximum charging voltage of 250 V d.c. Bank B contained 97 capacitors each having a capacitance of $20000 \text{ } \mu\text{F}$ and rated at 150 V d.c., providing a total capacitance of 1.94 F. The choice of capacitor bank for a given experiment depended on the range of heating rates required, the tube mass, and the tube resistance.

To charge the capacitor bank and the cutoff capacitor, a Nobatron model DCR-300, 2.5 A constant current d.c. power supply (Sorensen Co. Inc., Manchester, N.H., USA) was used. The constant current mode of operation of the d.c. power supply made possible rapid charging of the

capacitor bank [85]. Current limiting resistors, R-1 and R-2 in Fig. 20, were used to protect the power supply from overload. The voltage applied to the capacitor bank was monitored with a model 1350 digital multimeter (Data Precision Co., Wakefield, Mass., USA) and could be manually controlled to ensure reproducible setting of the furnace heating rates.

An auxiliary power supply, in the form of a step-down transformer, was used for the drying and charring stages. The auxiliary power supply was also employed to hold the temperature constant after the furnace was heated by the capacitor bank discharge. The power input to the graphite furnace from the step-down transformer was controlled by two silicon controlled rectifiers (SCR), shown as SCR-1 and SCR-2 in Fig. 20.

A capacitor bank of large capacitance and high voltage can store a large amount of electrical energy. The amount of energy from the capacitor bank used to heat the furnace to a desired temperature was only a small fraction of the total energy stored. The way to control the amount of the energy drawn by the furnace was to control the discharging time interval.

At the end of charring stage, the SCR-3 was switched on. It resulted in discharging the capacitor bank to heat the furnace. As soon as the atomization temperature was attained, it was necessary to switch off the high level power output from the capacitor bank and to turn on the transformer to hold the atomization temperature constant. Technically, the SCR could not be switched off unless zero current passed through it. Therefore, a switching circuit associated with a

high voltage capacitor, a so-called "cutoff capacitor", was employed to turn off the SCR-3. Normally, the voltage of the "cutoff capacitor" was about 40 volts higher than the voltage of the charged capacitor bank. When SCR-4 was switched on, a transient high voltage, which must be higher than the voltage on the capacitor bank, appeared on the cathode of the SCR-3. The appearance of this transient high voltage resulted in a transient zero current through the SCR-3, and made it possible to switch off the SCR-3.

III) Temperature-Measuring Devices

The drying and charring temperatures were measured with an automatic optical pyrometer, Ircon series 300, model 300 (Ircon Inc., Skokie, Ill., USA) which responded over the spectral region of 2.0-2.6 μm and had a maximum response time of 5 ms. This pyrometer provided a range of temperature measurement from 380 to 3000 K. The temperature was continuously monitored during each drying and charring cycle. This provided a means of checking variations in temperature due to changes in the resistance and the mass of the graphite tube. Appropriate voltage adjustment of the power supply maintained a constant, predetermined temperature.

The atomization temperature was measured with a separate, automatic optical pyrometer, Ircon series 1100, model 11x30 (Ircon Inc.), which responded in the spectral region of 0.6-1.1 μm and had a 1.5 ms response time. This pyrometer provided the range of temperature measurement from 1050 to 4000 K. The voltage output from this pyrometer was recorded with a Nicolet 2090-III, model 201 plug-in,

dual-channel digital oscilloscope (Nicolet Instrument). Oscilloscopic traces were converted into temperature profiles using the pyrometer calibration curve supplied by the manufacturer.

MEASUREMENT PROCEDURE

The capacitor bank and the "cutoff capacitor" were charged to the desired voltage. Test solutions of 5 μL were injected into the furnace with an Eppendorf pipette (Brinkman Instruments Inc., Westbury, New York, USA) fitted with disposable plastic tips. Generally, the sequence of steps making up the heating program for a measurement was as follows. A drying stage of 30 s at a temperature slightly above the boiling point of the solvent was used for the three types of furnaces. An appropriate charring temperature was applied to the sample for 60 s for both the type 1 and the type 2 furnace, and 120 s for the type 3 furnace. The duration of the discharge of the capacitor bank at the atomization stage depended on factors such as the voltage on the capacitor bank, the charring temperature, the mass and the resistance of the graphite tube used, etc. The settings of the capacitive discharge were established empirically, and will be detailed in the following section. The time during which the atomization temperature was held constant depended on the sample composition.

External sheath gas for the three types of atomizer was maintained at 3.0 L min^{-1} , whereas a flow rate of 0.4 L min^{-1} was used for the internal purge gas. The internal purge gas flow was interrupted 3 s before the end of the charring cycle and remained off throughout the atomization cycle.

A nominal spectral bandpass of 0.16 nm was used for all elements studied. The following resonance lines (nm) were used: Cd 228.8, Co 240.7, Mn 279.5, Mo 313.2, Ni 232.0, and Pb 283.3. The quartz plano-convex lenses were focussed for maximum throughput of the radiation from the emission source (the hollow cathode lamps) at the above wavelengths. A parallel beam of radiation was obtained which illuminated the interior of each furnace completely.

The absorbance and temperature signals were simultaneously recorded with the Nicolet 2090-II, dual-channel, digital oscilloscope and stored in the disk recorder. The integrated absorbance was obtained by using an integration program supplied by Nicolet Corporation with the Nicolet model 4094, 4-channel, programable digital oscilloscope fitted with an XF-44 disk recorder (Nicolet Instrument Corporation). Hard copies of the absorbance and temperature profiles were obtained by interfacing a plotter, model HP-7470A (Hewlett-Packard Co.) with the Nicolet model 4094 oscilloscope.

RELATIONSHIP BETWEEN THE POWER AND THE HEATING RATE OF THE FURNACES

The amount of energy, U , stored in a capacitor bank is given by the following equation.

$$U = \frac{C \cdot V^2}{2} \quad 3.1$$

where C and V stand for capacitance and voltage of the capacitor bank, respectively. When the furnace is heated by electrical discharge of the capacitor bank, the power output from the capacitor bank can be

described as the rate of expenditure of the stored energy at any instant, t ,

$$P_t = - \frac{dU_t}{dt} = - C \cdot V_t \frac{dV_t}{dt} \quad 3.2$$

According to Kirchhoff's voltage law, the instantaneous voltage, V_t , across the capacitor bank in the discharging circuit in Fig. 20 can be expressed as

$$V_t + i \cdot R(t) = 0 \quad 3.3$$

where i is the instantaneous current passing through the furnace having resistance R . As mentioned earlier, the resistance of the anisotropic pyrolytic graphite is temperature-dependent, and the temperature of the graphite furnace is a function of time. The resistance of the furnace is therefore a function of time as shown by Eqn 3.3. Since $i = C(dV_t/dt)$, solving for the V_t in Eqn 3.3, and then substituting the results into Eqn 3.2, one can describe the power output from the capacitor bank at any instant, t , as follows:

$$P_t = \frac{V_o^2}{R(t)} e^{-\int_0^t \frac{2}{C \cdot R(t)} dt} \quad 3.4$$

As the product of the capacitance and the resistance is very high, the value of the exponential term on the right hand-side of Eqn 3.4 is approximately one when the duration of the discharge is very short. The instantaneous output power from the capacitor bank is mainly

determined by the initial voltage and the reciprocal of the instantaneous resistance across the furnace.

Figure 21 shows the characteristic temperature-time curves of type 1 atomizer when the capacitor banks A and B are used as the source of electrothermal energy. The temperature is measured by focussing the pyrometer on the interior surface through the sample injection hole. The results show that an increase in the initial voltage of the capacitor banks increased the heating rate of the furnace. The curvature of the temperature-time curve in Fig. 21 with capacitor bank A as the electrothermal energy source may be attributed to the progressive and large voltage drops across the low capacitance of bank A during the discharging period resulting in a significant change in the output power level. The heating performance of type 1 furnace is better with the high capacitance of bank B in terms of the linearity of the temperature-time curve over a wide range of heating rates. Since the type 1 and the type 2 furnace have general similarities, capacitor bank B was used for both furnaces throughout the studies.

Figure 22 illustrates the temperature-time curves for the interior surface at the centre of the type 3 furnace with the capacitor banks A and B as the electrothermal energy source. Since the resistance of the graphite tube used in the type 3 furnace is about 8 times higher than that used in the type 1 and the type 2 furnace, Eqn 3.4 indicates that a higher initial voltage is required to maintain the same output level with the type 3 furnace. With tube having dimensions 3.0 mm i.d., 6.0 mm o.d. and 15.0 mm long, maximum heating rates of 10 and 35 K ms⁻¹ can be achieved by fully charging the capacitor banks B and A to 150 and

Figure 21. Temperature-time curves of the type 1 furnace when the capacitor bank is discharged at various initial voltages.

Figure 22. Temperature-time curves of the type 3 furnace when the capacitor bank is discharged at various initial voltages.

250 V, respectively. Since the voltage on the capacitor bank does not significantly drop during the short discharging period, Eqn 3.4 suggests that the non-linear heating curves for the type 3 furnace in Fig. 22 may be attributable to a decrease in the resistance across the furnace with rising temperature. However, this effect was not observed for the type 1 furnace with the bank B as energy source (Fig. 21). The cause of the difference in the characteristic temperature-time curves may be the difference in the rate of the heat loss at the central lamellar of the furnaces where the temperature was measured. For the type 1 furnace, the central lamellar of the furnace is too close to the contact electrodes, and the latter act as an effective heat sink. A significant heat loss via the contact electrodes compensates for the increase in the power level due to a decrease in the resistance.

The heating rate reported has been calculated using the time taken for the temperature to increase from the charring temperature (measured with the Ircon-300 pyrometer) to the predetermined atomization temperature (measured with the Ircon-1100 pyrometer).

The total input power consumed by the furnace is equal to the sum of the rate of heat loss to the environment by radiation, conduction, and convection, and rate of heat storage by the furnace. At relatively low temperatures at the middle interior surface of the furnace, the heat loss by radiation, conduction and convection should be small in comparison with the input power. Consequently, at relatively low temperatures, the rate of increase in the temperature of the furnace can be approximately equated to the input power as follows:

$$\frac{dT}{dt} = \frac{P}{mc} \quad 3.5$$

where P , m and c are the input power ($J s^{-1}$), the mass of the graphite tube (kg) and the specific heat ($J kg^{-1} K^{-1}$), respectively.

Figure 23 shows the experimental results of the heating rate as a function of the calculated input power for both the type 1 and the type 3 furnace. The input power has been calculated using the initial voltage on the capacitor bank and the measured resistance of the graphite furnace at room temperature. A higher charring temperature increases the heating rate at the same calculated power level for both furnaces. This may be attributable to the difference in the resistance of the graphite furnace at various charring temperatures which has not been taken into account.

ELECTRONIC MEASUREMENT SYSTEM

As shown in Fig. 23, heating rates up to $60 K ms^{-1}$ can be achieved with the capacitive-discharge-heated anisotropic pyrolytic graphite furnace used in this work. Theoretical studies of the effect of the heating rate on the atom-population time curves (Fig. 1) shows that the atomization of samples is facilitated by higher heating rates. Consequently, a sharp rise in the atom population inside the furnace with high heating rates results in the absorption pulse reaching the peak within a few milliseconds. Such fast, transient signals require a fast-response detection system in order to follow rapidly-changing signals without any distortion.

The amplifier assembly used for the present studies was provided

Figure 23. Heating rate as a function of the calculated input power delivered by the capacitor bank for the type 1 and the type 3 furnace.

○ type 1 furnace; ▲ type 3 furnace. ○ initial temperature
 = 873 K; ● initial temperature = 1273 K. Dimensions of tube are 3.0 mm
 i.d., 6.0 mm o.d., and 15.0 mm long.

with a variable time constant made of an active low-pass RC filter, located at the output of the logarithmic converter. The time constant corresponding to each damping was measured by partially blocking the light beam with a metal shaft (driven by a compressed air cylinder) having forward speed of 1.0 mm ms^{-1} . Since the response time of the photomultiplier is less than $0.5 \text{ } \mu\text{s}$, it may be reasonable to assume that an input of a square pulse to the photomultiplier is the result of quick change in the light throughput caused by the blocking mechanism (metal shaft). The time constants measured in this manner are presented in Table 6.

To assess the time constant of the detection system required for measuring fast, transient absorbance signals, the absorbance-time traces obtained by atomizing Cd and Pb in both the type 1 and type 3 furnace were obtained as a function of increasing damping. Cadmium and lead were selected as representative of volatile elements producing very fast transient absorbance pulses which were difficult for the amplifier to follow. Figures 24 and 25 show the effect of the time constant on the absorbance-time characteristics of Cd and Pb with the type 1 and the type 3 furnace at heating rates of 40 and 32 K ms^{-1} , respectively. As can be seen from these figures, an increase in damping resulted in a shift of the peak position, a reduction of the amplitude of the peak, as well as distortion of the shape of the absorbance pulse. However, the study was limited to the fastest available time constant of 4 ms . Figures 24 and 25 provide no reason to support the assumption that the time constant of 4 ms is fast enough to follow, without distortion, the rapid rise in the absorbance signals

Table 6. Measured time constant of the detection system*.

Damping position	Time constant, ms
A	4.0
B	8.0
C	16.0
D	52.0
E	104.0

*Rise time is defined as the time taken for the output signal to rise from 10 to 90% of its maximum value. The time constant is calculated by the following equation [86]:

$$0.9 = 1 - e^{-t_r/\tau}$$

where t_r and τ are rise time and time constant, respectively.

Figure 24. Effect of time constant, τ_{RC} , on the atomic absorption signal profiles of Cd and Pb generated by the type 1 furnace at a heating rate of 40 K ms^{-1}

1 - $\tau_{RC} = 4 \text{ ms}$; 2 - $\tau_{RC} = 8 \text{ ms}$; 3 - $\tau_{RC} = 16 \text{ ms}$; 4 - $\tau_{RC} = 52 \text{ ms}$.

Figure 25. Effect of time constant, τ_{RC} , on the atomic absorption signal profiles generated by the type 3 furnace at heating rates of 30 K ms^{-1} for Cd, and 32 K ms^{-1} for Pb.

1 - $\tau_{RC} = 4 \text{ ms}$; 2 - $\tau_{RC} = 8 \text{ ms}$; 3 - $\tau_{RC} = 16 \text{ ms}$; 4 - $\tau_{RC} = 52 \text{ ms}$.

of relatively volatile elements (such as Cd and Pb) produced at high heating rates.

Alternatively, the reliability of the signals measured with a time constant of 8 ms at a low heating rate can be determined by comparing the output absorbance signal with that measured with the time constant of 4 ms. Table 7 shows the temporal half-width and rise time of Cd and Pb signals at various heating rates. The maximum heating rates that can be used for reliable recording of the absorbance signals with the time constant of 8 ms have also been listed in Table 7. The "-" symbol indicates that the output signals measured with the 8 ms time constant differ from those measured with the 4 ms time constant, i.e., the 8 ms time constant is not fast enough to respond to the rapid rise of the signal. The "+" symbol indicates that the output signals measured with the 8 ms time constant are the same as those measured with the 4 ms time constant. Although temporal half-width has been used to determine the time constant required for detection systems [87], no correlation has been observed between this parameter and the reliability of recording signals. However, reliability of the recorded signals shows a correlation between the rise time of the signal and the time constant used. When the rise time of the signal pulse is greater than 3 times the time constant used for the measurement, the signal can be reliably recorded. The factor of 3 is further justified by the results obtained by atomizing Co at low heating rates and using the 16 ms time constant. On the basis of the above argument, it can be inferred from Table 7 that a 3 ms time constant is required for reliably recording the Pb signal at a heating of 32 K ms^{-1} using the type 3 furnace. The 4 ms

Table 7. Temporal half-width, rise time and reliability of recording of Cd and Pb absorption signals at various heating rates*.

Furnace	Analyte	Heating rate, $K\ ms^{-1}$	Temporal half-width, ms	Rise time [§] , ms	Reliability of recording [†]
Type 1	Pb	40	60 ± 3	20 ± 2	-
		30	72 ± 8	25 ± 2	+
	Cd	40	68 ± 5	20 ± 3	-
		30	88 ± 11	26 ± 3	+
Type 3	Pb	32	17 ± 1	9 ± 1	-
		20	21 ± 1	13 ± 1	-
		10	36 ± 3	20 ± 1	-
		8	50 ± 4	25 ± 2	+
	Cd	30	20 ± 2	11 ± 1	-
		20	28 ± 2	16 ± 2	-
		10	45 ± 4	31 ± 1	+

*Cd - mass = 5.0×10^{-15} kg; charring temperature = 470 K, atomization temperature = 1900 K.
 Pb - mass = 3.2×10^{-13} kg; charring temperature = 870 K, atomization temperature = 2300 K.
 §Rise time is defined as the time taken for the output signal to rise from 10 to 90% of its maximum value. Time constant = 4 ms.

†The reliability of recording is determined by comparing two output signals - one is measured using 4 ms time constant and the other is measured using 8 ms time constant. "+" sign indicates that the two signals are identical; whereas "-" sign indicates that the two signals are different.

time constant is generally fast enough for the Pb and Cd absorbance signals with all heating rates listed for both furnaces. In Table 7, the difference in temporal half-width and rise time given by the two furnaces suggests some difference between them. The cause for this difference will be discussed in Chapter 5.

SUMMARY

With capacitive discharge technique, heating characteristics of the furnace are complicated because of the change in the electrical resistivity of the tube and the progressive drop of voltage of the capacitor bank during the discharge cycle. In general, the heating rate of the furnace is determined primarily by the voltage on the capacitor bank. However, the voltage is limited to a certain level because high voltage power input causes electrical arcs at the contact points between the tube and the electrodes.

The rise time of the transient atomic absorption signal becomes shorter with increasing heating rate of the furnace. Therefore, the response time of the detection system must be shorter in order to record the signal without distortion.

CHAPTER 4

TEMPERATURE DISTRIBUTION IN THE CAPACITIVE-DISCHARGE-HEATED ANISOTROPIC PYROLYTIC GRAPHITE FURNACE

Earlier workers [88-94] have made theoretical and experimental studies of surface temperature gradients across the contact electrodes of graphite furnaces used for atomic absorption spectrometry. VAN DEN BROEK et al. [95] have theoretically modelled the temperature difference between the graphite surface and the vapour phase, and have predicted a direct proportionality between the heating rate of the graphite furnace and the temperature difference observed. Although the effect of non-uniform temperature distribution in the graphite furnace on chemical reactions and physical processes occurring during atomization has not been theoretically analyzed, severe matrix interferences and reduced sensitivities in conventional graphite furnace atomic absorption spectrometry have been frequently attributed to a non-uniform distribution of temperature.

In the present studies, the instantaneous temperature distribution of a graphite furnace has been expressed in the form of a differential equation. A finite-difference form of the differential equation has been used in a computer program to calculate the temperature at each time step. Heating of the gas inside the furnace by conduction of heat from the surface is considered to be a major process of heat transfer. As shown in Fig. 19 in Chapter 3, three configurations of the furnace have been constructed from an anisotropic pyrolytic graphite tube. The

type 1 and the type 2 furnace are similar to each other except for the design of one of the contact electrodes. The surface temperature distribution of these two furnaces is assumed to be unaffected by the difference in the configuration of the contact electrodes because of the high thermal conductivity and low electrical resistivity in the ab-plane of anisotropic pyrolytic graphite relative to its c-direction. Therefore, only two types of furnaces were selected for detailed study: the type 1 and the type 3. The importance of the study of temperature distribution lies not only in knowledge of temperature-time characteristics of the anisotropic pyrolytic graphite furnace (heated by capacitive discharge) but also in the application of the above knowledge in predicting absorption pulse characteristics and in their experimental verification.

THEORETICAL MODELLING

Two factors have been included in the mathematical formulation of a model to describe the resistive heating of a cylindrical graphite tube and the heat transfer to the gas inside the tube from the interior surface of the tube towards its centre. The first concerns the geometrical description of the furnace and is important when a numerical solution with explicit finite-difference approximation is used in the modelling process. The second concerns the thermodynamics and the boundary conditions which allow simplification of the theoretical framework for formulation of finite-difference equations.

The Temperature Distribution in the Interior Surface of the Graphite Furnaces

i) The type 1 furnace

The type 1 furnace was constructed with the lamellar planes (ab-plane) of the anisotropic pyrolytic graphite tube stacked parallel to the optical axis, with two contact electrodes in horizontal position across the diameter of the tube (Fig. 19). Since the tube is symmetrical about a vertical plane, only half of the cross-section needs to be considered. Figure 26a illustrates the nodal geometry for the finite-difference approximation of the temperature distribution in the type 1 furnace. Since regular (isotropic) graphite electrodes and the ab-plane of the anisotropic pyrolytic graphite have high thermal conductivities [58,78-81], it is assumed that the temperature is uniformly distributed over the sectional planes around each node. In other words, no temperature gradient along the length of the tube of the type 1 furnace at any particular node in Fig. 26a is assumed. The two-dimensional view of the furnace is therefore reduced to a line of nodes, as shown in Fig. 26b. There are j nodes across the external radius of the graphite tube. The region from node $j-m+1$ to node j forms the contact between the regular graphite electrode and the anisotropic pyrolytic graphite tube. At each node on the line, the true volume and surface area are used in the finite-difference approximation.

In considering the boundary conditions for modelling the surface temperature distribution in the type 1 furnace, it is assumed that the electrode support and the bulk environment of the argon-filled furnace

(a)

(b)

Figure 26. Nodal geometry of the type 1 furnace for the finite-difference approximation of the surface temperature distribution.

housing (which resembles the Varian-Techtron CRA-63 atomizer head) remain at a temperature of 300 K. This is because the brass electrode support is water-cooled to prevent it from overheating, and a large amount of argon is flushed into the housing to avoid the oxidation of the graphite tube.

The thermal resistance associated with the contacts between the electrodes and the tube would tend to insulate the tube from the cooling effect of the water-cooled electrodes. The corresponding enhanced electrical resistance of the contacts would tend to heat the surface of the graphite tube. These two effects would reduce the temperature gradient around the tube, but would increase the possibility of electrical arcs when a high voltage is applied from the capacitor bank. Since no electrical arcs were noticed nor tolerated during the heating of the furnace, it is assumed that a perfect contact has been made between the electrodes and the graphite tube, i.e., the thermal and the electrical contact resistance are negligible.

As summarized in Table 8, the properties: thermal conductivity, electrical resistivity and emissivity of both regular graphite and anisotropic pyrolytic graphite are temperature dependent. However, these property-values at any node are considered to be constant over each time step. At any instant, $t=p$, the total resistance across the electrode supports, $R(p)$, equals twice the resistance from the centre of the graphite tube to the electrode support, and is expressed as follows.

Table 8. Property values of regular (isotropic) graphite, anisotropic pyrolytic graphite and argon as a function of temperature

Material	Property	Unit	Function	Reference
Regular (isotropic) graphite	Density, ρ	g cm^{-3}	$\rho(T) = 1.87$	
	Heat capacity, C_p	$\text{J g}^{-1} \text{K}^{-1}$	$C_p(T) = 6.71 \times 10^{-2} + 2.60 \times 10^{-3} T - 1.11 \times 10^{-6} T^2 + 1.58 \times 10^{-10} T^3$	96, 97
	Thermal conductivity, k_{cond}	$\text{W cm}^{-1} \text{K}^{-1}$	$k_{\text{cond}}(T) = 1.73 - 1.67 \times 10^{-3} T + 6.84 \times 10^{-7} T^2 - 9.41 \times 10^{-11} T^3$	98
	Electrical resistivity, ϕ	ohm-cm	$\phi(T) = 1.17 \times 10^{-3} - 2.70 \times 10^{-7} T + 7.51 \times 10^{-11} T^2 + 1.50 \times 10^{-14} T^3$	98
	Emissivity, ϵ		$\epsilon(T) = 0.788 + 1.88 \times 10^{-5} T$	99
Anisotropic pyrolytic graphite	Density, ρ	g cm^{-3}	$\rho(T) = 2.20$	
	Heat capacity, C_p	$\text{J g}^{-1} \text{K}^{-1}$	$C_p(T)$ for anisotropic pyrolytic graphite is taken to be the same as $C_p(T)$ for regular graphite	58, 81
	Thermal conductivity in the c-direction, k_{cond}	$\text{W cm}^{-1} \text{K}^{-1}$	$k_{\text{cond}}(T) = 2.18 \times 10^{-2} - 9.76 \times 10^{-6} T + 1.24 \times 10^{-9} T^2$	98
	Electrical resistivity in the c-direction, ϕ	ohm-cm	$\phi(T) = 0.808 - 7.91 \times 10^{-4} T + 3.22 \times 10^{-7} T^2 - 4.51 \times 10^{-11} T^3$	80, 84
	Emissivity of the c-plane, ϵ		$\epsilon(T) = 0.978 + 1.47 \times 10^{-5} T - 2.47 \times 10^{-8} T^2$	99
Argon*	Density, ρ	g cm^{-3}	$\rho(T) = 1.784 \times 10^{-3} \times (273.15/T)$	
	Heat capacity, C_p	$\text{J g}^{-1} \text{K}^{-1}$	$C_p(T) = 0.52$	100
	Thermal conductivity, k_{cond}	$\text{W cm}^{-1} \text{K}^{-1}$	$k_{\text{cond}}(T) = 1.774 \times 10^{-4} \times (T/303.15)^{0.68}$	101

* $C_v = C_p - R$ where R is gas constant.

$$\begin{aligned}
 R(p) &= 2 \sum_{u=1}^n R_u^p(T) = 2 \left[\sum_{u=1}^{j-m} R_u^p(T) + \sum_{u=j-m+1}^j R_u^p(T) + \sum_{u=j+1}^n R_u^p(T) \right] \\
 &= 2 \Delta x \left[\sum_{u=1}^{j-m} \frac{\phi 1_u^p(T)}{A 1_u} + \sum_{u=j-m+1}^j \frac{\phi 1_u^p(T) \phi 2_u^p(T)}{A 2_u \phi 1_u^p(T) + A 1_u \phi 2_u^p(T)} + \sum_{u=j+1}^n \frac{\phi 2_u^p(T)}{A 2_u} \right] \quad 4.1
 \end{aligned}$$

where $R_u^p(T)$, $\phi 1_u^p(T)$ and $\phi 2_u^p(T)$ are resistance, resistivity of the anisotropic pyrolytic graphite along the c-direction, and resistivity of the regular graphite, all as functions of temperature, T , respectively. The subscript, u , denotes the position of a node, and the superscript, p , specifies the time, $A 1$ and $A 2$ represent the average area of two cross-sectional planes on each side of the node which is associated with the anisotropic pyrolytic graphite and the regular graphite, respectively; Δx is the distance between nodes. Since the electrical resistivity of the anisotropic pyrolytic graphite in the ab-plane is about 1000 times less than that along the c-direction and is similar to that of the regular graphite, uniform currents through each area ($A 1$ and $A 2$) in the region of $j-m+1$ to j are implicitly assumed in Eqn 4.1. Furthermore, since it is assumed that the resistance of any particular node is constant in a finite time interval, Δt , the power input to that node by ohmic heating, P_u , can be described by the following equation

$$P_u = i^2 R_u^p \quad 4.2$$

where i is the instantaneous current passing through the furnace having a resistance, $R(p)$, and R_u^p is the resistance of the node at time p .

Figure 27 shows the estimated ratio between the rate of heat loss

by radiation and that by convection from the heated graphite surface at various uniformly-distributed surface temperatures. The results indicate that heat loss by radiation dominates at high temperature of the graphite surface (> 1000 K). Since the observed temperature gradients along the tube and the electrode [102] result in regions of low temperature, convection will have some effects on heat loss. However, the present model neglects heat loss by convection from the outer surface of the tube and the electrodes, since the high average outer surface temperature results in heat loss by predominantly radiational processes. Therefore, the modes of heat loss from the type 1 furnace are considered to be thermal radiation from the outer surface to the surroundings and conduction of heat to the water-cooled electrode support. Since the heat capacity of the gas volume inside the cylindrical tube is much smaller than the heat capacity of the furnace housing, the amount of heat dissipated from the interior surface of the graphite tube is not taken into account.

Around any particular node, u , the rate of heat storage, Q_u , can be described as

$$Q_u = P_u + Q_u(\text{cond}) + Q_u(\text{rad}) \quad 4.3$$

where P_u is the power of ohmic heating given by Eqn 4.2, $Q_u(\text{cond})$ is the rate of heat transfer by conduction from/to adjacent nodes, $Q_u(\text{rad})$ is the rate of heat transfer by radiation between the node and its surrounding. The rate of heat conduction, $Q_u(\text{cond})$, can be expressed [103] by a partial differential equation (Eqn 4.4a), and then approximated in a finite-difference form as Eqn 4.4b.

Figure 27. The estimated ratio of the rate of heat loss by radiation and the rate of heat loss by convection from the heated graphite surface as a function of the uniformly-distributed surface temperature.

$\dot{q}_c$ - the rate of heat loss by convection.

$\dot{q}_r$ - the rate of heat loss by radiation.

Parameters used in the estimation such as the emissivity of graphite and the property values - viscosity, Prantle number, thermal conductivity - of argon at atmospheric pressure as a function of the temperature taken from reference 93.

$$Q_u(\text{cond}) = A_u(\text{cond}) k_u \left(\frac{\partial^2 T}{\partial x^2} dx \right)_{x=(u-\frac{1}{2})\Delta x} \quad 4.4a$$

$$\approx \frac{A_u(\text{cond}) k_u}{\Delta x} (T_{u+1} + T_{u-1} - 2 T_u) \quad 4.4b$$

where $A_u(\text{cond})$ is the average area of the interfacing cross-sectional plane between nodes u and $u+1$ and that between nodes u and $u-1$. k_u stands for the thermal conductivity of the graphite around node u . Since the area surrounding the tubular furnace, i.e., the interior surface area of the furnace housing, is much larger than the outer surface area of any particular node, and the temperature of the surrounding is much lower than the node temperature, the rate of heat loss from the node to its surrounding by radiation, $Q_u(\text{rad})$, can be described as follows [103, p.337].

$$Q_u(\text{rad}) = \sigma \epsilon_u A_u(\text{rad}) [T_s^4 - T_u^4] \quad 4.5a$$

$$= h_u A_u(\text{rad}) (T_s - T_u) \quad 4.5b$$

where σ is Stefan-Boltzmann constant ($5.699 \times 10^{-12} \text{ W cm}^{-2} \text{ K}^{-4}$), ϵ_u is the emissivity of graphite at node u , $A_u(\text{rad})$ is the radiating outer surface area around the node, T_s is the surrounding temperature (K), and h_u is the equivalent radiation heat transfer coefficient as shown in Eqn 4.5c.

$$h_u = \sigma \epsilon_u \frac{T_s^4 - T_u^4}{T_s - T_u} \quad 4.5c$$

The rate of the heat storage at any node which results in the time rate of change in the temperature, $\partial T_u / \partial t$, can be described as follows:

$$Q_u = V_u \rho C_p \frac{\partial T_u}{\partial t} \quad 4.6$$

where V_u is the volume of node u (cm^3), C_p is the heat capacity ($\text{J g}^{-1} \text{K}^{-1}$), and ρ is density (g cm^{-3}). The time derivative is expressed in finite-difference form as

$$\frac{\partial T_u}{\partial t} \approx \frac{T_u^{p+1} - T_u^p}{\Delta t} \quad 4.7$$

where superscript $p+1$ denotes the time explicitly in terms of the previous time p by a finite increment of time, Δt .

Substituting and rearranging Eqns 4.2-4.7, the temperature at node u after finite time increment can be described as follows:

$$T_u^{p+1} = \frac{\Delta t}{V_u C_p \rho} [i^2 R_u^p + \frac{A_u(\text{cond}) k_u^p}{\Delta x} (T_{u+1}^p - T_{u-1}^p) + h_u^p A_u(\text{rad}) T_s] + T_u^p [1 - 2Fo - Bi Fo \frac{A_u(\text{rad})}{A_u(\text{cond})}] \quad 4.8$$

$$\text{where } V_u \approx A_u(\text{cond}) \Delta x ; Fo = \frac{k_u^p \Delta t}{C_p \rho (\Delta x)^2} ; Bi = \frac{h_u^p \Delta x}{k_u^p}$$

The stability criterion is determined by the coupling of the two independent variables, Δx and Δt , in Eqn 4.8 in order to keep a positive coefficient for the T_U^P term [31, 103-105].

The change in the total resistance across the electrode support with increasing temperature of the furnace and of the electrode, as described earlier in Eqn 4.1, implies a variation of electric current during the heating cycle if a constant voltage across the assembly is considered. With the capacitive-discharge heating technique, the instantaneous electric current passing through the heating element by discharge of a capacitor bank is further complicated by a progressive drop in the voltage of the capacitor bank during the heating of the furnace. However, it is assumed that the resistance across the electrode support remains constant in the finite time interval, Δt . The voltage drop in the discharging RC-circuit within this finite time interval can be described as [105]:

$$\Delta V = V^{p+1} - V^p = V^p [\exp(-\Delta t / (R(p) \cdot C)) - 1] \quad 4.9$$

where C is the capacitance of the capacitor bank. The instantaneous current passing in such a circuit can be expressed by the following equation.

$$i = -C \frac{dV}{dt} \approx -C \frac{\Delta V}{\Delta t} = -\frac{C \cdot V^p}{\Delta t} [\exp(-\Delta t / (R(p) \cdot C)) - 1] \quad 4.10$$

Since the resistance of the type 1 furnace is considered to be the sum of the resistance of each node in series, current passing through each

node at a given instant is therefore the same. Once the preset atomization temperature is attained in the first node, i.e. $u=1$ in Fig. 26b, the electric current required to maintain a constant temperature in the first node is supplied by a transformer to the tube and electrode assembly. This current can be determined from Eqn 4.8 by setting $T_{u=1}^{p+1} = T_{u=1}^p$, i.e., the rate of heat storage in Eqn 4.6 equals zero.

ii) The type 3 furnace

The type 3 furnace was constructed with lamellar planes of the anisotropic pyrolytic graphite stacked perpendicular to the optical axis, with two contact electrodes across the graphite tube length (Fig. 19). Figure 28 shows the nodal geometry for the finite-difference approximation of the surface temperature distribution in the type 3 furnace. Under the same assumptions and boundary conditions as for the type 1 furnace, the surface temperature distribution of the type 3 furnace is formulated in essentially the same way as Eqn 4.8. However, it should be noted that only the first and third term of Eqn 4.1 will be needed for the type 3 furnace, since there is no region in this furnace that the electric current flows parallel through different graphite material.

Temperature Distribution in the Gas Phase in the Type 1 and the Type 3 Furnace

i) The type 1 furnace

The geometry of the gas-filled space of the type 1 furnace is approximated by an equally-spaced, orthogonal grid of nodes shown as

Figure 28. Nodal geometry of the type 3 furnace for the finite-difference approximation of the surface temperature distribution.

the solid dots and open circles in Fig. 29. Heating of the gas inside the furnace is the result of heat dissipation from the interior graphite surface. The points positioned near the interior graphite wall with the "*" symbol in Fig. 29 are considered to be at the temperature of the graphite surface. Only one quadrant needs to be considered because of symmetry, if the effects of the sample-injection hole are neglected. The actual circular cross-sectional plane of the tube is approximated by the saw-shaped dashed line as shown in Fig. 29. Although a cylindrical coordinate system would more accurately describe the geometry of a cylindrical tube, non-uniform surface temperature distribution around the circumference of the type 1 furnace would be more difficult to model.

As to the modes of heat transfer from the graphite wall to the stagnant argon gas inside the tube, CHAKRABARTI et al. [106] have demonstrated that conduction dominates the overall heat transfer process. The small diameter of the cylindrical tube inhibits heat transfer by free convection. The thermal spectrum shows that the radiation lies in the region of 0.1-100 μm , and the shift of the peak of thermal spectrum follows Wien's Displacement Law. Since monatomic argon gas, which is the predominant species inside the furnace, has no strong characteristic emission and absorption spectral lines around the peak, heating of the argon gas inside the graphite furnace by radiational heat transfer is unlikely and is not taken into account in the model. Since gas conduction is the only mode of heat transfer within the furnace, it is assumed that there is no thermal boundary

Figure 29. Nodal geometry of the gas-filled space of the type 1 furnace for the finite-difference approximation of the gas temperature distribution.

layer between the surface and the adjacent gas. The validity of the assumption is the result of the low velocity of the gas along the furnace's length throughout the heating cycle [93]. The temperature of the gas next to the surface symbolized by open circles in Fig. 29 is therefore the same as the adjacent surface temperature or the average of two adjacent surface temperatures symbolized by "*" (see Fig. 26).

Two-dimensional, transient heat transfer in the gas phase by conduction alone is given as follows [103]:

$$k \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right) = \rho C_v \frac{\partial T}{\partial t} \quad 4.11$$

where C_v is the heat capacity of the argon gas at constant volume, x and y represent the two independent space coordinates shown in Fig. 29. The heat capacity at constant volume, C_v , is used in the energy storage term of Eqn 4.11 even though the gas in the furnace remains at essentially constant pressure during the transient. The reason for the use of C_v instead of C_p has been given by CHAKRABARTI et al. [93]. Since the gas-filled space inside the tube is approximated by an equally-spaced, orthogonal grid of nodes, Eqn 4.11 can be re-expressed in its finite-difference form with these approximations.

$$\begin{array}{l} \text{conduction along} \\ \text{the x-axis} \end{array} \quad \frac{\partial^2 T}{\partial x^2} \approx \frac{1}{(\Delta x)^2} [T_{u+1,v} + T_{u-1,v} - 2T_{u,v}] \quad 4.12$$

$$\begin{array}{l} \text{conduction along} \\ \text{the y-axis} \end{array} \quad \frac{\partial^2 T}{\partial y^2} \approx \frac{1}{(\Delta y)^2} [T_{u,v+1} + T_{u,v-1} - 2T_{u,v}] \quad 4.13$$

temperature change
with time

$$\frac{\partial T}{\partial t} \approx \frac{1}{\Delta t} [T_{u,v}^{p+1} - T_{u,v}^p] \quad 4.14$$

where subscripts u and v denote the node position on the x and y coordinate, respectively. When Δx equals Δy , and if the temperatures of the nodes are known at any particular time, the temperature at an arbitrary node in the gas phase after a time increment, Δt , can be determined with the following equation which is obtained by rearranging and substituting Eqns 4.12-4.14 into 4.11.

$$T_{u,v}^{p+1} = Fo_{u,v}^p (T_{u+1,v}^p + T_{u-1,v}^p + T_{u,v+1}^p + T_{u,v-1}^p) + T_{u,v}^p (1 - 4Fo_{u,v}^p) \quad 4.15a$$

$$Fo_{u,v}^p = \frac{\xi_{u,v}^p \Delta t}{(\Delta x)^2} \quad \text{and} \quad \xi_{u,v}^p = \left(\frac{k}{\rho c_v} \right)_{u,v}^{t=p} \quad 4.15b$$

where Fo and ξ are the Fourier number and volumetric thermal diffusivity, respectively. The stability criterion of Eqn 4.15a is determined by the coupling of the two independent variables, Δx and Δt , in Eqn 4.15b, in order to keep a positive coefficient for the $T_{u,v}^p$ term in Eqn 4.15a i.e., $Fo < 0.25$ [31,103,104]. The property values of the gas around any node in the gas-filled space of the furnace are constant over each time step. These property values of argon as a function of temperature are summarized in Table 8.

Furthermore, the increase in the gas phase temperature inside the furnace causes expansion of the gas when the pressure inside the furnace is maintained constant (1 atm). Since the gas-filled volume inside the furnace is also constant for a given tube, the increase in the volume occupied by the gas with increasing temperature means that a part of the gas is expelled from the furnace. The rate of gas expulsion is related to the gas expulsion velocities at each end and at the sample-injection hole of the furnace. With the analogy of mass and energy conservation laws, CHAKRABARTI et al. [93] have theoretically investigated the rate of gas expulsion as a function of time during pulse-heating of the furnace by assuming no temperature gradient along the axial length of the furnace. However, the temperature gradient on the interior surface as well as the non-uniform gas phase temperature distribution in the type 1 furnace makes the analysis of the rate of gas expulsion more complex. In the model considered here, the volumetric expulsion rate is simply estimated on the basis of the ideal gas law. This has been calculated using the increase in the volume occupied by the gas based on the increase in the weighted-average gas phase temperature over each time step.

ii) The type 3 furnace

Gradients in the surface temperature along the axial length of the type 3 furnace have been observed. However, the surface temperature around the circumference at any node along the tube's axial length is uniform because of the high thermal conductivity in the ab-plane of the anisotropic pyrolytic graphite.

The modes of heat transfer inside the gas-filled space of the furnace by free convection and radiation are neglected using similar considerations as in the modelling the gas phase temperature in the type 1 furnace. The gas expansion with increasing gas temperature causes the axial transfer of thermal energy. However, this axial heat transport becomes less significant with increasing temperature because of decreasing gas density [93]. Heating of the gas inside the furnace is therefore attributed to only radial conduction of the thermal energy from the surface of a given axial node.

Figure 30 shows the nodal geometry of the gas-filled space of any node along the axial length of the tube of the type 3 furnace for finite-difference approximation of the gas phase temperature. Transient heat transfer inside the gas-filled space of any node by gas conduction alone in the radial direction, using cylindrical coordinates, may be expressed as follows [103,104]:

$$\frac{k}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) = \rho c_v \frac{\partial T}{\partial t} \quad 4.16$$

Re-expressing Eqn 4.16 in its finite-difference form, the temperature around each annular node, $T_{u,v}$, after a finite time increment can be derived as:

$$T_{u,v}^{p+1} = Fo_{u,v}^p [T_{u,v+1}^p (1 + \frac{\Delta r}{2r}) + T_{u,v-1}^p (1 - \frac{\Delta r}{2r})] + T_{u,v}^p (1 - 2Fo_{u,v}^p) \quad 4.17$$

Figure 30. Nodal geometry of the gas-filled space of the type 3 furnace for the finite-difference approximation of the gas temperature distribution.

where $\Delta r = \frac{r_o}{n}$; $2 \leq v \leq n-1$; $1 \leq u \leq j$;

$$Fo_{u,v}^p = \frac{\xi_{u,v}^p \Delta t}{(\Delta r)^2} ; \text{ and } \xi_{u,v}^p = \left(\frac{k}{\rho C_v} \right)_{u,v}^{t=p}$$

The subscripts u and v of the above equation represent the position of a node along the axial length of the type 3 furnace and the position of the annular node in the radial direction, respectively. The stability criterion of the above equation is $Fo \leq 0.5$. However, the problem of approximating the temperature at the central zone, $T_{u,1}$, with the cylindrical coordinate finite-difference equation (Eqn 4.17) should be noted. This equation cannot be used to solve for the centre node because the radius, r , equals zero. In the model considered here, $T_{u,1}$ is assumed to be the same as $T_{u,2}$. In order to minimize the propagated error, Δr should be a small value so that the total heat capacity involved in the central zone does not significantly alter the simulated results.

The average gas temperature of a cross-section at an axial node along the tube's length is calculated by the weighted-average gas temperature of all annular nodes in that section. The average gas phase temperature over the entire gas-filled space of the graphite tube is obtained by taking weighted-average of these average sectional gas temperatures.

Initial Condition

The time corresponding to charring and atomization temperatures of the furnace is that when the surface temperature of the first node, i.e., $u=1$ in Figs. 26 and 28, reaches the preset temperature. As mentioned before, the boundary conditions of the model are that the surrounding temperature and the temperature of node n in Figs. 26 and 28 are held constant at 300 K. In order to initiate the simulation of the distribution in the surface and the gas phase temperature with the finite-difference equations, the initial temperatures of all the nodes of the electrode, tube, and the gas are required.

However, a non-uniform temperature distribution is expected once the furnace is heated above the room temperature. The temperature distribution at the initiation of the atomization stage is set equal to the quasi-steady-state temperature at the termination of the charring stage. This quasi-steady-state temperature distribution is first obtained using 300 K as the initial temperature of all the nodes except that of the first node in Figs. 26 and 28. The temperature of the first node is set equal to the charring temperature. The electric current passing through the furnace is therefore calculated as the current required to maintain the temperature of the first node at the charring temperature. This distribution of the quasi-steady-state temperature is further employed as the initial temperature of each node at the initiation of the atomization stage.

EXPERIMENTAL

Apparatus

Computation was done with a Honeywell CP-V computer which employs two Sigma 9 central processing units. Programs were written in FORTRAN IV.

The capacitive-discharge-heated furnace made of anisotropic, pyrolytic graphite together with the atomic absorption spectrometer described earlier were used. The surface temperature of the graphite furnace was measured by optical pyrometry. Optical pyrometers, Ircon series 1100, model 11x30, and Ircon series 300, model 300 (Ircon Inc.) were used.

Measurement of the Distribution of the Surface Temperature

Figure 31 shows the experimental set-up for simultaneous measurement of the temperature distribution in the type 1 furnace. The temperature at two places (90 degrees apart on the interior tube surface), specified as zones A and B, were measured using two identical, automatic, optical pyrometers, series 1100, model 11x30 (Ircon Inc.). Temperature distribution in the type 3 furnace was measured sequentially with the optical pyrometer mentioned above along the axial length of the outer surface of the graphite tube. The voltage output of each pyrometer was recorded by a Nicolet 2090, model 201 plug-in, dual-channel digital oscilloscope (Nicolet Corporation).

Figure 31. The instrumental set-up for simultaneous temperature measurement at two zones, 90 degrees apart, of the type 1 furnace with two automatic optical pyrometers.

Zone A - the central lamellar plane across the two contact electrodes; zone B - the interior surface at one of the contact electrodes.

Measurement of the Gas Phase Temperature

The gas phase temperature was determined by the two-line absorption method [107-109]. The line pairs of Pb 368.3/280.2 nm, Sn 286.3/284.0 nm and Ni 229.0/232.6 nm were used. The working range of the thermometric species: Pb, Sn and Ni, used in the determination of the gas phase temperature was discussed by CHAKRABARTI et al. [106]. The gas phase temperature was calculated from two separate absorption measurements of each line pair in the same way as done by others [28,95,106,110].

RESULTS AND DISCUSSION

Errors in the Temperature Measurement by Optical Pyrometry and their Correction

When the furnace temperature is measured through the sample injection hole by optical pyrometry, the systematic errors in the measured temperature are associated with the ratio of the half-length and the radius of the graphite tube, the operational wavelength of the pyrometer, the emissivity of the graphite surface, the final temperature, and the temperature distribution [111]. In the experimental conditions described in Fig. 31, the ratio between the half-length and the radius of the graphite tube is 5.0 (7.5mm/1.5mm). The operational wavelength of the narrow-band spectral pyrometer, Ircon series 1100, model 11x30 (Ircon Inc.), is 0.85 μm which is determined from its calibration graph. Since the graphite surface is not an ideal blackbody radiator, i.e., the emissivity is not unity, the error in

each single measurement is mainly attributable to non-uniform temperature distribution along the graphite surface. When the temperature difference between zones A and B of the type 1 furnace is determined by optical pyrometry, the systematic error in each of the two simultaneously-measured temperatures is not expected to be the same. The higher amount of reflected radiation from zone B, due to its higher surrounding temperature, increases the systematic error in the measured temperature of zone B.

According to the principles of temperature measurement using narrow-band spectral pyrometers [112,113], the measured temperature, T_m , its true temperature, T_t , and the surrounding temperature, T_s , are related as follows:

$$\frac{1}{\exp(c_2/\lambda_c T_m)-1} = \frac{\epsilon_\lambda(T_t)}{\exp(c_2/\lambda_c T_t)-1} + \frac{1 - \epsilon_\lambda(T_t)}{\exp(c_2/\lambda_c T_s)-1} \quad 4.18$$

where c_2 , λ_c and $\epsilon_\lambda(T_t)$ are the second universal radiation constant (1.4388 cm K), the characteristic effective central wavelength, and the spectral emissivity of the object as a function of the temperature, respectively. However, the above equation is derived under the assumption that the surrounding temperature is uniform.

Figure 32 shows the correlation of the measured temperature and the true temperature of the object at various surrounding temperatures and the emissivities at $\lambda_c = 0.85 \mu\text{m}$. As can be seen, the higher the emissivity of the object the less the relative error in the measurement

Figure 32. Correlation of the measured temperature, T_m , with the true temperature, T_t , of the object at various surrounding temperatures, T_g , and with various emissivities.

Dashed lines represent perfect correlation. $\lambda_c = 0.85 \mu m$.

a $T_g = 2800 K$; b $T_g = 2600 K$; c $T_g = 2300 K$; d $T_g = 1900 K$; e $T_g = 1500 K$.

since a good emitter is also a good absorber, and hence less radiation is reflected. In the temperature range of 1000 to 2800 K, the relative error between the measured temperature and the true temperature of the object is small when the temperature of the object is higher than that of the surrounding. However, a large error in the temperature measurement due to reflected radiation is expected when the temperature of the object is much lower than that of the surrounding. The horizontal part of the curves in Fig. 32 indicates a potential difficulty in correcting the measured temperature using the above equation when the object's true temperature is much lower than the surrounding temperature. A slight variation in the temperature measurement in such a circumstance results in a variation of a few hundred degrees in the corrected temperature. Comparison of Fig. 32-I with Fig. 32-II shows that uncertainties in the measurement increase with decreasing emissivity.

To minimize error in measuring the temperature of an object with low emissivity and/or when the temperature of an object is much lower than its surrounding, a long operational-wavelength pyrometer is better than a short-operational-wavelength one because an increase in the characteristic central wavelength of the pyrometer decreases significantly the ratio of the radiance reflected from the object and the radiance emitted by the object, and hence, decreases the error in measuring the temperature. This is illustrated in Fig. 33. Also, when the temperature of the object is much lower than its surrounding, the smaller error in the temperature measurement with the long-operational-wavelength pyrometer means a correspondingly smaller correction factor

Figure 33. Effect on the correlation of the measured temperature, T_m , with true temperature, T_t , of an object having emissivity of 0.7 at a given surrounding temperature, T_s , with effective central wavelength, λ_c , as a parameter.

Dashed lines represent perfect correlation. a $\lambda_c = 0.85 \mu\text{m}$; b $\lambda_c = 2.0 \mu\text{m}$; c $\lambda_c = 8.0 \mu\text{m}$.

and less uncertainty in the corrected value of the temperature. Figure 33 also predicts a larger error in the temperature measured with a long-operational-wavelength pyrometer when the surrounding temperature is below the true temperature of the object; hence, a long-operational-wavelength pyrometer should not be used in such a case.

Theoretical studies suggest that: 1) to obtain high precision in the temperature measurement of zone A of the type 1 furnace, a short-operational-wavelength pyrometer should be used; 2) to achieve a smaller error in the measurement or a correctable error in the zone B temperature measurement, a long-operational-wavelength pyrometer should be used. However, long-operational-wavelength pyrometers normally suffer from slow response. Fast heating of the furnace by the capacitive discharge technique required that the measurement be made with the short-operational-wavelength pyrometer, Ircon series 1100, model 11x30 (Ircon Inc.).

Geometry of the Type 1 and the Type 3 Furnace

To simulate the surface temperature distribution of the type 1 furnace with a finite difference approximation, the nodal geometry in Fig. 26a was set with $n=60$ across the assembly half (15.0 mm long). When a graphite tube of internal radius 1.5 mm was used, the interior surface of the graphite tube was described by 6 nodes. One face of the control volume about the seventh node is tangential to the interior surface of the graphite tube. The calculated temperature distribution of the first seven nodes represents the theoretical temperature distribution of the interior surface of type 1 furnace around the

circumference. Since the internal radius of the furnace was divided into 6 segments, the nodal geometry of the gas-filled space inside the furnace is approximated by a 6x6 matrix.

The surface temperature distribution of the type 3 furnace was calculated using $n=35$, $j=15$ (Fig. 28b); the total length of the assembly was 35.0 mm (with a tube length of 15.0 mm). The temperature distribution of the gas-filled space of each axial node was calculated using $n=10$ (Fig. 30).

In the theoretical studies, the heating rate of the furnace was calculated from the time taken for the temperature of the first node ($n=1$ in Figs. 26 and 28) of the furnace to reach the preset, steady-state value from the initial temperature (i.e., the charring temperature).

Temperature-Time Curves of the Furnace Heated by the Capacitive Discharge Technique

When the furnace is heated by the capacitive discharge technique, the instantaneous input power can be described by Eqn 3.4, as discussed earlier in Chapter 3. Since the heating of the furnace is directly related to its input power, factors such as the initial voltage, the total capacitance of the capacitor bank, and the resistance of the furnace, will affect the characteristics of the temperature-time curve of the furnace.

Figure 34 shows the results of the effect of the capacitance of the capacitor bank on the simulated temperature-time curves. The solid-line curves a, b, c and d are the characteristic temperature-time

Figure 34. Theoretically predicted effect of the capacitance of capacitor bank on the temperature-time profiles of the type 1 and the type 3 furnace.

Dashed lines are voltage-time curves. Solid lines are temperature-time curves of the first node, i.e., $u=1$ in Figs. 26 and 28. Capacitance: a, 1 — 2.0 F; b, 2 — 1.0 F; c, 3 — 0.5 F; d, 4 — 0.25 F.

curves of the first node of the type 1 and the type 3 furnace which are simulated with the capacitor bank having capacitance values of 2.0, 1.0, 0.5 and 0.25 F, respectively. The dashed-line curves 1, 2, 3 and 4 present the instantaneous voltage of the capacitor bank having capacitance values of 2.0, 1.0, 0.5 and 0.25 F, respectively, during the heating of the furnace. Figure 34 shows that the temperature-time curve bends towards the time axis when a capacitor bank of low capacitance is used, whereas it bends towards the temperature axis for a capacitor of high capacitance. The large voltage drop in the low capacitance case results in a decrease in the power level, and hence, a decrease in the heating rate. However, the bending of the temperature-time curve towards the temperature-axis in the high capacitance case is mainly a result of a decrease in the furnace resistance with increase in temperature of the graphite tube.

Figure 35 shows the theoretical results of the effect of the initial voltage on the characteristic temperature-time curves of the first node of the type 1 and the type 3 furnaces. As expected from Eqn 3.4, the increase in initial voltage increases the heating rate of the furnace. Since the electrical resistance of the type 3 furnace is higher than that of the type 1 furnace, for the type 3 furnace the initial voltage of the capacitor bank is higher than that of the type 1 furnace in order to achieve the same heating rate.

As shown in Chapter 3, Figs. 21 and 22, the temperature-time curves of the type 1 and the type 3 furnace were measured at the central interior surface of the graphite tube through the sample

Figure 35. Theoretically predicted effect of the initial voltage on the temperature-time profiles for the type 1 and the type 3 furnace at the first node, i.e., $u=1$ in Figs. 26 and 28.

injection hole by optical pyrometry using various initial voltages as well as various capacitances of the capacitor bank. The simulation results of the model are in agreement with the experimental observation. For a given capacitance and initial voltage, a slight variation between the theoretical and the experimental results on the heating rate of the type 1 furnace may be attributable to the variation in the contact area between the electrodes and the tube in the experimental set-up. The details of this contact area effect on the heating rate of the furnace will be discussed in a later section. However, the theoretically predicted and the experimentally measured heating rates of the type 3 furnace show that their difference is greater than that for the type 1 furnace. At a given capacitance and initial voltage, the heating rate predicted by the model is consistently lower than the experimentally measured heating rate. Since electrical resistance is the major variable in determining the input power level, this suggests that the electrical resistivity of the anisotropic pyrolytic graphite in Table 8 may be over-estimated. The effect is not shown by the results of the type 1 furnace, but is shown by the results of the type 3 furnace. The above difference in the results may be attributable to the difference in the actual path length followed by the current in the two furnace-tubes - the path length of the type 3 furnace is about 30 times greater than that of the type 1 furnace because of the difference in their configurations.

Temperature Distribution in the Type 1 Furnace

i) Distribution of the interior surface temperature

As mentioned before, the anisotropic pyrolytic graphite tube used for the type 1 furnace was manufactured in such a way that the lamellar plane (ab-plane) of the graphite was parallel to the length of the tube. Since thermal conductivity of the anisotropic pyrolytic graphite in the ab-plane is about 150 times greater than that along the c-direction, there is a negligible temperature gradient along the length of the tube. However, the heat flow by conduction from the central lamellar of the tube to the water-cooled electrode support results in a non-uniform temperature distribution across the assembly.

Figure 36 shows the theoretical temperature-time curves of the first, fifth, and seventh nodes which are denoted by $T_{u=1}$, $T_{u=5}$ and $T_{u=7}$, respectively. The dots in Fig. 36 represent the temperature of other nodes, i.e., $u=2, 3, 4$ and 6 , at the time when the temperature of the first node reaches its steady-state, final value. Figure 37 shows an example of the temperature measured simultaneously with two identical, automatic, optical pyrometers (Ircon 1100), focussed on zones A and B which were 90 degrees apart. The oscilloscopic traces a and b of temperatures of zones A and B, respectively, measured with the two pyrometers, were converted into the temperature profiles A and B, respectively, using the pyrometer calibration curve. In Fig. 37, the temperature difference, ΔT , is the difference between the temperatures of zones A and B at the instant when zone A reaches its final, steady-state temperature.

Figure 36. Theoretically predicted distribution of the temperature of the interior surface of the type 1 furnace.

Initial voltage = 70 V; capacitance = 2.0 F; number of nodes within the contact region (i.e., value of m in Fig. 26) = 3; tube dimension - 3.0 mm i.d., 6.0 mm o.d., and 15.0 mm long.

Figure 37. Simultaneously-measured temperature profiles of zones A and B of the type 1 furnace.

Temperature profiles A and B are derived from the oscilloscopic traces a and b, respectively. ΔT is the temperature difference at the instant of time when the temperature at zone A attains its predetermined, final temperature. Dimensions of tube are the same as in Fig. 36.

Similar to the pyrometrically measured temperature-time curves in Fig. 37, the temperature of the seventh node in Fig. 36 shows a slow increase after the temperature of the first node attains its steady-state, final temperature. When the temperature was measured with an optical pyrometer, the target area of the pyrometer was defined by the optical arrangement. In the present studies, the Ircon series 1100, model 11x30, pyrometer has a minimum target area of 0.15 mm^2 . The coverage of the target area indicates that the temperature measurement is effectively restricted to the region corresponding to the sixth node described in the model, as the seventh node is tangential to the interior surface of the graphite tube. In order to compare the pyrometrically measured temperature difference, ΔT , in Fig. 37 with the theoretically calculated results in Fig. 36, the latter is taken as the difference between the temperatures of the first and sixth nodes. The results in Fig. 36 show that the difference in the theoretically calculated temperature is about 750 K for the combination of the final temperature of 2600 K and the heating rate of 21 K ms^{-1} , both determined at the first node. The pyrometrically measured difference in temperature between zones A and B in Fig. 37 is 550 K for a final temperature of 2600 K and heating rate of 20 K ms^{-1} , both determined at zone A. The difference between the heating rates is not sufficient to account for the 200 K difference. This difference may be attributed to the systematic error involved in the temperature measurement by optical pyrometry.

It is reasonable to assume that the pyrometrically measured temperature of T_A in Fig. 36 is the true temperature of zone A because

of the high emissivity of anisotropic pyrolytic graphite in the c-plane and the short-operational-wavelength pyrometer used. Since Eqn 4.18 is derived under the assumption that the object is completely enclosed in a uniform temperature, the maximum error in the temperature measurement of zone B due to reflected radiation from the high-temperature surroundings can be estimated by assuming that the spectral emissivity is 0.85-0.90 at $\lambda_c = 0.85 \mu\text{m}$. Figure 37 shows that when the temperature of zone A is 2600 K, the maximum difference between the pyrometrically measured temperature (2050 K) and the corrected temperature of zone B is 370-170 K (depending on the emissivity value chosen for the correction). Since the spectral emissivity of anisotropic pyrolytic graphite is highly dependent on the surface [99], quantitative corrections for the complex temperature distribution of the type 1 furnace can hardly be achieved by a simple method. However, both theoretical and experimental results agree qualitatively on the temperature distribution as well as the heating performance of the type 1 furnace.

An increase in the initial voltage of the capacitor bank increases the input power, and hence the heating rate. Figure 38 shows both the theoretical and experimental results on the effect of heating rate on the temperature difference. The difference in pyrometrically measured temperature is consistently lower than the temperature difference predicted from the theoretically simulated results. However, both experimental and theoretical results agree that, for a given rate, an increase in the final temperature of zone A will increase the

Figure 38. Theoretical and experimental results of the effect of the heating rate on the temperature difference, ΔT , of the type 1 furnace.

Solid line with open symbol: experimental results of the temperature difference between zones A and B measured by optical pyrometry. Dashed line with solid symbol: theoretical results of the temperature difference between the first and the sixth node. Dimensions of tube are the same as in Fig. 36.

$\triangle T_A = 2600$ K, $\blacktriangle T_{u=1} = 2600$ K; $\square T_A = 2300$ K, $\blacksquare T_{u=1} = 2300$ K;
 $\circ T_A = 2000$ K, $\bullet T_{u=1} = 2000$ K.

temperature difference. Also, an increase in the input power, and hence the heating rate, will tend to enhance the difference between the temperatures of zone A and zone B slightly. A slow heating rate increases the time taken for the temperature to reach a given value. A slow heating rate also tends to heat the electrode to a higher temperature by conduction, and hence decreases the temperature difference.

A decrease in the contact area between the tube and the graphite electrode tends to make the temperature distribution uniform because of a decrease in the rate of heat loss to the electrode by conduction. In the model considered, the change in contact area is made by changing the value of m in Fig. 26b, i.e., by changing the number of nodes in the region of $j-m+1$ to j . When $j=12$ is set for a tube of 3.0 mm i.d. and 6.0 mm o.d., a change in the value of m from 1 to 5 corresponds to an increase in the contact area from 4.7 to 21.8 mm².

The theoretical results show a significant change in the temperature distribution across the assembly with a change in the contact area, although only a slight increase in the temperature difference (< 100 K) between the first node and the seventh node occurs when the contact area increases from 4.7 to 21.8 mm². The temperature difference would be expected to be much greater because of conduction loss through the larger contact area. However, the low thermal conductivity of the anisotropic pyrolytic graphite in the direction of heat flow and the high input power effectively counteract this.

Additionally, an increase in the contact area implies that more nodes are involved in the parallel path of low resistance of the

regular graphite electrode, and hence the resistance across the assembly decreases. Conversely, a decrease in the contact area increases the resistance. When the furnace is heated from 300 to 2600 K with a 2.0 F capacitor bank charged to 70.0 V, the theoretical results predict that the change in contact area from 4.7 to 21.8 mm² will produce an increase in the average heating rate from 14.4 to 32.0 K ms⁻¹. The experimental results agree with those theoretically predicted.

The theoretical model also predicts a decrease in, but not elimination of, the temperature difference between the first and the seventh node due to an increase in the thickness of the graphite tube wall. This may be attributable to isolation of the central region of the graphite tube of low thermal conductivity from the regular graphite electrodes of high thermal conductivity, resulting in a decrease in the rate of heat loss. However, the great increase in the mass of the graphite tube with increase in its external radius drastically decreases the heating rate of the furnace with the same initial conditions.

Optimization of the geometrical shape of the anisotropic pyrolytic graphite tube and the regular graphite contact electrode may make the temperature distribution of the type 1 furnace more uniform, but it is not the subject of the present theoretical model.

ii) Distribution of the gas phase temperature and the rate of expulsion of gases from the furnace

Figure 39 shows the results for the simulation of the gas phase temperature distribution inside the type 1 furnace of dimension 3.0 mm i.d. and 6.0 mm o.d. Temperature-time curves, $T_{u=1}$ and $T_{u=7}$, are the surface temperatures at nodes 1 and 7, respectively. In Fig. 39, the dashed-line curves, T_a , T_b , T_c and T_d , are theoretical temperature-time curves for the selected places, a, b, c and d, respectively, in the gas-filled space of the furnace. The solid-line curve, T_{ave} , is the weighted average of the gas phase temperature. As can be seen from Fig. 39, during the first few milliseconds of the heating cycle, the rate of increase of the T_{ave} is much lower than that of the interior surface temperatures at any node. Thereafter, it increases nearly linearly with the increase in temperature of the surface. Throughout the entire heating cycle, T_{ave} lies in between the surface temperatures of the first and seventh nodes which the theory predicts to be the highest and the lowest temperature, respectively, of the interior surface of the type 1 furnace.

Physically, the motion of the gaseous species inside the furnace is governed by thermal flux, diffusion flux, and expansion force. The transport of the gaseous species is from the high temperature region to the low temperature region. As can be seen from Fig. 39, positions a and c have the same temperature. The line through these two positions is an isothermal line. The lines depicting theoretically predicted isothermal gas phase temperatures inside the type 1 furnace are nearly parallel to this line. The direction of thermal flux, therefore, is

Figure 39. Theoretical distribution of the gas temperature of the type 1 furnace.

$T_{u=1}$ and $T_{u=7}$ are the surface temperature at nodes 1 and 7, respectively. T_a , T_b , T_c and T_d are the temperatures at the selected positions a, b, c and d inside the furnace, respectively, as a function of time. T_{ave} is the weighted-average of gas temperature inside the type 1 furnace. Dimensions of tube are the same as in Fig. 36.

such that the gaseous species travel perpendicular to the isothermal line to cross the temperature gradient from the highest temperature region near the surface of the first node to the lowest temperature region around the seventh node.

Figure 40 shows both the experimentally determined gas temperature (by the two-line absorption method) and the theoretically-simulated, weighted-average gas temperature of the type 1 furnace at different heating rates. Since gas temperature determined by the two-line method is affected by factors such as the spatial distribution of the thermometric species, light beam geometry relative to the tube geometry, etc., the measured gas temperature has been called "effective temperature" [1,109]. The experimentally determined "effective temperature" agrees well with the theoretically-simulated, weighted-average gas temperature when the surface temperature of zone A

> 2300 K. However, Fig. 40 shows that the "effective temperatures" are consistently lower than the theoretically-simulated, weighted-average temperatures when the surface temperatures of zone A are below 2300 K. The lower "effective temperature" may be due to greater contributions from the thermometric species that have diffused to the cooler part of the graphite tube and less contributions by those at the hotter part of the tube in determining the "effective temperature" by the two-line absorption method. The theoretical model predicts that the surface temperature around zone B is 1500 K when the surface temperature of zone A is 2000 K.

Figure 40 also shows the theoretically simulated instantaneous

Figure 40 (I-IV). Effect of the heating rate of the type 1 furnace on the gas temperature and the rate of expulsion.

Dashed line of T_{ave} is the theoretical weighted-average gas temperature. Experimentally measured effective temperature by two-line absorption method with Sn (Δ), and Pb ($\bigcirc$) as the thermometric species. Curve e is the rate of volumetric expulsion as a function of time.

Dashed lines of $T_{u=1}$ and $T_{u=7}$ are the theoretically predicted surface temperature at the first node and the seventh node, respectively. Solid line of T_A is the experimentally measured temperature of zone A obtained by optical pyrometry.

Heating rate of zone A: (I) 39.0 K ms^{-1} ; (II) 27.3 K ms^{-1} ; (III) 18.5 K ms^{-1} ; (IV) 8.5 K ms^{-1} .

Fig. 40 (I-II).

(III)

(IV)

Fig. 40 (III-IV).

expulsion rates which increase with increasing heating rates of the furnace. At a given heating rate and initial temperature, the maximum rate of expulsion is independent of the final temperature of the furnace since the attainment of this maximum rate occurs shortly after the temperature begins to increase from its initial value. However, the results of the theoretical model suggest that when a furnace is operated at a high heating rate, an increase in the initial temperature of the furnace reduces the instantaneous expulsion rate.

Temperature Distribution in the Type 3 Furnace

i) Distribution of the interior surface temperature

Unlike the type 1 and the type 2 furnace, type 3 furnace was constructed in such a way that the c-axis of the anisotropic pyrolytic graphite was collinear with its optical axis. Temperature was uniformly distributed over the tube circumference (ab-plane) because of high thermal conductivity.

Figures 41 and 42 show the theoretically simulated and experimentally measured temperature distribution, respectively, along the length of the tube at various times during a heating cycle. Comparison of Fig. 41 with Fig. 42 shows qualitative agreement in the temperature distribution of the furnace as a function of time. During the temperature ramping stage, temperature is uniformly distributed over the length of the graphite tube because of low thermal conductivity of the anisotropic pyrolytic graphite in the direction of heat flow (c-direction) and the high input power level. However, once the temperature at the centre of the graphite tube reaches the preset

Figure 41. Theoretically simulated distribution of the surface temperature of the type 3 furnace.

Heating rate of the first node in Fig. 28 = 13.6 K ms^{-1} .

Dimensions of tube are 3.0 mm i.d., 6.0 mm o.d., and 15.0 mm long.

Time: A 0.0 ms; B 45.6 ms; C 107.8 ms; D 129.8 ms;

E 147.3 ms; F 294.6 ms; G 441.8 ms.

Figure 42. Distribution of the surface temperature of the type 3 furnace measured by optical pyrometry.

Heating rate = 12.8 K ms^{-1} . Initial temperature = 300 K .

Dimensions of tube are the same as in Fig. 41.

Time: A 125 ms; B 140 ms; C 155 ms; D 300 ms;

E 500 ms.

value, less power was required to maintain this temperature. Also, a large difference between the temperature at the ends of the tube and that of the electrodes at that time is both experimentally observed and theoretically predicted. This results in a drop of the temperature at the ends of the graphite tube with time, which agrees with the reported temperature distribution of the conventional, end-contacted graphite tube furnace [94]. However, the drop in temperature at the ends of the anisotropic pyrolytic graphite tube is much smaller than that of the above conventional graphite tube furnace because of the lower thermal conductivity of the anisotropic pyrolytic graphite relative to that of regular graphite in the direction of heat flow. Furthermore, the temperature at the ends of the graphite tube predicted by the theoretical model is consistently higher than that measured by optical pyrometry. The over-estimation of the temperature at the ends of the graphite tube by the theoretical model is due to the heat transfer by internal surface radiation not being taken into account. The low temperature of the contact electrode of the type 3 furnace results in a large heat loss by radiation from the internal surface at the ends of the graphite tube relative to its centre.

Increasing the heating rate by increasing in the input power level does not change the temperature distribution along the length of the graphite tube of the type 3 furnace.

ii) Gas temperature and the rate of expulsion of gases from the furnace

Figure 43 shows the theoretically simulated surface and weighted-average gas temperatures and experimentally-measured surface temperature, and measured "effective temperatures" of gas at various heating rates of the type 3 furnace. The "effective temperature" measured by the two-line absorption is consistently lower than the weighted-average gas temperature predicted by the model because of over-estimation of the temperature at the ends of the graphite tube mentioned earlier. No significant change in temperature difference between the surface and gas phase due to an increase in the heating rate from 6 to 40 K ms⁻¹ was observed experimentally nor theoretically predicted.

Curve e in Fig. 43 shows theoretically simulated results of the volumetric expulsion rate of the type 3 furnace at various heating rates. Similar to the phenomenon observed in type 1 furnace, the volumetric expulsion rate increases with increasing heating rate. At the same heating rate, type 3 furnace shows a higher instantaneous rate of volumetric expulsion than the type 1 furnace.

SUMMARY

The temperature distribution of the anisotropic pyrolytic graphite furnace heated with the capacitive discharge power supply was theoretically and experimentally studied. Non-uniform temperature distribution over the circumference of the type 1 furnace was theoretically predicted and experimentally observed. The effect of a

Figure 43 (I-IV). Effect of the heating rate of the type 3 furnace on the gas temperature and the rate of expulsion.

Dashed line of T_{ave} is the theoretical weighted-average gas temperature. Experimentally measured effective temperature by two-line absorption method with Sn (Δ), Pb ($\circ$) and Ni ($\square$) as the thermometric species.

Curve e is the rate of volumetric expulsion as a function of time. Dashed line of $T_{u=1}$ is the theoretically predicted surface temperature at the first node. Solid line of T_m is the experimentally measured surface temperature at the centre of the graphite tube obtained by optical pyrometry.

Heating rate: (I) 39.0 K ms^{-1} ; (II) 23.8 K ms^{-1} ; (III) 12.3 K ms^{-1} ; (IV) 6.0 K ms^{-1} .

Fig. 43 (I-II).

Fig. 43 (III-IV).

decrease in the contact area between the graphite tube and the contact electrodes does not significantly alter the distribution of the interior surface temperature of the type 1 furnace, but reduces the initial voltage required to achieve the same heating rate of the furnace at its central lamellar plane.

Surface temperature distribution of the type 3 furnace across the contact electrodes does not show a significant temperature gradient during the ramping part of the temperature-time profiles. This may be attributable to the low thermal conductivity of the anisotropic pyrolytic graphite tube in the direction of heat loss and high input power level. Once the temperature at the central lamellar plane of the type 3 furnace attains its predetermined, final, steady-state value, there is a gradual drop in the temperature at the ends of the tube while the temperature at the tube centre remains constant.

The gas temperature distribution inside the type 1 and the type 3 furnace was also theoretically and experimentally studied. The experimentally measured "effective gas temperatures" at different heating rates were in reasonable agreement with the theoretically predicted, weighted-average gas temperatures. Increase in the heating rate of the type 1 furnace from 8 to 40 K ms⁻¹ and of the type 3 furnace from 6 to 40 K ms⁻¹ produced no significant change in the difference between the surface temperature and the weighted-average gas temperature at the instant when the central lamellar plane of the graphite tube attained its pre-determined, final temperature. This may be due to the small interior radius of the graphite tubes used. The

model also predicts that an increase in the heating rate of the furnaces increases the instantaneous rate of expulsion. The maximum rate of volumetric expulsion seems to be dependent on the initial temperature and the heating rate, but independent of the final temperature of the furnaces.

CHAPTER 5

STUDIES ON THE CAPACITIVE DISCHARGE TECHNIQUE IN GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY

Early development of electrothermal atomizers for atomic absorption spectrometry followed two different approaches. One approach, used by L'VOV [114] and WOODRIFF et al. [115] created a high, constant-temperature environment using relatively large graphite furnaces. The other approach [69] was made for commercial development of graphite furnaces using small, pulse-heated, tubular, graphite furnaces which were simple to operate and easily applied to routine analysis. However, deposition of sample on the furnace wall meant that the analysis cell and the sample were heated simultaneously, and atomization of the analyte from various matrices occurred over different temperature ranges with unpredictable effect on the peak-height and the integrated absorbance [116]. In addition, samples were sometimes vaporized at temperatures too low to effect complete dissociation of analyte molecular vapour, which resulted in decreased atomic absorption signals [118-122].

Attempts that have been made to reduce and/or to eliminate matrix interferences in conventional graphite furnace atomic absorption spectrometry (GFAAS) are: chemical modifications of the analyte species or the sample matrix [119-123]; atomization of the sample in a nearly isothermal environment with the following devices: graphite platform [42,124-129], microboats [130], tungsten wire probes

[131,132], graphite probes [133-136], dual-power-supply atomizers [137-139] as well as modification of the existing atomizers [140-144],

If atomization of a sample occurs at a time when the atomization surface and the gas phase have attained a high, nearly-constant temperature, such atomization is called "isothermal atomization" [127]. The term "isothermal atomization" will be used in this chapter in the above context.

In this chapter, another approach to isothermal atomization, the capacitive-discharge technique (CDT), is described. The description contains a report on the analytical performance of three furnaces of different configurations based on the orientation of the lamellar plane of the anisotropic pyrolytic graphite tube relative to the furnace's optical axis.

EXPERIMENTAL

Apparatus

Unless otherwise stated, the atomic absorption spectrometer and the capacitive-discharge-heated graphite furnaces used in this study were the same as discussed in Chapter 3.

Reagents

Chemicals used were of ACS reagent grade purity. A stock solution containing 1000 µg/mL of each metal studied (except Mo) was prepared from pure metal or its oxide by dissolving it in ULTREX nitric acid (J.T. Baker Chemical Co., Phillipsburgh, N.J., USA). The stock solution of Mo was prepared by dissolving MoO₃ (99.5% minimum purity)

in 40% (v/v) ammonia-water mixture. The stock solutions of 10% (w/v) CuCl_2 and 10.5% (w/v) CuSO_4 were separately prepared by dissolving appropriate masses of CuCl_2 and CuSO_4 salts, respectively, in ultrapure water. Ultrapure water of resistivity 18.3 M Ω -cm was obtained direct from a Mill-Q2 water purification system (Millipore Corporation, Mississauga, Ontario, Canada). 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 graphite tube surface exactly below the sample injection port with an Eppendorf microlitre pipette fitted with disposable plastic tips. Argon gas of 99.995% purity was used as internal purge gas and external sheath gas.

RESULTS AND DISCUSSION

The Type 1 and the Type 2 Furnace

i) Effect of the heating rate on the atomic absorption signals

Figure 44 presents the atomic absorption signals of Pb at different heating rates of the type 1 furnace; the absorption pulses are superimposed on the temperature profiles of the graphite surface which are measured by focussing the optical pyrometer on zone A through the sample injection hole. The characteristics of the absorption pulse and the corresponding temperature profile shown in Fig 44 have been summarized in Table 9. Comparison of Fig. 44 with Fig. 1 in Chapter 1 shows that the characteristic changes in the shape and the peak-height

Figure 44. Atomic absorption pulse of 1.6×10^{-13} kg Pb (as NO_3^-) obtained with the type 1 furnace at various heating rates, superimposed on the temperature profiles of zone A plotted as the output voltage of the optical pyrometer.

Analytical wavelength = 283.3 nm, charring temperature = 770 K, atomization temperature = 2470 K. Dimensions of tube are 3.0 mm i.d., 6.0 mm o.d., and 15.0 mm long. Atomic absorption pulses 1, 2, 3 and 4 were obtained using the temperature profiles a, b, c and d, respectively.

Table 9. Characteristics of the atomic absorption pulse of Pb and the corresponding temperature profile of zone A in the type 1 furnace*.

Heating rate, K/ms	T _{app} , K	t _{app} , ms	Peak-height absorbance	Integrated absorbance, Abs-ms	T _{peak} , K	t _{peak} , ms
5.7	1560	105	0.203	21.6	2270	232
11.0	1520	64	0.250	21.0	2310	139
19.5	1550	40	0.303	26.4	2470	86
40.5	1520	18	0.272	24.6	2470	44

* Data are obtained from Fig. 44. T_{app}, t_{app}, T_{peak} and t_{peak} are appearance temperature, appearance time, temperature at the peak of the absorption pulse and time to reach the peak of the absorption pulse, respectively.

of the absorption pulse agree qualitatively up to a heating rate of 20 K ms^{-1} . The peak maxima drop slightly with further increase in the heating rate. This drop in the peak-height absorbance of the type 1 furnace can hardly be attributed to the response of the detection system since 4 ms time constant was used for all the measurements (see Table 7). The difference between the theoretical and experimental results may be due to other processes during atomization which have not been taken into account in the development of the theoretical model, such as the loss of the analyte vapour by expulsion. Since the furnace is open to the ambient atmosphere, pressure inside the furnace should be constant (1 atm). According to the ideal gas law, $pV=nRT$, increasing the gas temperature by heating the furnace results in expansion of the gas. The amount of gas expelled from the furnace depends on the difference between the initial and the final temperature of the furnace rather than the heating rate. At constant pressure, the time derivative of the ideal gas law can be obtained as follows:

$$\left(\frac{dV}{dt}\right)_p = \frac{R}{p} T \left(\frac{dn}{dt}\right)_{p,T} + \frac{nR}{p} \left(\frac{dT}{dt}\right)_{p,n} \quad 5.1$$

where T is the gas temperature inside the furnace. Equation 5.1 indicates that the rate of volumetric expulsion depends on the time rate of change of the gas temperature and the rate of vaporization of the species from the condensed phase. With the present experimental conditions, only a very small amount of the analyte was introduced into the furnace; hence, the first-term on the right-hand side of Eqn 5.1

can be neglected. However, it should be noted that this term may not be neglected for much larger amounts of matrix and/or analyte introduced into the furnace. Since the increase in the gas phase temperature closely follows the increase in surface temperature of the furnace, Eqn 5.1 indicates that an increase in the heating rate of the furnace increases the rate of expulsion; this supports the theoretical results shown in Fig. 40 and also suggests that the gas species are expelled out of the furnace within a short period of time. If the analyte is vaporized or atomized during the rapid heating of the furnace, it may be lost with the expelled internal purge gas. Thus, the expansion of the purge gas inside the furnace plays an important role in the atom removal process during the fast heating of the furnace, particularly for elements having low appearance temperatures.

Figure 45 shows the effect of heating rates on the peak-height absorbance of four elements for both the type 1 and the type 2 furnace. The peak-height absorbance was obtained using the optimum atomization temperatures which were earlier established using a heating rate of 10 K ms^{-1} . The temperature of both the type 1 and the type 2 furnace was measured by focussing the optical pyrometer on the central lamellar plane of the graphite tube across the place where contact electrodes were positioned. The heating rate represents the average heating rate measured over the temperature range from the final charring temperature to the preset, final atomization temperature. Comparison of the simulated and the experimental plots (Figs. 8 and 45, respectively) of the peak-height absorbance as a function of the

Figure 45. Peak-height absorbance as a function of the heating rate of the type 1 and the type 2 furnace.

Aqueous solutions of the analyte were used. Open symbols: type 2 furnace; closed symbols: type 1 furnace; T_c and T_f stand for charring temperature and atomization temperature, respectively. Dimensions of tube are 3.0 mm i.d., 6.0 mm o.d., and 15.0 mm long.

- ■ 8.0×10^{-14} kg Mn (as NO_3^-). λ : 279.5 nm, T_c : 880 K, T_f : 2800 K.
- ● 1.6×10^{-13} kg Pb (as NO_3^-). λ : 283.3 nm, T_c : 770 K, T_f : 2470 K.
- ● 5.0×10^{-15} kg Cd (as NO_3^-). λ : 228.8 nm, T_c : 470 K, T_f : 1800 K.
- △ 5.0 $\times 10^{-13}$ kg Co (as NO_3^-). λ : 240.7 nm, T_c : 1020 K, T_f : 3000 K.
- ▲ 1.0×10^{-12} kg Co (as NO_3^-). λ : 240.7 nm, T_c : 1020 K, T_f : 3000 K.

heating rate shows a reasonable agreement between the effect predicted by the model and that observed experimentally. However, Fig. 45 shows that the type 2 furnace gives higher peak-height absorbances for Pb, Mn and Co, whereas the reverse is observed for Cd. For Mn, the peak-height absorbance increases very rapidly with increasing heating rate up to 20 K ms^{-1} for both types of furnace. Beyond this, the peak-height absorbance levels off, and finally decreases slightly. The only other element which shows a similar, but less rapid, increase in the peak-height absorbance with increasing heating rates is Cd. Above 13 K ms^{-1} the peak-height absorbance of Cd then levels off, and remains nearly constant up to a heating rate of 18 K ms^{-1} . The signal finally falls off with further increase in the heating rate. Another element which follows the above trend of Cd, but with less pronounced effects, is Pb. Both Cd and Pb exhibit a very small range of heating rates over which the peak-height absorbance remains constant. This is especially true of cadmium, the low appearance temperature [28] of which occurs at a time when the purge gas inside the furnace is expanding very rapidly, with consequent increase in the rate of atom removal.

For the type-2 furnace, the temperature of the spot on which the sample is deposited, i.e., zone B, has been found to be lower than that for the type 1 furnace at a time corresponding to the onset of constant temperature in zone A (see Fig. 36). For the type 2 furnace, this lower temperature results in a delay in the vaporization of the sample, similar to that which occurs with the platform technique [106]. The analyte species thus enters a gas phase which has attained a higher

temperature than that of the gas phase in the type 1 furnace at the time of vaporization of the analyte species. Since the degree of dissociation of analyte molecular species increases with increasing temperature, and the delay in the vaporization of the sample till the gas temperature is higher reduces the loss of analyte species by expulsion with the internal purge gas, the type 2 furnace gives higher peak-height absorbance for most of the elements studied.

An additional difference between the two furnaces is the characteristics of the surface on which the sample is deposited. In the type 1 furnace the aqueous solution is deposited on the edges of the ab plane (Fig. 19). There are generally more reactive sites at this carbon surface than on the face of the ab-plane [145,146]. Thus, carbide formation will be more favourable at the edges of the ab-plane than on the pyrolytic graphite-coated surface where only the basal plane is exposed to the sample. Although the sample was deposited mainly on the basal plane of the type 2 furnace, the sample spread to the edges of this plane. Therefore, depression of the peak-height absorbance due to carbide formation in the type 2 furnace should be less likely than that in the type 1 furnace, but greater than that in a graphite tube coated with pyrolytic graphite where only the basal plane is exposed to the analyte. Even in the absence of carbide formation, in the type 2 furnace there should be decreased soaking of analyte solution into the furnace wall because of the lower porosity of the basal plane. This should enhance the rate of release of analyte atoms from the graphite surface into the gas phase. Table 10 lists the

Table 10. Characteristic mass of Pb, Ni and Mo.

Analyte	λ , nm	T_o , K	T_f , K	α , K ms ⁻¹	Capacitive discharge technique		P-E HGA-500 characteristic mass, kg
					Type 1	Type 2	
Pb	283.3	770	2470	20	$2.4 \times 10^{-15} \pm 5.8\%$	$2.0 \times 10^{-15} \pm 3.4\%$	1.3×10^{-14}
Ni	232.0	870	3100	30	$1.5 \times 10^{-14} \pm 8.0\%$	$5.2 \times 10^{-15} \pm 2.8\%$	1.0×10^{-14}
Mo	313.3	1000	3200	30	$5.8 \times 10^{-14} \pm 7.0\%$	$2.5 \times 10^{-14} \pm 7.1\%$	9.0×10^{-15}

λ , T_o , T_f and α are wavelength, charring temperature, atomization temperature and heating rate, respectively. Dimensions of both the type 1 and the type 2 furnace are 3.0 mm i.d., 6.0 mm o.d., and 15.0 mm long. Values shown with $\pm$ signs are percent relative standard deviations. The characteristic mass for the Perkin-Elmer HGA-500 was confirmed in this laboratory using The Perkin-Elmer atomic absorption spectrophotometer, model 5000.

characteristic mass for peak-height absorbance, defined as the mass of analyte required to give 0.0044 absorbance [147]. The values of characteristic mass for Pb, Ni, and Mo by the CDT have been compared with those reported for the Perkin-Elmer atomic absorption spectrophotometer, model 5000, equipped with a heated graphite atomizer (HGA), model 500, and Perkin-Elmer graphite tubes coated with pyrolytic graphite. The purpose of this comparison is to examine the change in characteristic mass for each graphite furnace when the analyte is changed from a non-carbide-forming element to an element known to form stable carbides. For optimized heating rates and temperatures used, the characteristic mass for the anisotropic pyrolytic graphite furnace used in the CDT is reduced by a factor of 5.4 for Pb, but is increased by a factor of 6.4 for Mo relative to the characteristic masses for the HGA-500. The Pb data for the CDT furnace indicate that high heating rates improve its sensitivity relative to that of the HGA-500. Also, in earlier work [70] in this laboratory with a modified HGA-2100 furnace heated at 4.3 K ms^{-1} , a 2.2-fold decrease in the characteristic mass for Pb relative to that of the Perkin-Elmer atomic absorption spectrophotometer, model 603, equipped with an HGA-76B was reported. Molybdenum may form an intercalation (layered) compound [148] with the pyrolytic graphite of the CDT furnace, inhibiting the release of molybdenum and increasing the characteristic mass.

A similar, though less severe, signal depression was observed with nickel. The characteristic mass for the type 1 furnace is 1.5 times greater than that for the HGA-500. Atomization of Ni or Mo from the type 2 furnace resulted in a 2-fold decrease in their characteristic

mass relative to that of the type 1 furnace. Both the temperature and the furnace configurations are probably responsible for determining the characteristic mass in the peak-height absorbance mode. However, the above data do not allow differentiation of their relative contributions.

ii) Effect of the tube length on peak-height absorbance.

Figure 46 shows the peak-height absorbance of Pb, Mn and Co as a function of the tube length. For both the type 1 and type 2 configuration, the tube length was varied from 10.0 to 25.0 mm. The effect on peak-height absorbance was similar in each case, i.e., there was an increase with increasing tube length. Since longer tubes provide a longer path over which diffusion and expulsion must occur, the residence time of atoms increases with increasing tube length [4,149]. Although 25.0 mm tube length gave the highest absorbance, constraints of greater mass requiring higher voltages and higher currents (to attain a given heating rate) than that for a 15.0 mm tube length led to the choice of 15.0 mm tube length for further studies. The capacitor bank B of 1.94 F was capable of supplying adequate power to heat large tubes rapidly. However, high power levels required for high heating rates generated loud electric arcs producing large cracks in the graphite tube, and sometimes even minor explosions which shattered the tube. Heating rates were therefore limited to a maximum of 20 K ms^{-1} .

Figure 46. Peak-height absorbance as a function of the tube length of the type 1 and the type 2 furnace.

Aqueous solutions of the analyte were used. Open symbols: type 2 furnace; closed symbols: type 1 furnace. Charring and atomization temperatures and analytical wavelengths used were the same as in Fig. 45.

□, ■ 8.0×10^{-14} kg Mn (as NO_3^-). ○, ● 1.6×10^{-13} kg Pb (as NO_3^-).
 △, ▲ 5.0×10^{-13} kg Co (as NO_3^-).

iii) Matrix interferences with the type 1 and the type 2 furnace

Figures 47 and 48 show the recovery of Pb signal by the peak-height absorbance mode from a CuCl_2 matrix and a CuSO_4 matrix with the type 1 and type 2 furnace. The recovery was higher with the type 2 furnace but the magnitude of recovery varied with the particular analyte-matrix combination. A higher gas phase temperature and the delay in vaporization of analyte in the type 2 furnace were probably the cause for its higher recoveries. Figures 47 and 48 show that 100% recovery of the peak-height absorbance of Pb was obtained with the type 2 furnace with the CuCl_2 matrix, and with both furnaces in the presence of the CuSO_4 matrix at a matrix/analyte mass ratio of roughly $10^5:1$. Recovery fell off at higher matrix/analyte mass ratios. It will be shown later in this chapter that, in the case of matrix interferences, peak-area absorbance gives better signal recoveries than peak-height absorbance. However, Figs. 47 and 48 show that even the peak-height absorbance gave 100% recoveries of the Pb signal up to a matrix/analyte mass ratio of roughly $10^5:1$. The above peak-height absorbance recoveries may be compared with the peak-area absorbance recoveries of Pb signals from the CuCl_2 matrix reported by other workers using their laboratory-made furnaces. SIEMER [137,140] reported 100% recovery of peak-area absorbance signals for Pb at a CuCl_2 matrix/analyte mass ratio of $5 \times 10^3:1$ for his tube-cup atomizer, and $5 \times 10^4:1$ for his home-made cup atomizer.

Figure 49 shows that at a matrix/Pb mass ratio of $> 10^5:1$, Pb signal recoveries as measured by peak-height absorbance are far better with the type 2 furnace than with the type 1 furnace for both the CuCl_2

Figure 47. Recoveries of Pb signal (2.0×10^{-13} kg as Cl^-) from CuCl_2 matrix (in aqueous solutions) in the type 1 and the type 2 furnace.

Heating rate = 35 K ms^{-1} . Dimensions of tube are 3.0 mm i.d., 6.0 mm o.d., and 15.0 mm long. $\square$ — Type 1 furnace;

$\bigcirc$ — type 2 furnace.

Figure 48. Recoveries of Pb signal ($2.0 \times 10^{-13} \text{ kg as NO}_3^-$) from CuSO_4 matrix (in aqueous solutions) in the type 1 and the type 2 furnace.

Heating rate = 35 K ms^{-1} . Dimensions of tube are 3.0 mm i.d., 6.0 mm o.d., and 15.0 mm long. $\square$ Type 1 furnace; $\circ$ type 2 furnace.

Figure 49. Recoveries of Pb signal from CuCl_2 and CuSO_4 matrices (in aqueous solutions) in the type 1 and the type 2 furnace as a function of the heating rate.

$T_c = 920 \text{ K}$, $T_f = 2500 \text{ K}$. Dimensions of tube are 3.0 mm i.d., 6.0 mm o.d., and 15.0 mm long. $\circ \square$ recovery of $2.0 \times 10^{-13} \text{ kg}$ Pb (as Cl^-) from $5.0 \times 10^{-8} \text{ kg}$ CuCl_2 . $\triangle \square$ recovery of $2.0 \times 10^{-13} \text{ kg}$ Pb (as NO_3^-) from $3.0 \times 10^{-8} \text{ kg}$ CuSO_4 . $\square \circ$ type 1 furnace: $\triangle \circ$ type 2 furnace.

and the CuSO_4 matrix. Except for the type 2 furnace with the CuSO_4 matrix, Pb signal recoveries are independent of the heating rate in the range of 5 to 35 K ms^{-1} . With the type 2 furnace, Pb signal recovery from the CuSO_4 matrix increases with increasing heating rates, and finally levels off at a heating rate $> 30 \text{ K ms}^{-1}$.

The Type 3 Furnace

i) Effect of the heating rate on atomic absorption signals

The type 3 furnace (graphite tube 10.0 mm in length) was fitted with quartz end-windows and was therefore more of a closed system than the open furnace of the type 1 or the type 2. Figure 50 shows the atomic absorption signals of Pb at different heating rates of the type 3 furnace. The absorption pulses are superimposed on the temperature profiles of the graphite surface - the temperature was measured by focussing the optical pyrometer through the sample injection hole. Table 11 summarizes the characteristics of the atomic absorption pulse and the corresponding temperature profile shown in Fig. 50. Figure 50 shows that the change in the shape and peak-height of the absorption pulse with increasing heating rates agrees qualitatively with the results predicted by the theoretical model shown in Fig. 1, up to a heating rate of 15 K ms^{-1} . The drop in the signal with further increase in the heating rate of the type 3 furnace may be attributed to the slow response time of the detection system (see Table 7) as well as the loss of analyte by expulsion.

Figure 51 shows the change in the peak-height absorbance as a

Figure 50. Atomic absorption pulses of 3.2×10^{-13} kg Pb (as NO_3^-) obtained with the type 3 furnace at different heating rates, superimposed on the surface temperature profiles of the centre of the graphite tube (plotted as the output voltage of the optical pyrometer).

Analytical wavelength = 283.3 nm, charring temperature = 770 K, atomization temperature = 2470 K. Dimensions of tube are 3.0 mm i.d., 6.0 mm o.d., and 10.0 mm long. Atomic absorption pulses 1, 2, 3, 4 and 5 were obtained using the temperature profiles a, b, c, d and e, respectively.

Table 11. Characteristics of the atomic absorption pulse of Pb and the corresponding temperature profile of the centre of the type 3 furnace*.

Heating rate, K/ms	T _{app} , K	t _{app} , ms	Peak-height, absorbance	Integrated absorbance, Abs-ms	T _{peak} , K	t _{peak} , K
4.8	1300	180	0.288	20.2	1670	236
9.6	1280	93	0.388	16.9	1690	123
14.2	1320	64	0.390	13.1	1750	88
22.8	1400	37	0.360	8.5	1933	56
44.1	1400	20	0.351	5.5	2223	33

*Data are obtained from Fig. 50. T_{app}, t_{app}, T_{peak} and t_{peak} are appearance temperature, appearance time, temperature at the peak of the absorption pulse, and time to reach the peak of the absorption pulse, respectively.

Figure 51. Peak-height absorbance as a function of the heating rate of the type 3 furnace.

Aqueous solutions of the analyte were used. Charring and atomization temperatures and analytical wavelengths used were the same as in Fig. 45. Dimensions of tube are 3.0 mm i.d., 6.0 mm o.d., and 10.0 mm long.

□ 8.0×10^{-14} kg Mn (as NO_3^-). ○ 3.2×10^{-13} kg Pb (as NO_3^-).
 ○ 5.0×10^{-15} kg Cd (as NO_3^-). △ 5.0×10^{-13} kg Co (as NO_3^-).

function of the heating rate for the type 3 furnace. The peak-height absorbance of Mn increases very rapidly with increase in the heating rate up to a limiting value of 20 K ms^{-1} . The peak-height absorbance of the other three elements, Co, Pb and Cd, increases less rapidly; Co and Pb up to a limiting heating rate of 15 K ms^{-1} , and Cd up to a limiting heating rate of 10 K ms^{-1} . As shown in Figs. 3-7 in Chapter 1, the appearance temperature of elements is very sensitive to changes in the rate of atom formation, but less sensitive to changes in the rate of atom loss. Low activation energies as well as high frequency factors provide high rates of atom formation at relatively low temperatures. The linear relationship between the activation energies and the appearance temperatures of some elements has been reported by STURGEON and CHAKRABARTI [28, p. 162]. Figure 52 has been plotted using the activation energies and the appearance temperatures of the elements reported by L'VOV et al. [20] and L'VOV [42]; its two straight line plots agree with the findings of STURGEON and CHAKRABARTI [28]. From these plots it may be conjectured that the magnitude of frequency factors involved falls into at least two different ranges [19]. In Fig. 52, both Cd and Pb are located in the low-activation-energy region in each of the two lines. Atomization of these elements should be more sensitive to changes in the heating rate if the loss process is diffusion-controlled [149]. However, rapid heating of this semi-enclosed furnace (the type 3) may force much of the expanding internal purge gas (and any analyte atoms present in the gas) out through the sample injection port because this is the only opening to relieve any pressure increase. In pulse-heated furnaces,

Figure 52. Correlation plot of the activation energy and the appearance temperature of elements

loss of analyte species by expulsion may contribute significantly to the total loss of analyte atoms if the analyte species are present in the gas phase during the period of rapid increase in the gas temperature [2,21]. The above explanation for the CDT furnace (the type 3) is supported by the fact that vapour plumes were observed to flow out through the sample injection port when several micrograms of a volatile salt were vaporized in the furnace. The higher activation energies of Mn and Co (relative to Cd and Pb) in each of the line groups of Fig. 52 result in higher appearance temperatures. The relatively high appearance temperatures of Mn and Co allow them to avoid partly or fully the drastic loss of analyte vapour by expulsion with the internal purge gas during the earlier part of the temperature rise. Hence, the loss of analyte vapour by expulsion should be less for these elements. Enhancements in their peak-height absorbance with increasing heating rates (up to their limiting heating rates) should therefore be expected, as predicted by the atomization model mentioned in Chapter 1, and are experimentally observed. These enhancements are similar to those observed with the type 1 and the type 2 furnace. The striking difference in the dependence of the peak-height absorbance of Mn and Co on heating rate, despite their similar appearance temperatures [28, p. 146;20], may be related to the difference in their mechanisms of atomization. Carbon reduction of $\text{MnO}_{(s)}$ at the Mn appearance temperature is thermodynamically unfavourable, whereas carbon reduction of $\text{CoO}_{(s)}$ at the Co appearance temperature is thermodynamically a highly favourable reaction [28, p. 147]. In

Fig. 51, the dramatic increase in the peak-height absorbance of Mn in contrast with the much smaller increase in the peak-height absorbance of Co with increasing heating rates (up to their limiting heating rates) is consistent with the postulation that atomization of Mn, involving thermal dissociation of $MnO(s)$, is more sensitive to higher heating rates than atomization of Co, which proceeds via carbon reduction of $CoO(s)$. At the appearance temperature of Co, the spontaneity of thermal dissociation of $CoO(s)$ would be determined by the instantaneous partial pressure of oxygen inside the furnace, whereas the above postulation would require that the actual atomization mechanism for Co is by carbon reduction of $CoO(s)$ rather than by thermal dissociation.

ii) Effect of the tube length on peak-height absorbance

Table 12 shows that an increase in the tube length of the type 3 furnace from 10.0 mm to 15.0 mm increases the peak-height absorbance, which agrees with the results of the theoretical model in Fig. 10. Further increase in the tube length beyond 15.0 mm was limited by higher resistance and greater mass of a longer furnace. Unlike the type 1 and the type 2 furnace in which an increase in the tube length decreases the resistance, in the type 3 furnace, the resistance increases with increasing tube length because the optical axis is collinear with the c-axis of the anisotropic pyrolytic graphite. Doubling the tube length of the type 3 furnace with the same internal and external diameters results in a 2-fold increase in both the mass and the electric resistance of the tube. Hence, the longer furnace

Table 12. Effect of the tube length of the type 3 furnace on the peak-height absorbance.

Analyte	Wavelength, nm	Mass of analyte, kg	Peak-height absorbance	
			Tube length 10.0 mm	Tube length 15.0 mm
Pb	283.3	3.2×10^{-13}	$0.383 \pm 3.8\%$	$0.447 \pm 3.3\%$
Cd	228.8	5.0×10^{-15}	$0.198 \pm 6.6\%$	$0.292 \pm 5.9\%$
Mn	279.5	8.0×10^{-14}	$0.676 \pm 3.8\%$	$0.832 \pm 3.7\%$
Co	240.7	5.0×10^{-13}	$0.331 \pm 3.9\%$	$0.370 \pm 1.9\%$

Charring and atomization temperatures and analytical wavelengths used were the same as in Fig. 45. Dimensions of the tube are 3.0 mm i.d. and 6.0 mm o.d. Heating rate = 15 K ms^{-1} . Values shown with $\pm$ signs are percent relative standard deviations.

would require much higher voltage and capacitance to attain the same heating rate (Eqns 3.4 and 3.5). Also, for the longer furnace, the final temperature could not be held constant using the available step-down transformer (32 V maximum). Therefore, capacitive discharge heating of the type 3 furnace with a tube longer than 15.0 mm was not attempted.

iii) Matrix interferences with the type 3 Furnace

Figures 53-55 show the results of studies of the recovery of the Pb signal using the peak-height and peak-area modes of absorbance measurement. The following observations are made. In all cases, when matrix interferences occur, the peak-area mode gives higher recoveries than the peak-height mode. The Pb signal recovery is 100% for the matrix/Pb mass ratio of $10^4:1$. At higher matrix/Pb mass ratios, signal recoveries drop for both modes of measurement, but the peak-height mode has a steeper drop than the peak-area mode.

Similar to the type 1 and the type 2 furnace, with the type 3 furnace at CuSO_4/Pb or CuCl_2/Pb mass ratio of $\sim 10^5:1$, Pb signal recoveries are independent of the heating rate in the range of 4 to 35 K ms. The low recovery of Pb from the CuCl_2 matrix was probably due to the loss of lead as a volatile chloride species [119,150]. The depression of the Pb signal in the presence of sulphate may be due to an increase in the partial pressure of oxygen because of thermal dissociation of CuSO_4 [151].

Figure 53. Recoveries of Pb signal ($2.0 \times 10^{-13} \text{ kg as } \text{PbO}_3^-$) from CuCl_2 matrix (in aqueous solutions) in the type 3 furnace.

$T_c = 1020 \text{ K}$, $T_f = 2500 \text{ K}$, heating rate = 35 K ms^{-1} .

Dimensions of tube are 3.0 mm i.d., 6.0 mm o.d., and 15.0 mm long.

○ — Peak-height mode; □ — peak area mode.

Figure 54. Recoveries of Pb signal ($2.0 \times 10^{-13} \text{ kg as NO}_3^-$) from CuSO_4 matrix (in aqueous solutions) in the type 3 furnace.

$T_c = 1020 \text{ K}$, $T_f = 2500 \text{ K}$, heating rate = 35 K ms^{-1} .
 Dimensions of tube are 3.0 mm i.d., 6.0 mm o.d., and 15.0 mm long.

○ — Peak-height mode; □ — peak area mode.

Figure 55. Recoveries of Pb signal (2.0×10^{-13} kg as NO_3^-) from synthetic seawater matrix in the type 3 furnace.

$T_c = 870$ K, $T_f = 2300$ K, heating rate = 32 K ms^{-1} . Dimensions of tube are 3.0 mm i.d., 6.0 mm o.d., and 15.0 mm long.

○ — Peak-height mode; □ — peak area mode.

SUMMARY

The results of all three furnace configurations agree with the predictions of a simple theoretical model presented in Chapter 1 that peak-height absorbance will increase with increasing heating rates up to a limiting heating rate. Beyond this limiting heating rate, peak-height absorbance will either remain constant or decrease, depending on the role of expulsion loss in the mechanism for analyte vapour loss.

Comparison of the characteristics of the atomic absorption pulse of Pb generated by the type 1 and the type 3 furnace, given in Tables 9 and 11 suggests that the difference in the absorption pulses from different furnace configurations may be due to differences in their temperature distribution. Since the temperature of zone B is much lower than that of zone A for the type 1 furnace, some analyte vapour might condense on the cooler spot of zone B following its vaporization from zone A where it had been earlier deposited. The longer rise time (Table 7) and the slow decay of the tailing part of the signal generated by the type 1 furnace is due to the relatively low heating rate and the low final temperature of zone B. The latter leads to a slow revaporization of the analyte from zone B. The great decrease in the peak area of lead with increasing heating rates of the type 3 furnace (shown in Table 11) indicates that a large fraction of the analyte vapour is lost with the expelled purge gas during the period of rapid increase in the temperature.

REFERENCES

- [1] B.V. L'VOV, J. Quant Spectrosc Radiat. Transfer 12, 651 (1972).
- [2] W.M.G.T. VAN DEN BROEK and L. DE GALAN, Anal. Chem. 49, 2176 (1977).
- [3] R.E. STURGEON and S.S. BERMAN, Anal. Chem. 55, 191 (1983).
- [4] B.V. L'VOV, "Atomic Absorption Spectrochemical Analysis", Adam Hilger, London (1976).
- [5] B.V. L'VOV, Pure Appl. Chem. 23, 11 (1970).
- [6] D.A. KATSKOV and B.V. L'VOV, Zh. Prikl. Spektrosk. 15, 783 (1971).
- [7] G. TORSI and G. TESSARI, Anal. Chem. 45, 1812 (1973).
- [8] S.L. PAVERI-FONTANA, G. TESSARI and G. TORSI, Anal. Chem. 46, 1032 (1974).
- [9] G. TORSI and G. TESSARI, Anal. Chem. 47, 839 (1975).
- [10] G. TORSI and G. TESSARI, Anal. Chem. 47, 842 (1975).
- [11] G. TESSARI, "Proceedings of the Symposium on Electrothermal Atomization in Atomic Absorption Spectrometry", p. 81, Chlum u Trebone, Czechoslovakia. 1977.
- [12] S.L. PAVERI-FONTANA, G. TESSARI and G. TORSI, Ann. Chimica 68, 943 (1978).
- [13] G. TESSARI and G. TORSI, Ann. Chimica 68, 967 (1978).
- [14] G. TORSI and G. TESSARI, Ann. Chimica 68, 991 (1978).
- [15] C.W. FULLER, Analyst 99, 739 (1974).
- [16] D.J. JOHNSON, B.L. SHARP, T.S. WEST and R.M. DAGNALL, Anal. Chem. 47, 1234 (1975).
- [17] J. ZSAKO, Anal. Chem. 50, 1105 (1978).

- [18] H. FALK, Spectrochim. Acta 33B, 695 (1978).
- [19] B. SMETS, Spectrochim. Acta 35B, 33 (1980).
- [20] B.V. L'VOV, P.A. BAYUNOV and G.N. RYABCHUK, Spectrochim. Acta 36B, 397 (1981).
- [21] J.A. HOLCOMBE, Spectrochim. Acta 38B, 609 (1983).
- [22] G. TESSARI and G. TORSI, Anal. Chem. 51, 2039 (1979).
- [23] J. ZSAKO, Anal. Chem. 51, 2040 (1979).
- [24] J.A. HOLCOMBE, G.D. RAYSON and N. AKERLIND, JR., Spectrochim. Acta 37B, 319 (1982).
- [25] G.D. RAYSON and J.A. HOLCOMBE, Anal. Chim. Acta 136, 249 (1982).
- [26] G.D. RAYSON and J.A. HOLCOMBE, Spectrochim. Acta 38B, 987 (1983).
- [27] J.A. HOLCOMBE and G.D. RAYSON, Prog. Anal. Atom. Spectrosc. 6, 225 (1983).
- [28] R.E. STURGEON and C.L. CHAKRABARTI, Prog. Anal. Atom. Spectrosc. 1, 5 (1978).
- [29] G.I. NIKOLAEV and V.B. ALEKSOVSKII, Zh. Tekh. Fiz. 34, 753 (1964).
- [30] A.C. NORRIS, "Computational Chemistry", John Wiley, New York (1981).
- [31] C.F. GERALD, "Applied Numerical Analysis", 2nd Edn, Addison-Wesley, Don Mills, Ontario, Canada (1978).
- [32] W.C. CAMPBELL and J.M. OTTAWAY, Talanta 21, 837 (1974).
- [33] W. FRECH, J.-A. PERSSON and A. CEDERGREN, Prog. Analyt. Atom. Spectrosc. 3, 279 (1980).

- [34] C.L. CHAKRABARTI, C.C. WAN, R.J. TESKEY, S.B. CHANG, H.A. HAMED and P.C. BERTELS, *Spectrochim. Acta* 36B, 427 (1981).
- [35] R.E. STURGEON, C.L. CHAKRABARTI and C.H. LANGFORD, *Anal. Chem.* 48, 1792 (1976).
- [36] B. WELZ, "Proceedings of the Symposium on Electrothermal Atomization in Atomic Absorption Spectroscopy", p. 126, Chlum u Trebone, Czechoslovakia, 1977.
- [37] H.S. WAHAB and C.L. CHAKRABARTI, *Spectrochim. Acta* 36B, 475 (1981).
- [38] O. GENC, S. AKMAN, A.R. OZDURAL, S. ATES and T. BALKIS, *Spectrochim. Acta* 36B, 163 (1981).
- [39] J. AGGETT and A.J. SPROTT, *Anal. Chim. Acta* 72, 49 (1974).
- [40] D.A. KATSKOV, *Zh. Prikl. Spectrosk.* 30, 612 (1979).
- [41] W. FRECH, N.G. ZHOU and E. LUNDBERG, *Spectrochim. Acta* 37B, 691 (1982).
- [42] B.V. L'VOV, *Spectrochim. Acta* 33B, 153 (1978).
- [43] A.A. PUPYSHEV and V.K. NAGDAEV, *Zh. Prikl. Spectrosk.* 33, 227 (1980).
- [44] V.K. NAGDAEV and A.A. PUPYSHEV, *Zh. Prikl. Spectrosk.* 36, 373 (1982).
- [45] C. DUVAL, "Inorganic Thermogravimetric Analysis", Elsevier Publishing Co., New York, 1963.
- [46] D.L. STYRIS and J.H. KAYE, *Anal. Chem.* 54, 864 (1982).
- [47] R.E. STURGEON, D.F. MITCHELL and S.S. BERMAN, *Anal. Chem.* 55, 1059 (1983).

- [48] R.E. STURGEON, C.L. CHAKRABARTI, I.S. MAINES and P.C. BERTELS, Anal. Chem. 47, 1240 (1975).
- [49] R.E. STURGEON, C.L. CHAKRABARTI and P.C. BERTELS, Anal. Chem. 47, 1250 (1975).
- [50] J.P. BYRNE, Aust. J. Chem. 32, 249 (1979).
- [51] B.V. L'VOV and G.N. RYABCHUK, Spectrochim. Acta 37B, 673 (1982).
- [52] R.E. STURGEON, K.W.M. SIU and S.S. BERMAN, Spectrochim. Acta 39B, 213 (1984).
- [53] A. CEDERGRÉN, W. FRECH and E. LUNDBERG, Anal. Chem. 56, 1382 (1984).
- [54] C.TH.J. ALKEMADE and P.J. TH. ZEEGERS, "Spectrochemical Methods of Analysis", Ed. by J.D. WINEFORDNER, p. 12, Wiley, New York, 1971.
- [55] I. BARIN and O. KNACKE, "Thermochemical Properties of Inorganic Substances", Springer-Verlag, Berlin, 1973.
- [56] I. BARIN, O. KNACKE and O. KUBASCHEWSKI, "Thermochemical Properties of Inorganic Substances", Springer-Verlag, Berlin, 1977.
- [57] JANAF Thermochemical Tables, D.R. STULL, Dow Chemical Co., Midland, Michigan (1965 and subsequent supplements).
- [58] W.C. RILEY "High Temperature Materials & Technology", Ed. by I.E. CAMPBELL and E.M. SHERWOOD, Chapter 7, John Wiley & Sons, New York, 1967.
- [59] I.S. KULIKOV, "Thermal Dissociation of Chemical Compounds", Translated from Russian by J. SCHMORAK, Israel Program for Scientific Translations Ltd., Jerusalem, 1967.
- [60] R.T. YANG, and C. WONG, J. Phys. Chem. 84, 678 (1984).
- [61] R.C. BANSAL, F.J. VASTOLA, P.L. WALKER, Jr., Carbon 8, 443 (1970).

- [62] H. EYRING and S.H. LIN, "Heterogeneous Kinetics at Elevated Temperatures", Ed. by G.R. BELTON and W.L. WORRELL, p. 1, Plenum Press, New York, 1970.
- [63] J. NAGLE and R.F. STRICKLAND-CONSTABLE, "Proceedings of the Fifth Conference on Carbon", Vol. 2. p. 154, 1961.
- [64] J.R. WALLS and R.F. STRICKLAND-CONSTABLE, Carbon 1, 333 (1964).
- [65] R.F. STRICKLAND-CONSTABLE, "Second Conference on Industrial Carbon and Graphite", p. 235, 1966.
- [66] L.C.F. BLACKMAN "Modern Aspects of Graphite Technology" Academic Press, New York, 1970.
- [67] P.W. ATKINS, "Physical Chemistry", 2nd Edn, W.H. Freeman and Company, San Francisco, 1982.
- [68] C.J. GEANKOPLIS, "MASS Transport Phenomena", Holt, Rinehart and Winston, Inc., New York, 1972.
- [69] H. MASSMANN, Spectrochim. Acta 23B, 215 (1968).
- [70] C.L. CHAKRABARTI, H.A. HAMED, C.C. WAN, W.C. LI, P.C. BERTELS, D.C. GREGOIRE and S. LEE, Anal. Chem. 52, 167 (1980).
- [71] C.L. CHAKRABARTI, C.C. WAN, H.A. HAMED and P.C. BERTELS, Canadian Research 13, 31 (1980).
- [72] C.L. CHAKRABARTI, C.C. WAN, H.A. HAMED and P.C. BERTELS, Nature 288, 246 (1980).
- [73] C.L. CHAKRABARTI, C.C. WAN, H.A. HAMED and P.C. BERTELS, Anal. Chem. 53, 444 (1981).
- [74] C.L. CHAKRABARTI, C.C. WAN, S.B. CHANG, H.A. HAMED, and P.C. BERTELS, "Recent Advances in Analytical Spectroscopy", Ed. by

- K. FUWA, p. 103, Pergamon Press, New York, 1982.
- [75] M.S. CRESSER and C.E. MULLINS, Anal. Chim. Acta 68, 377 (1974).
- [76] K. MANTHEY, German Patent 2245610, 1974, The Perkin-Elmer Corporation.
- [77] W.H. SMITH and D.H. LEEDS, Modern Materials 7, 139 (1970).
- [78] A. MOORE, Chem. Phys. Carbon 11, 69 (1972).
- [79] B.T. KELLY, "Physics of Graphite", Applied Science Publishers, London, 1981.
- [80] J. PAPPIS and S.L. BLUM, J. Am. Ceramic Soc. 44, 592 (1961).
- [81] D. SCHIFF, Metals Engineering Quarterly 2, No. 4, 32 (1962).
- [82] Y.S. TOULOUKIAN, R.W. POWELL, C.Y. HO, and P.G. KLEMENS, "Thermophysical Properties of Matter - Vol. 2, Thermal Conductivity of Nonmetallic Solid", IFI/Plenum, New York, 1970.
- [83] S. MROZOWSKI, Phys. Rev. 85, 609 (1952).
- [84] K. AOKI and S. YAJIMA, J. Material Sci. 6, 1338 (1971).
- [85] B. HAYWORTH and D. WARRILOW, Electro-Optical System Design 10, No. 3, 42 (1978).
- [86] J.J. BROPHY, "Basic Electronics for Scientists", 3rd Edn, McGraw-Hill Book Co., New York, 1977, p. 211.
- [87] E. LUNDBERG and W. FRECH, Anal. Chem. 53, 1437 (1981).
- [88] W. SLAVIN, S.A. MYERS and D.C. MANNING, Anal. Chim. Acta 117, 267 (1980).
- [89] H.G.C. HUMAN, N.P. FERREIRA, C.J. RADEMEYER and P.K. FAURE, Spectrochim. Acta 37B, 593 (1982).
- [90] L.A. PELIEVA, E.V. PROS TETSOVA and V.G. BUKHANTSOVA, Zh. Prikl. Spectrosk. 36, 898 (1982).

- [91] L.A. PELIEVA, V.G. BUKHANTSOVA and O.A. DAVIDYUK, Zh. Prikl. Spectrosk. 38 533 (1983).
- [92] C.L. CHAKRABARTI and R. DICK, internal report, 1982, unpublished data.
- [93] C.L. CHAKRABARTI, S. WU, R. KARWOWSKA, J.T. ROGERS and R. DICK, submitted for publication.
- [94] H. FALK, A. GLYSMANN, L. BERGANN, G. MINKWITZ, M. SCHUBERT and J. SKOLE, Spectrochim. Acta, Part B, in press.
- [95] W.M.G.T. VAN DEN BROEK, L. DE. GALAN and J.P. MATOUSEK, Anal. Chim. Acta 100 121 (1978).
- [96] A.R. UBBELOHDE and F.A. LEWIS, "Graphite and Its Crystal Compounds", Oxford University Press, London, 1960.
- [97] Y.S. TOULOUKIAN and E.H. BUYCO, "Thermophysical Properties of Matter - Vol. 5, Specific Heat of Nonmetallic Solid", IFI/Plenum, New York, 1970.
- [98] Y.S. TOULOUKIAN, "Thermophysical Properties of High Temperature Solid Matter - Vol. 1, Elements", The Macmillan Co., New York, 1967.
- [99] Y.S. TOULOUKIAN, and D.P. DeWITT, "Thermophysical Properties of Matter - Vol. 8, Thermal Radiative Properties of Nonmetallic Solids", IFI/Plenum, New York, 1972.
- [100] Y.S. TOULOUKIAN and C.Y. HO, "Properties of Nonmetallic Fluid Elements", McGraw-Hill Book Co., New York, 1981.
- [101] J.C. BAILAR, H.J. EMELEUS, S.R. NYHOLM, and A.F. TROTMAN-DICKENSON, "Comprehensive Inorganic Chemistry - Vol. 1",

Pergamon Press, New York, 1973.

[102] C.L. CHAKRABARTI, S.B. CHANG, S.R. LAWSON and P.C. BERTELS,
Spectrochim. Acta 38B, 000 (1984).

[103] J.P. HOLMAN, "Heat Transfer", 5th Edn, McGraw-Hill Book Co.,
New York, 1981.

[104] C.L. SMITH, R.W. PIKE and P.W. MURRILL, "Formulation and
Optimization of Mathematical Models", International Textbook Co.,
Scranton, Pennsylvania, 1970.

[105] H.W. JACKSON, "Introduction to Electronic Circuits", 5th Edn,
Prentice-Hall Inc., New Jersey, 1981.

[106] C.L. CHAKRABARTI, S. WU, R. KARWOWSKA, J.T. ROGERS, L. HALEY,
P.C. BERTELS and R. DICK, Spectrochim. Acta 39B, 415 (1984).

[107] I. REIF, V.A. FASSEL and R.N. KNISELEY, Spectrochim. Acta
28B, 105 (1973).

[108] R.F. BROWNER and J.D. WINEFORDNER, Anal. Chem. 44, 247 (1972).

[109] B.V. L'VOV and N.A. ORLOV, Zh. Analit. Khim. 30 1653 (1975).

[110] D.D. SIEMER, E. LUNDBERG and W. FRECH, Appl. Spectrosc. 38, 389
(1984).

[111] H. FALK, Spectrochim. Acta 39B, 387 (1984).

[112] W. HEIMANN and U. MESTER, "Temperature Measurement, 1975-Inst.
Phys. Conf. Ser. No. 26", Ed. by B.F. BILLING and T.J. QUINN,
p. 219, The Institute of Physics, London, 1975.

[113] J.D. RAY, "Report on the Steel Industry/Research Workshop", p. 99,
The Holiday Inn, Burlington, Ontario, Canada, May 8-9, 1984.

[114] B.V. L'VOV, Spectrochim. Acta 17, 761 (1961).

[115] R. WOODRUFF and J. RAMELOW, Spectrochim. Acta 23B, 665 (1968).

- [116] J. SMEYERS-VERBEKE, Y. MICHOTTE and D.L. MASSART, *Anal. Chem.* 50, 10 (1978).
- [117] K. JOHANSSON, W. FRECH and A. CEDERGREN, *Anal. Chim. Acta* 94, 245 (1977).
- [118] B.V. L'VOV and L.A. PELIEVA, *Prog. Analyt. Atom. Spectrosc.* 3, 65 (1980).
- [119] W. FRECH and A. CEDERGREN, *Anal. Chim. Acta* 82, 83 (1976).
- [120] E.J. CZOBK and J.P. MATOUSEK, *Anal. Chem.* 50, 2 (1978).
- [121] D.J. HODGES, *Analyst* 102, 66 (1977).
- [122] E.L. HENN, *Anal. Chem.* 47, 428 (1975).
- [123] D.J. HYDES, *Anal. Chem.* 52, 959 (1980).
- [124] B.V. L'VOV, L.A. PELIEVA and A.I. SHARNOPOL'SKII, *Zh. Prikl. Spektrosk.* 27, 395 (1977).
- [125] C.L. CHAKRABARTI, C.C. WAN and W.C. LI, *Spectrochim. Acta* 35B, 93 (1980).
- [126] C.L. CHAKRABARTI, C.C. WAN and W.C. LI, *Spectrochim. Acta* 35B, 547 (1980).
- [127] C.L. CHAKRABARTI, S. WU and P.C. BERTELS, *Spectrochim. Acta* 38B, 1041 (1983).
- [128] W. SLAVIN and D.C. MANNING, *Anal. Chem.* 51, 261 (1979).
- [129] W. SLAVIN and D.C. MANNING, *Spectrochim. Acta* 35B, 701 (1980).
- [130] J.J. SOTERA, L.C. CRISTIANO, M.K. CONLEY and H.L. KAHN, *Anal. Chem.* 55, 204 (1983).
- [131] D.C. MANNING, W. SLAVIN and S. MYERS, *Anal. Chem.* 51, 2375 (1979).

- [132] E.J. CZOBIAK and J.P. MATOUSEK, *Spectrochim. Acta* 35B, 741 (1980).
- [133] S.K. GIRI, D. LITTLEJOHN and J.M. OTTAWAY, *Analyst* 107, 1095 (1982).
- [134] W. SLAVIN and D.C. MANNING, *Spectrochim. Acta* 37B, 955 (1982).
- [135] S.K. GIRI, C.K. SHIELD, D. LITTLEJOHN and J.M. OTTAWAY, *Analyst* 108, 244 (1983).
- [136] C.L. CHAKRABARTI, S. WU, R. KARWOWSKA, S.B. CHANG and P.C. BERTELS, *At. Spectrosc.* 5, 69 (1983).
- [137] D.D. SIEMER, *Anal. Chem.* 55, 692 (1983).
- [138] W. FRECH and S. JONSSON, *Spectrochim. Acta* 37B, 1021 (1982).
- [139] W. FRECH, A. CEDERGREN, E. LUNDBERG and D.D. SIEMER, *Spectrochim. Acta* 38B, 1435 (1983).
- [140] D.D. SIEMER, *Anal. Chem.* 55, 99 (1983).
- [141] S.R. LAWSON and R. WOODRIFF, *Spectrochim. Acta* 35B, 753 (1980).
- [142] D.D. SIEMER, *Anal. Chem.* 54, 1659 (1982).
- [143] J.A. HOLCOMBE and M.T. SHEEHAN, *Appl. Spectrosc.* 36, 631 (1982).
- [144] T.M. RETTBERG and J.A. HOLCOMBE, *Spectrochim. Acta* 39B, 249 (1984).
- [145] J.A. HOLCOMBE, *Anal. Chem.* 53, 324 (1981).
- [146] J.M. TRHOMA, *Chem. Phys., Carbon* 1, 121 (1965).
- [147] "Nomenclature, Symbols, Units and Their Usage in Spectrochemical Analysis", *Pure and Applied Chemistry* 45, 99 (1976).
- [148] F.A. COTTON and G. WILKINSON, "Advanced Inorganic Chemistry", 4th Edn, p. 359, John Wiley & Sons, New York, 1980.

- [149] C.L. CHAKRABARTI, S.B. CHANG, S.R. LAWSON and S.M. WONG,
Spectrochim. Acta 38B, 1287 (1983).
- [150] W. SLAVIN, G.R. CARRICK and D.C. MANNING, Anal. Chem. 56,
163 (1984).
- [151] R.H. EKLUND and J.A. HOLCOMBE, Anal. Chim. Acta 109, 97 (1979).

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