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STUDIES ON ELECTROTHERMAL ATOMIZATION IN
GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY

RALPH E. STURGEON, B.Sc. (Hons.)

A Thesis

Submitted to the School of Graduate Studies
in Partial Fulfilment of the Requirements

for the Degree
Doctor of Philosophy
Carleton University

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ABSTRACT

A study of the factors affecting the dynamics of growth and decay of absorbance signals generated in graphite electrothermal atomizers (tube-type) and an investigation into the fundamental parameters governing the mechanisms of atomic vapour formation in and its loss from these atomizers were made.

Transient atomic absorption signals generated during continuous heating of tube-type electrothermal atomizers can be characterized by at least two quantities; the peak absorbance corresponding to the peak of the pulse, and the integrated absorbance representing the pulse area. A comparison of analytical figures of merit is given for both methods of signal measurement using two commercial atomizers - a modified Varian Techtron Carbon Rod Atomizer model 63 (CRA-63) and a Perkin-Elmer Heated Graphite Atomizer model 2100 (HGA-2100). For the elements studied, Cd, Zn, Cu, Al, Sn, Mo and V, detection limits and precision are essentially the same for both methods of measurement in each atomizer. With the CRA-63, sensitivity by the integration method of measurement is approximately the same as, or less than, that obtained by the peak height method. With the HGA-2100, 2- to 8-fold increases in sensitivity are obtained with the integration method of measurement. With both atomizers, greater linear dynamic range in calibration curves was obtained with the integration method of measurement.

Peak absorbance is inversely proportional to the cross-sectional area, S , of the graphite tube, whereas integrated absorbance is

proportional to l^2/S , where l is the effective length of the tube. With these commercial atomizers, in addition to being dependent on the geometry of the graphite tube, the peak and the integrated absorbance are highly dependent on the rate of heating of the tube, the physicochemical properties of the graphite surface and the temporal and spatial non-isothermality within the tube.

The excitation temperature of the atomic vapour was measured as a function of time using a two-line atomic absorption method. Vapour temperature varies with the thermometric species and the rate of heating of the furnace. The time dependence of the temperature is primarily determined by the time-dependent thermal gradient along the axial length of the tube. The excitation temperature of the vapour is equal to the temperature at the centre of the furnace only for 200 - 300 ms immediately following the appearance time of the signal. Thereafter, the difference between the two temperatures is approximately a linear function of time.

The mechanisms of loss of atomic vapour from the HGA-2100 furnace were determined from the rate of decay of Mo and V absorbance signals under isothermal conditions. The major mechanisms of loss are condensation of the vapour on the cooler extremities of the furnace, chemical losses through the formation of involatile and/or undissociated species, and expulsion and/or diffusion of vapour through the sample introduction port.

The mechanism of atom formation in the HGA-2100 was studied using a combined thermodynamic and kinetic approach. With the assumptions that analyte condensed-gas phase quasi-equilibrium exists within the furnace, and that the production of atoms is characterized by a unimolecular

rate constant, a plot of the logarithm of the absorbance as a function of the inverse of the absolute temperature yields a straight line from which the activation energy, E_a , of the last steps in the sequence of reactions leading to atomic vapour can be obtained. Three major atomization mechanisms are operative: thermal dissociation of the metal oxide; reduction of the oxide by carbon followed by vaporization of the metal; thermal dissociation of the metal halide.

Atomization above atmospheric pressure was achieved using a specially constructed furnace and pressurizable housing capable of operation at $1.3 \times 10^6 \text{ N}\cdot\text{m}^{-2}$ (13 atm) of Ar. High pressure broadens the absorption line profile and decreases the absorption coefficient of the atomic vapour in the furnace, leading to decreased peak height and integrated sensitivity, increased linear dynamic range of calibration curves, and freedom from variation in discharge conditions of the emission-line source.

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LIST OF PUBLICATIONS ARISING FROM THIS RESEARCH

1. Atomization in Graphite Furnace Atomic Absorption Spectrometry -- Peak Height Method vs. Integration Method of Measuring Absorbance: Carbon Rod Atomizer 63; R.E. Sturgeon, C.L. Chakrabarti, I.S. Maines and P.C. Bertels, Anal. Chem., 47, 1240 (1975).
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5. The Temperature of the Atomic Vapour in Graphite Furnace Atomic Absorption Spectrometry; R.E. Sturgeon and C.L. Chakrabarti, Spectrochim. Acta, 32B, 0000 (1977).
6. Atomization Above Atmospheric Pressure in Graphite Furnace Atomic Absorption Spectrometry; R.E. Sturgeon, C.L. Chakrabarti and P.C. Bertels, Spectrochim. Acta, 32B, 0000 (1977).

7. The Mechanism of Atomic Vapour Loss in Graphite Furnace Atomic Absorption Spectrometry; R.E. Sturgeon and C.L. Chakrabarti, Anal. Chem., 49, 0000 (1977).

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INTRODUCTION

Although a flame is the most widely used medium for atomizing samples in atomic absorption spectrometry (AAS), the demand for better sensitivity and detection limits, the necessity for more economical use of the sample and the fundamental disadvantages of flame techniques has led to the development of a variety of electrothermal atomizers as an alternative atomization medium. These atomizers have utilized heated graphite tubes, carbon rods and filaments, sampling boats and cups, loops, rods and metal filaments. Comprehensive reviews of these atomizers have been published by Kirkbright (1), Syty (2) and Woodruff (3) and recent developments have been reviewed by Hieftje et al. (4).

Electrothermal atomizers are more difficult to build, cost more to purchase and are physically more bulky than a typical nebulizer-burner (flame), as they require a large supply of power and fairly elaborate equipment to control the power supplied and record the analytical signal. However, the most commonly employed electrothermal atomizers (graphite tubes and rods) offer tremendous analytical advantages and further development potential over atomization by the flame technique, as shown below.

1. Electrothermal atomizers require only a few microlitres of sample per injection.
2. Viscous liquids that are difficult to nebulize in the flame can be conveniently handled by electrothermal techniques of atomization.

3. Analysis of samples in the vacuum ultraviolet is possible with electrothermal atomization (using a system purged free of air), whereas such a measurement with a flame is prevented by the intense absorption by oxygen.

4. Electrothermal atomizers produce a low background signal, resulting in superior signal-to-noise ratios (i.e., better detection limits) over those given by the flame technique.

5. The chemical and thermal environment of the atomic vapour can be much better controlled when electrothermal atomizers are employed.

6. The efficiencies of vaporization and atomization in electrothermal atomizers are usually superior to those in the flame, especially in the cases of elements which tend to form thermally stable oxides. This is a consequence of the smaller volume of the electrothermal atomizer, the absence of dilution of the analyte by expanding flame gases, the highly reducing environment inside an incandescent graphite tube and the more complete vaporization and dissociation.

7. Enhancements in sensitivity of the order of $10^4 - 10^5$ over the flame technique are attainable with electrothermal atomizers as a result of the above characteristics and the increased lifetime of the atomic vapour within the analytical volume.

8. The capability of direct solid sampling exists when electrothermal atomizers are used.

9. The speed of analysis by flame and electrothermal techniques is similar.

The possibility of determining a large number of elements (≈ 70) with high sensitivity, selectivity, accuracy and speed, coupled with the simplicity and relatively low cost of apparatus, makes AAS with electrothermal atomization potentially ideal for trace and ultratrace analysis. Correspondingly, the technique has been shown to be of considerable value for the detection and analysis of trace amounts of metals in a variety of matrices (2 - 4).

RESEARCH AIMS

In most cases, emphasis in research concerning atomic absorption measurements with electrothermal atomizers has been placed on the construction of these devices and their empirical application to practical analytical problems. Only a relatively few authors have paid attention to a systematic investigation into the more fundamental aspects of electrothermal atomization. This is in striking contrast with the large amount of theoretical material which has been published dealing with the flame technique. The primary reason for the difficulty in explaining the behaviour of atomic populations produced by electrothermal atomizers lies in the transient nature of the atomic vapour cloud. The distribution of free atoms and their lifetime depend not on the equilibrium temperature of the atomizer but on the rate of atomization of analyte compounds or their decomposition products on the graphite surface. An understanding of the processes of vaporization and atomization is important since it will ultimately enable prediction of optimum conditions for analysis based on theoretical principles (as opposed to empirical determinations), and provide information about the

mechanism of interference from concomitants in the analyte matrix. The nature of the signal profile is also important because proper recording of the atomic absorption and therefore, correct design of equipment, is a prerequisite to obtaining accurate and precise analytical data. To this end, a fundamental study of the time-dependent processes which occur during analyte atomization within tube-type graphite electrothermal atomizers was undertaken. During the time this thesis research was in progress, the following papers were published: characterization of the signals and various methods of their measurement (5), the influence of the response time of the amplifier • recorder system on the signals (5 - 8), the influence of the rate of heating of the atomizer on the analytical sensitivity (8, 10), the effects of atomizer geometry and construction material on the signals (11 - 14), the mechanism of atom formation (10, 12, 15 - 17), the temperature of the atomic vapour within the atomizer (18), and the interferences due to compound formation and the composition of the matrix (19 - 24). By far the most important work to date is that by L'vov (11) who has explained the phenomenon of production of atomic vapour and the concept of the temporal signal profile.

ORGANIZATION OF THE THESIS

The thesis has been divided into two sections. The first section is a general study of the dynamics of growth and decay of the analytical signal within tube-type graphite atomizers with a view to assessing the relative merits of both the peak and integration

methods of signal measurement. The second section consists of an investigation into the fundamental parameters governing the mechanisms of formation of atoms in and their loss from a heated graphite atomizer. The greater part of the research was conducted with two commercially available electrothermal atomizers, viz., the Varian Techtron Carbon Rod Atomizer model 63 (CRA-63) and the Perkin-Elmer Heated Graphite Atomizer model 2100 (HGA-2100). Chapters 1 and 2 deal with the characterization of the atomizers and the transient signals generated within them, as well as discuss the peak and integration methods used for measuring these signals. The measurement of the time-dependent excitation temperature of the atomic vapour produced within both atomizers is discussed in Chapter 3. Chapters 4 and 5 deal with the mechanisms of formation of atoms in and their loss from the HGA-2100. Chapter 6 discusses the theoretical and practical aspects of analyte atomization under high pressures (1 - 11 atm) of inert gas. Each chapter consists of a short introduction describing the purpose of the chapter and its relationship with the preceding chapters, a description of the experimental procedures and a discussion of the results. The nomenclature and terminology used throughout this thesis follow the recommendations of IUPAC as given in Pure Appl. Chem., 30, 653 (1972).

Chapter 1

CHARACTERIZATION OF TRANSIENT SIGNALS AND THEIR MEASUREMENT

Analytical signals obtained with electrothermal atomizers are, in general, curves having peaks (2), their exact shape for a given element being determined by the physical and chemical properties of the matrix, by the properties of the sample cell (geometry, construction material), by the heating rate of the atomizer and by the distortion of the signal caused by the finite response time of the amplifier-recorder system used. The selection of an optimum method of atomization in atomic absorption spectrometry is therefore a complicated problem which still remains largely unresolved, the main reason for this being the purely empirical approach to its solution taken by the majority of the investigators in this field.

The most widely used method of measuring signals given by electrothermal atomizers is the measurement of the maximum or peak absorbance attained (11). An alternative method is to measure the integrated absorbance, obtained by summing the absorbance values over the time period during which free atoms reside within the analytical volume (defined by the beam of radiation from the emission source).

Theory of Signal Shape

To assess the relative merits of the peak and integration methods of measurement of signals from a theoretical viewpoint and to consider the influence of various physicochemical factors on the analytical characteristics of the signals, L'vov (5, 25) and L'vov et al. (26, 27) devised a mathematical model to describe the time-dependent characteristics of the atom population within an isothermal cuvette. For the sake of simplicity, only the processes of the transfer of sample vapour through the analytical volume were considered; all intermediate stages in the transformation of the sample before it entered the analytical volume (i.e., the mechanism of atom formation) were not taken into account. The following assumptions were made in constructing the mathematical model: the element to be determined is completely atomized; all of the atoms of the element enter the analytical volume; the removal of atomic vapour from the analytical volume is determined solely by diffusion under a concentration gradient. The following variables are introduced: N_0 is the number of atoms of the element to be determined in the sample; N is the total number of atoms of the element within the analytical volume at the moment of time t ; τ_1 is the atomization time -- the time duration of transfer of atoms into the analytical volume; τ_2 is the residence time of atoms within the cuvette -- the mean length of time spent by an atom within the analytical volume, and τ_3 is the length of time during which the signal is recorded

$$(\tau_3 = \tau_1' + 5\tau_2').$$

The change in the number of atoms within the analytical volume — at any instant of time t is determined by the difference between the number of atoms entering the analytical volume, $n_1(t)$, and the number of atoms escaping from it $n_2(t)$, in unit time:

$$dN/dt = n_1(t) - n_2(t) \quad (1-1)$$

With a diffusional mechanism of vapour loss, the function $n_2(t)$ may be approximated by:

$$n_2(t) = N/\tau_2' \quad (1-2)$$

Introduction of sample into the analytical volume takes place via a process of accelerated vaporization of the sample due to the continuously rising temperature of the evaporation surface. Hence, $n_1(t)$ may be approximated by:

$$n_1(t) = At \quad (1-3)$$

From the condition of normalization, A may be determined:

$$\int_0^{\tau_1'} n_1(t) dt = N_0 \quad (1-4)$$

Hence,

$$n_1(t) = (2N_0/\tau_1'^2)t \quad (1-5)$$

and equation 1-1 becomes:

$$dN/dt = (2N_0/\tau_1'^2)t - N/\tau_2' \quad (1-6)$$

. This is a general linear first-order differential equation which may be solved with the aid of an integrating factor ($\exp(t/\tau_2')$) to yield the following integral:

$$N_{t \leq \tau_1'} e^{t/\tau_2'} = (2N_0/\tau_1'^2) \int t e^{t/\tau_2'} dt + C \quad (1-7)$$

Integrating, and evaluating C from the boundary condition $N = 0$ at $t = 0$ yields:

$$N_{t \leq \tau_1'} = 2N_0 \frac{\tau_2'^2}{\tau_1'^2} \left[\frac{t}{\tau_2'} - 1 + e^{-t/\tau_2'} \right] \quad (1-8)$$

When the sample has been completely atomized ($t = \tau_1'$), N_t attains a maximum:

$$N_{t=\tau_1'} = 2N_0 \frac{\tau_2'^2}{\tau_1'^2} \left[\frac{\tau_1'}{\tau_2'} - 1 + e^{-\tau_1'/\tau_2'} \right] \quad (1-9)$$

At $t \geq \tau_1'$, equation 1-1 must be modified to account for the fact that the sample introduction step has been completed and only diffusional loss follows, i.e.,

$$dN/dt = -N/\tau_2' \quad (1-10)$$

$$\int_{N_{\tau_1'}}^{N_t} \frac{dN}{N} = \int_{\tau_1'}^t -\frac{dt}{\tau_2'} \quad (1-11)$$

$$N_{t \geq \tau_1'} = N_{\tau_1'} e^{-(\tau_1' - t)/\tau_2'} \quad (1-12)$$

Substitution of the value of $N_{\tau_1'}$ given by equation 1-9 results in equation 1-13.

$$N_{t \geq \tau_1'} = 2N_0 \frac{\tau_2'^2}{\tau_1'^2} \left[\frac{\tau_1'}{\tau_2'} - 1 + e^{-\tau_1'/\tau_2'} \right] e^{(\tau_1' - t)/\tau_2'} \quad (1-13)$$

Equations 1-8 and 1-13 describe the kinetics of change in the number of atoms in the analytical volume as a function of time. A graphical representation of this is shown in Figure 1 where the pulse shapes for various τ_1'/τ_2' ratios have been plotted (according to equations 1-8 and 1-13).

Methods of Recording Atomic Absorption

The pulses shown in Figure 1 may be conveniently characterized by two quantities; the peak value, N_p , corresponding to the peak of the pulse, and the area under the pulse, Q_N . A simplified expression describing the peak of the pulse may be obtained from equation 1-9 if it is assumed that $\tau_1'/\tau_2' \ll 1$. Under such conditions, a series expansion of the exponential term gives, to a first approximation:

$$N_{t=\tau_1'} = N_p = N_0 \quad (1-14)$$

The pulse area, Q_N , is obtained by measuring the integral value of the atom population during the entire period for which atoms are produced and remain in the analytical volume, i.e.,

$$Q_N = \int_0^{\tau_3} N(t) dt \quad (1-15)$$

Substituting equations 1-8 and 1-13 into 1-15 and integrating yields

TIME (in τ_2 units)

Figure 1: Variation in the number of atoms in an analytical volume for different τ_1'/τ_2' ratios. 1. $\tau_1'/\tau_2' = 0.2$ 2. $\tau_1'/\tau_2' = 1.0$ 3. $\tau_1'/\tau_2' = 5.0$

(for large τ_3):

$$Q_N = N_0 \tau'_2 \quad (1-16)$$

The measured peak and integrated absorbances are directly related to the expressions for N_p and Q_N , i.e.,

$$A_{t=\tau'_1} = A_p = k_A N_0 = A_0 \quad (1-17)$$

$$\int_0^{\tau_3} A_t dt = k_A N_0 \tau'_2 = A_0 \tau'_2 \quad (1-18)$$

where, for simplicity, k_A is a proportionality constant relating the measured absorbance to atomic population and A_0 is the absorbance which would result if all of the analyte atoms were confined within the analytical volume at a single instant of time.

If a sample is completely atomized in a time $t \ll \tau'_2$, the peak absorbance must correspond to the total number of atoms in the sample. Provided $\tau'_1/\tau'_2 \ll 1$, small variations in the value of τ'_1 and/or τ'_2 , which may take place during measurements, have only a minor effect on the relationship expressed by equation 1-17. If, however, $\tau'_1 > \tau'_2$, the peak absorbance depends on both τ'_1 and τ'_2 , such that a simple relationship between A_p and N_0 is possible only if $\tau'_1/\tau'_2 = \text{constant}$.

The integrated absorbance is neither dependent on the rate, $n_1(t)$, nor on the time, τ'_1 , of entry of sample vapour into the analytical volume. This is extremely significant, since, first, the measurement of $\int A_t dt$ permits one to prevent varying sample composition from affecting the analytical results, and, second, the absolute amount of sample atomized may be increased, which will result in an increase

in the relative sensitivity of a determination. The amount of sample that can be used for analysis is limited only by the rate of atomization, the limiting condition being the accumulation of atoms within the analytical volume above some critical value at which their concentration becomes so large that the assumption of a purely diffusive mechanism of vapour loss from the absorption cell is no longer valid. With the peak method, absorbance measurements are restricted by the relatively narrow range of proportionality between the amount of analyte atomized and the measured A_p , this range usually being no larger than 0.5 absorbance. With the integration method of measurement the rate of atomization can be adjusted in such a way that the A_t values do not exceed the absorbance at which the linear relationship between vapour density and absorbance no longer exists. In this manner, larger absolute masses of sample may be atomized, thus increasing both the relative sensitivity of a determination and the linear dynamic range of the calibration curves. The only conditions to be fulfilled with the integration method of measurement are that the magnitude of τ'_2 remains constant and that complete atomization of the sample occurs.

By considering the distortion of pulse shape introduced by the time constant of the recording circuit, Katskov and L'vov (27) have determined the conditions for the attainment of optimum detection limits and precision by both methods of measurement. With the peak method, instantaneous atomization of the sample ($\tau'_1 \ll \tau'_2$) gives the highest signal-to-noise (S/N) ratio when the time constant of the recording circuit, $\tau_{RC} = \tau'_2$. As τ'_1/τ'_2 increases, maximum S/N occurs

at $\tau_{RC} > \tau'_2$. With the integration method of measurement maximum S/N occurs when $\tau_{RC} = 0$. Whereas the peak height sensitivity is a decreasing function of τ_{RC} , the integrated signal sensitivity is independent of τ_{RC} . A comparison of the S/N ratios for both methods of measurement indicates that, in principle, identical limits of detection can be attained by both methods, provided that the signals are recorded under optimum conditions.

Signal integration requires both simpler equipment and a simpler measurement procedure. The avoidance of peak height measurement allows for less demanding power requirements and consequent lower operating temperatures of the atomizer. As a result, the possibility of measuring the absorption given by low-volatility metals arises, such as tungsten, whose peak height sensitivity is extremely poor. In addition, the measurement method is much easier, since simple capacitor-type accumulator circuits can be employed.

Because of the severe limitations imposed on the recording system for the accurate measurement of peak height, the possibilities offered by the integration method have been explored by several groups of workers (26 - 33). L'vov et al. (26) atomized 2.5×10^{-13} kg Tl in a graphite cuvette at various levels of additional electrode heating and without additional heating. Their data (26), reproduced in Table 1, show that the integrated absorbance remains practically constant despite the considerable difference in atomization rates which are reflected, indirectly, in the magnitude of the peak absorbance. Thus, the integration method of measurement is not influenced by the kinetics of sample entry into the analytical volume. L'vov and Plyushch (28)

Table 1

Integrated Absorbance by 2.5×10^{-13} kg Tl for
Various Rates of Sample Atomization^a

A_p/A	$\int A_t dt / A \times s$
0.72	1.7
0.66	1.7
0.51	1.8
0.32	2.0
0.24	1.7
0.16	1.7
0.13	1.9
0.09	1.7

^aReproduced from reference 26; cuvette: length 40 mm,
diameter 2.5 mm, $T = 1670$ K, $p = 405$ kPa (4 atm) Ar,
 $\lambda = 276.8$ nm.

employed a technique of sample evaporation from a tungsten wire heated with an air-acetylene flame and found that the integration method was applicable only to solutions of highly volatile elements and not to solid samples. Borzov et al. (29) used the integration method to measure, in a flame, the signals resulting from the atomization of both solutions and solid samples in a graphite atomizer which was independently heated by an alternating current. The results obtained by these authors (29) for the determination of Cu in various powdered materials are presented in Table 2. The Cu content was calculated using a calibration curve prepared from an aqueous solution of pure copper. The excellent agreement between the certified and measured contents is experimental confirmation of the advantage of the integration method of measurement because the analytical results were independent of the sample composition. In the above cases, a graphical method of integration (cutting and weighing the recorder chart tracings) was employed. An attempt to use an integrating circuit for atomic absorption measurements with an arc atomizer was made by Belyaev et al. (30). These authors employed accumulation of the signal expressed in terms of an intensity difference, not of absorbance values; because of this their method of measurement was less satisfactory. Pickford and Rossi (31) reported the results of signal integration using a background correction system (with a non-resonance line) and a graphite tube atomizer and commented on the improved precision obtained. These authors (31) also drew attention to the fact that, over a limited range, changes in the rate of atomization had a relatively minor effect on the integrated absorbance as compared to the peak absorbance.

Table 2

Determination of Copper in Solid Materials^a

Sample	Copper, %	
	Certified	Found
MgO	0.003	0.0027
Fe ₂ O ₃	0.003	0.0028
Cr ₂ O ₃	0.003	0.0027
Al ₂ O ₃	0.003	0.0028
ZnO	0.003	0.0027
Al-Mg ferrite	0.003	0.0034
Ni-Zn ferrite	0.003	0.0030
BaCO ₃	0.003	0.0029
BaCO ₃	0.01	0.0088

^aReproduced from reference 29.

Minor increases in precision with the integration method of measurement were also reported by McIntyre et al. (32). Schramel (33) reported increases in the linear dynamic range of calibration curves of integrated signals over those for peak signals.

Despite the theoretical advantages offered by the integration method of measurement, the few applications reported in the literature are those mentioned above. Unfortunately, apart from the data reported by L'vov and co-workers, the results of signal integration reported by others are in arbitrary units only and are not useful for quantitative comparisons. In those studies where the integration method of measurement of signals produced by a graphite tube atomizer have been recorded in absorbance $\times$ seconds (11, 26, 27), such measurements were carried out using an isothermal graphite cuvette (11, 34, 35) employing separate arc-heating to vaporize and atomize the sample. Because of the widespread use and general availability of commercial tube-type graphite atomizers, it is instructive to determine the influence of fundamental parameters such as the rate of heating of the atomizer (i.e., kinetics of sample introduction into the analytical volume), its geometry, the time constant of the recording system and the physical and chemical properties of the analyte element on the analytical characteristics of the signals generated by such atomizers. Additionally, it is important to compare the practical advantages and disadvantages of the peak and integration methods of recording such signals.

EXPERIMENTAL

Apparatus. A Varian Techtron single-beam atomic absorption spectrometer, model AA-5 (Varian Techtron Pty. Ltd., Melbourne, Australia) with a 0.5 m Ebert mount monochromator (50 x 50 mm grating ruled with 638 lines mm^{-1}) was used. In place of the burner the spectrometer was fitted with either one of two electrothermal atomizers, a Varian Techtron Carbon Rod Atomizer model 63 (CRA-63) or a Perkin-Elmer Heated Graphite Atomizer, model 2100 (HGA-2100, The Perkin-Elmer Corporation, Norwalk, Conn., U.S.A.). The baseplate of the HGA-2100 was modified so that it could be fitted to the optical rail of the spectrometer. The CRA-63 working head and adjustable mount are shown in Figure 2; the HGA-2100 furnace is shown in Figure 3. Both atomizers employ a three-stage resistive heating program: a low current/voltage to dry the sample, an intermediate current/voltage to char and ash the sample, and a high current/voltage to heat the atomizer to incandescence and to atomize the sample. The CRA-63 power supply utilizes a feedback loop to maintain a constant, preselected voltage in each of the stages, whereas the HGA-2100 power supply uses a constant current feedback control to provide automatic compensation for small variations in line voltage and contact resistances. Modifications made to the CRA-63 power supply to obtain a faster rate of heating and a higher final temperature (ca. 3800 K) have been described elsewhere (36). The HGA-2100 power supply was used as supplied, except for minor changes made in the purge gas control. Whereas the sheath gas for the CRA-63 exits in

Figure 2: CRA-63 with mount for optical rail.

Figure 3: HGA-2100 with mount for optical rail.

a laminar flow from a baffle screen below the tube and streams upward, the sheath gas for the HGA-2100 consists of two separate gas flows. One such flow, maintained continuously throughout all three heating stages, prevents oxidation of the graphite tube and circulates in the concentric space between the graphite tube and the end cones. A second, independent flow, illustrated in Figure 4, enters from both ends of the graphite tube and exits through the sample introduction port. When the furnace is operated in the internal interrupt mode, this internal purge gas flow is automatically stopped during the atomization stage. The solenoid valve used for this purpose resumes the gas flow after a period of 12 seconds. As it is often necessary to operate the atomization stage for periods greater than this, the internal purge gas flow was manually regulated with a three-way stopcock.

Single element hollow cathode lamp sources (Perkin-Elmer and Varian Techtron), operated at the recommended current, were used. Source radiation was collimated and focussed with 5 cm diameter, 10 cm focal length quartz plano-convex lenses. Signals were detected with a Hamamatsu R446-NR photomultiplier tube (Hamamatsu Corp., Middlesex, New Jersey, U.S.A.) which was enclosed within a magnetically and electrostatically shielded housing to reduce interferences. To further reduce spurious noise and minimize 60 Hz pickup, a model 164 preamplifier (Ithaco Inc., Ithaca, New York, U.S.A.) was installed directly on the output of the photomultiplier tube. The preamplifier provided a maximum gain of 100.

Measurements of surface temperature were made with a series

Purge Gas Flow

Cooling Water Flow

Figure 4: Cross-section of the HGA-2100.

1100 automatic optical pyrometer (Ircon Inc., Niles, Illinois, U.S.A.).

For measuring integrated absorbance, an electronic integrator consisting of a timing circuit, a lock-in amplifier and an integrating digital voltmeter (DVM, which functions as a direct absorbance $\times$ second readout) was assembled to replace the Varian Techtron amplifier.

(Circuit diagrams for the amplifier-integrator unit are available upon request). A simplified schematic of the amplifier-integrator assembly is shown in Figure 5. Continuous 5-digit display of either percentage transmittance or absorbance was possible using the DVM. In addition, analog display of either of these was also possible using a voltmeter incorporated into the amplifier module of the spectrometer. The operation of the unit is as follows. The signal from the photomultiplier tube is passed through the preamplifier into a lock-in amplifier, the reference signal to which is the same 285 Hz trigger voltage used to modulate the hollow cathode lamp emission source. The amplified signal is then passed through a logarithmic converter and into a Dymec model 2401 C integrating digital voltmeter (Hewlett-Packard Co. Ltd., Los Angeles, Calif., U.S.A.) where the absorbance signals are summed over a preset time interval. Digital display of the integrated output on the DVM occurs simultaneously with the peak absorbance recording on a fast-response (0.25 s full scale) Electronik 194 strip-chart recorder (Honeywell Ltd., Scarborough, Ontario, Canada). The absorbance-time trace of the pulse is also recorded on a model 549 storage type oscilloscope (Tektronix Inc., Portland, Oregon, U.S.A.) fitted with a Type 1A7A high-gain differential amplifier plug-in. The trace can be subsequently photographed with a "Polaroid" camera (Tektronix Inc.).

Figure 5: Amplifier - integrator assembly.

Reagents. All chemicals used were of Fisher CERTIFIED grade or of the highest purity commercially available. Stock solutions of metal standards were prepared as follows for each metal and contained $1 \times 10^{-3} \text{ kg/dm}^3$ of that metal only; solutions of Cu, Sn, Al, Zn, Ni, Mn, Fe, Cr and Co were prepared from the metals, Cd, Pb, Ca and Mg from their carbonates and Mo and V from the trioxide and pentoxide, respectively. The above metals or their compounds were dissolved in pure acids or bases where required and diluted with ultrapure water obtained direct from a Milli-Q water system (Millipore Corp., Mississauga, Ontario, Canada). All test solutions were prepared immediately prior to their use by dilution with ultrapure water.

Gases. High purity (99.95%) argon, helium and nitrogen gases were used to sheath the atomizers. Hydrogen gas (99.995% purity) was used for some selected studies with the CRA-63. Prior to flowing past the atomizers, each gas passed through a model 6183 T gas filter (Matheson Co., Whitby, Ontario, Canada) to remove all particulates of diameter larger than $0.3 \mu\text{m}$ (99.999% efficiency).

Procedure. Test solutions of $5 \times 10^{-6} \text{ dm}^3$ volume were injected into the atomizers with an Eppendorf syringe (Brinkmann Instruments Inc., Westbury, New York, U.S.A.) fitted with disposable plastic tips. Sheath gas for the CRA-63 was maintained at $7.5 \times 10^{-2} \text{ dm}^3 \cdot \text{s}^{-1}$ (4.5 l min^{-1}), while a flow rate of $1.3 \times 10^{-3} \text{ dm}^3 \cdot \text{s}^{-1}$ (0.08 l min^{-1}) was used for the internal purge and a rate of $1.7 \times 10^{-2} \text{ dm}^3 \cdot \text{s}^{-1}$ (1.0 l min^{-1}) for the external sheath gas on the HGA-2100. The

influence of a hydrogen diffusion flame on the sensitivity of a number of elements atomized with the CRA-63 was studied. For reasons detailed in a later chapter, no attempt was made to suppress any ionization of any of the elements used.

A nominal spectral bandpass of 0.08 nm was used for all elements except Ca, Co and Sn for which 0.16 nm was used. The following resonance lines (nm) were used: Al 309.3, Ca 422.7, Cd 228.8, Co 240.7, Cu 324.7, Cr 357.8, Fe 248.3, Mg 285.2, Mn 279.5, Mo 313.2, Ni 232.0, Pb 283.3, Sn 224.6, V 318.4 and Zn 213.9. The quartz plano-convex lenses were focussed for maximum throughput of the radiation from the emission source at the wavelengths used. A parallel beam of radiation was obtained which illuminated completely the interior of each furnace. Whereas a 0.2 cm diameter aperture stop was placed immediately following the CRA-63, both to define the radiation beam emerging from the graphite tube and to reduce the intensity of emission from the incandescent tube entering the monochromator, the enclosed design of the HGA-2100 is such that the graphite tube housing serves as its own aperture stop (cf. Figure 3).

The sequence of operations for the integration control unit of the amplifier-integrator assembly (Figure 5) is described below. The initiation and duration of the integration period is controlled by an automatic timing circuit activated by a trigger pulse from the power supply unit of either atomizer. The trigger signal is synchronous with the start of the atomization stage. The absorbance pulse from the analyte is displayed on the storage oscilloscope and the magnitude of the appearance time, i.e., the time elapsed from the start of the atomization stage to the point at which the absorbance

signal is first perceived to depart from the baseline noise, is manually introduced into the delay cycle of the timing circuit of the integration control unit. The time duration of the absorbance pulse is then measured and entered into the integration cycle of the timing circuit. Both of the above times can be accurately and reproducibly set to within ± 0.5 ms and are selected such that integration over spurious baseline noise is minimized. In this study, the integration time period was extended to cover an additional 20 - 30 ms preceding and following the absorbance pulse. Such a precaution was taken to ensure that integration over the total width of the pulse was carried out. Except where stated otherwise, all peak and integrated absorbance measurements were made with an amplifier time constant of 18 ms.

RESULTS AND DISCUSSION

Because of the diversity of the areas included in this thesis, it is most convenient to present the results and discussion in a number of subsections, commencing with a characterization of the instrumentation. Presentation of data dealing with the influence of various parameters on the shapes of signals, analytical figures of merit, etc., has been divided into two sections; those data pertaining to signals obtained with the CRA-63 and those obtained with the HGA-2100. These data have been compared and contrasted in an attempt to correlate the signal characteristics of each atomizer with its respective physical characteristics.

Power Characteristics of the Atomizers

As indicated earlier, the HGA-2100 and CRA-63 are resistively heated devices which utilize a three-stage constant current and a constant voltage program, respectively, for heating the atomizing element. By maintaining the resistance (at room temperature) of the atomizer at a preselected, reproducible value (22 m Ω for the HGA-2100, 65 m Ω for the CRA-63), power-controlled heating may be achieved. Since the temperature-time characteristics of the atomizer are largely determined by the power consumption (37, 38), the power characteristics of both atomizers were determined. The voltage drop across the workhead terminals was measured with a rectifier-type ac meter, model Avo. 8 (Avometer Inc., Plainview, New York, U.S.A.); the current passing through the power cables was measured with an Amprobe RS-34 clip-on ammeter (Amprobe Inc., Lynbrook, New York, U.S.A.), and the atomizer resistance was measured across the workhead terminals of each device with a model 4328 A milliohmeter (Hewlett-Packard Co. Ltd.).

Figures 6 and 7 show the effect of variation of the power supply settings on the output power for the atomization stage of the CRA-63 (operated in the step mode) and the HGA-2100, respectively. The CRA-63 settings are arbitrary dial points and correspond to successively higher, non-linear increases in the voltage applied to the workhead. The HGA-2100 settings correspond to the manufacturer's pre-calibrated temperatures indicated on the front panel of the power supply. The modified power supply of the CRA-63 provides higher operating voltages

Figure 6: Power output of the CRA-63 as a function of power supply setting.

Figure 7: Power output of the HGA-2100 as a function of power supply setting.

(maximum 11.6 V) and power than the HGA-2100 power supply (maximum 6.8 V).

Temperature-Time Characteristics of the Atomizers

The temperature of the atomizer is a complicated function of time and various other factors, such as the input power, the mass of the atomizer, and its heat losses by convection, conduction and radiation (37, 38). The temperature-time characteristics of the surfaces of both atomizers were obtained by monitoring with the automatic optical pyrometer the intensity of blackbody radiation emitted from their interior surfaces through their sample introduction ports.

In all temperature measurements the parameter of importance is the thermal time constant of the measuring device. With electrothermal atomizers the temperature continuously changes with time and it is necessary to measure these temperature changes instantaneously. For very fine thermocouples, the response time ranges from ms to s. Even when it may be assumed that the thermocouple is in perfect thermal contact with the heating device, a temperature jump in the system results in the temperature of the thermocouple approaching a steady-state value after several (≈ 4.6) time constants. This type of device can produce a large error in the measured temperature-time characteristics of the atomizer. In addition, thermocouples are generally limited in their upper temperature range (< 2200 K). The above problems are particularly severe when temperature-time measurements are made of electrothermal atomizers for which large temperature jumps occur.

in short time intervals. The automatic optical pyrometer employed for these studies has a time constant of 1 ms, and therefore does not suffer from these drawbacks.

Figures 8 and 9 present temperature-time curves at various power consumptions for the CRA-63 and HGA-2100, respectively.

The voltage-temperature calibration provided by the manufacturer of the optical pyrometer was experimentally confirmed by measuring the temperature of the HGA-2100 furnace with thermocouples and by checking the temperature calibration with the melting points of a number of pure elements placed within the furnace. In this manner it was determined that the pyrometer output, and hence the surface temperature-time curves reported here, are accurate to within $30 - 40^{\circ}$ at 2500 K (i.e., $\pm 2\%$ error). From a number of such surface temperature curves, obtained throughout a three-year interval, it was established that the reproducibility of the data was ± 15 K at all temperatures. This figure represents the sum of the uncertainties due to variations in the optical focussing of the pyrometer on the tube surface, the reproducible setting of the furnace resistance and the temperature (atomization) program, and the contribution to the variation of temperature caused by the variability in the flow rate and temperature of the cooling water. This latter factor has been reported by others (38, 39) to cause an increase in the atomizer temperature with increasing rate of water flow, probably because of a negative temperature coefficient of the contact resistances present in the furnace power circuit. In addition, there is a possible contribution due to small variations in the emissivity of the graphite with different tubes

Figure 8: Temperature-time characteristics of the interior surface of the CRA-63 at various power outputs of the atomization stage.

● 5.3 kW ○ 4.9 kW △ 3.6 kW ▲ 2.6 kW

Figure 9: Temperature-time characteristics of the interior surface of the HGA-2100 at various power outputs of the atomization stage.

● 3.2 kW ○ 2.6 kW △ 1.8 kW ▲ 1.3 kW

and with the aging of their surface.

The 500 K intercept, common to each of the temperature-time curves, is the temperature of the atomizer at the completion of the ashing stage of the heating cycle. This temperature, measured with an iron-constantan thermocouple placed in contact with the interior surface of each atomizer, directly opposite the sample injection port, is the steady-state temperature attained after 15 seconds of heating. The power output of the drying and ashing stages of the CRA-63 is 80 and 275 W, respectively. The corresponding values for the HGA-2100 are 60 and 220 W.

In all cases, the temperature-time curves rise linearly and asymptotically approach an upper steady-state temperature (not evident in Figure 8, as the atomization time is too short) which reflects the balance ultimately attained between the input power and the heat losses. The power supplied to the atomizer is dissipated by radiation, conduction, convection and in raising the temperature of the atomizer. At low temperatures, and at the centre of the interior surface of the atomizer, heat losses due to radiation, conduction and convection should be small; consequently, the rate of increase in the temperature of the atomizer is related to the input power by equation 1-19:

$$dT/dt = \gamma = P/mc \quad (1-19)$$

where P is the power consumption of the atomizer ($J \cdot s^{-1}$), m is the mass of the carbon tube (kg) and c its specific heat capacity ($J \cdot kg^{-1} \cdot K^{-1}$). According to equation 1-19, there is a linear relationship

between the initial rate of heating of the atomizer (low temperatures) and its power consumption. Such a relationship was experimentally confirmed and is shown graphically in Figure 10 for both the CRA-63 and the HGA-2100 (the required data were obtained from Figures 6 - 9). Johnson et al. (10) and Torsi and Tessari (9) also observed such a relationship with a filament-type atomizer. The more rapid rate of rise of temperature with input power for the CRA-63 ($\approx 25\%$ greater) is largely the result of the smaller mass of this tube compared with that of the HGA-2100 (2.4×10^{-4} kg versus 7.9×10^{-4} kg). Differences in their heat capacities (the CRA-63 is coated with pyrolytic graphite (40, 41)) may also contribute to the difference in the heating rates of the two tubes.

Effect of Sheath Gas on Atomizer Temperature

The influence of the sheath gas on the temperature-time characteristics of the interior surfaces of both atomizers was investigated. The differential amplifier plug-in unit of the oscilloscope was used in the dc offset mode, allowing the output from the optical pyrometer to be recorded with high sensitivity (0.5 mV cm^{-1}). The measured temperatures could then be determined with greater accuracy. The temperature-time characteristics of both atomizers are presented in Figures 11 and 12. The CRA-63 (Figure 11) was operated in the step atomization mode at an atomization power of 5.3 kW. A sheath gas flow rate of $7.5 \times 10^{-2} \text{ dm}^3 \text{ s}^{-1}$ (4.5 l min^{-1}) was maintained for each gas. The HGA-2100 (Figure 12) was operated

Figure 10: Initial rate of heating of the atomizer surface as a function of atomization power.

● CRA-63 ▲ HGA-2100

Figure 12: Effect of various sheath gases on the temperature-time characteristics of the HGA-2100.

at an atomization power of 3.4 kW with an external sheath gas flow rate of $1.7 \times 10^{-2} \text{ dm}^3 \text{ s}^{-1}$ (1.0 l min^{-1}). Because of their different heat transfer properties (42), the amount of heat lost to each gas by the atomizer surface varies in proportion to their thermal conductivities, for which the relative values for the gases are listed in Table 3. The decrease in surface temperature of the atomizer when N_2 or He is substituted for Ar as a sheath gas is consistent with the differences in the thermal conductivities of the gases. With the CRA-63, substitution of He for Ar reduces the surface temperature by approximately 100 K, whereas with the HGA-2100, the same substitution reduces the surface temperature by 300 K. This observation is anomalous in view of the fact that the CRA-63 is an open system in which the sheath gas flows freely past the atomizer. As such, the extent to which He cools the CRA-63 should be more pronounced than that for the HGA-2100. The efficiency with which thermal energy is transferred from the atomizer surface to the sheath gas (as translational kinetic energy) is characterized by an accommodation coefficient, a , which is a function of the properties of both the heated surface and of the colliding species. The accommodation coefficient can be defined as standing for the fractional extent to which those molecules that fall on the surface and are reflected or re-emitted from it, have their mean energy adjusted or 'accommodated' toward what it would be if the returning molecules were issuing as a stream out of a mass of gas at the temperature of the wall (43, pp. 311 - 315). The accommodation coefficient should approach unity if the gas atoms are adsorbed on the surface as they strike it and then subsequently

Table 3

Relative Thermal Conductivities of Various Sheath
Gases at 300 K

Gas	Relative Thermal Conductivity
He	1.0
N ₂	0.2
Ar	0.1

From reference 42.

desorbed at the temperature of the surface, or if the surface is so irregular and cavernous that most of the atoms strike it a number of times before escaping, even though the accommodation coefficient for a single impact is less than unity. Thermal accommodation coefficients tend to be smaller for large differences in temperature between the heated surface and the ambient gas or for high rates of shear, i.e., convection of the gas past the heated surface (44). Because of the high velocity at which the gas flows past the CRA-63 (high rate of shear), the accommodation coefficient for He on this surface is much smaller than that for He on the surface of the HGA-2100. Consequently, the heat losses by conduction are smaller for the CRA-63, as observed.

Electronic Measurement System

Amplifier

The electronic measurement system in AAS can be divided into three subsystems, the detector, the amplifier and the recorder. Either the amplifier or the recorder is the dominant factor determining the response time of the system, since the response time of the photomultiplier tube is $< 0.1 \mu\text{s}$ (45, p. 309). The amplifier assembly described earlier was provided with variable time constants, situated at the output of the logarithmic amplifier. By examining, on the oscilloscope, the amplifier response to a step input function, the time constant corresponding to each damping position was measured. The modulation was bypassed and a square wave of variable width from a model 164 function generator (Wavetek Inc., San Diego, Calif., U.S.A.) was

applied to the input of the linear amplifier. The spectrometer was operated in the absorbance mode and a single dominant time constant was calculated for each damping position by measuring the time for the absorbance output to rise to 63% of its maximum. An approximate, dominant time constant of the amplifier-pen recorder assembly was also measured (in the absorbance mode) for full-scale response on the strip-chart recorder. The time constants measured in this manner are presented in Table 4.

To assess the effect of the time constant of the measurement system on the analytical signals, the absorbance-time traces obtained by the atomization of Cd and Cu in both the CRA-63 and HGA-2100 were examined under conditions of increasingly damped response. Cd was selected for study as it is representative of a class of volatile elements producing transient absorbance pulses which are the most difficult (for the amplifier) to follow. Cu is representative of the medium volatility elements and is useful for comparative purposes. Figures 13 and 14 illustrate the effect of the time constant of the recording system on the signal response. The rise time (10 - 90% output) of the Cd signal in the CRA-63 is 0.1 s. The signal can be reliably recorded with an amplifier time constant of 18 ms but becomes severely distorted with increased damping. The rise time of the Cu signal is much larger and, as a consequence, there is less distortion of this signal with increasing amplifier damping. The influence of the physical characteristics of the furnace on determining the extent to which the absorbance-time profiles for each element are affected by the recording time constant is evident from these figures. Signals generated by the

Table 4

Time Constants of the Recording System^a

Damping Position	τ_{RC}/ms	
	Linear-Log Amplifier	Amplifier-Recorder ^b
1	0.5	240
2	18	240
3	160	240
4	300	430
5	840	860
6	1480	1500
7	1750	1800
8	2200	2200
9	3200	3200
10	3700	3700
11	4800	4800

^aDefined as the time taken to achieve 63% of the maximum output in response to a step input function.

^bFor full scale response.

Figure 13: Effect of amplifier time constant, τ_{RC} , on the absorbance-time characteristics of Cd and Cu in the CRA-63 at an atomization power of 5.3 kW.

1. $\tau_{RC} = 0.5 \text{ ms}$ 2. $\tau_{RC} = 18 \text{ ms}$ 3. $\tau_{RC} = 160 \text{ ms}$

Figure 14: Effect of amplifier time constant, τ_{RC} , on the absorbance-time characteristics of Cd and Cu in the NGA-2100 at an atomization power of 3.2 kW.

1. $\tau_{RC} = 0.5$ ms	2. $\tau_{RC} = 18$ ms	3. $\tau_{RC} = 160$ ms
4. $\tau_{RC} = 300$ ms	5. $\tau_{RC} = 840$ ms	6. $\tau_{RC} = 1480$ ms

HGA-2100 are broader, with larger rise times than those generated by the CRA-63 (the reasons for this will be discussed in a subsequent section). Consequently, the HGA-2100 signals, at equivalent time constants, are less subject to severe distortion than the CRA-63 signals.

If the response of the measurement system is too slow both the peak height and the area under the absorbance-time curve (i.e., the integrated absorbance) are not governed solely by the physical and chemical processes which take place in the sample cell, but also by instrumental parameters. For theoretical studies, undistorted signals are required; otherwise, all measurements from which conclusions will be drawn will be influenced by instrumental parameters. The signals obtained with an amplifier time constant of 18 ms are identical with those obtained with a time constant of 0.5 ms, but the noise level is lower. Consequently, all subsequent optical measurements, unless specified otherwise, were made with an amplifier time constant of 18 ms. To improve further the signal-to-noise ratio recorded with the oscilloscope, the amplifier bandwidth on the differential plug-in unit was maintained at 100 Hz. Whereas no information on the signal was lost under such conditions, the noise level was greatly reduced. A 100 Hz bandwidth allows reliable recording of signals whose rise times are as short as 3.5 ms (45, p. 49).

Integrator

The integrating digital voltmeter, which utilizes a voltage-to-frequency converter, integrates by counting. The input

voltage is converted into a series of pulses whose frequency is proportional to the magnitude of the signal voltage. The pulses are then added in the counter stage over a specified time, giving a total number of counts relative to the area under the absorbance-time curve. The integration time is manually controlled and preset for each absorption pulse, as described earlier. The response of the integrator to various signal amplitudes and integration times was examined. The spectrometer was operated in the absorbance mode using a Mn hollow cathode lamp source ($\lambda = 279.5$ nm) and a spectral bandpass of 0.08 nm. By manually "stopping down" an iris diaphragm placed immediately before the entrance slit of the monochromator, various constant, reproducible absorbances varying from 0.025 to 0.950 absorbance were produced as square-wave input signals. At each absorbance, the signal was integrated for various, reproducible times ranging from 0.500 s to 20.000 s. Figure 15 shows the integrated absorbance plotted as a function of the integration time for a number of input absorbance signals. The response of the integrator is linear to better than 1% over a 760-fold range of integrated output (0.025 A·s to 19.000 A·s). All signals generated in either atomizer can be reliably integrated with this measurement system.

CRA-63

Characterization of Transient Signals

Oscilloscopic traces showing the absorbance-time pulses for Cd, Zn, Cu, Al, Sn, Mo and V atomized in the CRA-63 are presented in

Figure 15: Output of the integrator as a function of integration time for various absorbances.

● 0.95 ○ 0.70 ▲ 0.50 △ 0.30 ■ 0.10 □ 0.05

Figures 16 - 22. Whereas Cd, Zn, Cu, Al and Sn were sampled from a 5% HNO_3 aqueous solution, Mo and V were sampled from an alkaline aqueous solution. Atomization conditions were adjusted to give maximum values for the peak and integrated absorbance. Continuous heating of the atomizer was maintained over a time which extended beyond the duration of each absorbance signal. The time axis in these figures begins after a variable delay period, suitably chosen for each element so as to exclude unnecessary display of the baseline signal. Taking the time scale into account for each element, it is evident that the absorption pulses of fairly volatile elements are characterized by sharper and narrower curves having higher peak absorbance values than the elements of medium or low volatility, or those elements which tend to form compounds of low volatility in graphite furnaces, e.g., Mo and V, which may form refractory carbides (46, 47). For Cd, Zn, Cu, Al and Sn, heating of an unloaded (blank) tube produced no background signal. For Mo and V however, heating of the unloaded tube resulted in a signal which increased with the temperature of the atomizer, as shown for V in Figure 22. This blank signal arises as a result of scattering of the source radiation by carbon particles ejected from the graphite surface at high temperatures. Consequently, the signal increases with time and is responsible for what appears to be a second analytical peak at the tail end of the Mo trace, shown in Figure 21.

The influence of various sheath gases on the signals was studied using Ar, N_2 and He. In all cases the peak and integrated absorbance decreased with decreasing molecular weight of the sheath gas. Figure

Figure 16: Oscilloscope showing absorbance by 5.0×10^{-15} kg Cd in the CRA-63; absorbance = 0.10/scale div., time = 50 ms/scale div. Trigger delay time = 50 ms

Figure 17: Oscilloscope showing absorbance by 5.0×10^{-15} kg Zn in the CRA-63; absorbance = 0.10/scale div., time = 100 ms/scale div. Trigger delay time = 200 ms.

Figure 18: Oscilloscope showing absorbance by 4.0×10^{-13} kg Cu in the CRA-63; absorbance = 0.20/scale div., time = 200 ms/scale div. Trigger delay time = 200 ms.

Figure 19: Oscilloscope showing absorbance by 7.5×10^{-13} kg Al in the CRA-63; absorbance = 0.10/scale div., time = 100 ms/scale div. Trigger delay time = 700 ms. H_2 diffusion flame with H_2 flow rate = $8.3 \times 10^{-3} \text{ dm}^3 \text{ s}^{-1}$ (0.5 l min^{-1}).

Figure 20: Oscilloscope showing absorbance by 1.0×10^{-12} kg Sn in the CRA-63; absorbance = 0.2/scale div., time = 100 ms/scale div. Trigger delay time = 300 ms. H_2 diffusion flame with H_2 flow rate = $2.5 \times 10^{-2} \text{ dm}^3 \text{ s}^{-1}$ (1.5 l min^{-1}).

Figure 21: Oscilloscope showing absorbance by 5.0×10^{-13} kg Mo in the CRA-63; absorbance = 0.10/scale div., time = 500 ms/scale div. Trigger delay time = 600 ms.

Figure 22: Oscillogram showing absorbance by 2.0×10^{-12} kg $V^{2/3}$ (curve A) and an unloaded tube (curve B) in the CRA-63; absorbance = 0.10/scale div., time = 500 ms/scale div. Trigger delay time = 700 ms.

23 shows the effect of Ar, N₂ and He on the signal from Cu. Each sheath gas was maintained at a flow rate of $7.5 \times 10^{-2} \text{ dm}^3 \text{ s}^{-1}$ (4.5 l min^{-1}). Since the time spent by an atom within the analytical volume is inversely proportional to the diffusion coefficient, the residence time of atoms within the furnace, and hence, the peak and integrated absorbance, will be affected by the sheath gas. For a gaseous binary system, the diffusion coefficient is given by equation 1-20 (48):

$$D_{1,2} = 2.66 \times 10^{-22} \frac{T^{3/2} \sqrt{(M_1 + M_2)/2M_1M_2}}{p\sigma_{1,2}^2} \quad (1-20)$$

where $D_{1,2}$ is the diffusion coefficient for species 1 in medium 2 ($\text{m}^2 \text{ s}^{-1}$), T is the absolute temperature, M_1 and M_2 are the masses of the diffusing species and those of the diffusion medium (amu), p is the pressure ($\text{N} \cdot \text{m}^{-2}$) and $\sigma_{1,2}$ is the collision diameter for the two species, which is further given by:

$$\sigma_{1,2} = (\sigma_1 + \sigma_2)/2 \quad (1-21)$$

where σ_1 and σ_2 are the individual diameters of the colliding particles (m). Normalized diffusion coefficients for Cu in Ar, N₂ and He, calculated from equation 1-20, are presented in Table 5. Also given are the normalized peak and integrated absorbances obtained for Cu in each sheath gas. Since the various sheath gases do not influence the atomizer surface temperature to any great extent (Figure 11), the thermal atomization conditions are hardly affected by the kind of sheath gas used; consequently, the influence of possible differences in the temperature

Figure 23: Effect of various sheath gases on the absorbance by 2.0×10^{-13} kg Cu in the CRA-63. Flow rates of Ar, N₂ and He = $7.5 \times 10^{-2} \text{ dm}^3 \text{ s}^{-1}$ (4.5 l min^{-1}).

Table 5

Relative Values of the Diffusion Coefficient of Cu in Various Sheath Gases and Relative Values of the Peak and Integrated Absorbance by Cu^a

Gas	^b $\sigma_{\text{gas}}/\text{nm}$	^c $D_{1,2}$	A_p	$\int A_t dt$
Helium	0.200	3.63	0.47	0.40
Nitrogen	0.316	1.01	0.87	0.88
Argon	0.286	1.00	1.00	1.00

^aTaken from the results shown in Figure 23.

^bDiameters of the gas molecules (both monatomic and diatomic) taken from reference 49, p. 157.

^cCalculated from equation 1-20 with the assumption that $T_{\text{He}} = T_{\text{N}_2} = T_{\text{Ar}}$.
Atomic diameter for Cu = 0.254 nm (50).

are not accounted for in the calculation of $D_{1,2}$. Although greatly influenced by the diffusion medium, the variation in the peak and integrated signals with sheath gas is not quantitatively accounted for by the relative values of the diffusion coefficient. The major reason for this is that the CRA-63 is an open system and losses of atomic vapour occur not only by diffusion but by convection as well. Because maximum sensitivity is achieved with an Ar sheath gas, it was used throughout the remainder of this study.

The effect of a H_2 diffusion flame on the analytical characteristics of the signals was investigated; only Sn and Al were influenced by its presence. In the absence of a H_2 diffusion flame, Al gave multiple absorption peaks, indicative of the formation of a number of intermediate species having significantly different volatility. Such a trace is shown in Figure 24. In the presence of a H_2 diffusion flame, the first peak disappears (cf. Figure 19). The influence of the H_2 diffusion flame on the absorbance by Sn is shown in Figure 25, which illustrates that the H_2 diffusion flame shifts the absorption pulse to an earlier appearance time, increases the peak absorbance and decreases the pulse width. The H_2 diffusion flame creates and maintains a more highly reducing chemical environment in which the extremely low partial pressure of oxygen does not favour the formation of oxides of Sn and Al (51 - 53). Although the flame produced no measurable increase in the surface temperature of the atomizer, the burning H_2 increases the excitation temperature of the atomic vapour (Chapter 3), thus enhancing the atomization efficiency of these elements.

Figure 24: Oscilloscope showing absorbance by 1.2×10^{-12} kg Al in the CRA-63 in the absence of a H_2 diffusion flame; absorbance = 0.10/scale div., time = 100 ms/scale div. Trigger delay time = 700 ms.

Figure 25: Oscilloscope showing the effect of a H_2 diffusion flame on the absorbance by 1.2×10^{-13} kg Sn in the CRA-63; absorbance = 0.20/scale div., time = 100 ms/scale div. Trigger delay time = 300 ms.
 A) H_2 flow rate = $2.5 \times 10^{-2} \text{ dm}^3 \text{ s}^{-1}$ (1.5 l min^{-1})
 B) H_2 flow rate = $0.0 \text{ dm}^3 \text{ s}^{-1}$.

Absorption Pulse Characteristics

The pulse characterization times are shown in Figure 26. The following times are defined: $\tau_{\text{appearance}}$ is the time elapsed from the start of the atomization stage to the point at which the observed absorbance signal extrapolates back to the baseline noise; τ_{peak} is the time elapsed from the start of the atomization stage to the point at which the absorbance maximum occurs; τ_{end} is the time elapsed from the start of the atomization stage to the point at which the pulse returns to the baseline noise; τ_{display} is the total duration of the pulse ($\tau_{\text{end}} - \tau_{\text{appearance}}$). Additionally, the atomization time, τ_1 , and the residence time, τ_2 are shown. The atomization time is defined by the relationship $\tau_{\text{peak}} - \tau_{\text{appearance}}$. The residence time is defined as the time taken for the absorbance signal to decrease from its maximum to a value e times smaller (e is the base of the Napierian logarithms) measured from the decay side of the pulse. A discussion of the relationship of the experimental values of τ_1 and τ_2 to the theoretical values of τ'_1 and τ'_2 introduced by Livov in his model is given in Appendix I.

The pulse characterization times for each element, obtained from the oscilloscopic traces, are presented in Table 6. Also shown are the optimum atomization conditions under which the data were obtained. Each element possesses a characteristic appearance time and a time to attain peak absorbance which are well defined for a given atomization power input (rate of heating of the atomizer). Within the limits of experimental error, these times are independent of the mass of analyte atomized. As an example, the $\tau_{\text{appearance}}$

Figure 26: Pulse characterization times.

Table 6

Pulse Characterization Times under Optimum Conditions
with the CRA-63

Element	Atomization Conditions ^a		Characterization Times/ms			
	Power/W	Time/ms	τ_{appear}	τ_{peak}	τ_{end}	τ_{display}
Cd	4750	1000	85	200	550	465
Zn	4750	1000	250	490	690	440
Cu	4750	2000	350	800	1800	1450
Al	4750	1500	890	1230	1420	530
Sn	4750	1500	420	600	900	490
Mo	5300	2600	900	1650	3000	2000
V	5300	2000	875	1570	2600	1725

^aFor both the peak and the integration methods of measurement.

and τ_{peak} values for different masses of Cu are presented in Table 7. The constancy of these values is a consequence of the small amount of energy absorbed by the analyte during its physicochemical transformation to atomic vapour, relative to the total thermal energy received by the atomizer.

The melting and boiling points of the elements studied as well as the temperatures of the interior surface of the graphite tube at all characterization times are presented in Table 8. These temperatures, which are reproducible to ± 20 K, are taken from the temperature - time curves in Figure 8 and do not equal the temperatures of the atomic vapour except at the appearance times (cf. Chapter 3). Table 8 indicates that relatively low temperatures are required for the atomization of low volatility elements such as Mo and V and that there is no consistent relationship between the appearance temperatures and the melting and boiling points of the elements. The reason for this is that the exact mechanism of atom formation varies with each element and, hence, the physicochemical properties of the elements may not reflect the physicochemical properties of the actual reaction intermediate(s). Additionally, the appearance temperatures are influenced by the detection limit of the element and are determined by the absorption coefficient of the atomic vapour. The physical significance of the appearance time, therefore, is that it is a measure of the time taken by the atomizer to reach a sufficiently high temperature for atomization to become rapid thereafter. As the atomization power or rate of heating of the atomizer increases, the time required to achieve this temperature decreases but the appearance temperature remains unaltered. Since

Table 7

Effect of Analyte Mass on the Characteristics of the
Absorption Pulse of Cu with the CRA-63^a

10^{12} x Mass of Cu/kg	Characterization Times/ms			
	τ_{appear}	τ_{peak}	τ_1	τ_2
0.25	350	800	450	310
0.50	330	800	470	300
0.75	330	760	430	330
1.00	350	780	430	320
1.25	340	780	450	340

^aAtomization program: dry, 50 W; ash, 175 W; atomize, 4750 W.

Table 8

Pulse Characterization Temperatures with the CRA-63

Element	Melting Point/K	Boiling Point/K	Temperature/K		
			τ_{appear}	τ_{peak}	τ_{end}
Cd	594	1038	730	950	1660
Zn	693	1180	1110	1560	1870
Cu	1356	2848	1220	2020	3140
Al	933	2740	2080	2560	2760
Sn	505	2543	1520	1750	2160
Mo	2890	4885	2050	3000	3650
V	2163	3653	2030	2930	3580

the rate of a physicochemical reaction is exponentially dependent upon the activation energy barrier, the temperature at which rapid atomization commences is uniquely determined by the physicochemical properties of each element, or the properties of the major intermediate species in the sequence of steps leading to free atoms.

The atomization times for the elements are listed in Table 9. It is difficult to use the appearance temperature as a measure of the atomization energy as it is influenced by a number of instrumental parameters and by the sensitivity of the element. The atomization time, however, is a measure of the total time taken for conversion of the sample into atomic vapour; therefore, relative values of this parameter are dependent on fewer instrumental variables. Since the atomization times are also independent of the mass of analyte atomized (Table 7) they may be taken as a measure of the relative energy for atomization of each element. If the elements are divided into two groups and arranged in order of increasing τ_1 within each group, one gets the following two sequences:

The elements have been divided into the above two groups according to their mechanism of atom formation (cf. Chapter 5). Sn, Cu, V and Mo initially form atoms predominantly through vaporization of the metal, whereas atomization of Cd, Zn and Al proceeds predominantly through oxide dissociation. The first sequence parallels the heat of formation

Table 9

Atomization Times with the CRA-63

Element	τ_1/ms
^a Cd	115
^a Zn	240
^a Cu	450
^a Al	340
^a Sn	180
^b Mo	750
^b V	695

^aAtomization power of 4750 W.

^bAtomization power of 5300 W.

of gaseous atoms from their standard state at 298 K, i.e., 300, 340, 460 and 660 kJ mol⁻¹ for Sn, Cu, V and Mo. The second sequence closely parallels the bond dissociation energy of the metal oxide, i.e., 280, 276 and 485 kJ mol⁻¹ for Cd, Zn and Al. The relative position of Zn, however, is anomalous with respect to the bond energies listed.

Effect of Atomization Power on Absorbance Signals

The effect of atomization power (rate of heating of the atomizer) on the peak and integrated absorbance for Cd, Zn, Cu, Al and Sn is presented in Table 10. The peak absorbance increases with the atomization power, whereas the integrated absorbance remains constant for the fairly volatile elements (Cd, Zn) and Cu but increases with the atomization power for the medium volatility elements (Al, Sn). The effect on Mo and V could not be studied as incomplete atomization of these elements occurs even with maximum available atomization power. Also, incomplete atomization of Sn and Al results below an atomization power of 3.6 kW. In order to explain these observations, it is necessary to consider the processes of formation of atoms in and their loss from the analytical volume. Although the mechanisms of atom formation in electrothermal atomizers are quite complex (Chapter 5), for simplicity, they may be treated as an evaporation phenomenon and L'vov's approach (5, 11) to the process adopted. If it is assumed that atomic vapour arises solely by evaporation from a condensed phase, then its rate of production is determined by the rate of evaporation. The rate of evaporation is exponentially dependent upon the temperature and may be

Table 10

Effect of Atomization Power on Peak and Integrated Absorbance^a

Heating Rate/K ms ⁻¹	Power/W	Element									
		Cd		Zn		Cu		Al		Sn	
		A _p	^b ∫A _t dt	A _p	∫A _t dt	A _p	∫A _t dt	A _p	∫A _t dt	A _p	∫A _t dt
2.72	5900	-	-	-	-	-	-	0.355	0.118	0.319	0.073
2.21	4750	0.266	0.082	0.228	0.040	0.166	0.092	0.347	0.113	0.315	0.073
1.87	4000	0.263	0.085	0.225	0.040	0.160	0.095	0.272	0.085	0.293	0.066
1.68	3600	0.262	0.083	0.219	0.040	0.144	0.095	0.125	0.038	0.263	0.060
1.40	3000	0.240	0.084	0.210	0.040	0.133	0.096	-	-	-	-
1.26	2600	0.216	0.084	0.199	0.041	0.115	0.096	-	-	-	-
0.89	1900	0.178	0.085	0.152	0.042	-	-	-	-	-	-
0.66	1400	0.128	0.085	-	-	-	-	-	-	-	-

^aCRA-63; Ar sheath gas flow rate = $7.5 \times 10^{-2} \text{ dm}^3 \text{ s}^{-1}$ (4.5 l min^{-1}).^bIntegrated absorbance in units of absorbance x second.^cH₂ diffusion flame with flow rates for: Al $8.3 \times 10^{-3} \text{ dm}^3 \text{ s}^{-1}$ (0.5 l min^{-1}); Sn $2.5 \times 10^{-2} \text{ dm}^3 \text{ s}^{-1}$ (1.5 l min^{-1}).

described by the following equation (54):

$$R(T) = A \exp(-\Delta H^0/RT) \quad (1-22)$$

where A is a constant, ΔH^0 is the latent heat of evaporation of the substance and R is the gas constant. Since evaporation occurs simultaneously with increasing atomizer temperature, equation 1-22 may be expressed as:

$$R(t) = A \exp(-\Delta H^0/R(T_0 + \gamma t)) \quad (1-23)$$

where $T_0 + \gamma t$ defines the initial temperature-time characteristics of the atomizer (i.e., γ is the initial slope of the T - t curve and T_0 is the temperature intercept). It is evident from these equations that a minimum temperature must be attained in order to achieve a rapid rate of evaporation. Thereafter, an increase by 100 - 200 K close to this temperature will increase the atomization (evaporation) rate by an order of magnitude. Equations 1-22 and 1-23 indicate that a minimum temperature (appearance temperature) must be attained before the analytical signal will appear. Thereafter, signal growth is very rapid. This is experimentally observed. With accelerated vaporization, the time-dependent number of atoms in the analytical volume is given by equations 1-8 and 1-13. Maximum population (signal) is achieved when τ_1 is a minimum, i.e., the rate of evaporation is a maximum. According to equation 1-23, the sample evaporation time, τ_1 , should vary in an inverse exponential manner with the rate of heating of the atomizer or the power delivered in the atomization stage (since these two parameters are linearly related according to equation 1-19).

Correspondingly, the peak absorbance (given by equation 1-9) should vary exponentially with the atomization power (assuming τ_2 to be constant). Figure 27 shows the variation of τ_1 for Cd, Zn, Cu and Sn with atomization power. As predicted by equation 1-23, the atomization time varies inversely with the atomization power, the dependence being most pronounced for Sn and Cu but approximately the same for Cd and Zn. This is a result of the relative magnitude of their atomization energies (Chapter 5). The relationship of the peak absorbance to atomization power is shown in Figure 28. The peak absorbance is not exponentially dependent on the atomization power but rises to a steady-state maximum with increasing power. The influence of power on the signal is greatest for the more difficult-to-volatilize elements. A similar variation in the peak absorbance with power was noted by Posma et al. (8). These authors reported a parabolic relationship of the peak absorbance by Cu to the heating rate of a CRA-63. Although Torsi and Tessari (9) reported a linear relationship between the peak absorbance and the atomization power for Cr atomized in a carbon rod device, their data can also be interpreted as showing a parabolic relationship. Johnson et al. (10) reported a linear relationship for Zn using a carbon filament atomizer although their data suggest an exponential relationship.

The attainment of a constant peak absorbance at high atomization power reflects the balance attained between the rates of production and loss of atomic vapour. This, and the fact that an exponential relationship does not exist between the input power and

Figure 27: Effect of atomization power on τ_1 in the CRA-63.

▲ Cu △ Sn ○ Zn ● Cd

Figure 28: Effect of atomization power on the peak absorbance in the CRA-63.

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the peak absorbance, indicates that the signal maximum is not determined solely by the rate of production of atoms. According to equation 1-9, there is an inverse exponential relationship between the peak absorbance and the τ_1/τ_2 ratio. The influence of the atomization power on the τ_1/τ_2 ratio is presented in Table 11. The residence time is a decreasing function of the atomization power since diffusional, convectional and chemical losses of atomic vapour are temperature-dependent. The term chemical loss will be used to mean loss of analyte atoms by formation of a compound or compounds by the analyte element with other species present within the atomizer, including incandescent graphite. In qualitative agreement with equation 1-9, the decrease in the τ_1/τ_2 ratio with the atomization power results in an increase in the peak absorbance. Although such treatment qualitatively describes some of the trends in Figure 28, it does not explain the constant signals obtained at high atomization powers, it cannot account for the rapid decrease in the signals from Al and Sn and their incomplete atomization at low atomization powers nor can it satisfactorily explain the dependence of the integrated absorbance on the atomization power (to be presented in a later section).

The rapid decrease in the peak absorbance for Sn and Al with decreasing atomization power and their incomplete atomization below power settings of 3.6 kW may be accounted for by considering the possibility of chemical loss through carbide formation. A decrease in the atomization power causes a decrease in the rate of heating of the atomizer, and hence, a decrease in the rate of evaporation of the analyte (equation 1-23). Consequently, the longer time during

Table 1

Effect of Atomization Power on τ_1/τ_2 with CRA-63

Element	Power/W	τ_1 /ms	τ_2 /ms	τ_1/τ_2
Cd	4750	115	150	0.77
	4000	125	155	0.81
	3600	140	155	0.90
	3000	170	160	1.06
	2600	200	165	1.20
Zn	4750	240	110	2.18
	3600	280	120	2.35
	2600	350	140	2.50
Sn	4750	180	140	1.28
	4000	250	150	1.65
	3600	420	190	2.20

which the analyte is in contact with the hot graphite permits greater penetration of the analyte into its pores with a resulting increase in the extent of carbide formation. The above leads to incomplete atomization and memory effects. This problem is particularly severe for Mo and V because of their high appearance temperatures and reactivity toward incandescent graphite. Additionally, at lower rates of heating, a greater amount of analyte may be lost from the analytical volume by diffusion before the appearance temperature is attained.

The variation of the integrated absorbance with atomization power (Table 10) can only be explained as above. According to equation 1-18, the integrated absorbance is dependent only on the magnitude of the residence time of the atomic vapour. For each element, the residence time increases as the atomization power decreases (Table 11). Assuming that the efficiency of atom formation is independent of the applied power (which is a reasonable assumption, as the appearance temperature is independent of the heating rate) the integrated absorbance should therefore increase with decreasing atomization power. This is not observed; the integrated absorbance remains constant for Cd, Zn and Cu but decreases for Al and Sn. There are two possible explanations for the above results: (1) the constancy of the integrated absorbance for Cd, Zn and Cu is due to a fortuitous balance between the rates of atom formation and loss, hence, the area under the absorption pulse remains unchanged as the atomization power is varied; (2) with lower rates of heating (i.e., with longer time for analyte evaporation) an increasing fraction of the analyte atoms is lost through penetration into the pores and subsequent

carbide formation. The latter explanation appears more likely, particularly for Sn and Al.

Irrespective of the model used to describe signal shape, one aspect of atomization is clear; because the rate at which the sample evaporates (and also the rate of molecular dissociation) depends on the rate of increase of temperature, at temperatures at which the analyte has a significant vapour pressure, it is important that the atomizer reach a sufficiently high temperature before a sizable fraction of the element disappears from the analytical volume. On the other hand, the temperature should not be increased more than necessary to completely vaporize (and dissociate) the analyte, as the rate of loss of atomic vapour becomes too large. It is the inseparability of the rate of heating of the atomizer and the maximum temperature which it attains that presents a major problem with commercial electrothermal atomizers. The advantages of employing the maximum rate of heating cannot be fully realized because of this effect. Such conditions contribute to the levelling off of the peak absorbance at high heating rates. L'vov (11) has overcome this problem by passing the atomic vapour into an isothermal cuvette subsequent to its evaporation (atomization) from a separately heated electrode.

Residence Time and Sensitivity

The residence time of each element was calculated from equation 1-13 (at $t = \tau_2$) assuming that the loss of atomic vapour is solely by diffusion. The residence times, presented in Table 12, do not

Table 12

Residence Times with the CRA-63

Element	τ_2/ms
^a Cd	150
^a Zn	110
^a Cu	310
^a Al	120
^a Sn	140
^b Mo	510
^b V	550

^aAtomization power of 4750 W.

^bAtomization power of 5300 W.

support this assumption, even when the increase in surface temperature beyond the absorbance maximum is accounted for. Vanadium has the largest residence time, despite the fact that the decay of this signal occurs during the highest temperature period of the atomizer. According to the model for signal shape, it is possible to evaluate τ_2 from the tail of the absorption pulse provided that atomization is complete at the time $t = \tau_{\text{peak}}$. For the elements of low volatility (Mo and V), atomization has not been completed at this point. As the maximum simply marks the point of balance between the rate of introduction of atoms into and their loss from the analytical volume, the tail of the absorption pulse must contain a contribution from the continuing atomization of the analyte beyond the absorbance maximum. Calculation of τ_2 on the basis of equation 1-13 gives, at best, only a qualitative measure of the true residence time of the atomic vapour. In all cases the residence times are less than one second. These small values are the result of the short length and high temperature of the atomizer.

The absolute sensitivities obtained for each element by both methods of measurement are presented in Table 13. The absolute sensitivity is defined as the slope of the calibration curve, i.e., the mass of element which gives a peak absorbance of 0.0044 or an integrated absorbance of 0.0044 absorbance x second. In all cases, the integrated sensitivity is lower than the peak sensitivity by factors ranging from 1 - 5. The integrated sensitivity is determined by the product of the residence time and the number of atoms in the sample. Because it is based on the mass of an element which gives a signal of 0.0044 absorbance x second, it follows from the small

Table 13

^aAbsolute Sensitivity/kg

Element	Method of Measurement		
	Peak (oscilloscope)	Peak (recorder)	Integration
Cd	9.5×10^{-17}	1.6×10^{-16}	5.2×10^{-16}
Zn	8.4×10^{-17}	1.1×10^{-16}	6.3×10^{-16}
Cu	2.7×10^{-15}	3.7×10^{-15}	6.7×10^{-15}
Al	1.3×10^{-14}	1.6×10^{-14}	4.8×10^{-14}
Sn	9.1×10^{-15}	1.1×10^{-14}	4.8×10^{-14}
Mo	7.5×10^{-15}	7.9×10^{-15}	7.7×10^{-15}
V	3.1×10^{-14}	4.5×10^{-14}	5.5×10^{-14}

^aDefined as the slope of the calibration curve i.e., the mass of element which gives a peak absorbance of 0.0044 and an integrated absorbance of 0.0044 absorbance x second.

values of the residence times (i.e., $\tau_2 < 1$ s, Table 12), that the integrated sensitivities are all less than the corresponding peak height sensitivities.

Peak absorbances, obtained from the oscilloscopic traces of elements of high volatility, are considerably greater than those given by a strip-chart recorder. This is due to the distortion of the signals introduced by the larger effective time constant of the recorder (cf. Table 4). The distortion in peak amplitude introduced by the recorder must increase as the peaks themselves increase (the effective time constant for the recorder depends on the distance of pen travel). Additionally, the distortion is also dependent on the magnitude of τ_1 for a given element. Large values of τ_1 (e.g., Mo and V) result in the signals rising more slowly with time with the result that the recorder is capable of following them more accurately. Pen-recorded peaks of every element therefore suffer variable degrees of distortion. The use of an oscilloscope as the measurement device overcomes this limitation.

Limit of Detection

The limit of detection is defined as the mass of the element that gives a signal equal to three times the standard deviation of 10 replicate measurements with the same solution containing a low concentration of the element. Detection limits for both methods of measurement are presented in Table 14. All integrated measurements were made with a time constant of 0.5 ms, peak absorbance signals

Table 14

Limit of Detection^a

Element	Peak/kg	Integration/kg
Cd	2.6×10^{-16}	4.5×10^{-16}
Zn	2.7×10^{-16}	4.1×10^{-16}
Cu	7.5×10^{-15}	2.0×10^{-14}
Al	3.0×10^{-14}	3.0×10^{-14}
Sn	2.7×10^{-14}	4.7×10^{-14}
Mo	4.8×10^{-14}	2.3×10^{-14}
V	2.0×10^{-14}	1.2×10^{-14}

^aDefined as the mass of the element that gives a signal equal to three times the standard deviation of 10 replicate measurements with the same solution containing a low concentration of the element.

were measured with a system time constant of approximately 80 ms using the pen recorder (calculated from the full scale response time of the pen recorder and the fact that the signals were limited to one-third of the recorder span). A scale expansion of 4 was used in all cases. Although the measurements were not carried out under the ideal recording conditions specified in reference 27, the detection limits by both methods of measurement agree closely and differ, at most, by a factor of 2.

Analytical Calibration Curves

In theory, the integration method should yield calibration curves with a larger linear dynamic range than those given by the peak method. With the integration method, the rate of sample vaporization can be adjusted such that the absorption values do not exceed a value at which the absorbance is no longer proportional to the mass of analyte. In this study, however, maximum vaporization rates were used in order to attain maximum sensitivity. The linear dynamic range for each element, given in Table 15, is defined as the range in absolute mass of the element from the limit of detection to the upper mass limit where a 5% deviation from linearity results. The calibration curves by the integration method have a larger linear dynamic range, this being most marked for Cd and Zn and to a lesser extent for Cu, Al and Sn. Typical calibration curves by both methods of measurement are shown for Cu in Figure 29. Because the strip-chart recorder was used for the peak absorbance measurements, additional bending of this curve was introduced by the inadequate response of the recorder.

Table 15

Upper Limit for Linear Calibration Curves^a

Element	Peak/kg	Integration/kg	$\int A_t dt / A_p$
Cd	1.0×10^{-14}	6.0×10^{-14}	6.0
Zn	7.5×10^{-15}	1.1×10^{-13}	14.7
Cu	5.0×10^{-13}	2.7×10^{-12}	5.4
Al	2.0×10^{-12}	3.5×10^{-12}	1.7
Sn	5.0×10^{-13}	8.0×10^{-13}	1.6
Mo	3.0×10^{-12}	3.0×10^{-12}	1.0
V	7.0×10^{-12}	7.0×10^{-12}	1.0

^aDefined as the range in absolute mass of the element from the limit of detection to the upper mass limit where a 5% deviation from linearity occurs.

Figure 29: Calibration curves for Cu in the CRA-63.

○ peak absorbance ● integrated absorbance

Beyond the point of strict linearity, the calibration curve by the integration method has, in most cases, a more gentle curvature than that of the peak absorbance curve, hence, the working range is even longer for the integration method. By suitably adjusting the vaporization rates, it may be possible to extend the linear ranges of both curves.

For Mo and V, the calibration curves by the peak method of measurement did not pass through the origin but intercepted the absorbance axis at 0.02 and 0.05 absorbance, respectively. It is evident from the oscilloscopic traces for these elements, shown in Figures 21 and 22, that the "blank" heating of an unloaded tube produces an absorption peak caused by scattering of the source radiation by carbon particles ejected from the incandescent graphite tube at high temperatures. This blank signal peak appears at a different point in time from that of the analytical signal peak. Additionally, there is a small contribution from this blank signal which occurs at the analyte absorption peak. Subtraction of the pen recorded peak of this blank signal would lead to over-correction of the results. This is of considerable practical importance since the peak method is usually used for the analysis of real samples with the assumption that blank signals can be fully corrected for. Because of the origin of this problem, other elements requiring high temperature for atomization would experience the same problem. In such cases, integration of the analytical signal, followed by correction for the integrated blank signal, would yield the correct analytical result.

Precision

The percentage relative standard deviations of the peak and integrated signals are presented in Table 16. The values were calculated from 10 replicate measurements using solutions of sufficient concentration to give peak absorbances of 0.3 to 0.4, provided these values fell within the linear range of the calibration curves. The precision obtained with both methods of measurement is comparable, and in this respect the results are in agreement with those reported by McIntyre et al. (32). The precision values for the integration method were obtained by measuring the absorbance signal over its entire duration. Recently, Piepmeier (55) indicated that improvements in precision by up to a factor of six may be expected when transient absorbance signals with long tails are only partially integrated. The reason for this is that the contribution to the signal from the tail of the pulse will decrease with time, whereas the noise will increase.

The precision values are a complex function of the atomization characteristics of each element, the wavelength, the stability of the emission source (particularly for integrated measurements lasting a period of several seconds), the age of the graphite tube (extent and reproducibility of the scattering of the source radiation by carbon particles), the reproducibility of the rate of heating of the atomizer and the reproducibility of the sample delivery step.

Table 16

Element	Precision ^a	
	Peak	Integration
Cd	2.4	2.5
Zn	2.1	4.5
Cu	0.5	1.2
Al	4.0	3.1
Sn	4.8	5.5
Mo	1.3	1.7
V	1.8	1.7

^aExpressed as a percentage relative standard deviation of 10 replicate measurements made with the same solution of the element.

HGA-2100

Characterization of Transient Signals

In addition to the seven elements studied with the CRA-63, viz., Cd, Zn, Cu, Al, Sn, Mo and V, the characteristics of the absorption pulses of the following eight additional elements were studied with the HGA-2100: Pb, Fe, Cr, Co, Mn, Mg, Ni and Ca. Analytical figures of merit for the first seven elements only were obtained, the latter eight elements were only qualitatively studied.

Oscilloscopic traces showing the absorbance-time characteristics of each of the elements are presented in Figures 30 - 44. The atomization conditions are identical for all elements, i.e., dry, 60 W, ash, 220 W, atomize, 3150 W, and correspond to HGA-2100 power supply meter settings of 100 C, 300 C and 2700 C, respectively. Although such conditions are not optimum for proper measurement of the signal from many of the elements, these traces allow direct intercomparison of the absorption pulses under the same heating conditions. In contrast to those obtained with the CRA-63, the signals from the HGA-2100 are considerably more drawn out, the peaks being more rounded with the rise to and decay from the maximum being more gentle. As attempted earlier, the elements may be qualitatively classified into three groups, based on the general appearance of the pulse: Pb, Cd, Zn and Mg show the most transient-like behaviour, characteristic of the more volatile analytes; Cu, Sn, Al, Fe, Mn, Co and Cr are intermediate in signal shape, and hence, in volatility, whereas Ni, Ca, V and Mo show pulse features which are characteristic of the least volatile of the analyte

Figure 30: Oscilloscope showing absorbance by 2.0×10^{-14} kg Cd in the HGA-2100; absorbance = 0.05/scale div., time = 200 ms/scale div. Trigger delay time = 50 ms.

Figure 31: Oscilloscope showing the absorbance by 1.0×10^{-11} kg Pb in the HGA-2100; absorbance = 0.10/scale div., time = 200 ms/scale div. Trigger delay time = 100 ms.

Figure 32: Oscillogram showing absorbance by 2.0×10^{-14} kg Zn in the HGA-2100; absorbance = 0.10/scale div., time = 200 ms/scale div. Trigger delay time = 250 ms.

Figure 33: Oscillogram showing absorbance by 2.5×10^{-12} kg Cu in the HGA-2100; absorbance = 0.20/scale div., time = 500 ms/scale div. Trigger delay time = 300 ms.

Figure 34: Oscilloscope showing absorbance by 2.5×10^{-12} kg Co in the HGA-2100; absorbance = 0.20/scale div., time = 500 ms/scale div., Trigger delay time = 500 ms.

Figure 35: Oscilloscope showing absorbance by 1.5×10^{-12} kg Fe in the HGA-2100; absorbance = 0.2/scale div., time = 500 ms/scale div., Trigger delay time = 500 ms.

Figure 36: Oscilloscope showing absorbance by 8.0×10^{-14} kg Mg in the HGA-2100; absorbance = 0.10/scale div., time = 200 ms/scale div. Trigger delay time = 550 ms.

Figure 37: Oscilloscope showing absorbance by 3.0×10^{-13} kg Mn in the HGA-2100; absorbance = 0.10/scale div., time = 500 ms/scale div. Trigger delay time = 600 ms.

Figure 38: Oscilloscope showing absorbance by 4.0×10^{-12} kg Sn in the HGA-2100; absorbance = 0.20/scale div., time = 500 ms/scale div. Trigger delay time = 500 ms.

Figure 39: Oscilloscope showing absorbance by 2.5×10^{-12} kg Ni in the HGA-2100; absorbance = 0.05/scale div., time = 500 ms/scale div. Trigger delay time = 500 ms.

Figure 40: Oscilloscope showing absorbance by 1.2×10^{-12} kg Cr in the HGA-2100; absorbance = 0.20/scale div., time = 500 ms/scale div. Trigger delay time = 500 ms.

Figure 41: Oscilloscope showing absorbance by 1.5×10^{-12} kg Ca in the HGA-2100; absorbance = 0.20/scale div., time = 1000 ms/scale div. Trigger delay time = 100 ms.

Figure 42: Oscilloscope showing absorbance by 2.5×10^{-12} kg Al in the HGA-2100; absorbance = 0.20/scale div., time = 500 ms/scale div. Trigger delay time = 500 ms.

Figure 43: Oscilloscope showing absorbance by 6.0×10^{-12} kg Mo in the HGA-2100; absorbance = 0.10/scale div., time = 1000 ms/scale div. Trigger delay time = 1000 ms.

Figure 44: Oscilloscope showing absorbance by 3.0×10^{-11} kg V in the HGA-2100; absorbance = 0.10/scale div., time = 1000 ms/scale div. Trigger delay time = 1000 ms.

elements.

The internal purge gas was interrupted during the atomization cycle, leading to increases in both the height and breadth of the absorbance pulses. The effect is illustrated in Figure 45 for the atomization of Cu. Interruption of the internal purge gas increases the residence time by preventing the sweeping out of the atomic vapour from the analytical volume. The initial few hundred ms following the appearance of the copper signal are unaffected by the internal purge gas (curve B) because atoms produced during this time period do not have time to escape from the analytical volume by diffusion and mechanical expulsion. The increased rate of convectional loss due to the purge gas decreases both the peak height and the width of the pulse. Since the peak of the pulse marks the point of balance between the rates of formation and loss of atoms, an increase in the rate of loss decreases the peak height and shifts the maximum to an earlier point in time.

Whereas the effect of a H_2 diffusion flame on the analytical characteristics of the elements could not be studied using the HGA-2100, the influence of various sheath gases was investigated. Ar, N_2 and He sheath gases were each maintained at a flow rate of $1.7 \times 10^{-2} \text{ dm}^3 \text{ s}^{-1}$ (1.0 l min^{-1}). The effect of each gas on the signal from $1.5 \times 10^{-12} \text{ kg}$ Cu is shown in Figure 46. Table 17 presents the relative values of the diffusion coefficient of Cu in each gas as well as the relative values of the peak and integrated absorbances by Cu (taken from Figure 46). Figure 12 shows that the temperature of the surface of the atomizer is 300 K lower for He and 40 K lower for N_2 than that measured with Ar as the sheath gas. Assuming that the sheath gases are equilibrated

Figure 45: Oscillogram showing the effect of internal purge gas (Ar) on the absorbance by 1.5×10^{-12} kg Cu in the HGA-2100; absorbance = 0.10/scale div., time = 500 ms/scale div. Trigger delay time = 500 ms.

- A) Internal purge gas interrupt mode.
- B) Internal purge gas flow rate = 1.0×10^{-3} $\text{dm}^3 \text{s}^{-1}$ (0.08 l min^{-1}).

Figure 46: Oscillogram showing the effect of various sheath gases on the absorbance by 1.5×10^{-12} kg Cu in the HGA-2100; (internal purge gas interrupt mode) absorbance = 0.10/scale div., time = 500 ms/scale div. Trigger delay time = 500 ms.

A) Ar B) N_2 C) He

External sheath gas flow rate = $1.7 \times 10^{-2} \text{ dm}^3 \cdot \text{s}^{-1}$.

Table 17

Relative Values of the Diffusion Coefficient of Cu in Various Sheath Gases and Relative Values of the Peak and Integrated Absorbance by Cu^a

Gas	^b $\sigma_{\text{gas}}/\text{nm}$	^c $D_{1,2}$	^d $T_{\tau_{\text{peak}}}/\text{K}$	^e $D_{1,2}T_{\tau_{\text{peak}}}^{1.5}$	A_p	$\int A_t dt$
He	0.200	3.63	2200	3.0	0.53	0.48
N ₂	0.316	1.01	2460	1.0	0.88	0.86
Ar	0.286	1.00	2500	1.0	1.00	1.00

^aTaken from the results shown in Figure 46.

^bDiameters of gas molecules—(both monatomic and diatomic) taken from reference 49, p. 157.

^cCalculated from equation 1-20 with the assumption that $T_{\text{He}} = T_{\text{N}_2} = T_{\text{Ar}}$.
Atomic diameter for Cu = 0.254 nm (50).

^dTemperature of the HGA-2100 graphite tube surface at the peak of the Cu signal.

^eRelative diffusion coefficients corrected for temperature according to equation 1-20.

to the surface temperatures, and selecting τ_{peak} as a convenient, but arbitrary reference point, the relative diffusion coefficients were corrected, according to equation 1-20, for the surface temperature at the peak of the Cu signal. As with the CRA-63, the peak and integrated signals are highly dependent upon the diffusion medium. Although the temperature-corrected diffusion coefficients give a better approximation to the effect of various sheath gases on the signal, the results are still not quantitatively accounted for. The assumption that the temperature of the gaseous diffusion medium is equal to the surface temperature is only a rough approximation.

In addition to the effect of diffusion, chemical reaction of the sheath gas with the atomic vapour may occur at high temperature when N_2 is used. Figure 47 shows the effect of substitution of N_2 for Ar on the absorbance signal given by Al. The large decrease is not due to increased diffusional losses but to chemical reaction of the aluminium with nitrogen in the presence of graphite. The formation of AlCN (56) under such circumstances is very favourable. Despite the fact that the bond dissociation energy of Al-CN is comparable to that of Al-O, i.e., 485 kJ mol^{-1} (57), the degree of dissociation of AlCN is much lower because the partial pressure of CN molecules in the under-mentioned relation is much higher than that of atomic oxygen (which determines the extent of dissociation of AlO):

$$p_{\text{Al}}/p_{\text{AlCN}} = K_{\text{AlCN}}/p_{\text{CN}} \quad (1-24)$$

where p denotes the partial pressure of the species and K_{AlCN} is the equilibrium constant for the dissociation of AlCN. Atomization of

Figure 47: Oscilloscope showing absorbance by 1.5×10^{-12} kg Al in the HGA-2100;
absorbance = 0.10/scale div., time = 500 ms/scale div. Trigger delay
time = 500 ms.

A) Ar B) N₂

aluminium from tantalum- and tungsten-lined atomizers equalizes the sensitivities obtained in Ar and N_2 sheath gases (58). The large decrease in Al atomic absorption in the presence of N_2 is not observed with the CRA-63. This may be a consequence of its short length and open nature with the result that the partial pressure of CN generated within this tube is smaller than that in the HGA-2100. Additionally, the CRA-63 graphite tubes are coated with pyrolytic graphite (40,41) which is less reactive than regular graphite. The effect on the Al signal of the substitution of N_2 for Ar in the HGA-2100 is reduced by 25% when pyrolytic-graphite-coated tubes are used (Chapter 2).

A second feature of these Al signals is that, in contrast with those from the CRA-63, only one Al maximum is obtained in the absence of a H_2 diffusion flame. The formation of a second maximum in the CRA-63 is related to the fact that the surface is coated with pyrolytic graphite (cf. Chapter 2); only one maximum is obtained with uncoated tubes.

Absorption Pulse Characteristics

The pulse characterization times for each element, taken from its respective oscilloscopic trace, are presented in Table 18. The increased characterization times for Cd, Zn, Cu, Al, Sn, Mo and V in the HGA-2100 (compared to the CRA-63) are a consequence of a lower rate of heating and a decreased rate of loss of atomic vapour from this atomizer. This conclusion is supported by the pulse characterization temperatures presented in Table 19. Despite the increased appearance times, the corresponding temperatures for Mo and V are within 100 K

Table 18

Pulse Characterization Times with the HGA-2100^a

Element	τ_{appear}	τ_{peak}	τ_{end}	τ_{display}
Cd	190	410	1800	1600
Pb	440	640	2100	1660
Zn	510	740	2400	1920
Cu	630	1560	4800	4170
Co	780	1800	7600	6780
Fe	820	1780	7700	6880
Mg	820	1070	2550	3280
Mn	830	1400	3600	6670
Sn	850	1630	4500	3650
Ni	900	2130	6500	5600
Cr	960	1920	8200	7230
Ca	1100	2700	> 17000	> 16000
Al	1290	2050	7500	6210
Mo	1340	2400	> 17000	> 16000
V	1400	2450	> 17000	> 13600

^aAtomization program: dry, 60 W; ash, 220 W; atomize, 3150 W.

Ar sheath gas, internal purge gas interrupt mode.

Table 19

Pulse Characterization Temperatures with the HGA-2100

Element	Melting Point/K	Boiling Point/K	Characterization Temperatures/K		
			τ_{appear}	τ_{peak}	τ_{end}
Cd	594	1038	720	990	2510
Pb	601	2013	1040	1250	2710
Zn	693	1180	1160	1380	2850
Cu	1356	2848	1270	2300	3030
Co	2690	3143	1430	2510	3050
Fe	1808	3023	1500	2490	3050
Mg	922	1363	1500	1800	2900
Mn	1517	2235	1510	2160	3000
Sn	505	2543	1540	2370	3030
Ni	1728	3005	1610	2730	3050
Cr	2163	2755	1670	2590	3050
Ca	1112	1757	1845	2930	3050
Al	933	2740	2055	2690	3050
Mo	2890	4885	2100	2850	3050
V	2163	3653	2150	2870	3050

of those recorded with the CRA-63 and within 30 K for Cd, Zn, Cu, Al and Sn. Variations in the furnace heating rate change the characterization times but not the characterization temperatures. As with the CRA-63, the characterization times and temperatures are independent of the mass of analyte atomized. This is presented in Table 20, which shows the constancy of $\tau_{\text{appearance}}$ and τ_{peak} of Cu over a 16-fold change in the analyte mass.

There is no relationship between the appearance temperature of the element and its melting and boiling point. Table 19 indicates that, whereas relatively low temperatures are required for the atomization of low volatility elements such as Mo, V and Co, relatively high temperatures are required for some high volatility elements, e.g., Zn, Mg and Ca. The reason for this apparent anomaly is that the physicochemical properties of the elements do not reflect the physicochemical properties of the intermediate(s) in the sequence of steps leading to atom formation.

The atomization time for each element is presented in Table 21. The τ_1 values for Cd, Zn, Cu, Al, Sn, Mo and V are all greater than the respective values obtained with the CRA-63 (Table 9). There are two reasons for this. First, the rate of heating of the HGA-2100 at an atomization power of 3150 W is two-fold lower than that of the CRA-63 at an atomization power of 5300 W ($\gamma = 1.23 \text{ K ms}^{-1}$ versus 2.48 K ms^{-1}); consequently, the time taken for analyte evaporation is much longer with the HGA-2100 (cf. equation 1-23). Secondly, the time taken to attain the absorbance maximum with the HGA-2100 is subject to less influence from the rate of loss of atomic vapour,

Table 20

Effect of Analyte Mass on the Characteristics of the
Absorption Pulse of Cu with the HGA-2100^a

10 ¹² x Weight of Cu/kg	Characterization Times/ms			
	τ_{appear}	τ_{peak}	τ_1	τ_2
1.0	630	1610	980	1150
1.5	630	1610	980	1200
2.0	630	1560	930	1200
3.0	630	1560	930	1150
4.0	630	1560	930	1150
6.0	630	1560	930	1100
7.0	630	1560	930	1225
16.0	630	1560	930	1150

^aAtomization program: dry, 60 W; ash, 220 W; atomize, 3150 W.

Ar sheath gas, internal purge gas interrupt mode.

Table 21

Atomization Times with the HGA-2100^a

Element	τ_1 /ms
Cd	220
Pb	200
Zn	230
Cu	930
Co	1020
Fe	960
Mg	250
Mn	570
Sn	820
Ni	1230
Cr	960
Ca	1600
Al	760
Mo	1060
V	1050

^aAtomization program: dry, 60 W; ash, 220 W; atomize, 3150 W. Ar sheath gas, internal purge gas interrupt mode.

whereas with the CRA-63, the loss of atomic vapour is so rapid that this parameter has greater effect in determining the experimental τ_1 .

If the elements are divided into two groups on the basis of their mechanism of atom formation (cf. Chapter 5) and arranged in order of increasing τ_1 , one gets the following two sequences:

The first of the above series contains those elements which initially form atoms predominantly by vaporization of the metal; the second corresponds to those elements which initially form atoms predominantly by dissociation of an oxide. Except for the anomalous positions of Ni and Ca, both sequences parallel the order of increasing energy of atomization. The anomalously high τ_1 for Ca and Ni may be the result of extensive penetration of these elements into the pores of the graphite tube at high temperature and/or the possible formation of an involatile carbide.

Effect of Atomization Power on Absorbance Signals

The effect of the atomization power (rate of heating of the furnace) on the peak and integrated absorbance by Cd, Zn, Cu, Al and Sn is presented in Table 22. The atomization power and time were individually adjusted to maximize the peak and integrated absorbance. Mo and V are not included in this study because of incomplete atomization, even with maximum available atomization power. Unlike the CRA-63,

Table 22

Effect of Atomization Power on Peak and
Integrated Absorbance^a

Element	Power/W	A_p/A	$\int A_t dt/A \cdot s$
Cd	3150	0.144	0.066
	2580	0.155	0.091
	1800	0.171	0.137
	1320	0.142	0.178
	1000	0.108	0.195
	600	0.048	0.220
	460	0.022	0.198
Zn	3150	0.257	0.145
	2580	0.298	0.214
	1440	0.273	0.263
	830	0.141	0.332
	680	0.135	0.273
Cu	3150	0.220	0.430
	2800	0.215	0.450
	2370	0.140	0.420
Al	3150	0.236	0.436
	2580	0.196	0.380
	1950	0.040	0.186
Sn	3150	0.312	0.482
	2580	0.214	0.442
	1950	0.128	0.404

^aHGA-2100; Ar sheath gas, internal purge gas
interrupt mode.

the greatest sensitivity by the peak method for Cd and Zn is not obtained with the fastest rate of heating of the furnace. Cu is the only element for which the integrated absorbance remained constant as the atomization power was varied, until a lower limit was reached below which incomplete atomization occurred. The integrated absorbance for Cd and Zn showed a sharp increase as the atomization power was lowered.

The relationship of the peak absorbance and atomization time to atomization power is shown in Figures 48 and 49, respectively. Whereas there is an inverse, exponential relationship between the atomization time and power, in agreement with equations 1-19 and 1-23, no such relationship is observed with the peak absorbance. According to equation 1-9, the peak absorbance has an inverse exponential relationship with the τ_1/τ_2 ratio. The effect of variation of atomization power on the τ_1/τ_2 ratio is presented in Table 23. Except for Cd, for which the ratio decreases, the τ_1/τ_2 ratio increases for Zn, Cu, Al and Sn as the atomization power increases. It is evident from Tables 22 and 23 that in no case does the maximum peak absorbance occur at the minimum τ_1/τ_2 ratio, as predicted by equation 1-9. As with the CRA-63, the peak absorbance in the HGA-2100 is not determined solely by the rate of production of atoms. The absorbance-time characteristics of each pulse, as well as the variation of the peak and integrated absorbance with the atomization power, are more conveniently described in terms of the rates of production and loss of atomic vapour.

Figure 48: Effect of atomization power on the peak absorbance in the HGA-2100.

Figure 49: Effect of atomization power on τ_1 in the HGA-2100.

Δ Cu $\circ$ Sn $\blacktriangle$ Al $\square$ Zn $\bullet$ Cd

Table 23

Effect of Atomization Power on τ_1/τ_2 Ratio with the HGA-2100

Element	Power/W	τ_1 /ms	τ_2 /ms	τ_1/τ_2
Cd	3150	220	220	1.00
	2580	240	260	0.92
	2200	270	270	1.00
	1800	320	310	1.03
	1440	390	360	1.08
Zn	3150	230	260	0.89
	2580	250	280	0.89
	2200	290	380	0.76
	1440	425	640	0.67
	1240	500	880	0.57
Cu	3150	930	1140	0.82
	2580	1060	1360	0.78
	2200	1190	1520	0.78
Al	3150	760	1180	0.65
	2580	1010	1690	0.60
	2200	1470	3420	0.43
Sn	3150	820	700	1.17
	2580	1190	1110	1.08
	2200	1450	1360	1.07

Residence Time and Sensitivity

The residence times for Cd, Zn, Cu, Al, Sn, Mo and V, under optimum atomization conditions for both the peak and integration methods of measurement, are presented in Table 24. Compared with the CRA-63, residence times with the HGA-2100 are greater by factors ranging from 3 to 18. The large increases are a result of an increased path length for diffusion, decreased convective losses and a large thermal gradient within the furnace. Non-uniform heating of the furnace allows the atomic vapour, produced from analyte evaporation in the hot, central zone, to diffuse outward and condense at the cooler extremities. With continued heating, the hot zone spreads outward, reevaporating the condensate. Although there is not much of a problem with the high volatility elements, an extensive broad tail develops in the absorbance pulses of low volatility elements. Such an effect is dependent on the physical characteristics of the individual element. This relationship is more evident from Table 25, which shows the residence times for 15 elements, each obtained with the same atomization program. The τ_2 values are randomly ordered with respect to the atomic weights of the elements. This is a consequence of the temporal and spatial non-isothermality of the furnace, the unique temperature-dependence of the signal for each element and the fact that the method of evaluation of τ_2 is questionable because of the assumption that atomization is complete at the absorbance maximum. When the elements are arranged in increasing order with respect to τ_2 , one obtains the following sequence:

Table 24

Optimum Residence Times with the HGA-2100

Element	Power/W	τ_2 /ms
Cd (peak)	1800	310
Cd (int)	560	1000
Zn (peak)	2580	280
Zn (int)	830	1100
Cu	3150	1140
Al	3150	1180
Sn	3150	700
Mo	3150	8300
V	3150	3600

Table 25

Residence Times with the HGA-2100^a

Element	τ_2 /ms
Cd	220
Pb	240
Zn	260
Cu	1140
Co	2180
Fe	1600
Mg	740
Mn	750
Sn	700
Ni	2430
Cr	1880
Ca	6300
Al	1180
Mo	8300
V	3600

^aAtomization program: dry, 60 W; ash, 220 W;
atomize, 3150 W.

$\text{Cd} \leq \text{Pb} \leq \text{Zn} \ll \text{Sn} \leq \text{Mg} \leq \text{Mn} < \text{Al} \leq \text{Cu} < \text{Fe} < \text{Cr} < \text{Co} < \text{Ni} \ll \text{V} < \text{Ca} < \text{Mo}$

The elements can be separated into three groups (Cd to Zn; Sn to Ni; V to Mo), which are characterized by a smooth variation in τ_2 values within each group and large variation in τ_2 values between the groups. The first three elements are highly volatile and unreactive toward graphite. The second group includes a number of elements which have an increasing tendency toward reaction with incandescent graphite. The last three elements are highly reactive toward graphite.

Table 26 presents the absolute sensitivities obtained for Cd, Zn, Cu, Al, Sn, Mo and V by both methods of measurement. In contrast to the results obtained with the CRA-63, the sensitivity by the peak method of recording is approximately the same for both the oscilloscopic and pen-recorded methods of measurement. This is the consequence of the lower rate of heating of the HGA-2100, producing comparatively broad, slowly-rising absorbance signals. Compared to the peak method of measurement, integration yields superior sensitivities for Cu, Al, Sn, Mo and V and similar sensitivities for Cd and Zn. Improved integrated sensitivities with the HGA-2100 are the result of increased residence times (generally greater than 1 s). Maximum advantage with the integration method of measurement occurs with the relatively involatile elements (eg. Mo and V) for which the signal display time is greatest and the pulse height small.

Comparison of Tables 13 and 26 indicates that peak height sensitivities are higher with the CRA-63 (with the modified power supply), whereas the HGA-2100 generally gives superior sensitivities with the integration method of measurement. Absorbance is proportional

Table 26

^aAbsolute Sensitivity/kg

Element	Method of Measurement		
	Peak (oscilloscope)	Peak (recorder)	Integration
Cd	3.5×10^{-16}	4.0×10^{-16}	4.2×10^{-16}
Zn	2.6×10^{-16}	3.0×10^{-16}	3.7×10^{-16}
Cu	2.1×10^{-14}	2.1×10^{-14}	1.1×10^{-14}
Al	1.7×10^{-14}	1.9×10^{-14}	1.1×10^{-14}
Sn	2.9×10^{-14}	3.3×10^{-14}	1.9×10^{-14}
Mo	8.8×10^{-14}	8.8×10^{-14}	9.1×10^{-15}
V	4.0×10^{-13}	4.0×10^{-13}	5.2×10^{-14}

^aDefined as the slope of the calibration curve, i.e., the mass of element which gives a peak absorbance of 0.0044 or an integrated absorbance of 0.0044 absorbance x second.

not to the total number of atoms present within the furnace, but to the effective length of the absorbing volume $\int_0^1 N(x)dx$ (analogous to the Beer Lambert law) where $N(x)$ is the concentration of atoms at point x in an absorbing volume of total length l . If it is assumed that the atoms are uniformly distributed over the cross-section, S , of the furnace, the total number of atoms in the furnace at any time t is given by:

$$N_t = S \int_0^1 N_t(x) dx \quad (1-25)$$

The effective length of the absorbing volume along the furnace axis is therefore:

$$\int_0^1 N_t(x) dx = N_t / S \quad (1-26)$$

Under the assumption that $\tau_1/\tau_2 \ll 1$, the number of atoms in the furnace at the peak of the absorbance pulse is given by equation 1-14, i.e.,

$$N_{\text{peak}} = N_0 \quad (1-14)$$

Substituting equation 1-14 into 1-26 one gets the effective length of the absorbing volume at the peak of the absorbance pulse:

$$\left(\int_0^1 N_t(x) dx \right)_{\text{peak}} = \frac{N_{\text{peak}}}{S} = \frac{N_0}{S} \quad (1-27)$$

The integral value of the number of atoms is dependent only on τ_2 , as given by equation 1-16:

$$Q_N = \int_0^\infty N_t dt = N_0 \tau_2 \quad (1-16)$$

The integral value of the effective length of the absorbing volume can be obtained by substituting equation 1-16 into 1-26:

$$Q_{N1} = \int_0^{\infty} dt \int_0^l N_t(x) dx = \frac{\tau_2}{S} N_0 \quad (1-28)$$

The residence time of atoms within the analytical volume is dependent on the rate of loss of atoms. If the atomic vapour is lost only by diffusion, the rate of diffusion can be assessed from equation 1-29 (11, p. 204):

$$dM/dt = -D(dp/dx)S \quad (1-29)$$

where dM/dt is the rate of diffusion by mass, dp/dx is the density gradient in the direction of diffusion, D is the diffusion coefficient and S is the cross-sectional area of a (imaginary) plane across which diffusion occurs. Assuming that the atomic vapour is lost through diffusion to the extremities of the furnace where it condenses, and that the density of the atomic vapour falls linearly from the value of ρ at the centre of the furnace, where the sample is atomized, to zero where it is lost, a distance l away, one can derive the following equation:

$$\frac{dp}{dx} = \frac{\rho}{1/2} = \frac{M}{(1/2)(V/2)} = \frac{4M}{Sl^2} \quad (1-30)$$

Substituting equation 1-30 into 1-29 and integrating (allowing for diffusion of vapour from the centre to both sides) yields:

$$M_t = M_0 \exp(-8Dt/l^2) \quad (1-31)$$

where M_0 is the mass of the vapour at the initial instant of time.

The mean time spent by atoms in the analytical volume may be calculated

from equation 1-31:

$$\tau_2 = l^2/8D \quad (1-32)$$

Substitution of equation 1-32 into 1-28 gives the integral value of the effective length of the absorbing volume:

$$Q_{N1} = (l^2/8DS)N_0 \quad (1-33)$$

For comparison of the performance of different atomizers, the ratio of the effective length of the absorbing volume to the total number of atoms of an element is important. With the peak method of measurement, one gets:

$$\left(\int_0^1 N_t(x) dx \right)_{\text{peak}} / N_0 \approx \frac{1}{S} \quad (1-34)$$

and for the integration method of measurement, one gets:

$$Q_{N1}/N_0 = l^2/8DS \quad (1-35)$$

The differences in sensitivity in the peak and integration methods of measurement for the two electrothermal atomizers used in this study may be compared by using equations 1-34 and 1-35 (56). Table 27 gives the values of the atomizer parameters for the CRA-63 and the HGA-2100. A diffusion coefficient of $5 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$ has been selected as a reasonable value in an Ar atmosphere at 2000 K (11, p. 288). It is evident from Table 27 that, whereas the HGA-2100 offers a 2.5-fold theoretical increase in the integration method of measurement over that given by the CRA-63, the peak height method of measurement with the CRA-63 offers a 4-fold theoretical increase over that given by the HGA-2100. The above

Table 27

Characteristic Atomizer Parameters^a

Parameters	HGA-2100 ^b	CRA-63 ^c	HGA/CRA Ratio
τ_2/s	0.20	0.02	not applicable
S^{-1}/m^{-2}	3.5×10^4	1.4×10^5	4.0
$Q_{N_1}N_O^{-1}/m^{-2}s$	6.9×10^3	2.8×10^3	2.5

^aCalculated from equations 1-32 and 1-35.

^b $l = 0.028$ m, $d = 0.006$ m, $D = 5 \times 10^{-4} m^2 s^{-1}$.

^c $l = 0.009$ m, $d = 0.003$ m, $D = 5 \times 10^{-4} m^2 s^{-1}$.

calculation has been made without considering the dependence of N_{peak} on the actual τ_1/τ_2 ratio. These theoretical estimates may be compared with the experimental results for the sensitivities determined for Cd, Zn and Sn using both atomizers. Table 28 shows that, on the average, the difference in sensitivity between the atomizers is 3.3-fold in favour of the CRA-63 for the peak absorbance measurements (versus a theoretical estimate of 4) and 1.7-fold in favour of the HGA-2100 for measurements of the integrated absorbance (versus a theoretical estimate of 2.5).

Agreement between theoretical and experimental values for other medium and low volatility elements is poor because of the non-isothermality of the HGA-2100 furnace along its length as compared to the uniformly heated CRA-63. This is evident from the data given in Table 29. With high volatility elements, this problem is not severe, since with constant heating, the subsequent temperature increases at the extremities of the furnace reevaporate the condensate into the analytical volume. With low volatility elements, the final temperature of the furnace extremities is not sufficient for rapid reevaporation of the condensate. As a result, the effective residence time of atoms in the furnace is decreased, i.e., the characteristic value of l for the HGA-2100 (equation 1-32) is not the geometric length of the furnace but the length of the hot working zone of the furnace.

Limit of Detection

Detection limits for Cd, Zn, Cu, Al, Sn, Mo and V are given

Table 28

Experimental

Sensitivity Ratios between the HGA-2100 and CRA-63

Element	Peak Method/kg		HGA/CRA Ratio	Integration Method/kg		HGA/CRA Ratio
	HGA	CRA		HGA	CRA	
Cd	3.5×10^{-16}	9.5×10^{-17}	3.7	4.2×10^{-16}	5.2×10^{-16}	0.81
Zn	2.6×10^{-16}	8.4×10^{-17}	3.1	3.7×10^{-16}	6.3×10^{-16}	0.59
Sn	2.9×10^{-14}	9.1×10^{-15}	3.2	1.9×10^{-14}	4.8×10^{-14}	0.40

Table 29

Experimental Sensitivity Ratios between the
HGA-2100 and CRA-63

Element	Peak Method/kg		HGA/CRA Ratio	Integration Method/kg		HGA/CRA Ratio
	HGA	CRA		HGA	CRA	
Cu	2.1×10^{-14}	2.7×10^{-15}	7.8	1.1×10^{-14}	6.7×10^{-15}	1.6
Al	1.7×10^{-14}	1.3×10^{-14}	1.3	1.1×10^{-14}	4.8×10^{-14}	0.23
Mo	8.8×10^{-14}	7.5×10^{-15}	12	9.1×10^{-15}	7.7×10^{-15}	1.2
V	4.0×10^{-13}	3.1×10^{-14}	13	5.2×10^{-14}	5.5×10^{-14}	0.95

in Table 30. The measurement conditions have been reported earlier in connection with the CRA-63. Both methods of measurement yield comparable detection limits.

Analytical Calibration Curves

The linear dynamic range of the calibration curves by both methods of measurement is given in Table 31. Little gain is obtained with the integration method of measurement because the signals obtained with slow heating of the furnace can be faithfully recorded with the strip-chart recorder. Figure 50 presents typical calibration curves of Cu by both methods of measurement.

Precision

The precision of replicate determinations for Cd, Zn, Cu, Al, Sn, Mo and V is given in Table 32. The values listed for the integration method of measurement were obtained by measuring the absorbance signal over its entire duration. No significant difference in precision between the two methods of measurement is observed.

Summary

The advantages of the integration method of measurement predicted by the theory have not been realized with commercial electrothermal atomizers. The reason for this is that these atomizers do not meet the requirements of correct use of the integration method mainly because of the temporal and spatial non-isothermality of the graphite tube. Commercial

Table 30

Limit of Detection^a

Element	Peak/kg	Integration/kg
Cd	4.5×10^{-16}	5.6×10^{-16}
Zn	4.1×10^{-15}	2.9×10^{-15}
Cu	2.1×10^{-14}	3.0×10^{-14}
Al	3.9×10^{-14}	4.7×10^{-14}
Sn	3.6×10^{-14}	3.0×10^{-14}
Mo	3.6×10^{-13}	3.2×10^{-13}
V	5.4×10^{-13}	5.1×10^{-13}

^aDefined as the mass of the element that gives a signal equal to three times the standard deviation of 10 replicate measurements with the same solution containing a low concentration of the element.

Table 31

Upper Limit for Linear Calibration Curves^a

Element	Peak/kg	Integration/kg	$\int A_t dt / A_p$
Cd	5.0×10^{-14}	5.0×10^{-14}	1.0
Zn	5.0×10^{-14}	1.0×10^{-13}	2.0
Cu	3.5×10^{-12}	5.0×10^{-12}	1.4
Al	7.5×10^{-13}	1.0×10^{-12}	1.3
Sn	2.0×10^{-12}	2.0×10^{-12}	1.0
Mo	1.0×10^{-11}	1.0×10^{-11}	1.0
V	4.0×10^{-11}	4.0×10^{-11}	1.0

^aDefined as the range in absolute mass of the element from the limit of detection to the upper mass limit where a 5% deviation from linearity occurs.

Figure 50: Calibration curves for Cu in the HGA-2100.

○ peak absorbance ● integrated absorbance

Table 32

Precision^a

Element	Peak	Integration
Cd	3.1	4.3
Zn	3.2	1.6
Cu	2.6	2.6
Al	2.0	2.3
Sn	3.5	2.5
Mo	4.1	2.7
V	3.6	3.2

^aExpressed as a percentage relative standard deviation of 10 replicate measurements made with the same solution of the element.

atomizers serve both to thermally produce the atomic vapour and to contain it; the continuous rise in temperature over the duration of the absorption pulse and the inseparability of the rate of heating and the maximum temperature attained by these devices allow no control to be maintained over the residence time of the atomic vapour as atomization conditions are varied. Consequently, the integration method of measurement becomes dependent on the kinetics of atomization. Additionally, because of their open nature and hence, short residence times, the sensitivity of the integration method of measurement is not greatly increased over that given by the peak height method.

L'vov's mathematical model developed for electrothermal atomizers makes it possible to quantitatively interpret some of the observed differences in the sensitivity between the two methods of measurement. Although quantitative interpretation of pulse shapes was not realized, the concept of an atomization time and a residence time is useful for the purposes of both characterizing the absorption pulses and semi-quantitatively accounting for the physicochemical factors which influence them. For this reason, these concepts will be used throughout the remainder of this thesis.

Comparison of the results from the CRA-63 and the HGA-2100 point to a number of factors which are instrumental in determining the peak and integrated sensitivities: the atomizer geometry, its rate of heating, the temporal and spatial non-isothermality of the atomizer, and the physicochemical properties of its surface. It is this latter factor which will be examined in greater detail in Chapter 2. As the rate of heating of the atomizer is decreased, the surface properties

of the graphite assume greater importance. This is particularly evident with the more difficult-to-volatilize elements, some of which may form refractory carbides. Differences in the surface porosity and reactivity of the atomizer can also influence the atomization characteristics of some elements.

Chapter 2

Surface Effects in Graphite Furnace Atomic Absorption Spectrometry

The physical characteristics of the surface of a graphite tube can influence both the kinetics of atomization (hence, the sensitivity of a determination) and the principal mechanism of atom formation. Whereas the CRA-63 tubes are manufactured from high density spectrographic grade graphite and subsequently coated with a layer of pyrolytic graphite (40, 41), those for the HGA-2100 have no pyrolytic graphite coating.

L'vov (11) has advocated the use of pyrolytic graphite for the construction of electrothermal atomizers on the grounds of its low permeability to gases, low porosity, high purity, a higher sublimation point (3970 K) than standard graphite, a high resistance to oxidation and a high thermal conductivity. Atomizers constructed of pyrolytic graphite should offer the advantages of improved confinement of vapour, decreased penetration of the analyte into the pores of the graphite surface, increased lifetime and uniform heating. As a result, an improvement in sensitivity, detection limit and precision in graphite furnace atomic absorption spectrometry may be expected when pyrolytic graphite is substituted for conventional graphite. Atomizers made of standard graphite and coated with a layer of pyrolytic graphite can also be expected to provide such improvements (11, 59, 60).

Despite the number of advantages offered by pyrolytic graphite, many instrument manufacturers have failed to make use of this material for the construction of atomizers. Recently, however, The Perkin-Elmer Corp. described and evaluated a technique for coating HGA-2100 tubes with pyrolytic graphite by an in situ pyrolysis of a mixture of 10% methane - 90% nitrogen (14).

This study was undertaken to evaluate the effects of a coating of pyrolytic graphite over spectrographic graphite on the atomization and analytical characteristics of the absorbance signals produced in a HGA-2100 furnace.

EXPERIMENTAL

Apparatus. Pyrolytic-graphite-coated tubes (0.001 in. thick coating of PT-101 pyrolytic graphite) were supplied by Ultra Carbon Corporation (Bay City, Michigan, U.S.A.). Conventional tubes, obtained from The Perkin-Elmer Corporation, were subsequently coated with pyrolytic graphite by Ultra Carbon Corporation. Additionally, a number of tubes coated with pyrolytic graphite according to the procedure described by Manning and Ediger (14), were supplied by the The Perkin-Elmer Corporation. All other instrumentation has been described in Chapter 1.

Electron micrographs were obtained with a JEOL model JSM-U3 Scanning Electron Microscope.

Reagents. Reagents and sheath gases have been given in Chapter 1.

Procedure. Sample volumes of $5 \times 10^{-6} \text{ dm}^3$ were introduced into the HGA-2100 furnace with an Eppendorf syringe fitted with disposable plastic tips. The furnace was operated in the internal purge gas interrupt mode with Ar as the sheath gas. Lamp currents, wavelengths and spectral bandwidths used in this study have been presented in Chapter 1.

RESULTS AND DISCUSSION

The useful lifetime of a graphite tube is determined both by the conditions under which it is operated (i.e., steady-state temperature attained by the furnace as well as its duration) and the analyte element. In addition to determining the wavelength at which spectroscopic measurements are made and hence, the amount of scattering of the source radiation by carbon particles ejected from the incandescent graphite surface, the physicochemical properties of the analyte element are also important. This is particularly the case with the relatively involatile elements, some of which may also form refractory carbides. As the tube ages and becomes more porous, the penetration of the analyte into the graphite pores as well as carbide formation may be so extensive that the tube may suffer from memory effects, irreproducible atomization as well as scattering of the source radiation. Whereas the tube becomes useless for further analytical determinations of such an element, it may perform satisfactorily with other, more volatile elements. Consequently, it is difficult to present a definite figure regarding the lifetime of a particular tube. The useful lifetime of the graphite tube is, however, greatly

extended if the tube is coated with pyrolytic graphite. More than 100 atomization cycles at ~ 3000 K maintained for a period of 10 seconds (for the atomization of Mo and V) with an Ultra Carbon coated tube, failed to produce as much visible wear (powdery surfaces) or scattering of the source radiation as 20 such cycles with an uncoated tube.

To accurately compare the performances of coated and uncoated tubes, their electrical characteristics were considered. With the contact tension between the furnace tube and the cones set to an arbitrary value, the measured resistance of the furnace assembly was $29\text{ m}\Omega$ for the pyrolytic-graphite-coated tubes processed by Ultra Carbon Corporation, $22\text{ m}\Omega$ for the uncoated tubes and $20\text{ m}\Omega$ for those pyrolytic-graphite-coated tubes prepared in situ. All subsequent measurements were made with a furnace assembly resistance of $22\text{ m}\Omega$ (contact tension was increased when the Ultra Carbon coated tubes were used in order to reduce the furnace resistance from $29\text{ m}\Omega$ to the above value; similarly, the tension was reduced for the Perkin-Elmer coated tubes). Under such conditions, the power delivered to the atomizer and hence, its rate of heating, will be determined solely by the physical and electrical characteristics of the tubes. In both cases, the pyrolytic-graphite-coated tubes showed lower rates of heating than the uncoated tubes. Figure 51 shows the temperature-time profiles of the atomizer surface for an uncoated (A) and an Ultra Carbon Corporation coated tube (B) at an atomization setting of 2700°C . The heating characteristics of the coated tubes supplied by The Perkin-Elmer Corporation were intermediate between curves A and B.

Figure 51: Temperature-time characteristics of the interior surface of the HGA-2100 at a power supply setting of 2700 C.

A) uncoated tube

B) pyrolytic-graphite-coated tube

The power delivered to the atomizer is related to the resistance of the heating element, R , and the current drawn, I , by

$$P = I^2 R \quad (2-1)$$

The resistivity of pyrolytic graphite is greater than that of regular, high-purity graphite (61, p. 98). The decreased resistance of the Perkin-Elmer coated tubes may be explained by considering that the low resistance graphite tube and its interior "jacket" of high resistance pyrolytic graphite form a parallel electrical circuit of two resistors, the net resistance being lower than that of an uncoated tube. The tube from Ultra Carbon Corporation has a layer of high-resistance pyrolytic graphite deposited over both the length of the tube and the ends which make electrical contact with the cones. The anisotropy ratio of specific resistance (c-axis/a-axis) is about 10^4 in pyrolytic graphite obtained by cracking CH_4 on a heated carbon surface at 2400 K (61, p. 98). Because of the orientation of the planes of graphite in the pyrolytic coating, parallel to the longitudinal axis of the tube, the current flow is perpendicular to these planes at the surface in contact with the cones; hence, the resistance of the furnace circuit is higher. Because of its lower resistance, the Perkin-Elmer coated tube is expected to heat up less rapidly than an uncoated tube and this has been experimentally observed. In contrast to the predictions of equation 2-1, however, the high-resistance coated tube from Ultra Carbon Corporation heats up at the slowest rate. Whereas the masses of the coated and uncoated tubes from The Perkin-Elmer Corporation are roughly the same, that of the Ultra Carbon tube is $\approx 25\%$ greater. The result is a larger heat capacity which decreases the rate of

heating of these tubes (cf. equation 1-19). Since the lower rate of heating of the graphite tube reduces the peak absorbance values, (8 - 10), pyrolytic-graphite-coated tubes may be a drawback in the peak absorbance method. Data on the performance of coated tubes reported throughout the remainder of this chapter refer exclusively to those obtained directly from Ultra Carbon Corporation. The performance characteristics of the Perkin-Elmer coated tubes agree with those reported by Manning and Ediger (14).

Absorption Pulse Characteristics

The effect of the atomization temperature on the peak and integrated absorbance is presented in Table 33. The influence of the rate of heating of the furnace on the signals is identical to that observed when uncoated tubes are used. These effects, which have been explained on the basis of the kinetics of formation and loss of analyte atoms within the furnace, have been described in Chapter 1.

Atomization of Mo and V is greatly improved with pyrolytic-graphite-coated tubes. These elements can be completely atomized at heating rates as low as 0.77 K ms^{-1} and 0.63 K ms^{-1} , respectively. This is a significant improvement over uncoated tubes, in which heating rates below 1.2 K ms^{-1} result in incomplete atomization of these elements, and hence, "memory effects".

Aluminium shows a radical change in signal characteristics in coated tubes. Figures 52 and 42 are absorbance-time traces for the atomization of Al from a coated and an uncoated tube. Two peaks are obtained with the coated tube, corresponding to the sequential

Table 33

Effect of Atomization Temperature on Peak and
Integrated Absorbance

Element	^a Temperature Setting/C	$\gamma/K \text{ ms}^{-1}$	Absorbance	
			A_p/A	$\int A_t dt/A \cdot s$
Cd	2700	0.91	0.253	0.118
	2100	0.51	0.271	0.216
	1700	0.40	0.266	0.322
	1000	0.21	0.235	0.525
	800	0.17	0.192	0.484
Zn	2700	0.91	0.344	0.188
	2100	0.51	0.327	0.267
	1700	0.40	0.292	0.289
	1400	0.29	0.170	0.290
Cu	2700	0.91	0.262	0.173
	2500	0.77	0.225	0.174
	2100	0.51	0.092	0.128
Al	2700	0.91	0.260	0.175
	2500	0.77	0.175	0.107
Sn	2700	0.91	0.238	0.431
	2500	0.77	0.182	0.370
	2100	0.51	0.051	0.164
Mo	2700	0.91	0.320	0.462
	2500	0.77	0.125	0.446
V	2700	0.91	0.250	0.315
	2500	0.77	0.145	0.281
	2300	0.63	0.043	0.145

^aThe temperature setting has been shown in the centigrade scale in accordance with that on the meter scale of the power supply for the furnace.

Figure 52: Oscillogram showing absorbance by 7.5×10^{-13} kg Al in the HGA-2100 with a pyrolytic-graphite-coated tube; absorbance = 0.10/scale div., time = 500 ms/scale div. Trigger delay time = 800 ms (curve A), 700 ms (curve B).

A) N_2 sheath gas B) Ar sheath gas.

atomization of two distinct species of significantly different volatility. A possible explanation for this is given below. In its outermost layers, graphite can form lamellar compounds with water (61, p. 176). Recent work by Frech and Cedergren (62, 63) indicates that hydrogen is formed at high temperatures (~ 1000 K) by the reaction of graphite with surface-adsorbed water remaining in the graphite tube after the drying step. The amount of hydrogen produced by a regular graphite tube was found to be considerably larger than that produced by a tube coated with pyrolytic graphite. This is presumably due to differences in the adsorptive capacities of the two surfaces for water and their intrinsic reactivity. In the absence of a hydrogen diffusion flame, two distinct absorption peaks are obtained for Al with the CRA-63 (coated tube), whereas in the presence of a hydrogen diffusion flame, only a single peak occurs (compare Figures 19 and 24). This observation, as well as those made by Frech and Cedergren (62, 63) lead to the conclusion that the change in the atomization characteristics of aluminium in a pyrolytic-graphite-coated tube may be related to its inability to produce sufficient hydrogen. It is reasonable to postulate that the larger amount of hydrogen generated by an uncoated tube plays a role in the elimination of one of the aluminium peaks presumably by forming a different species as an intermediate in the atomization of aluminium.

Optimum atomization conditions and the corresponding pulse characterization times are presented in Table 34. The major difference between the two tubes is the decreased display times for Mo and V obtained with the uncoated tubes (compare Tables 18 and 34). This is a significant advantage in analysis as shorter atomization and integration

Table 34.

Pulse Characterization Times Under Optimum Conditions

Element	Atomization Conditions		Characterization Times/ms			
	Heating Rate/K ms ⁻¹	Time/s	$\tau_{\text{appearance}}$	τ_{peak}	τ_{end}	τ_{display}
Cd (peak)	0.51	3	300	620	1600	1300
Cd (int)	0.21	9	800	2050	7700	6900
Zn (peak)	0.91	3	700	1020	2050	1350
Zn (int)	0.40	4	600	1650	3300	2700
^a Cu	0.91	5	850	1510	4100	3250
^a Al	0.91	7	1750	2030	5500	3550
^a Sn	0.91	9	1100	2100	8000	6900
^a Mo	0.91	9	1800	2700	8000	6200
^a V	0.91	8	1850	2350	6500	4650

^aFor both the peak and the integration methods of measurement.

times become adequate for these elements. This aspect is particularly important when the long-term stability of the source is poor and in the absence of a double-beam system, when baseline drift is significant, thus limiting the precision and accuracy of the integrated absorbance measurements.

Pulse characterization temperatures are given in Table 35.

The appearance temperatures are, within experimental error, equal to those obtained when uncoated tubes are used.

Effect of Tube Surface Structure on Atomization

The extent and ease of atomization of Mo and V in coated tubes may be attributed to the low surface porosity of the pyrolytic graphite. Porosity is defined as the percentage by volume of the pores in relation to the total volume. The porosity of pyrolytic graphite is effectively zero, as compared to 17% for regular high-purity graphite (64).

Figures 53 and 54 are electron micrographs of the interior surfaces of unused pyrolytic-graphite-coated and uncoated tubes. The surface of the coated tube is much smoother and less porous than that of the uncoated tube. Its nodular appearance is a characteristic growth feature of the pyrolytic coating. This occurs as a result of surface imperfections in the substrate graphite and the possibility that supersaturation levels of carbon vapour cause gas-borne nuclei to form and grow during the coating process (65). Figures 55 and 56 are electron micrographs of the interior surfaces of both tubes after approximately 150 high-temperature atomization cycles. Little change

Table 35

Pulse Characterization Temperatures^a

Element	Melting Point/K	Boiling Point/K	Temperature/K		
			$\tau_{\text{appearance}}$	τ_{peak}	τ_{end}
Cd	594	1038	780	1070	1960
Zn	693	1180	1140	1430	2280
Cu	1356	2840	1280	1880	2920
Al	933	2740	2070	2270	3000
Sn	505	2543	1500	2310	3000
Mo	2890	4885	2100	2620	3000
V	2173	3653	2140	2460	3000

^aCorresponding to the surface temperatures of the furnace at a heating rate of 0.91 K ms^{-1} .

Figure 53: Electron micrograph of the interior surface of an unused pyrolytic-graphite-coated tube, x 500

Figure 54: Electron micrograph of the interior surface of an unused, uncoated tube, x 500

Figure 55: Electron micrograph of the interior surface of a used pyrolytic-graphite-coated tube (after ≈ 150 atomization cycles at 2700 C), x 500

Figure 56: Electron micrograph of the interior surface of a used, uncoated tube (after ≈ 30 atomization cycles at 2700 C), x 500.

is observed in the appearance of the coated tube (compare Figures 53 and 55), whereas there is significant alteration in the surface of the uncoated tube (compare Figures 54 and 56); its surface structure has developed a loose and extremely porous sponge-like appearance. Figures 57 and 58 show the fracture edge of the pyrolytic coating of a new and used tube. With the new tube (Figure 57) the coating is evenly bonded to the underlying graphite body of the tube. After extensive use (Figure 58) the coating shows signs of shrinkage and increased brittleness, causing poorer bonding to the body of the tube but at no point are breaks observed in the pyrolytic surface.

The higher surface porosity of uncoated tubes allows for increased penetration of the analyte into the pores at high atomization temperatures (40, 41, 66, 67). Once the analyte has penetrated into the pores of the graphite surface, atomization becomes more difficult and is accompanied by well-known memory effects (66). As the tube ages, these problems become progressively more acute (compare Figures 54 and 56). Atomization of relatively involatile elements is greatly facilitated in coated tubes. Not only may lower rates of heating be employed, but the time taken for complete atomization is also significantly reduced.

Residence Time

The residence time and atomization time, for each element in both tubes, are presented in Table 36. In each case, the reported values are those obtained under optimum conditions both for the peak and the integration methods of measurement. Although the decreased permeability

Figure 57: Electron micrograph of the fracture edge of an unused pyrolytic-graphite-coated tube, x 500

Figure 58: Electron micrograph of the fracture edge of a used pyrolytic-graphite-coated tube, x 500.

Table 36

Atomization Times, τ_1 , and Residence Times, τ_2

Element	Coated tube		Uncoated tube	
	τ_1 /ms	τ_2 /ms	τ_1 /ms	τ_2 /ms
Cd (peak)	320	580	320	310
Cd (int)	2100	1500	1600	1000
Zn (peak)	320	290	250	280
Zn (int)	1050	600	1450	1100
^a Cu	660	440	930	1140
^a Al	280	300	760	1180
^a Sn	1000	1000	820	700
^a Mo	900	850	1060	8300
^a V	500	1580	1050	3600

^aFor both the peak and the integration methods of measurement.

of the pyrolytic graphite should improve the confinement of atomic vapour, leading to residence times longer than those in uncoated tubes, residence times for most of the elements are in fact significantly shorter in the coated tubes. Since the tail of the absorption pulse, from which τ_2 is evaluated, may be influenced by the continued atomization of the analyte beyond the absorption maximum (as discussed in Chapter 1), the residence time is influenced by the atomization time of the analyte. This is particularly true with the more difficult-to-atomize elements. With the exception of Sn, all of the elements (in the peak absorbance method) have shorter atomization times in the coated tube despite its lower rate of heating. The lower τ_1 values, a consequence of the decreased penetration of the analyte into the pores of the graphite surface, serve also to decrease the measured residence times. With the coated tubes, there is less tendency for the atomization process to extend much beyond the absorbance maximum. Tessari and Torsi (67) have also found evidence for this effect. As the temperature increases, some analyte diffuses into the pores of the graphite tube; the direction of this diffusion is reversed with the depletion of the surface layer of the analyte.

Sensitivity

The absolute sensitivities, for both the peak and the integration methods of measurement, are presented in Table 37. Absolute sensitivities obtained with coated tubes are comparable to or better than those obtained with uncoated tubes (compare data given in Table 26). Increased peak height sensitivity given by coated tubes is a consequence of increased

Table 37

^aAbsolute Sensitivity/kg

Method of Measurement

Element	Peak (oscilloscope)	Peak (recorder)	Integration
Cd	5.4×10^{-16}	5.6×10^{-16}	3.3×10^{-16}
Zn	2.2×10^{-16}	2.9×10^{-16}	4.1×10^{-16}
Cu	8.7×10^{-15}	8.8×10^{-15}	1.1×10^{-14}
Al	1.1×10^{-14}	1.7×10^{-14}	2.7×10^{-14}
Sn	7.9×10^{-14}	8.5×10^{-14}	4.7×10^{-14}
Mo	1.1×10^{-14}	1.1×10^{-14}	6.3×10^{-15}
V	4.6×10^{-14}	5.0×10^{-14}	2.7×10^{-15}

^aDefined as the slope of the calibration curve, i.e., the mass of element which gives a peak absorbance of 0.0044 or an integrated absorbance of 0.0044 absorbance x second.

rates of atomization. However, maximum advantage in using coated tubes is realized only for involatile analytes. The sensitivity improvement in coated tubes is the result of an increase in the rate of atomization, not the fraction of analyte atoms converted to atomic vapour. This is supported by the observation that, while 8- and 9-fold enhancements in the peak height sensitivities are obtained for Mo and V, respectively, their integrated sensitivities increase by less than a factor of 2.

The decreased sensitivities listed for Sn are the result of a change in the hollow cathode lamp used with the coated tubes (necessitated by failure of the lamp used earlier for the study of the uncoated tubes). The new Sn hollow cathode gave much poorer spectral output and gave poorer sensitivity than the previous lamp.

Using a graphite furnace (Perkin-Elmer HGA-70) whose surface had been treated with such carbide-forming elements as Zr, La, Si, V, B, Mo and Ba, Runnels et al. (47) reported sensitivity enhancement factors ranging from 2.2 to 12.8 for difficult-to-volatilize elements. These authors (47) have attributed such increases to the formation of a coating of metal carbide on the surface of the tube; physical contact between the graphite and subsequent samples is prevented, precluding carbide formation by elements in the analysis of subsequent samples. The following is advanced as an alternative explanation for such behaviour. Carbide-forming metals, such as those listed above, are active catalysts for graphitization (68 - 70). Graphitization can decrease the reactivity of the graphite surface. During the pretreatment stage of the graphite tube a carbide is formed. The carbide penetrates the pores of the graphite surface dissolving the disordered carbon and precipitating

it as nonreactive, small graphite crystallites, without a significant change in the composition of the graphite. This process occurs very rapidly above 2000 K and with continued heat treatment, the precipitated graphite crystallites slowly grow in size. The carbide particles burrow through the surface of the tube wall, dissolving disordered carbon on the leading surface and depositing it as graphite at the trailing surface (71). The improved sensitivities obtained for difficult-to-volatilize elements using a carbide-treated tube (47) may, therefore, be the result of a more highly ordered graphite surface, similar in structure to the pyrolytic coating on the tubes used in this study.

Limit of Detection

The limit of detection for each element in a coated tube is given in Table 38. No significant improvement is realized with coated tubes.

Precision

Table 39 compares the precision of replicate determinations of the elements in the coated and uncoated tubes. A slight improvement with the integration method of measurement is indicated when coated tubes are used. The precision does not differ significantly between the two types of tube - this agrees with the conclusions of Manning and Ediger (14).

Table 38

Limit of Detection^a

Element	Peak/kg	Integration/kg
Cd	2.0×10^{-15}	8.7×10^{-16}
Zn	3.9×10^{-15}	2.7×10^{-15}
Cu	1.8×10^{-14}	2.7×10^{-14}
Al	8.6×10^{-14}	9.9×10^{-14}
Sn	2.9×10^{-13}	3.0×10^{-13}
Mo	1.0×10^{-13}	1.2×10^{-13}
V	4.4×10^{-13}	3.5×10^{-13}

^aDefined as the mass of the element that gives a signal equal to three times the standard deviation of 10 replicate measurements with the same solution containing a very low concentration of the element.

Table 39

Precision^a

Element	Coated Tube		Uncoated Tube	
	Peak	Integration	Peak	Integration
Cd.	3.1	1.1	3.1	4.3
Zn	3.4	3.0	3.2	1.6
Cu	3.6	2.0	2.6	2.6
Al	4.7	3.5	2.0	2.3
Sn	4.8	2.6	3.5	2.5
Mo	2.8	1.6	4.1	2.7
V	2.1	2.1	3.6	3.2

^aExpressed as a percentage relative standard deviation of 10 replicate measurements made with the same solution of the element.

Summary

The decreased surface porosity of the pyrolytic coating reduces the extent of penetration of the analyte into the surface of graphite tubes. This is particularly advantageous with the more difficult-to-atomize elements whose appearance temperatures are of the order of 2000 K. Coated tubes are useful for the determination of such elements because of their increased lifetime at high temperatures, increased sensitivity, shorter atomization times and relative freedom from memory effects. Since the pyrolytic graphite coating can be applied in situ and maintained in good condition by periodically recoating the tube, such coated tubes are extremely attractive because of their excellent cost-benefit ratio.

Chapter 3

The Temperature of Atomic Vapour in Graphite Furnace Atomic Absorption Spectrometry

In atomic absorption spectrometry it is frequently of interest to determine such parameters as the degree of dissociation of analytes, the extent of ionization of metal vapours, diffusion coefficients of atoms and thermochemical constants. As such, it is necessary to know the temperature of the atomic vapour under investigation. Additionally, such information is required in the study of mechanisms of metal atom formation (Chapter 5) and loss (Chapter 4) in graphite atomizers. Although several reports concerning the temperature of the graphite tube wall have been published (7, 10, 15, 37, 38, 72, 73) little has appeared concerning the excitation temperature of the atomic vapour within the atomizer.

In an exact sense, a temperature may only be defined for systems in thermodynamic equilibrium. In such a case, a unique value of the temperature is sufficient to describe:

1. The velocity distribution function of all the particles according to Maxwell's equation.
2. The population of the excited states according to Boltzmann's equation.
3. The distribution of molecules and their dissociation products according to the mass action law of Guldberg and Waage.

4. The distribution of atoms and their ionization products according to Saha's equation.

5. The distribution of the electromagnetic radiation field according to Planck's law.

When the various forms of energy are not equilibrated, it is still useful to measure the 'temperature' of a particular process, e.g., translational temperature, vibrational temperature, etc. The more closely the above temperatures coincide, the closer the approach to equilibrium and the more physical meaning the temperature of the system possesses.

Whereas there are a variety of methods available for determining flame temperatures (74), only a few spectroscopic techniques are conveniently adaptable to the measurement of transient signals generated by graphite furnace atomizers. For example, Massmann and Gucer (75), have succeeded in measuring the temperature of the vapour phase within a graphite furnace by observing the Boltzmann distribution of vibrational and rotational (emission) bands of C_2 and CN produced within the atomizer. Similarly, the metal vapour itself may be conveniently used as a spectroscopic thermometric species. L'vov et al. (76) measured the effective excitation temperature of an absorbing layer of Sn vapour in an isothermal graphite cuvette by a two-line atomic absorption method using a sharp-line source. Bratzel and Chakrabarti (77) also employed a two-line atomic absorption technique (78) using an uncalibrated continuum source to measure the excitation temperature of Ga and In vapour above a carbon filament atomizer and within a "mini-Massmann" atomizer. Ide et al. (79) measured the

excitation temperature of Pb vapour above both an electrically heated tantalum strip and a glassy carbon strip, also by a two-line absorption method.

Commercial graphite furnaces do not function as isothermal cuvettes because their temperature varies in an essentially parabolic manner with time (Chapter 1). Additionally, these furnaces are dynamic systems, the time-dependent atomic population being governed by the rate of introduction of atoms into and their rate of loss from the analytical volume. Any thermometric species employed for the spectroscopic measurement of vapour temperature is detected at its characteristic appearance temperature, increases to a maximum population and then decreases as the temperature of the atomizer continues to increase. Excitation temperatures reported for In in Ref. 77 and for Pb in Ref. 79 correspond only to the temperature measured by the peaks of the absorbance pulses and, therefore, may not represent the maximum temperatures achieved. Matoušek (80) and Adams and Kirkbright (81) have measured the temperature-time characteristics of the atomic vapour. Using a CRA-63, Matoušek (80) reported that the excitation temperature, measured with Ni as the thermometric species, was approximately 300 K in excess of that of the surface of the graphite tube over most of the duration of the signal. Adams and Kirkbright (81) reported that the excitation temperature of In within a HGA-2000 increased as the atom population increased, attained a maximum at the signal maximum and thereafter decreased as the signal decayed. None of the above studies provide any detailed consideration of the mechanism of heat transfer to or

from the atomic vapour. This research was undertaken to establish the relationship between the temperature-time characteristics of the graphite wall and the excitation temperature-time characteristics of the atomic vapour produced within the HGA-2100 and the CRA-63.

Ionization of analytes in the HGA-2100 was also investigated, for although it has long been recognized and suitably treated in flame AAS (82, 83), the question of whether or not ionization occurs in electrothermal atomizers has not been resolved.

THEORY

Measurement of Vapour Temperature

The optical two-line method for measuring the excitation temperature of a vapour depends on the relative population of two different energy levels of a thermometric species. The absorption variant of this commonly used emission method is based on the measurement of atomic absorption by two lines of the same element corresponding to transitions from different lower sublevels.

There are two methods for measuring the excitation temperature of the atomic vapour by the two-line absorption method (76, 78), depending on the nature of the thermometric species employed, i.e., the presence or absence of developed hyperfine splitting (hfs) in the absorption profile of the atomic line. For those elements having appropriate pairs of lines for which hfs is either negligible or absent altogether, it is convenient to measure the sharp-line absorbance by the element with a hollow cathode lamp (76). In those cases where hfs is well

developed, it is more convenient to measure the relative absorption of the radiation from a continuum source by the thermometric species (78).

Case 1

When a hollow cathode lamp or other sharp-line source is used to measure the relative population of two atomic energy levels, L'vov et al. (76, 84, 85) have shown that the effective excitation temperature governing the atomic population ratio is given by the expression:

$$T_{\text{eff}} = \frac{E_2 - E_1}{2.303 k \log \left[\frac{A_1 \Delta\nu_{D_1} g_2 f_2 H_2(a, 0.725a)}{A_2 \Delta\nu_{D_2} g_1 f_1 H_1(a, 0.725a)} \right]} \quad (3-1)$$

where E_1 and E_2 are respectively the electronic energies of the lower and upper sublevels from which the transitions arise; k is Boltzmann's constant; A_1 and A_2 are the measured sharp-line absorbances; $\Delta\nu_{D_1}$ and $\Delta\nu_{D_2}$ are the Doppler half-widths of the absorption line profiles; $g_2 f_2$ and $g_1 f_1$ the products of the degeneracy (statistical weight) and oscillator strength for each transition, and $H_1(a, 0.725a)$ and $H_2(a, 0.725a)$ are the Voigt integrals, which are convolution integrals of the Doppler and Lorentz broadened absorption line profiles of each line (84, 86). The damping parameter, a , is defined by Equation 3-2:

$$a = \frac{\Delta\nu_N + \Delta\nu_L}{\Delta\nu_D} \sqrt{\ln 2} \quad (3-2)$$

where $\Delta\nu_N$ and $\Delta\nu_L$ are the natural and Lorentz half-widths of the atomic line, respectively. Because natural broadening is relatively insignificant, the damping parameter is effectively proportional to the ratio of the Lorentz-to-Doppler half-widths. The excitation temperature is dependent upon the wavelengths of the two transitions because of the influence of the Doppler half-widths and the line profiles. Doppler half-width is inversely proportional to wavelength, whereas Lorentz half-width is independent of wavelength. As a result, the damping parameter, a , is proportional to wavelength (86). The dependence of the Voigt integral on the damping parameter is shown graphically in Figure 59 (87). The slope of the curve varies continuously from zero at small values of a to 1 as $a \rightarrow \infty$. The entire range of a can be roughly divided into three regions in which the $H(a, 0.725a)$ curve can be approximated by linear segments with slopes 0.0, 0.5 and 1.0 (76), i.e.,

$$H(a, 0.725a) = \text{constant}, \quad 0 < a \leq 0.2$$

$$H(a, 0.725a) \propto 1/\sqrt{a}, \quad 0.2 \leq a \leq 0.8$$

$$H(a, 0.725a) \propto 1/a, \quad 0.8 \leq a < \infty$$

Accounting for the above relationships with respect to equation 3-1 one gets:

$$T_{\text{eff}} = \frac{E_2 - E_1}{2.303 k \log \left[\frac{A_1 g_2 f_2}{A_2 g_1 f_1} \right] + 2.303 k \log r(\lambda)} \quad (3-3)$$

where the function $r(\lambda)$ is given below:

Figure 59: Logarithm of the Voigt integral as a function of $\log a$.

$$\begin{aligned}
 r(\lambda) &= \lambda_2/\lambda_1 & 0 < a \leq 0.2 \\
 r(\lambda) &= \sqrt{\lambda_2/\lambda_1} & 0.2 \leq a \leq 0.8 \\
 r(\lambda) &= 1 & 0.8 \leq a < \infty
 \end{aligned}$$

In principle, vapour temperature measurements can be made with any element having electronic energy levels sufficiently close ($< 2 \times 10^{-19}$ J, i.e., $< 10,000 \text{ cm}^{-1}$) to its ground level to provide an appreciable excited state population. In practice, however, there are a number of limitations imposed by the measurement system itself. With constant concentration of the analyte, the error in the absorbance measurement will be higher for the spectral transition arising from the less populated energy level; therefore, the determination of the vapour temperature should be made with line pairs in which the transition arising from the higher energy level has the higher g_f factor (to equalize the sensitivity of the two lines). The element selected must provide adequate atomic absorption sensitivity; the two lines selected must be as close as possible so that the difference in their wavelengths does not require compensation for varying response of the photomultiplier tube to different spectral regions, and to avoid adjustments in the external optical system arising from the wavelength dependence of the focal length of the lenses; reliable values for the oscillator strengths must be available for the two lines, and the lines must be devoid of developed hfs. This latter factor rules out the use of In and Ga as thermometric species.

Case 2

If an atomic line source were used for In or Ga, the exact

profiles for both the source emission line and the atomic absorption line would be required. Since this information is generally not available, a continuum emission source is used, in which case the measured relative absorption is independent of the absorption line profile, and hence, the presence or absence of hfs in the selected lines (88, 89).

Browner and Winefordner (78) have described a two-line atomic absorption method for the measurement of flame temperature which may also be applied to electrothermal atomizers. By measuring the relative absorption, α (the ratio of the absorbed to incident light intensity, i.e., $(I_0 - I)/I_0$), from a continuum source for two atomic spectral lines originating from different lower sublevels of the same element, these authors (78) have shown that the effective temperature, measured at low optical densities, ($\alpha < 0.03$) is given by:

$$T_{\text{eff}} = \frac{E_2 - E_1}{2.303 k \log \left[\frac{g_2 f_2 \left(\frac{\lambda_2}{\lambda_1} \right)^2 \frac{\alpha_1}{\alpha_2}}{g_1 f_1} \right]} \quad (3-4)$$

and at high optical densities by:

$$T_{\text{eff}} = \frac{E_2 - E_1}{2.303 k \log \left[\frac{g_2 f_2 \left(\frac{\lambda_2}{\lambda_1} \right)^2 \left(\frac{\alpha_1}{\alpha_2} \right)^2 \frac{\Delta\lambda_{L_2}}{\Delta\lambda_{L_1}}}{g_1 f_1} \right]} \quad (3-5)$$

where λ_1 and λ_2 are the wavelengths of the two transitions and $\Delta\lambda_{L_1}/\Delta\lambda_{L_2}$ is the ratio of the Lorentz half-width of the two absorption

lines.

In the low optical density region measurements are restricted to $\alpha < 0.03$, which can result in systematic and random errors of up to $\pm 10\%$ in the measurement of T_{eff} (78). In order to determine the temperature by the measurement of α at high optical densities, it is necessary to know the ratio $(\Delta\lambda_{L_2}/\Delta\lambda_{L_1})$. It has been shown (78, 90) that if the growth curves ($\log \alpha$ versus $\log$ mass of the analyte) for the two wavelengths employed are parallel, and if the intersection point of the low (slope = 1) and high (slope = $\frac{1}{2}$) density asymptotes of each curve occurs at the same analyte mass, then the ratio of the Lorentz half-widths is equal to the ratio of the α values at the intersection point. In such case, equation 3-5 may be reduced to equation 3-4. Temperature measured in this manner is independent of the spectral bandwidth of the monochromator, provided it is maintained constant between the measurements (78). However, since a wider spectral bandwidth reduces the relative absorption (88), it is necessary to restrict the spectral bandwidth to less than 0.1 nm. As a result, α values are restricted to < 0.3 , in order to keep the wings of the absorption line from extending beyond the spectral bandwidth isolated.

Ionization in Graphite Furnace Atomizers

The influence of temperature and electron pressure on the ionization of a metal vapour may be considered using the following equilibrium:

for which the equilibrium constant $K_i(T)$ is given by the Saha equation (91):

$$\log K_i(T) = \frac{3}{2} \log T - \frac{3.18 \times 10^{22}}{T} E_i + \log \frac{Q_{M+}}{Q_M} + 15.684 \quad (3-6)$$

where E_i is the ionization energy of the metal (J), and Q_M and Q_{M+} are the partition functions of the metal atom and the metal ion, respectively. By introducing the term degree of ionization, α_i , defined by equation 3-7

$$\alpha_i = n_{M+} / (n_{M+} + n_M) \quad (3-7)$$

where n is the number density of the species denoted by the subscript of n , an expression relating the degree of ionization to the temperature and the electron pressure may be obtained:

$$\log \frac{\alpha_i}{(1 - \alpha_i)} = \log \frac{K_i(T)}{n_e} = -\log n_e + \frac{3}{2} \log T - \frac{3.18 \times 10^{22}}{T} E_i + \log \frac{Q_{M+}}{Q_M} + 15.684 \quad (3-8)$$

The above treatment assumes that second and higher ionization can be ignored at the temperature in question and that $n_e = n_{M+}$, i.e., that the concentration of electrons is governed solely by the ionization of the element being determined. In practice, a considerable number of foreign atoms are usually present in an atomic vapour. Na and K are constant impurities in most gases, and at S.T.P. the mean concentrations of these elements in the atmosphere are 10^{18} and 5×10^{16} atoms m^{-3} , respectively (92). At 2000 K, this concentration of Na ($\equiv$ detection limit level for Na with the HGA-2100) gives rise to an electron concentration of approximately 5×10^{14} m^{-3} (92).

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MICROCOPY RESOLUTION TEST CHART
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Besides this background of electrons causing a reduction in α_i , a second source of electrons must be considered, these being produced by incandescent graphite. Because of the low thermionic work function of graphite, a large partial pressure of electrons may be generated within the furnace. Consideration of the equilibrium:

leads to the thermionic emission equation (92, 93):

$$N_e = [2(2\pi m_e kT)^{3/2} / h^3] e^{-\phi/kT} \quad (3-9)$$

where N_e is the electron concentration, m_e the electron mass, h is Planck's constant, and ϕ the thermionic work function of graphite. At 3000 K, N_e is approximately $1.5 \times 10^{19} \text{ m}^{-3}$, and at 2000 K, $N_e \approx 1.1 \times 10^{15} \text{ m}^{-3}$. This additional source of electrons contributes to the suppression of the ionization of analyte. When the total electron concentration is dependent upon a number of sources, additional Saha equations must be considered for these species and a system of coupled Saha equations is required to be solved in order to calculate electron concentration. Rigorous calculation of α_i is difficult and, at best, an approximation is obtained. Additionally, such calculation assumes that equilibrium with respect to ionization has been established. This assumption may be unjustified as the ionization reaction may be slow in attaining equilibrium. The degree of ionization must therefore be determined experimentally. The most convenient means of measuring α_i is the Cs addition method (94) based upon the complete suppression of the ionization of an element by the addition

of a large excess of easily ionized Cs. The degree of ionization can then be found from the increase in the absorbance signal by the analyte element:

$$\alpha_i = 1 - A(\text{without Cs})/A(\text{Cs added}) \quad (3-10)$$

The absorbance by the analyte element must be corrected for the possible contribution of the analyte element (present as an impurity) in the added Cs itself or in other sources of adventitious contamination. Enough excess Cs must be added to suppress the ionization completely and the added Cs must not influence the atomization characteristics of the analyte.

EXPERIMENTAL

Apparatus. Hollow cathode lamp sources were used for sharp-line absorbance measurements. A 1000 watt xenon-arc lamp, model 976C-1 (Hanovia, Canrad Precision Inc.), employed for the relative absorption measurement by In and Ga, was modulated at 285 Hz with a mechanical chopper, type L42 HHD (American Time Products, Bulova Watch Co. Inc., N.Y.). The chopper was placed immediately before the first condensing lens on the optical rail. The spectral lines selected for In and Ga were peaked, prior to absorption measurements, using In and Ga hollow cathode lamps. All signals were recorded on the storage oscilloscope and subsequently photographed. The time constant of the recording system was 18 ms. The temperature of the surface of the graphite tube was measured with the automatic optical pyrometer. Cs and K hollow cathode lamps were used to investigate the extent of ionization

in the HGA-2100. All other instrumentation has been described in Chapter 1.

Reagents. Stock solutions containing 1×10^{-3} kg dm⁻³ of Fe, Sn, In and Ga were prepared from the metals. Standard solutions of Cs and K were prepared from their chlorides (Fisher CERTIFIED). All test solutions were prepared immediately prior to their use by dilution with ultrapure water.

Procedure. A spectral bandwidth of 0.08 nm was used for sharp-line absorbance measurements by Fe and Sn. The hollow cathode lamps were operated at their recommended currents so as to minimize self-absorption broadening. The continuum source was operated at 25 amperes and 20 volts. The spectral bandwidth employed for In and Ga was 0.03 nm. Test solutions of the metals were introduced into the atomizers in 5×10^{-6} dm³ volumes with an Eppendorf pipette fitted with disposable plastic tips.

Growth curves for In and Ga were constructed using the HGA-2100 in order to determine, under the experimental conditions used, the inter-relationship of the intersection points of the high and low optical density asymptotes for each of the lines.

The temperature of the gas phase as a function of time was obtained by measuring the appropriate signal-time characteristics (the sharp-line absorbance or the relative absorption) on the oscilloscope for the two lines of each thermometric species. When sharp-line absorbance measurements were made, care was taken to ensure that the mass of each analyte introduced into the furnace fell within the linear range of the calibration curves for both lines of the element. When relative

absorption was measured, the α values were limited to $\alpha < 0.3$. In each case, the temperature-time characteristics of the interior surface of the furnace, obtained with the optical pyrometer, were compared with those of the vapour phase. The vapour temperature of Fe produced in the CRA-63 was measured with and without the introduction of H_2 (i.e., a H_2 -diffusion flame) into the Ar sheath gas.

The possibility of ionization of analytes was investigated by the Cs addition technique.

RESULTS AND DISCUSSION

HGA-2100

Excitation Temperature of the Atomic Vapour

In order to be as thorough as possible, a number of thermometric species were used for measurement of the excitation temperature of the atomic vapour. Because optical measurements for any element can supply information about the vapour temperature only above its appearance temperature, a number of elements encompassing a range of volatilities, and hence, a range of temperatures over which vaporization occurs, is required. Figure 60 illustrates the relationship between the temperature of the surface of the furnace and the minimum temperature over which each of the selected elements may be used to obtain their excitation temperatures in the HGA-2100. For each element, the data range (time domain) over which the temperature could be reliably measured is indicated by a solid line. The complete absorbance traces could not be utilized because of prohibitively small signal-to-noise ratios at

Figure 60: Absorbance-time profile of the thermometric species superimposed on the temperature-time profile of the surface of the HGA-2100. Solid line represents that portion of the absorbance profile from which the data were taken.

the commencement and the completion of each of the signals. With Fe, Sn, In and Ga, vapour temperatures could be measured over the range of atomizer surface temperature 1250 - 3000 K. Table 40 presents the resonance lines, their gf ratios, energy levels and other pertinent data for the elements. Table 41 presents the equations used to calculate the effective vapour temperatures.

Growth curves ($\log \alpha$ v. $\log$ mass of the analyte) constructed for both In and Ga at both wavelengths for each element, using the HGA-2100, are shown in Figure 61. The peak of the absorption pulse served as the measure of α . At low concentrations the curves are parallel with slopes equal to unity, whereas the high optical density segments have slopes of 0.5. The intersection points of both the low and high optical density segments occur at the same analyte mass. In addition, it is evident that the ratio α_1/α_2 is, within the limits of experimental uncertainty, equal to the ratio α_1/α_2 at any other arbitrarily selected analyte mass for both In and Ga. As a result, equation 3-5 may be reduced to equation 3-4, allowing measurements to be made in the high optical density region for both elements where systematic errors may be reduced.

The temperature-time data reported for the atomic vapour are the average of at least 15 determinations for each line pair, corrected in each case for the blank. Typical oscillograms of the absorbance-time traces for In, Ga, Fe and Sn are shown in Figures 62-65, respectively. The time axis in each of these figures varies from 200 to 500 ms (scale division) and commences after a variable delay time following the initiation of the atomization

Table 40

Parameters used in Calculating T_{eff}

Element	Wavelength/nm	Spectral Term Value/cm ⁻¹		$\frac{92f_2}{91f_1}$	$r(\lambda)$
		Lower	Upper		
In	410.18	0	24,373	2.18 ± 0.13^a	-
	451.13	2,213	24,373		
Ga	403.3	0	24,789	1.57 ± 0.09^a	-
	417.21	826	24,789		
Sn	284.0	3,428	38,629	4.9 ± 0.2^b	1.004^d
	286.33	0	34,914		
Fe	358.12	6,928	34,844	9.4 ± 0.5^c	1.019^d
	371.99	0	26,875		

^aReference 107^bReference 108^cReference 85^dReference 85 and 76. (for $r(\lambda) = \sqrt{\lambda_2/\lambda_1}$)

Table 41

Equations Used in Calculating T_{eff}

Element	Effective Temperature/K
In	$T_{\text{eff}} = 1366./\log(2.64 \alpha_0/\alpha_1)$
Ga	$T_{\text{eff}} = 516.6/\log(1.68 \alpha_0/\alpha_1)$
Sn	$T_{\text{eff}} = 2143/\log(4.90 A_0/A_1)$
Fe ϕ	$T_{\text{eff}} = 4330/\log(9.22 A_0/A_1)$

Figure 61: Growth curves for In and Ga in the HGA-2100 with a heating rate of 1.23 K ms^{-1} of the furnace.

Figure 62: Oscillograms showing absorbance by 1.0×10^{-10} kg In in the HGA-2100 (absorption of radiation from a continuum source) at a heating rate of 1.23 K ms^{-1} of the furnace.

A) 410.18 nm line; absorbance = 0.05/scale div.,
time = 200 ms/scale div. Trigger delay time = 400 ms.

B) 451.13 nm line; absorbance = 0.02/scale div.,
time = 200 ms/scale div. Trigger delay time = 400 ms.

Figure 63: Oscilloscope showing absorbance by 1.0×10^{-10} kg Ga in the HGA-2100 (absorption of radiation from a continuum source) at a heating rate of 1.23 K ms^{-1} of the furnace; absorbance = 0.05/scale div., time = 200 ms/scale-div. Trigger delay time = 500 ms.

A) 417.21 nm line B) 403.3 nm line

Figure 64: Oscilloscope showing absorbance by 2.0×10^{-12} kg Sn in the HGA-2100 (absorption of radiation from a hollow cathode source) at a heating rate of 1.23 K ms^{-1} of the furnace; absorbance = 0.05/scale div., time = 500 ms/scale div. Trigger delay time = 50 ms.

A) 286.3 nm line B) 284.0 nm line

Figure 65: Oscillograms showing absorbance by Fe in the HGA-2100 (absorption of radiation from a hollow cathode source) at a heating rate of 1.23 K ms^{-1} of the furnace.

A) $7.0 \times 10^{-13} \text{ kg Fe}$; 372.0 nm line, absorbance = 0.10/scale div., time = 500 ms/scale div. Trigger delay time = 500 ms.

B) $1.4 \times 10^{-12} \text{ kg Fe}$; 358.1 nm line, absorbance = 0.02/scale div., time = 500 ms/scale div. Trigger delay time = 500 ms.

stage of the furnace. In all cases, the precision of the measurement (expressed as a standard deviation) was in the range $\pm 1 - 4\%$, being worse on either side of the signal maximum. The accuracy of the temperature is determined directly by the oscillator strengths (or transition probabilities) used. Although relative atomic transition probabilities are used, the values for many lines are inconsistent (85, 95 - 100). Table 42 presents some literature values of the gf ratio for the two Fe lines used. Additional examples could also be found for Fe and the other thermometric species used. The large variation in the gf ratio introduces a possible range of uncertainty of 120 K in the temperature measured by the peak of the Fe absorbance pulse (1950 K). The gf ratio of 9.4 ± 0.5 was selected for this study for the calculation of temperature because of the good agreement obtained between the calculated excitation temperature (using this gf ratio) and the surface temperature of the furnace at the appearance time of the Fe signal. It will be shown shortly that, at the appearance time of the signal, these two temperatures must necessarily coincide. The possible error introduced into the excitation temperatures as a result of the inaccuracy of the gf values is $\pm 5 - 10\%$.

Excitation temperature-time curves for In, Ga, Sn and Fe are shown in Figures 66 and 67. The time axis in these figures commences with the initiation of the atomization stage of the furnace. Some general conclusions may be drawn: a) in all cases the excitation temperatures rise linearly to a maximum, level off, and begin to decrease (not clearly evident for Ga); b) the maximum temperatures attained by the atomic species are lower than those of the furnace

Table 42

Some Literature Values for gf Ratios for Fe

	Wavelength/nm	$g_2 f_2 / g_1 f_1$ ratios		
		Ref. 85	Ref. 96	Ref. 97
Fe	358.12	9.4 ± 0.5	6.5 ± 1.1	6.9 ± 1.1
Fe	371.99

Figure 66: Excitation temperature-time profiles of the atomic vapour in the HGA-2100 with a heating rate of 1.23 K ms^{-1} of the furnace.

○ Sn ● Ga △ In

Figure 67: Effect of the rate of heating of the furnace on the excitation temperature-time profile of Fe atomic vapour in the HGA-2100.

surface (3000 K) by as much as 1300 K (In); c) the maximum temperatures attained by the elements vary in the order of their volatility[†] with respect to the relative positions of their absorption peaks i.e., $\text{In} > \text{Fe} \approx \text{Ga} > \text{Sn}$ (Figure 60); d) maximum temperature does not coincide with the peak of the absorption pulse for any of these elements.

These observations may be explained by considering the physical processes which occur during and following the atomization of the thermometric species. Intimate physical contact between the condensed phase and the furnace wall allows thermal energy to be rapidly transferred throughout the condensed phase by vibrational interaction involving frequency factors of the order of 10^{12} s^{-1} (101). Although this is the most efficient means of heat transfer, particularly if the analyte evaporates from a monolayer deposit, there are additional mechanisms of achieving thermal equilibration following vaporization of the sample. Collisions with the furnace wall (and the Ar sheath gas) transfer thermal energy to the atomic vapour. The efficiency of this process is characterized by the magnitude of the accommodation coefficient (Chapter 1). This assumes that the accommodation coefficient has the same value for the transfer of electronic energy as it has for that of the translational kinetic energy. However, by the principle of the equipartition of energy these two kinds of energy are distributed independently; in collisions they may not have the same mean rates of energy transfer. In addition to the above, the vapour is subject to a field of high-density blackbody radiation emitted by the incandescent graphite.

As vaporization proceeds, the atomic vapour distributes itself

[†] The correct volatility with respect to vapour pressure is $\text{In} > \text{Ga} > \text{Sn} > \text{Fe}$.

throughout the volume of the furnace. A concentration gradient is established between the centre (from which vaporization occurs) and the ends of the furnace. In addition to the concentration gradient, a thermal gradient also exists because the ends of the furnace are in electrical and thermal contact with the water-cooled cones whose temperature does not exceed 330 K. Both the concentration and thermal gradient are a complex function of time because of the direct (thermal) and indirect (increasing analyte vaporization) effects arising from the constantly increasing temperature of the furnace. The flux of atoms to the cooler ends of the furnace quenches the excited electronic states; the result is a lowering of the measured excitation temperature.

The measurement of vapour temperature by spectroscopic methods is equivalent to the measurement of the total population ratio of the absorbing species included in the viewing field of the spectrometer, and to the determination of an effective temperature that corresponds to this ratio according to a Boltzmann distribution:

$$\frac{g_2}{g_1} \exp[-(E_2 - E_1)/kT_{\text{eff}}] = \frac{\int_0^l n_2(x) dx}{\int_0^l n_1(x) dx} \quad (3-11)$$

where $n_1(x)$ and $n_2(x)$ are the densities of the thermometric species in the lower and upper quantum states of the transition and l is the optical path length. Consequently, an average or weighted average temperature is not measured (95), rather, the effective temperature is applicable only to the total population ratio of states 1 and 2. The measured excitation temperature is therefore highly dependent upon the thermal

gradient along the optical axis of the furnace.

Findlay et al. (39) measured a temperature difference of 500 K between the centre and ends of a HGA-70 furnace which had a central temperature of 1000 K. In the present case, where temperatures at the centre of the furnace approach 3000 K, much larger thermal gradients exist. Because the vapour temperature is quickly "accommodated" to that of the wall (i.e., the vapour in each section of the furnace is in thermal equilibrium with the wall at that point), the effective excitation temperature will be much lower than the wall temperature measured at the centre of the furnace.

Because the thermal gradient is time-dependent, (the gradient increasing with increasing temperature at the centre of the furnace), the excitation temperature-time curves measured with each thermometric species will be dependent on the volatility of the thermometric species. Additionally, the magnitude of the excitation energy corresponding to the spectral transition measured will also influence the measured temperature, as indicated by equation 3-11. The maximum excitation temperatures measured with Ga, Fe and Sn are similar (≈ 2350 K) because these elements have a similar volatility (compare their absorbance-time profiles shown in Figure 60). The influence of the time-dependent temperature gradient along the axis of the furnace on determining time-dependent excitation temperatures of Ga, Fe and Sn is therefore similar. Indium, however, is significantly more volatile than the other thermometric species, with the result that the temperature gradient exerts a substantially different effect on the excitation temperature measured with this element. The concentration of atomic

In at low surface temperatures is higher than that of the other thermometric species and extensive diffusion of In vapour to the cooler ends of the furnace occurs before a high surface temperature at the centre is attained. The measured excitation temperature is therefore comparatively low.

The plateau regions of steady-state excitation temperature measured with In, Fe and Sn represent the balance between the rate of heating of the atomic vapour, by all processes, and its rate of cooling by collisionally-induced quenching of excited states.

Ultimately, the excitation temperature decreases as more excited states are quenched, i.e., $\int_0^1 n_2(x)$ decreases as the atomic vapour diffuses to the cooler ends of the furnace.

Influence of the Sheath gas and the Rate of Heating of the Furnace

Figure 67 shows the influence of the rate of rise of temperature of the HGA-2100 furnace on the excitation temperature of Fe. Iron was used as the thermometric species in this study because of its large data range (Figure 60). Initial heating rates of 1.23, 1.06 and 0.73 K ms^{-1} were employed. Also shown in Figure 67 is the effect of substitution of N_2 for Ar as the sheath gas. The maximum excitation temperature measured is a function of the maximum temperature attained by the furnace. In addition, the rate at which the excitation temperature increases is proportional to the rate of heating of the furnace. Because the rate of vaporization of analyte increases with the heating rate of the furnace, the rate of introduction of high-temperature vapour into the gas phase becomes increasingly faster than the rate of quenching

of the excited-state population due to cooling. The data for vapour temperature reported for a furnace heating rate of 0.73 K ms^{-1} are limited in range because of the poor resolution of the signal from the background noise.

Figure 67 also indicates that substitution of N_2 for Ar as the sheath gas has no effect on the measured excitation temperature, despite the fact that the thermal conductivity of N_2 is 50% higher than that of Ar. Heat transfer from the furnace walls to the atomic vapour should be enhanced when N_2 is substituted for Ar and a higher excitation temperature should result when N_2 is used. The reason that this is not observed is that N_2 may act as an efficient quencher as well as a better (than Ar) thermal conductor, the effect of the former predominating over that of the latter.

Difference in Temperature between the Vapour and Surface

The difference between the measured excitation temperature and the surface temperature at the centre of the furnace, ΔT , for each of the thermometric species, is shown in Figures 68 and 69. In each case a similar profile is obtained, the temperature deviating from that of the surface in a roughly linear manner with time. The rate at which ΔT increases is proportional to the rate of heating of the furnace. This effect is illustrated in Figure 69, in which the ΔT for Fe is shown at three different rates of heating. At high rates of heating the extent of diffusion of atomic vapour is not increased in proportion to the rate of growth in the magnitude of the thermal gradient. Accordingly, the excitation temperature lags behind the reference

Figure 68: Temporal variation of the difference in temperature between the furnace wall and the atomic vapour in the HGA-2100 with a heating rate of 1.23 K ms^{-1} of the furnace. Arrow indicates the appearance time of the signal.

Figure 69: Temporal variation of the difference in temperature between the furnace wall and the atomic vapour in the HGA-2100 with the rate of heating as a variable. Arrows indicate the appearance times of Fe signals.

$\circ$ 1.23 K ms⁻¹ Δ 1.06 K ms⁻¹ $\bullet$ 0.73 K ms⁻¹

temperature of the centre of the furnace at a rate proportional to the rate of growth of the thermal gradient (i.e., the rate of heating of the furnace).

The arrows in Figures 68 and 69 indicate the appearance times of the signals - the three arrows shown in Figure 69 are, from left to right, the appearance times for Fe at heating rates of 1.23; 1.06 and 0.73 K ms^{-1} , respectively. The time elapsed between that indicated by the arrow and the time when a temperature difference of 15 K is measured is approximately 200 - 300 ms (the ΔT of 15 K was selected because this is the reproducibility of measurement of the surface temperature). Only over this time span following the appearance of the absorbance signal is the excitation temperature of the atomic vapour equal to the surface temperature at the centre of the furnace. This time period is related to the rate of diffusion of analyte vapour away from the hot centre of the furnace and to the magnitude of the thermal gradient within the furnace at the appearance time of the thermometric species. The "diffusion-induced" lowering of the excitation temperature requires a measurable "induction time" of approximately 200 ms.

CRA-63

Excitation Temperature of the Atomic Vapour

Excitation temperatures in the CRA-63 were measured with Fe at a furnace heating rate of 0.88 K ms^{-1} . Measurements were made with and without the use of a hydrogen diffusion flame ($2.5 \times 10^{-2} \text{ dm}^3 \text{ s}^{-1}$).

i.e., $1.5 \text{ l min}^{-1} \text{ H}_2$). Figure 70 shows that the H_2 diffusion flame increases the steady-state excitation temperature by approximately 100 K at 1900 K. The temperature of the surface of the furnace, however, remains unaltered (Chapter 1). This increase in the temperature of the vapour may partially account for the improvement in the atomization characteristics noted for Sn and Al (Chapter 1) when these elements are atomized in the presence of a H_2 diffusion flame. The chemical effects due to this flame (increased reducing nature of the gas phase) must also be taken into consideration.

As noted for the HGA-2100, the excitation temperature-time profile measured in the CRA-63 rises linearly to a plateau and then decreases (as the temperature of the furnace continues to rise). Also, as with the HGA-2100, the maximum excitation temperature attained is 500 - 600 K lower than that of the surface of the furnace. Because of the short length of the CRA-63 (9 mm long), the variation in the surface temperature with distance from the centre of the tube is small. Figure 71 shows the variation in the temperature of the CRA-63 along the length of the tube as a function of time. The five positions measured along the tube are the ends, the centre and the points midway between. The resolution of each position is $\pm 0.5 \text{ mm}$ because of the finite surface area sampled by the optical pyrometer. The rate of heating of the furnace was 1.10 K ms^{-1} . The maximum difference in the temperature measured between the centre and the ends of the CRA-63 is 240 K. This difference in temperature is slightly dependent upon the flow rate of Ar sheath gas and increases by 30 K for an increase in the flow rate from 5×10^{-2} to $7.5 \times 10^{-2} \text{ dm}^3 \text{ s}^{-1}$.

Figure 70: Effect of the H₂ diffusion flame on the excitation temperature-time profile of Fe atomic vapour in the CRA-63 at a heating rate of 0.88 K ms⁻¹ of the furnace.
 ○ H₂ diffusion flame (H₂ flow rate = $2.5 \times 10^{-2} \text{ dm}^3 \text{ s}^{-1}$ (1.5 l min⁻¹))
 ● without H₂ diffusion flame

Figure 71: Variation as a function of time of the surface temperature of the CRA-63 along the length of the graphite tube at a heating rate of 1.10 K ms^{-1} of the furnace. The time shown below represents the time elapsed after the commencement of the atomization stage.
 A) 0.45 s B) 0.65 s C) 0.85 s D) 1.05 s E) 1.25 s

(3.0 to 4.5 l min⁻¹). Although blackbody emission from the exterior surface of the furnace may not have been measured (the conditions for which the optical pyrometer was calibrated), the relative differences observed in the temperature as a function of the distance along the furnace are not in error. The small thermal gradient along the length of the CRA-63 cannot account for the low excitation temperature of the Fe vapour. The CRA-63 is an open system, however, and the sheath gas is considerably cooler than the end of the tube. The high linear flow rate of the gas from below the tube creates convection currents of cold gas at its ends. Diffusion of atomic vapour from the centre to either end (≈ 0.5 cm) results in quenching of the excited-state atoms. Therefore, although the measured thermal gradient along the surface of the tube is small, a large thermal gradient in the sheath gas entrained within the tube may be present.

Difference in Temperature between the Vapour and the Surface

Figure 72 shows the manner in which the excitation temperature of the atomic vapour deviates from the surface temperature as a function of time. The arrow indicates the appearance time of the iron signal. Identical appearance times were observed with and without the H₂ diffusion flame, it having no effect on the Fe signal. The time elapsed between that indicated by the arrow and the time when a temperature difference of 15 K is recorded is approximately 100 ms.

The larger effective thermal gradient in the CRA-63 accounts for the short time span over which the excitation temperature of the

Figure 72: Temporal variation of the difference in temperature between the furnace wall and Fe atomic vapour in the CRA-63 at a rate of heating of 0.88 K ms^{-1} of the furnace. Arrow indicates the appearance time of the signal.

○ H_2 diffusion flame (H_2 flow rate = $2.5 \times 10^{-2} \text{ dm}^3 \text{ s}^{-1}$)

● without H_2 diffusion flame

atomic vapour is equal to that of the surface of the furnace at its centre.

IONIZATION

Figure 73 presents oscilloscopic traces showing the absorbance-time signals of Cs (measured using the 852.1 nm line) and K (766.5 nm line). For reasons stated below, it is important to establish that the Cs and K signals overlap in time. Because of the different temperature-dependencies of various elements and the dynamic nature of the resulting signals, it is conceivable that most of the ionization buffer added may be dissipated or not produced at the time when the atomic vapour of the analyte is produced. In such circumstances, little or no buffering action could occur. It is evident from Figure 73 that any electrons generated by ionization of Cs are present within the furnace at the time when K atomic vapour is produced. From the appearance temperature and the absorbance-time characteristics of K, a "steady-state" temperature of approximately 2400 K may be assumed to have been attained by K vapour beyond the absorbance peak (based on a comparison with the temperature-time characteristics of Sn vapour, whose absorbance-time characteristics are similar to those of K, cf. Figures 66 and 73). To determine whether or not the atomization characteristics of K are affected by the addition of large excesses of Cs, the absorbance-time signal given by 2.5×10^{-14} kg K in various mass excesses of Cs (as CsCl) up to 10^4 -fold was measured. No change was observed in the signal characteristics of K with the exception of a depression of peak height beyond a Cs/K mass ratio of 10^2 .

Figure 73: Oscillograms showing absorbance by Cs and K in the HGA-2100.

- A) 4.5×10^{-12} kg Cs; absorbance = 0.20/scale div.,
time = 500 ms/scale div. Trigger delay time = 50 ms.
B) 2.5×10^{-14} kg K; absorbance = 0.05/scale div.,
time = 500 ms/scale div. Trigger delay time = 50 ms.

As a result, the effect of added Cs on the absorbance by K can be quantitatively accounted for below this Cs/K mass ratio. Figure 74 shows the peak and integrated absorbance by 2.5×10^{-14} kg K (at a furnace heating rate of 1.23 K ms^{-1}) as a function of the mass excess of added Cs. In each case only the K signal, corrected for the added K content present as an impurity in the Cs, is shown. It is evident that the degree of ionization, α_i , for K is zero (equation 3-10). Ionization of K does not occur to a measurable extent in the HGA-2100. Measurement of the absorbance by K^+ , using the 630.7 nm line, leads to the same conclusion, as no signal was obtained. This lack of ionization of K may be accounted for by the partial pressure of electrons emitted by the incandescent graphite walls of the tube. As noted earlier (equation 3-8), the electron pressure has an important effect on the degree of ionization. Increasing p_e by a factor of 10 has roughly the same depressing effect on α_i as reducing the temperature by 1000 K (91, p. 166).

Four independent studies on ionization of analytes in electrothermal atomizers have been published recently. Whereas Bancroft et al. (102) and Ottaway and Shaw (103) have reported that ionization of analytes is negligible in tungsten and graphite furnaces, Schrenk and Everson (104) and Epstein et al. (105) have concluded that ionization is appreciable and that ionization suppressants should be used. The latter two studies were made with an open tantalum boat sampling system (104) and a HGA-2100 furnace (105), respectively. It is possible that measurement of ionization in graphite furnaces depends not only on the ionization potential of the analyte but also on its

Figure 74: Effect of added Cs on the absorbance by 2.5×10^{-14} kg K.

○ peak absorbance ● integrated absorbance

volatility (i.e., its appearance temperature) and the method of measurement of α_i . Assessing α_i by the technique used here would give completely different results from that obtained from a measurement of the ratio of the emission intensities from the neutral atom line and an ion line. The reason for this is that emission is obtained only from the excited atom population which is located in the maximum temperature zone of the atomizer. It is evident from these conflicting observations that the question of ionization of analytes in electrothermal atomizers is far from resolved. In this connection, it would be very enlightening to measure p_e as a function of time within an unloaded furnace by an independent technique, e.g., the well-known technique of microwave absorption (106).

Summary

The excitation temperature of the atomic vapour arising from analyte atomization in a HGA-2100 and a CRA-63 atomizer is governed by the thermal gradient along the axial length of the atomizer, the appearance temperature of the analyte species, and the rate of heating of the atomizer.

Chapter 4

Mechanisms of Loss of Atomic Vapour from the Graphite Furnace

The sensitivity obtained with either the peak or the integration method of signal measurement in graphite furnace AAS is highly dependent on the rate of loss of atomic vapour from the analytical volume (Chapter 1). Because the peak of these transient signals is attained when the rate of production of atomic vapour is equal to its rate of loss, a decrease in the rate of loss results in an increase in the peak absorbance. Similarly, the integrated absorbance is inversely dependent on the rate of loss of atomic vapour from the analytical volume (equation 1-18 and 1-32). By determining the various modes of loss of atomic vapour from the graphite furnace and the factors which influence them, measures based on theoretical grounds may be taken to improve the vapour confinement, thereby enhancing the sensitivity of determination. This study was undertaken to determine the relative contribution of the individual modes of atomic vapour loss to the total rate of loss of the atomic vapour from the HGA-2100.

Five major factors may be cited as contributors to the loss of atomic vapour from commercial graphite furnace atomizers:

- (a) physical expulsion of excess atomic vapour if the volume occupied by the atomic vapour at the operating pressure and temperature of the furnace is greater than the analytical volume (as defined by the geometry of the incident light beam);
- (b) diffusion and convection of atomic

vapour through the aperture of the atomizer; (c) diffusion of atomic vapour through the walls of the graphite tube; (d) diffusion of atomic vapour to the cooler extremities of the atomizer where condensation may occur; (e) chemical loss of the atomic vapour by reaction with the hot graphite surface and/or by recombination with other gas phase species (e.g., entrained oxygen, sheath gases, etc.) to form involatile or undissociated species.

The rate of loss of atoms from the analytical volume may be conveniently studied by examining the decay portion of the absorbance-time signal. Assuming that loss of vapour occurs solely by diffusion, the rate of diffusion may be expressed by equation 1-29:

$$dM/dt = -D(dp/dx)S \quad (1-29)$$

The amount of diffusion taking place through the end apertures of a tubular cuvette of length l and cross-sectional area S is given by equation 1-31:

$$M_t = M_0 \exp(-8D_g t/l^2) \quad (1-31)$$

where M_0 is the mass of the vapour at an initial instant of time arbitrarily selected from the decay portion of the absorbance-time signal, M_t is the mass of the vapour at time t , and D_g is the gas phase diffusion coefficient. Similarly, the amount of diffusion which occurs through the porous walls of the cuvette is given by (11, p. 205):

$$M_t = M_0 \exp(-D_w S_w t/t_w V) \quad (4-1)$$

where D_w is the diffusion coefficient for mass transfer through the

wall, S_w is the internal area of the walls of the cuvette, t_w the wall thickness, V the volume of the cuvette, and M_0 and M_t are as defined above.

Since absorbance is proportional to M , a plot of $\log(A_0/A_t)$ versus t should yield a straight line from the slope of which D_g or D_w may be obtained. The general application of equation 1-29 to commercial graphite furnaces is complicated by the fact that the temperature of both the furnace and the atomic vapour is time-dependent (Chapter 3) and that the decay portion (tail) of the signal may contain a contribution from the continuing atomization of the analyte, especially when refractory species are atomized. To circumvent both of these difficulties, it is necessary to select, as probes for the measurement of the rate of vapour loss, elements which are sufficiently involatile that the decay regions of their absorbance-time profiles occur over the time period in which the graphite furnace has attained a steady-state temperature. Mo and V are two such elements which serve this purpose. Figure 75 shows the absorbance-time profiles for these elements superimposed on the temperature-time profile of a pyrolytic-graphite-coated tube. Although the temperature of the atomic vapour is somewhat lower than that of the surface of the furnace, the atomic vapour has attained a steady-state temperature over the decay region of the absorbance pulse (Chapter 3). The difficulty of working with either Mo or V is that the tail of their absorbance pulses may be supplied with a significant number of additional atoms which are produced by the continuing atomization of the element. This problem is minimized by using pyrolytic-graphite-coated tubes (Chapter 2). Penetration of analyte into the surface of coated tubes at high temperature is reduced

Figure 75: Absorbance-time profiles of Mo and V superimposed on the temperature-time profile of a pyrolytic-graphite-coated tube at a rate of heating of 0.91 K.ms^{-1} .

because of their low porosity. Such coated tubes yield high sensitivity and sharp absorbance pulses with well-defined decay regions.

Equation 1-29 may therefore be used to investigate the mechanism of loss of atomic vapour in commercial graphite furnaces provided elements such as Mo and V are used as analytical probes. Since the gas phase diffusion coefficient is inversely related to the ambient pressure of foreign gas, the influence of an applied pressure of an inert gas on the rate of loss of atomic vapour may be used to assess the importance of gas phase diffusional loss.

EXPERIMENTAL

Instrumentation. To investigate the effect of an external pressure on the rate of loss of atomic vapour, a special graphite furnace fitted with a pressurizable housing was constructed. The furnace was nickel-plated, fabricated from brass and was of a size and design similar to that of the HGA-2100. The commercially available graphite cones, tubes and quartz end windows were used in this furnace. Provision was also made for a system of external and internal sheath gases. The pressurizable furnace has been designed to provide larger water cooling ports and channels, solid unit construction for improved electrical contact and is capable of handling 1000 amperes at 15 volts. Figure 76 shows the furnace fitted on a stainless steel circular baseplate. Through this baseplate, which also serves as a mount on the optical rail, pass all of the service connections to and from the furnace. These include the electrical connections, the internal and external sheath gas lines, cooling water inlet and outlet lines, a gas pressure line input

Figure 76: Furnace mounted on its stainless steel baseplate.

Figure 77: Furnace enclosed within its pressure chamber.

and a gas pressure release valve. Each of the gas lines is equipped with an external regulator valve. The baseplate has a flange which is approximately 2 cm wide and is grooved to accept a rubber "O"-ring and 12 equally spaced hex-head screws. These fittings allow the furnace to be enclosed in a pressurizable chamber which can be attached to the baseplate by the screw-type mount. The stainless-steel pressure chamber, shown in Figure 77, is fitted with two demountable (in threaded receptacles) quartz windows (1 cm thick), a detachable quartz observation window mounted at 90° to the optical axis, and an injection port containing a quartz window through which the furnace may be sighted by a pyrometer during pressurized runs. The chamber is also fitted with a pressure gauge (calibrated in psi) and a safety release valve (arbitrarily set at 200 psi). The pressurizable furnace was powered by the commercially available HGA-2100 power supply. Unless stated otherwise, investigations carried out at atmospheric pressure were made with the commercial HGA-2100 furnace. Both regular and pyrolytic-graphite-coated tubes were used.

Reagents and gases have been described in Chapter 1.

Procedure. The sequence of operations followed for sample atomization under pressure is described below. Sample volumes of $5 \times 10^{-6} \text{ dm}^3$ were introduced through the injection port of the pressure chamber with an Eppendorf pipette fitted with disposable plastic tips. The sample was subjected to the usual drying and ashing with both internal and external sheath gases flowing. The heating sequence was then interrupted before the ashing stage was completed and the flow of both sheath gases was stopped. The injection port was then closed and the furnace was flushed once with the pressurizing gas (directly from a cylinder of the compressed

gas) and then pressurized to the desired pressure (reproducibly set to ± 2 psig). The heating cycle was reinitiated and absorbance measurements taken. The gas pressure was then released through a separate valve, the chamber repressurized and the blank signal obtained. This sequence of operations requires approximately two minutes for completion (including blank). The furnace was operated in the internal purge gas interrupt mode during runs at atmospheric pressure.

Absorbance-time profiles for each of the elements were recorded on a storage oscilloscope and photographed with a "Polaroid" camera. Plots of $\log(A_0/A_t)$ against t were constructed for Mo and V using the data obtained from the tail of their absorbance pulses.

RESULTS AND DISCUSSION

Effect of Internal Purge Gas

The effect of internal purge gas on the signal given by 4×10^{-12} kg of Cu is shown in Figure 45. The initial few hundred ms following the appearance of the Cu signal are unaffected by the internal purge gas (curve B) because the atoms produced during this period of time do not escape from the analytical volume. The increased rate of convectional loss decreases both the peak height and the width of curve B. Since the peak of the absorbance pulse marks the point of balance between the rates of formation and loss of atoms, an increase in the rate of loss decreases both the peak height and shifts the maximum to an earlier point in time.

Effect of Various Sheath Gases

The effect of various sheath gases on the absorbance signals has been discussed in detail in Chapter 1 (Figure 46, Table 17). Substitution of N_2 or He for Ar reduces the peak height and the integrated absorbance. Although such effects could not be quantitatively accounted for using equation 1-20, the data clearly show that the signals are highly dependent upon the composition of the diffusion medium. Variation of the flow rate of external sheath gas from 8.3×10^{-3} to $3.3 \times 10^{-2} \text{ dm}^3 \text{ s}^{-1}$ (0.5 to 2.0 l min^{-1}) produced no change in the absorbance-time traces for the elements. There is therefore no tendency for the flow of external sheath gas past the sample injection port to draw atomic vapour out of the furnace.

Measurement of Loss Rates

The relative rates of loss of atomic vapour from the analytical volume were investigated by plotting $\log(A_0/A_t)$ against time. The point A_0 was arbitrarily selected from the decay portion of the absorbance-time profile of the element, with the single condition that it be placed beyond the absorbance maximum. The difficulty in using elements such as Cd and Cu as working probes with this technique is illustrated in Figure 78. Straight lines are not obtained for these elements because the temperature of both the atomic vapour and the diffusion medium is rapidly increasing over the decay regions of these signals; hence, $D_{1,2}$ increases with time causing an accelerated diffusional loss of atomic vapour. A linear relationship is obtained with Mo and V, however. Figure 79 is a plot of $\log(A_0/A_t)$ versus time

Figure 78: Plot of $\log(A_0/A_t)$ versus time for Cd and Cu at $1.0 \times 10^{-5} \text{ N}\cdot\text{m}^{-2}$ Ar obtained with an uncoated graphite tube at a rate of heating of $1.2 \text{ K}\cdot\text{ms}^{-1}$.

● Cd ○ Cu

Figure 79: Plot of $\log(A_0/A_t)$ versus time for Mo and V at $1.0 \times 10^5 \text{ N}\cdot\text{m}^{-2}$ Ar with a pyrolytic-graphite-coated tube at a rate of heating of $0.91 \text{ K}\cdot\text{ms}^{-1}$.

● V ○ Mo

for these elements in a pyrolytic-graphite-coated tube using an Ar sheath gas at atmospheric pressure. Because the decay portion of their absorbance-time profiles lies in a region of steady-state temperature of the furnace (≈ 2800 K, Figure 75), straight lines are obtained. The slope of the plot is a measure of the rate of loss of atomic vapour by all processes. Because the volume occupied by the atomic vapour under these conditions is less than 1% of the volume of the furnace, the possibility of its expulsion from the furnace may be ignored. The remaining loss processes, diffusional and chemical, may each be considered as first-order processes. Correspondingly, a linear relationship between $\log(A_0/A_t)$ and time is expected in either case, with the slope of the curve being governed by the predominant mechanism of loss. Figure 79 shows that in an Ar atmosphere, the rate of loss of V > Mo by 17% (slopes are approximately 0.13 s^{-1} and 0.11 s^{-1} , respectively), which suggests that the mechanism of loss is a gas phase diffusional process. The ratio of $D_{1,2}$ for V and Mo, calculated from equation 1-20, is 1.16:1.00. The rate of loss of Mo atomic vapour in an Ar and N_2 sheath gas was found to be approximately the same. The rate of loss in a He atmosphere could not be investigated as the signals obtained were too small; larger analyte mass, necessary to obtain a measurable signal, could not be employed because of incomplete atomization (and hence, memory effects). The slope of the $\log(A_0/A_t)$ versus t plot (i.e., the rate of loss) was found to be independent of the mass of analyte taken for measurement provided that complete atomization occurs. This latter observation indicates that the loss follows first-order kinetics and is consistent with equations (1-31) and (4-1).

An estimate of the diffusion coefficient may be obtained by using equation 1-31. The slope of the $\log(A_0/A_t)$ versus t plot is related to D_g by:

$$D_g = (2.303 l^2) \text{slope} / 8 \quad (4-2)$$

from which $D_{Mo} \approx 1 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$ in Ar at atmospheric pressure. This calculation assumes that gas phase diffusion to the ends of the furnace is the only loss mechanism and that the effective length of the analytical volume is 5.5 cm (i.e., the distance between the quartz end windows). Although the exact temperature of the Mo vapour is unknown, 2500 K is not an unreasonable estimate (cf. Figure 75). The D_{Mo} calculated above is within a factor of 5 (smaller) of similar data reported by L'vov (11, p. 288) for Zn in Ar (taking into account the mass difference between Mo and Zn).

Effect of Injection Port Aperture

To calculate the relative importance of the aperture (0.17 cm diameter) of the injection port in determining the total rate of loss of atomic vapour, measurements were made with the port sealed with a small plug of spectrographic graphite, machined to provide a gas-tight seal. Measurements of loss were also made in a second graphite tube whose injection port diameter had been increased to 0.34 cm. A series of measurements showed that the rate of loss of atomic vapour was decreased by 20% when the injection port was plugged, and increased by 16% when the area of the port was increased by a factor of 4. These data indicate that diffusional (and convective) losses of atomic vapour through the

injection port are small in comparison to other loss mechanisms.

Effect of an External Pressure

The effect of an externally applied pressure of Ar gas on the rate of loss of atomic vapour from a pyrolytic-graphite-coated tube is shown in Figure 80. The effects of an applied pressure on the analytical characteristics of the absorbance signals will be presented in Chapter 6. As the ambient pressure increases, the rate of loss decreases. The slope of the $\log(A_0/A_t)$ versus t graph is directly proportional to the effective diffusion coefficient of the atomic vapour. Since the diffusion coefficient is inversely proportional to the pressure of the foreign gas (equation 1-20), a logarithmic plot of the slope versus the pressure should yield a straight line of unit slope. Such a plot is shown in Figure 81. Although a linear relationship has been drawn, the spread in the data points is too large to justify this relationship with certainty. The slope of the curve is 0.36. The effect of the applied pressure in lowering the rate of loss of the atomic vapour from the analytical volume is much less than what would be expected from a purely diffusional loss mechanism. An increase in the ambient pressure from 1.0×10^5 to $9.1 \times 10^5 \text{ N}\cdot\text{m}^{-2}$ (1 to 9 atm) reduces the loss rate by a factor of only 2. The low value of the slope of the curve in Figure 81 may be the result of other factors tending to increase the rate of loss of the atomic vapour at high pressure. High pressure reduces the mean free path of the atoms and decreases the rate of diffusional loss. Two other factors, however, tend to increase the rate of vapour loss. The decreased rate of diffusional loss allows a greater amount of the Mo atomic vapour to react

Figure 80: Plot of $\log(A_0/A_1)$ versus time for Mo at various pressures of Ar with a pyrolytic-graphite-coated tube at a rate of heating of $0.91 \text{ K}\cdot\text{ms}^{-1}$.

Figure 81: Effect of Ar pressure on the rate of loss of Mo atomic vapour from a pyrolytic-graphite-coated tube at a rate of heating of $0.91 \text{ K} \cdot \text{ms}^{-1}$.

with the incandescent graphite walls forming an involatile carbide (46, 47). At high pressure, the atomic vapour may be mechanically expelled as the expanding gases are forced out of the analytical volume during the heating of the furnace. Although the analyte atomic vapour occupies less than 1% of the volume of the furnace, mechanical loss of the vapour entrained within the expelled Ar may occur (109, 11, p. 211). Thus, chemical and mechanical loss of the Mo atomic vapour may occur to a greater extent as the ambient pressure is increased, thereby reducing the effect of the applied pressure in lowering the overall rate of loss of vapour from the analytical volume. Figure 82 illustrates the various forces acting on the atomic vapour at high pressure within the graphite tube; diffusion and mechanical expulsion tending to drive the vapour from the analytical volume and high pressure tending to contain it.

Loss Through the Graphite Wall

To determine the contribution of diffusion through the walls of the graphite tube to the total loss of atomic vapour, the rates of loss of Mo and V in a pyrolytic-graphite-coated tube were compared with those in an uncoated tube. Although uncoated tubes are subject to the problems discussed earlier, they may be used provided the tubes have not been used before, and the number of atomization cycles is kept extremely low (≈ 10). Figure 83 shows a $\log(A_0/A_t)$ versus t plot for Mo and V in an uncoated tube at atmospheric pressure (Ar sheath gas). The slopes are 0.13 s^{-1} and 0.14 s^{-1} for Mo and V, respectively. These values indicate that the rate of loss of Mo and V atomic vapour from uncoated tubes is increased

Figure 82: Distribution of atomic vapour within the graphite furnace and the tendency of pressure both to contain the vapour against diffusional flow and to mechanically expel the vapour.

Arrows indicate the direction of movement of the atomic vapour as a result of: — diffusion and mechanical expulsion;
 ----- pressure.

Figure 83: Plot of $\log(A_0/A_t)$ versus time for Mo and V at $1.0 \times 10^5 \text{ N.m}^{-2}$. Ar obtained with an uncoated graphite tube at a rate of heating of 1.2 K.ms^{-1} .

by 21% and 12%, respectively, over that obtained with coated tubes. These increases reflect the combined contribution to the rate of loss arising from both diffusion through the wall of the tube and possibly increased chemical loss as a result of reaction of the atomic vapour with the more reactive incandescent graphite of the uncoated tube. These results indicate that the rate of loss of atomic vapour through the wall of the graphite tube is small in comparison to other types of loss (assuming that no losses occur through the walls of the graphite tubes which have been coated with pyrolytic graphite). L'vov (11, p. 207) has shown that cuvettes made of either pyrolytic graphite, or standard graphite which is coated with a layer of pyrolytic graphite, prevent atomic vapour from diffusing through the walls. Whereas L'vov (11; p. 205) has shown that the rate of loss of atomic vapour through the porous walls of his uncoated cuvette is greater than the rate of loss of vapour from a similar but pyrolytic-graphite-coated cuvette, the results presented here indicate that diffusional loss through the graphite walls of an uncoated tube is rather small. The reason for this lies in the difference in geometry between the HGA-2100 furnace and L'vov's (11) cuvette. Assuming that only gas phase and wall-diffusional losses occur (equations 1-31 and 4-1), and considering the dimensions of the HGA-2100 furnace and L'vov's cuvette (11, p. 205) and the diffusion coefficients for gas and wall diffusion (11, p. 205), it can be shown that gas phase diffusional losses predominate over losses through the wall of the HGA-2100.

The results of all experiments, summarized in Table 43, indicate that gas phase diffusion plays a major role in the loss of atomic vapour

Table 43

Summary of the Rate of Loss of the Atomic Vapour
from the HGA-2100

Element	Slope of $\log(A_o/A_t)$ versus t plot/s ⁻¹			
	Coated tube	Plugged port	Enlarged port	Uncoated tube
Mo	0.107	0.090	0.125	0.130
V	0.125	-	-	0.140

from the analytical volume of the HGA-2100. Loss of vapour through the graphite walls is probably negligible in pyrolytic-graphite-coated tubes and accounts for approximately 20% of the losses in uncoated tubes. Gas phase diffusional and convectional losses of atomic vapour through the aperture of the injection port are also small. At atmospheric pressure, the major loss mechanism is diffusion of atomic vapour to the cool extremities of the furnace where condensation of analyte occurs. This can be easily demonstrated by atomizing mercury in the furnace - a deposit of mercury is formed on the quartz end windows, their brass receptacles and the graphite cones.

Effect of End Windows

The role of the quartz end windows in determining the rate of loss of atomic vapour from the analytical volume is complex. Atomization of relatively easy-to-volatilize elements, such as Cd and Pb and medium volatility elements, such as Cu, in a furnace without end windows produces no change in either the absorbance-time profiles of these elements or their peak height sensitivities. This effect was observed in both Ar and He sheath gases. Atomization of relatively involatile elements, such as Mo and V and elements whose appearance temperatures approach 2000 K, in a furnace containing no end windows results in large decreases in both the peak absorbance and the integrated absorbance. Figure 84 shows the absorbance-time profiles for 1.5×10^{-12} kg of Al in an Ar sheath gas. Curve A was obtained with both end windows present, curve B with one window present and curve C without end windows. The presence of the gas-tight quartz end windows prevents convective loss of atomic

Figure 84: Oscillogram showing absorbance by 1.5×10^{-12} kg Al at 1.0×10^5 N·m⁻² Ar in an uncoated tube at a rate of heating of 1.2 K·ms⁻¹. Absorbance = 0.10/scale div., time = 500 ms/scale div. Trigger delay time = 500 ms.

- A. End windows present.
- B. One window removed.
- C. Both windows removed.

vapour at the high temperature required for the atomization of this element. Although the HGA-2100 furnace is not symmetrical about the injection port (the left-hand side is longer than the right-hand side), removal of either end window affects the signal equally.

The increase in the geometric path length which results when the left-hand end window is removed does not increase the effective path length of the absorbing vapour. The reason for this is that the effective path length is not defined by the physical geometry of the graphite tube but by the distance from the centre of the tube to a point whose temperature is sufficiently low that condensation of the analyte occurs (i.e., the hot, working zone of the graphite tube). Although the path lengths are unsymmetrical with respect to the injection port, the temperature gradient is symmetrical; consequently, the atomic vapour is lost at its point of contact with the cold walls.

Table 44 shows the variation of the peak absorbance by Al with the rate of heating of the furnace. The ratio of the signals obtained with and without the end windows present indicates that the total amount of atomic vapour lost from the furnace increases as the rate of heating decreases. The appearance temperature of the Al signal is the same in each case (2080 K) and independent of the rate of heating of the furnace. The greater loss of atomic vapour at low heating rates is the result of the increased time available for diffusion before the signal attains its maximum.

The effect of varying the path length over which diffusion occurs, and hence, the time taken for losses to occur, is shown in Figure 85. Atomization of Al was carried out at $1.0 \times 10^5 \text{ N}\cdot\text{m}^{-2}$ (1 atm) Ar with a

Table 44

Effect of Rate of Heating of the Furnace on the Absorbance Signal
by Al with and without the End Windows Present ^a

Heating Rate/K·ms ⁻¹	Peak Absorbance/A		Ratio ^b
	With Windows	Without Windows	
1.23 ^c	0.360	0.155	2.3
0.90 ^c	0.145	0.045	3.2
0.79 ^d	0.175	0.035	5.0

^aAr sheath gas at $1.0 \times 10^5 \text{ N·m}^{-2}$ (1 atm) pressure, uncoated graphite tube.

^bThe ratio of the peak absorbance given by Al with the end windows present to that obtained without the end windows.

^cSample size = $1.5 \times 10^{-12} \text{ kg}$.

^dSample size = $4.0 \times 10^{-12} \text{ kg}$.

Figure 85: Oscillogram showing absorbance by 1.2×10^{-12} kg Al at 1.0×10^5 N·m⁻² Ar in an uncoated tube at a rate of heating of 1.2 K·ms⁻¹. Absorbance = 0.10/scale div., time = 500 ms/scale div. Trigger delay time = 500 ms.

- A. Sample placed at the centre of the graphite tube.
- B. Sample placed at either end of the grooved portion of the graphite tube.

furnace fitted with end windows. Curve A was obtained by placing the sample in the normal central position within the furnace. Curve B (two traces are shown) was obtained by placing the sample at either extreme end of the tube on the grooved portion of its surface. The sample placed close to either end window requires a longer period of time before the signal appears because the rate of heating of the tube at either end is slower than that in the middle. Additionally, the signal from the sample placed at either end is 60% smaller than that obtained with the centrally placed sample. This large decrease in sensitivity is the result of a shorter path length for diffusion between the sites of vapour production and loss (the cool extremes of the furnace).

Whether or not the vaporized sample reaches the window area of the graphite tube depends on the element determined. This is a consequence of the time-dependent thermal gradient along the axial length of the tube. Depending on the element (its vapour pressure-temperature characteristics), the vapour may reach the end of the tube and the end windows (as in the case of Hg) or it may condense within the tube somewhere between the injection port and the end of the tube. With the relatively involatile elements, removal of an end window increases the rate of transport of vapour to its ultimate site of condensation. Thus, a "wind" must be created by a pressure gradient within the graphite tube at high temperature when the thermal gradient is largest, increasing the rate of loss. This effect is additional to the increased diffusion coefficients for these elements at higher temperatures. In addition, the sites of vapour

condensation for involatile elements are closer to the centre of the graphite tube than those for easy-to-volatilize elements.

It may be concluded that the end windows on the HGA-2100 furnace are useful for reducing the mechanical expulsion of the analyte vapour at high temperature. However, the windows have little or no effect on absorbance signals produced at low temperature (e.g., those by Cd, Pb).

Chemical Loss of Analyte Vapour

Loss of the analyte vapour may occur as a result of formation of involatile and/or undissociated compounds between the analyte and the incandescent graphite and/or the matrix of the sample or gases in the atomizer. Chemical loss of Mo atomic vapour by formation of an involatile carbide through reaction with the incandescent graphite has been discussed earlier. Chemical loss of Al by reaction with nitrogen in the presence of incandescent graphite can occur as a result of the formation of undissociated AlCN (Chapter 1), the sensitivity being reduced by over 60% when N₂ is substituted for Ar as the sheath gas. Chemical loss of atomic vapour through the formation of involatile compounds is the cause of incomplete atomization, and hence, "memory effects" for some elements (i.e., Mo and V).

Summary

The mechanism of loss of the atomic vapour from the HGA-2100 graphite furnace varies with the physicochemical properties of the analyte species, the heating rate and steady-state temperature of the

atomizer, and the physicochemical properties of the surface of the furnace. The major factor contributing to loss of atomic vapour is diffusion to the cooler extremities of the furnace where condensation occurs. Loss through the aperture of the sample injection port accounts for approximately 20% of the total loss while loss through the graphite walls also contributes about 20%.

Chapter 5

Mechanisms of Atom Formation in the Graphite Furnace

The formation of analyte atoms in various flames has been discussed by many workers. As convenient cells for the study of high-temperature reactions, flames have been used to obtain spectroscopic evidence for reaction intermediates and bond dissociation energies of stable species (110 - 119). However, little has been reported on the atomization processes in graphite furnace atomizers. Whereas it is generally conceded that local thermodynamic equilibrium exists at various points throughout a flame (110), it may be questionable to assume that equilibrium is attained in electrothermal atomizers. High thermal gradients, rapid rates of rise of temperature and transient signals generated by these atomizers may not allow adequate time for physical and chemical processes to reach equilibrium before the atomic species have been lost. Despite the possibility that equilibrium may not be attained in electrothermal atomizers, several researchers have attempted to gain insight into the dominant processes of atom production based on the assumption that equilibrium has been attained. For example, Campbell and Ottaway (17) have assumed that reduction of metal oxides by carbon is rapid, and have correlated the appearance temperature of the signal with the temperature at which reduction of analyte oxides with solid carbon (the surface of the graphite cell) becomes thermodynamically favourable ($\Delta G_{\text{reaction}}^{\circ} \leq 0$):

Their study suggests that a large number of analyte species produce gaseous atoms through such a reduction reaction. Although correlation between the temperature and ΔG° of the above reduction reaction was observed for 18 of the 27 elements investigated, their data for the appearance temperature reflects the temperature of the tube wall at the point in time at which the peak, rather than the beginning, of the analyte signal occurs. Many of their appearance temperature values therefore tend to be too high. The difference between their reported appearance temperature and the true appearance temperature for each element is a function of the rate of heating of the graphite tube, the geometry of the tube, and the analyte species. On the other hand, Aggett and Sprott (12) have compared the appearance temperatures of various analytes in both graphite and tantalum atomizers. Comparison of the appearance temperatures from each atomizer, for the same analyte species, indicates whether or not oxide reduction plays a rôle in the formation of analyte atoms. Lower appearance temperatures from the graphite atomizer are indicative of a reduction process. The free energy change for equation 5-1 was evaluated at the appearance temperature to determine if reduction was thermodynamically possible. Of the 16 elements studied, only 4 (Fe, Ni, Co and Sn) offered evidence of a reductive mechanism. These authors (12) have implicitly assumed the surface of the tantalum atomizer to be coated with a layer of Ta_2O_5 . Thermodynamically, reduction of analyte oxides by tantalum at the temperatures employed is highly favourable:

The assumption that this reduction reaction can be ruled out is valid only if Ta_2O_5 forms a coherent stable film on the surface of the metal. It has been determined (120, p. 339) that growth of the surface oxide proceeds by a mechanism of diffusion of the metal through the film to the surface. Provided this step is slow in comparison to the atomization time of the analyte, reduction by tantalum is not likely to occur. The fact that a change in the appearance temperature was observed for some analytes when the tantalum atomizer was used can be interpreted as confirmation of the fact that the reduction of analyte oxides by Ta is hindered by the presence of a surface film of Ta_2O_5 (assuming that accurate measurements of the temperature were obtained for both atomizers).

Fuller (15, 121-123) has criticized the thermodynamic approach to atom production because it does not explain the fact that several elements may form thermodynamically stable carbides at and below the temperatures at which $\Delta G_{\text{reaction}}^0$ for equation 5-I is zero. In addition, the thermodynamic approach cannot give any indication of the rates of atomization, and consequently, predict shapes of absorbance-time curves. As a result, he has attempted to explain the dynamics of these transient signals using a kinetic approach. With copper as a working model, he obtained rate constants for the production and dissipation of atoms in a heated graphite atomizer and assigned an activation energy of $13.8 \times 10^4 \text{ J mol}^{-1}$ (33 kcal mol^{-1}) to the production of copper atoms. Whereas such treatment has the potential for predicting peak shapes and activation energies governing the production and dissipation of atoms, it is a necessary condition that an isothermal environment exist within the

atomizer, preferably throughout the entire duration of the signal. In addition, accurate temperatures of the atomic vapour are required. Commercially available atomizers cannot provide an isothermal environment over the entire duration of an absorbance pulse. As a result, a purely kinetic treatment of the entire absorption pulse is very difficult. In addition, Fuller (15, 121-123) has implicitly assumed that the atomic vapour temperature is equal to that of the graphite surface. Deviations from thermal equilibrium will cause large errors in the estimation of rate constants and activation energies, particularly when activation energies of the order of 400 kJ mol^{-1} are involved. Johnson et al. (10) have examined the nature of atom production from a non-mechanistic viewpoint. By assuming that a simple Boltzmann factor governs the vaporization of solid analyte, and hence, the concentration of gaseous analyte species, these authors have succeeded in modelling a single transient signal (molybdenum) arising from atomization with a West-type carbon filament atomizer. Unfortunately, poor agreement was obtained for those metals which vaporized at low temperatures. These authors (10) have implied that various energies are associated with the vaporization process, these energies being characteristic of the analyte and related to either the heat of vaporization of the metal or the metal oxide bond dissociation energy, whichever is larger. A comprehensive kinetic model for atomization developed by Torsi and Tessari (9,16,67,124,125) details the determination of such atomization energies using a filament type device. These authors have obtained an activation energy of 405 kJ mol^{-1} (96 kcal mol^{-1}) for the production of Ni atoms, suggesting that the atomic vapour

arises as a result of sublimation of the metal.

The major problem with such studies is that electrothermal atomizers do not function as cuvettes (with the exception of those used by L'vov (11) and Woodruff (3, 126)) in which isothermal conditions exist, but rather as furnaces in which an isothermal environment cannot be achieved over the time required for the production of the signal. As such, the characteristics of the transient signals are largely determined by kinetic parameters (rates of production and dissipation of atoms) as is evidenced by the magnitude of the effect of the rate of heating of the furnace on the resulting peak absorption (Chapter 1). Despite this limitation, it is interesting to examine the results of those models for atom formation which are based on the assumption that thermodynamic equilibrium exists. From such studies, however, only indirect evidence of the possible dominant reactions, which lead to the formation of free atoms has been provided, and no evidence of any intermediates in such reactions has been published.

It is important to establish the relationship of such energy values, as arise from the above models, to the nature of the atomization processes, and to quantitatively evaluate their magnitudes from the measurement of basic system parameters. This investigation attempts to provide some evidence as to the nature of the major atomization processes for a number of elements in the HGA-2100.

THEORY

The absorbance signals arising from analyte atomization in the HGA-2100 cannot be properly handled by a kinetic technique, since an accurate knowledge of vapour temperatures is required. The model developed by Torsi and Tessari (9,16,67,124,125) is applicable only to those atomizers in which the region above the vaporizing analyte behaves as an infinite sink for atomic species, i.e., an open system. No provision has been made in their model for analyte condensation and subsequent reevaporation, which occur in tube-type atomizers. As a result, their treatment is applicable only to those cases in which atomization occurs from a rod or filament device. With tube-type atomizers, such as the HGA-2100 employed in this study, analyte condensation and reevaporation can be shown to occur. It is for this reason that an entirely new approach to the problem was undertaken. The model presented here was designed to account for both the thermodynamic and kinetic aspects of atomization.

There are a number of potential pathways by which gas phase atoms may be formed. When the sample is in the form of a nitrate or sulphate, the metal oxide usually results on heating; even when the sample is in the form of a halide, this may still be true, since hydrolysis to oxygen-containing species frequently occurs. The majority of precursors to gas phase atoms are therefore either metal oxides (generally monoxides (11, p. 129)) or halides which, in the most general cases, may participate in such reactions as the following in the HGA-2100.

These equations will be used to formulate a simple model. The validity of this model will be tested by its ability to make predictions and to produce numbers coherently related to other experiments.

The oxygen and halogen atoms resulting from the dissociation of the metal compounds in equations 5-III and 5-V have been shown in the monatomic form. The reason for this is that the partial pressures of these species (as well as the metal) are extremely low. Since the mass of analyte atomized is of the order of 10^{-12} kg, the partial pressure of liberated oxygen or chlorine within the furnace at a temperature of 1500 K is approximately $0.01 \text{ N}\cdot\text{m}^{-2}$ (10^{-7} atm). Over the initial portion of the signal, where measurements are taken, these partial pressures are closer to $10^{-3} \text{ N}\cdot\text{m}^{-2}$. As such, the probability of collision of analyte fragments and their resulting recombination is negligible. The final step leading to free atom formation in the above equations (and those given throughout this chapter) is therefore not written with a reversible equilibrium arrow. It has been assumed that equilibrium with respect to bimolecular gas phase collisions does not exist (i.e., there is no formation of Cl_2 , O_2 , etc.). Gas phase-condensed phase equilibria are assumed to be established for such species as M_xO_y , MX_m and $M(s/l) - M_2(g)$ (the latter

system will be further discussed in a subsequent section). The gas phase-condensed phase equilibrium should more properly be labelled a quasi-equilibrium. Such equilibria may be written as (using equation 5-III as a typical example):

where k_f and k_r are rate constants for the forward and reverse reactions, respectively, k_f/k_r is the equilibrium constant for the phase equilibrium, and k_d is a rate constant introduced to account for diffusional losses of gas phase molecules. The viability of the model rests on the assumption that k_r competes favourably with k_d . This is not an unreasonable assumption when one considers the total internal area of the furnace walls on which condensation and reevaporation of MO may occur as compared to the velocity and mode of permanent loss of MO from the analytical volume (largely diffusional losses to relatively cool condensation points within the furnace, cf. Chapter 4). It is implicitly assumed that gas phase molecules have a longer lifetime in the furnace than the corresponding metal atoms. This is due to the latter's intrinsically higher reactivity towards the hot carbon (forming metal carbides (47)) and any gas phase scavengers present in this system.

It can be shown that the energy associated with the production of free atoms of the analyte may be obtained directly from atomic absorption measurements. Nikolaev and Nemets (127), for example, have determined the heats of sublimation of Ti and Mo from measurements made

with a graphite cuvette. By lining the cuvette with a thin layer of metal foil of the appropriate element and allowing equilibrium to be attained at each temperature, the heat of sublimation of the metal was calculated from the slope of a plot of the logarithm of the absorbance as a function of the inverse of the absolute temperature. Although these were "static" measurements, made with a graphite cuvette which is capable of maintaining an isothermal environment, it will be shown in the following sections that this same information may be obtained from "dynamic" measurements of the absorbance by metal vapours produced in a commercial graphite furnace whose temperature is constantly rising.

Consider the most general atomization processes illustrated by equations 5-III - 5-V. If the final step in the atomization process is characterized by a unimolecular rate constant k_1 , then according to equation 5-III, the rate of production of $M_{(g)}$ at any temperature is given by:

$$dp_{M_{(g)}}/dt = xk_1p_{M_{xO_y(g)}} \quad (5-1)$$

$$= k_1K_p a_s x \quad (5-2)$$

where $K_p = p_{M_{xO_y(g)}}/a_s$, a_s is the activity of the condensed phase on the surface of the graphite furnace, and p is the partial pressure of the species denoted by the subscript of p . The activity of the condensed phase will be maintained as a variable throughout the remainder of this model, since it is conceivable that it will vary with both temperature and analyte mass. For small analyte masses, the sample can penetrate

into the pores of the graphite tube. In such cases, the activity of the condensed phase on the surface will be different from that which would result if sufficient analyte were introduced both to penetrate into the pores and to form a homogeneous surface layer. Under these conditions, it is also easy to visualize variations of a_s with temperature. As the temperature rises, the surface layer is stripped off, exposing the subsurface layer of different activity.

Metal vapour is lost from the analytical volume by processes which are largely diffusional in nature (Chapter 4). The net rate of appearance of metal vapour is given by equation 5-3:

$$dp_{M(g)}/dt = k_1 K_p a_s x - R_D \quad (5-3)$$

where R_D is the rate of diffusional loss. It has been shown in Chapter 4 that the rate of loss of metal vapour from the furnace may be approximated by a simple first order process; hence,

$$R_D = k_D p_{M(g)} \quad (5-4)$$

in which k_D is the (slightly temperature-dependent) rate constant for loss of vapour. Under such conditions, the atomization processes in the furnace may be likened to a reaction in a flow system in which reactants ($M_x O_y(g)$) enter the reaction volume continuously while the product mixture ($M(g)$ and $O(g)$) leaves. During the short period when a_s is nearly constant, a steady-state is achieved (at each temperature) in which the number density of all species no longer changes with time. Rearranging equation 5-3 and substituting equation 5-4 for R_D one gets:

$$dp_{M(g)}/dt = 0 = k_1 K_p a_s x - k_D p_{M(g)} \quad (5-5)$$

which upon rearrangement yields:

$$p_{M(g)} = k_1 K_p a_s x / k_D \quad (5-6)$$

In atomic absorption spectroscopy, the measured absorbance is directly proportional to the concentration of atomic vapour; hence,

$$A_T = k_A p_{M(g)} = k_A k_1 K_p a_s x / k_D \quad (5-7)$$

where A_T is the absorbance by metal vapour at any temperature T and k_A is a proportionality constant relating absorbance to metal vapour concentration. According to transition-state theory, the rate constant k_1 can be formulated in thermodynamic terms by introducing the standard free energy change for the reaction:

$$\begin{aligned} k_1 &= \frac{kT}{h} e^{-\Delta G^{\ddagger}/RT} \\ &= (kT/h) e^{\Delta S^{\ddagger}/R} e^{-\Delta H^{\ddagger}/RT} \end{aligned} \quad (5-8)$$

where k and h are Boltzmann's and Planck's constants, respectively, and the quantities $\Delta G^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ are the free energy, the entropy and the enthalpy of activation, respectively. To a first approximation, the enthalpy of activation may be equated to the activation energy E_a for the reaction (49, p. 386). Not only is k_1 a function of temperature, but so also is K_p , the equilibrium constant for the gas-condensed phase equilibrium. The relationship of K_p to temperature is given by the well-known van't Hoff equation (128):

$$\left(\frac{\partial \ln K_p}{\partial (1/T)} \right)_p = - \frac{\Delta H^0}{R} \quad (5-9)$$

where ΔH^0 is the standard enthalpy change accompanying the phase transition (reactants and products at unit fugacity). In the integrated form, using common logarithms, equation 5-9 may be written as

$$\log K_p = -\Delta H^0/2.3RT + C \quad (5-10)$$

where C is an integration constant, and ΔH^0 is assumed to be independent of temperature. Substituting equations 5-8 and 5-10 into 5-7 one gets:

$$\log A_T = - \frac{E_a + \Delta H^0}{2.3RT} + \frac{\Delta S^{0+}}{2.3R} + \log \frac{k_A a_s k_T x C^i}{h k_D} \quad (5-11)$$

$$= - \frac{E_a + \Delta H^0}{2.3RT} + A_0 \quad (5-12)$$

Equation 5-12 expresses the relationship of the measured absorbance to the energy associated with the production of atomic vapour. A plot of the logarithm of the absorbance as a function of the inverse of the absolute temperature should yield a straight line with slope = $-(E_a + \Delta H^0)/2.3R$ and intercept = A_0 . In addition to the basic assumptions of this model which have been introduced up to this point, the construction of a $\log A_T$ versus $1/T$ plot requires that the temperature of the gas phase be equal to that of the surface of the graphite tube over the data range employed, that atomization of the analyte is of a thermal nature only, that E_a , ΔH^0 and ΔS^{0+} are approximately independent of the temperature over the temperature range employed in the above plot, and that the

temperature-dependence of k_D is sufficient to compensate for that introduced by the last term in equation 5-11 (i.e., the linear T factor and that arising from the fact that $k_A \propto T^{0.7}$ (11, p. 221)). This last assumption is a reasonable approximation based on the temperature-dependence $T^{3/2}$ reported for gas phase diffusion coefficients (48).

Although the slope of the $\log A_T$ versus $1/T$ plot yields an activation energy, the magnitude of E_a is an excellent approximation to the bond dissociation energies of gaseous species (129), and throughout this chapter will be so identified.

The above model for atom production is based on the reaction sequence given by equation 5-III. It is straightforward to see that consideration of either reaction sequence 5-IV or 5-V will lead to an identical result. Treatment of the absorbance data is therefore quite general - it is not necessary to know the reaction sequence *a priori*. By correlating the energy value obtained from the $\log A_T$ versus $1/T$ plot with a very limited set of possible primary steps in the atomization sequences, the utility of the model may be tested and the major precursors to free analyte atoms identified. More specifically, the energy term may be correlated for best agreement with one of the following values: (a) the dissociation energy of the metal oxide; (b) the dissociation energy of the metal halide; (c) the heat of atomization of the metal; (d) the metal-metal bond dissociation energy, or (e) the metal-carbon bond dissociation energy. The $\log A_T$ versus $1/T$ plot will henceforth be referred to as an E_a plot, and the associated energy obtained from the slope will simply be identified, for convenience, as E_a .

From a consideration of reaction sequences which involve more than one potential source of $M_{(g)}$, such as that outlined in equation 5-IV, it is evident that as the temperature of the system is increased, certain steps in the path to $M_{(g)}$ will be replaced by others, and hence, disappear from the E_a plot. As a result, the E_a plot may appear as a composite of two or more intersecting straight line segments of different slope, reflecting the transition which occurs when the major supply of $M_{(g)}$ changes from one species to another. Consider, once again, the reaction sequence given by equation 5-III:

At relatively low temperatures, when little of the oxide has been vaporized and a_s may be considered a constant, production of $M_{(g)}$ arises by way of the following path:

the energy associated with $M_{(g)}$ production being the combined energies of vaporization (the contribution from the K_p term, i.e., ΔH^0) and dissociation (the contribution from k_1 , i.e., E_a) of the oxide. At higher temperatures, when almost all of the condensed-phase oxide on the surface has vaporized ($a_s \rightarrow 0$), the major supplier of $M_{(g)}$ becomes $M_xO_y(g)$:

with the result that the energy now associated with $M_{(g)}$ production is that arising from oxide dissociation (i.e., the contribution from

k_1). It is evident that as the temperature of the system increases, certain earlier steps in the sequence to $M_{(g)}$ may disappear, just as the temperature dependence of K_p is lost when a sufficiently high temperature is reached to vaporize the surface oxide, that is, the equilibrium governed by K_p is shifted strongly to the product side. It follows, that if the sample mass is greatly increased, such that the $M_xO_y(s) \rightleftharpoons M_xO_y(g)$ equilibrium is maintained over the full range of temperature employed in these studies, then the temperature dependence arising from both the K_p and k_1 terms will be measured. This concept of energy terms being lost at high conversion of the reaction may be further illustrated by considering the reaction sequence shown in equation 5-IV. The first step in this reaction, reduction of the metal oxide by carbon, leaves the free metal on the surface of the graphite tube in a physical state (prior to atomization) that is determined by the temperature of the graphite tube. The energy involved in this step is not observable by the proposed technique. At the first appearance of free metal, the following reaction is established, the concentrations of the vapour phase species being determined by the temperature:

Initially, the concentration of $M_{2(g)}$ is very low and the measured energy corresponding to the production of $M_{(g)}$ is the heat of atomization of $M_{(s/l)}$, i.e., $M_{(s/l)} \rightarrow M_{(g)}$. When the temperature is sufficiently high that the bulk of $M_{(s/l)}$ has been evaporated and the dominant precursor to $M_{(g)}$ is the dimer, the production of $M_{(g)}$ arises predominantly from the reaction $M_{2(g)} \rightarrow M_{(g)}$, the measured energy corresponding to only

the dissociation energy of the dimer. As a result, the E_a plot will appear as a composite of two intersecting straight lines of different slopes. Those energy steps which "drop out" of the atomization sequence as the temperature is raised (or those which do not appear at all e.g., reduction) are those for which high conversion of the reactants to another form has occurred.

The formation of gaseous metal dimers upon evaporation of metals has been well documented (130 - 132). Honig (130) has shown that formation of dimeric and larger clusters of atoms in the gas phase must take place during the evaporation process itself; they are not restricted to forming in the gas phase at high monomer partial pressures. Figure 86 presents the energy level diagram for the sublimation of a metal (131). For $M_{(s/l)}$, $M_{(g)}$ and $M_{2(g)}$ in equilibrium, one gets:

$$\frac{d \ln p_M}{d(1/T)} = - \frac{\Delta H_M}{R} \quad (5-13)$$

$$\frac{d \ln p_D}{d(1/T)} = - \frac{\Delta H_D}{R} \quad (5-14)$$

If $\Delta H_D > \Delta H_M$, the dimer may be present in small amount at low temperatures but will become increasingly important the higher the temperature. Thus, unstable molecules with little probability of forming at low temperatures can become significant at high temperatures (131).

Just as energy steps may be lost from the reaction sequence because of high conversion of the reactants to another form, new reaction pathways may arise because of low conversion. An example of such a case is the reduction of metal oxides by carbon followed by sublimation of the

Figure 86: Energy level diagram for the sublimation of a metal. ΔH_M is the heat of vaporization of the monomeric species, ΔH_D the heat of vaporization of the dimeric species, and $D_{(M_2)}$ the dissociation energy of $M_2(g)$.

element. This is the result of the low "conversion" of the oxide to the gas phase below the temperature at which the reduction reaction becomes thermodynamically favourable.

Having obtained a value of E_a and a possible atomization sequence, it is necessary to ensure that the resulting intermediate satisfies additional physicochemical criteria. For example, if it is implied (from the E_a data) that the free metal was the immediate precursor to gaseous atoms, then reduction of the metal oxide must have occurred. The reduction reaction must therefore be thermodynamically favourable at or prior to the temperature at which the atomic absorption becomes detectable, i.e., the appearance temperature. In addition, the selected reaction sequence must reflect the physical and chemical form of the analyte at the appearance temperature, as indicated by melting and boiling point data and results of differential thermal analysis.

The second parameter arising from the model is the intercept ($\log A_0$) of the $\log A_T$ versus $1/T$ plot, which, according to equation 5-11, contains a number of physical constants, the variable quantity being the entropy factor for production of atomic vapour. Since the intercept also includes temperature-dependent parameters (k_A , k_D , a_s , ΔS^{0+} and T), its magnitude cannot be evaluated by a linear extrapolation of the $\log A_T$ versus $1/T$ curve (i.e., $1/T \rightarrow 0$ at $T \rightarrow \infty$). As a result, this term will not be considered further in this discussion.

EXPERIMENTAL

Apparatus. Details of the apparatus have been given in previous chapters.

The HGA-2100 was used throughout this study. Except where noted, uncoated graphite tubes were used.

Reagents. In addition to the stock solutions of metal standards described earlier, polystyrene - 2% divinylbenzene copolymer beads (200 - 400 mesh, Eastman Kodak Co.) and anhydrous oxalic acid (Fisher Scientific Co.) were used.

Gases. Except where noted otherwise, argon gas (99.95% purity) was employed to sheath the atomizer. Nitrogen gas (99.95% purity) was also used for some selected studies.

Procedure. Temperature-time curves of the atomizer surface were obtained using the automatic optical pyrometer. As the heating rate of the atomizer is dependent upon the quality of the electrical contacts between the graphite tube and the cones, care was taken to insure a reproducible temperature profile by measuring the furnace resistance prior to each study and maintaining it at a set arbitrary value of 22 m Ω by suitably adjusting the contact tension between the graphite cones and the graphite tube.

Aqueous test solutions of Cd, Zn, Mn, Ni, Sn, Pb, Cr, Cu, Fe, Co, Ca, Al and Mg taken as the chlorides containing 5% (v/v) HCl, and aqueous solutions of Cd, Zn, Mn, Ni, Cr, Pb, Cu, Fe, Co, Ca, Al and Mg taken as the nitrates containing 5% (v/v) HNO₃ were prepared. Aqueous test solutions of Sn and V in 5% (v/v) NaOH and Mo in 5% (v/v) NH₄OH were also prepared. All aqueous samples were introduced in 5×10^{-6} dm³ volumes into the atomizer with an Eppendorf pipette fitted with disposable plastic tips.

Solid samples of various copper and aluminium compounds were also atomized. Copper was taken in the following compound forms: CuI , CuBr_2 , CuCl_2 , Cu_2O , CuSO_4 , $\text{Cu}(\text{NO}_3)_2$ and CuCN . Aluminium was taken as AlCl_3 , Al_2O_3 and $\text{Al}_2(\text{SO}_4)_3$. Polystyrene beads were acid-leached free of copper and mixed with the above copper compounds as an inert matrix to provide a 10^6 -fold dilution for the test sample introduced into the atomizer (at the 10^{-12} kg level). This was accomplished by homogenizing a mass of each compound containing 10^{-6} kg of the metal into 10^{-3} kg of matrix. A 10^{-6} kg portion of this sample was further "diluted" with an additional 10^{-3} kg of matrix, thus ensuring a 10^6 -fold dilution. As the polystyrene beads could not be acid-leached free of Al, an oxalic acid matrix was employed for sampling the solid Al compounds. The oxalic acid was purified by sublimation under vacuum and mixed with the aluminium samples in a manner identical with that described above for Cu in polystyrene. Sampling was accomplished by placing approximately 10^{-6} kg of either mixture into the centre of the furnace by removing an end window cap from the atomizer and introducing the sample with a microspatula. The 217.9 nm and 256.8 nm lines were used for copper and aluminium, respectively, for solid sampling - these lines were employed instead of the resonance lines because the latter gave too high absorbance signals.

An absorbance-time profile was obtained for each element in the following manner: using a storage oscilloscope for recording signals and a sufficient mass of each analyte to obtain a peak absorbance of approximately 1, a high sensitivity (0.05 absorbance/cm), fast-scan 20 - 50 ms/cm) absorbance-time trace was photographed. From this trace

and the temperature-time characteristics of the furnace, a plot of the logarithm of the absorbance versus the reciprocal of the absolute temperature over a range of 100 - 300 ms (depending on the element) beyond the appearance time (covering absorbance values ≤ 0.25) was drawn. The activation energy, E_a , was evaluated from the slope of this plot by a least squares analysis. The E_a data reported in this study are the average of at least three separate determinations for each element.

Except where stated otherwise, all absorbance traces were obtained using the following temperature program, as indicated by the temperature setting on the HGA-2100 power supply: dry 100; ash 300; and atomize 2700. When solid samples of copper were atomized, the temperature setting of the ashing stage was increased to 500 in order to remove completely all traces of the polystyrene matrix. The oxalic acid used for aluminium solid sampling was completely removed prior to atomization at the temperature setting 300 for the ashing stage. In all cases, the HGA-2100 was operated in the internal purge gas interrupt mode during atomization.

RESULTS AND DISCUSSION

Since construction of a $\log A$ versus $1/T$ plot requires that the temperature of the atomic vapour be equal to that of the surface of the furnace, absorbance measurements were restricted to the initial few hundred ms of the absorption pulse (Chapter 3). A typical absorbance-time profile in the heated graphite atomizer is presented

in Figure 87. Also shown is an expanded portion of the profile following the appearance of the signal. Absorbance data taken from this region of the curve were used to construct the E_a plots.

Figure 88 is a typical E_a plot obtained from the atomization of 5.0×10^{-12} kg of iron, taken as the chloride. As predicted by the theory, a straight line relationship is observed from which E_a is evaluated.

As expected from equation 5-12, the E_a values were found to be independent of both the initial mass of the sample atomized and the rate of atomization. Figure 89 is an E_a plot obtained by atomizing 0.25, 0.30 and 1.0×10^{-12} kg of Mn, taken as the nitrate. Within the standard deviation of the slopes, the E_a values are equal.

Figure 90 is an E_a plot obtained by atomizing 4.0×10^{-13} kg Mg, taken as the nitrate, at various heating rates of the furnace, i.e., 1.23, 1.06 and 0.73 K ms^{-1} . Within the standard deviation of the slopes, the E_a values are independent of the rate of heating of the atomizer. It can be seen from this plot that, at the higher absorbance values corresponding to the higher temperature portion of the plot, the straight line begins to show negative curvature. This bending, characteristic of every plot, may be the result of a number of factors, including the fact that the temperature of the atomic vapour begins to deviate from the surface temperature of the furnace, the variation with temperature of the activity of the analyte on the surface of the furnace, the decrease in the flux of material entering the vapour phase as the area of the evaporating surface decreases with increasing time, i.e., with increasing temperature, and the possibility that E_a

Figure 87: Typical absorbance-time profile with the inset showing the magnified part of the curve from which the data were taken.

Figure 88: E_a plot for 5.0×10^{-12} kg Fe taken as the chloride, together with oscillogram from which the plot was drawn. Absorbance = 0.05/scale div., time = 50 ms/scale div. Trigger delay time = 700 ms.

Trace	Scope Trigger Delay/ms	Mass of Mn/kg
A	600	2.5×10^{-13}
B	650	3.0×10^{-13}
C	650	7.5×10^{-13}

Figure 89: Oscillograms showing absorbance by varying masses of Mn taken as the nitrate. Absorbance = 0.05/scale div.; time = 50 ns/scale div.

Figure 89(cont'd): E_a plots for varying masses of Mn taken as the nitrate.
 $\circ$ 2.5×10^{-13} kg Δ 3.0×10^{-13} kg $\bullet$ 7.5×10^{-13} kg

Trace	Scope Trigger Delay/ms	Heating Rate/K.ms ⁻¹
A	700	1.23
B	900	1.06
C	1450	0.73

Figure 90: Oscillograms showing absorbance by 4.0×10^{-13} kg Mg at various rates of heating of the atomizer.
Absorbance = 0.05/scale div., time = 50.ms/scale div.

Figure 90(cont'd): E_a plots for 4.0×10^{-13} kg Mg taken as the nitrate at various rates of heating of the atomizer.

$\bigcirc$ 1.23 K ms^{-1} $\triangle$ 1.06 K ms^{-1} $\bullet$ 0.73 K ms^{-1}

is not a temperature-independent parameter (contrary to the assumption made).

To consider the possible role of reduction reactions in the production of free atoms, the standard free energy change per mol of metal, $\Delta G^{\circ}_{\text{reaction}}$, for the reduction of the oxide at the appearance temperature was calculated for each element. The required thermodynamic data were obtained from a number of sources (133 - 136). The results of these calculations are presented in Table 45. The subscript given to each of the $\Delta G^{\circ}_{\text{reaction}}$ values is the temperature closest to the appearance temperature for which the calculation was made. The physical state of the reduced metal was, in contrast with the treatment given by Campbell and Ottaway (17), considered as being governed solely by the temperature of the furnace and the melting and boiling point of the element in question. Only those cases for which $\Delta G^{\circ}_{\text{reaction}} \leq 0$ is the reduction reaction thermodynamically favourable at the appearance temperature. It should be noted that although the standard free energy change, ΔG° , was evaluated assuming the solid components to be at unit activity and gases at unit fugacity, this is not the case in the furnace (where the partial pressure of CO is not $1.01 \times 10^5 \text{ N}\cdot\text{m}^{-2}$ (1 atmosphere)). As a result, the ΔG° values, as written, should be much more favourable than indicated. It is for this reason the standard free energy change $\Delta G^{\circ} \leq 0$ should not be used as the criterion for spontaneity, but simply $\Delta G \leq 0$. The equilibrium constants (calculated from the relationship $\Delta G^{\circ} = -RT \ln K_p$) have also been listed in Table 45. The magnitudes of these constants enable one to appreciate more easily the extent to which such reduction reactions occur. Thermodynamic

Table 45

Standard Free Energy Change for Reduction Reactions

Oxide	Element m.p./K	Element b.p./K	Oxide m.p./K	Oxide b.p./K	Appearance Temp./K	$\Delta G^\circ_{\text{reaction}}/\text{kJ mol}^{-1}$	Log K_{eq}	State of Aggregation of the Metal
CdO	594	1038	d 1173	subl 1832	720	12,700	-0.9	liquid
ZnO	693	1180	2248	-	1140	25,110	-1.2	liquid
PbO	601	2013	1161	-	1040	-92,1050	4.6	liquid
CuO	1356	2848	1599	-	1270	-184,1300	7.4	solid
CoO	2690	3143	2208	-	1430	-100,1400	3.7	solid
MnO	1517	2235	> 1923	-	1480	29,1500	-1.0	solid
FeO	1808	3023	1693	-	1500	-67,1500	2.3	solid
Fe ₃ O ₄	1808	3023	d 1811	-	1500	-113,1500	3.9	solid
MgO	922	1363	3073	3873	1510	180,1500	-6.3	gas
SnO ₂	505	2543	1400	subl 2073	1560	-289,1600	9.5	liquid
NiO	1728	3005	2263	-	1590	-155,1600	5.1	solid
Cr ₂ O ₃	2163	2755	2708	4273	1660	-50,1700	1.6	solid
CaO	1112	1757	2853	3123	1850	146,1900	-4.0	gas
Al ₂ O ₃	933	2740	2318	3253	2080	67,2100	-1.7	liquid
MoO ₃	2890	4885	1068	subl 1428	2100	-644,2100	16.0	solid
V ₂ O ₃	2163	3653	2243	-	2200	-109,2200	2.6	liquid

calculations, however, provide no information as to the rates of the reactions involved. A slightly favourable reaction, in the context of reaction energetics, may actually prove to be unfavourable due to kinetics, and hence, the extent of the reaction may be limited.

Table 46 lists the E_a values obtained for the elements sampled from aqueous solutions, the appearance temperature for each element, and the corresponding literature values for the dissociation energy. The E_a values have a standard deviation of the order of 10%, which represents the sum of the uncertainties in the measurement of temperature ($\approx 2\%$), the absorbance signal with respect to time ($\approx 3\%$), and the least squares slope of the E_a plot ($\approx 5\%$). For those cases in which the sequential processes contributing to the production of atomic vapour were measurable, the resulting E_a values and selected intermediates have been presented in Table 46 as being separated by a slash. The E_a plot for each element is presented in Appendix II.

The activation energies obtained in these studies arise from the fact that a unimolecular rate constant governs the production of observable atoms. Under normal circumstances, rate constant data are obtained from a number of discrete isothermal runs in which total vibrational, rotational and dissociation relaxation is maintained. In the present system, isothermal data points cannot be plotted because the temperature is continuously rising at a high rate. Even under conditions such as these, however, it is probable that thermal equilibrium at each temperature over all degrees of freedom is approximately established (indeed, the data indicate that this must be the case). Data obtained from measurements in shock tubes (137, 138) on the

Table 46

Atomization Energies of the Elements

Element/Form	Appearance Temp./K	E_a /kJ mol ⁻¹	Selected Literature Values Intermediate ^a	Energy/kJ mol ⁻¹	Reference
Pb/HCl	1040	190/120	Pb(l)/Pb-Pb	178/100	50
Pb/HNO ₃					
Cu/HCl	1270	320/180	Cu(s)/Cu-Cu	338/195	50
Cu/HNO ₃					
Co/HCl	1430	410/180	Co(s)/Co-Co	428/167	50
Co/HNO ₃					
Sn/HCl	1560	310/200	Sn(s)/Sn-Sn	302/195	50
Sn/NaOH					
Ni/HCl	1590	410/210	Ni(s)/Ni-Ni	430/232	50
Ni/HNO ₃					
Mo/NH ₄ OH	2100	690	Mo(s)	658	50
V/NaOH	2200	640/490	V-O/V(l)	644/460	50
Fe/HNO ₃	1500	410	Fe(s)	415	50
Cr/HNO ₃	1660	410	Cr(s)	397	50
Cr/HCl					
Mg/HCl	1510	380	Mg-O	393	136
Mg/HNO ₃					

Table 46 (cont'd)

Atomization Energies of the Elements

Element/Form	Appearance Temp./K	E_a /kJ mol ⁻¹	Selected Literature Values Intermediate ^a	Energy/kJ mol ⁻¹	Reference
Cd/HNO ₃	720	270	Cd-0	280	50
Zn/HNO ₃	1140	270	Zn-0	276	50
Mn/HCl					
Mn/HNO ₃	1480	390	Mn-0	402	50
Ca/HCl					
Ca/HNO ₃	1850	380	Ca-0	351	50
Al/HCl					
Al/HNO ₃	2080	980/480	----	---	--
Cd/HCl	670	210	Cd-Cl	209	50
Zn/HCl	940	200	Zn-Cl	205	136
Fe/HCl	1400	360	Fe-Cl	351	50

^aSubscript (s) denotes the heat of atomization of the element from its standard state at 298 K.

Subscript (l) denotes the heat of vaporization of the element.

vibrational and rotational relaxation times of many molecular species indicate that chemical equilibrium can be established despite the extreme rates of rise of temperature that accompany the shock wave. Dissociation relaxation times for many molecules are on the μs time scale (137, pp. 189 - 212), whereas the maximum rate of rise of temperature employed here is only $0.001 \text{ K } \mu\text{s}^{-1}$.

Mechanisms for Atomization of the Elements

Three major pathways leading to gaseous free atoms have been identified: reduction of the analyte oxide by carbon with subsequent sublimation of the metal, thermal dissociation of the metal oxide, and thermal dissociation of the metal chloride. Examples of the three mechanisms are given in the following sections. No attempt has been made to maintain mass balance with respect to the physicochemical transformations in the equations given. Only products for which evidence is available appear.

I. Reduction by Carbon followed by Vaporization

Lead. Two sequential atomization energies have been obtained for lead, 190 and 120 kJ mol^{-1} (46 and 28 kcal mol^{-1}), regardless of whether the analyte is taken as the nitrate or chloride. Figure 91 is the E_a plot for lead. It may be broken into two straight-line segments which intersect at a temperature of approximately 1160 K. In the low temperature region the slope corresponds to an E_a value of 190 kJ mol^{-1} . In the higher temperature region a value of 120 kJ mol^{-1}

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Figure 91: E_a plot for 2.0×10^{-12} kg Pb taken as the nitrate, together with oscillogram from which the plot was drawn. Absorbance = 0.05/scale div., time = 50 ms/scale div. Trigger delay time = 250 ms.

is obtained. These energies can be attributed to the heat of vaporization of lead and the bond dissociation energy of $\text{Pb-Pb}_{(g)}$, having values of 178 and 100 kJ mol^{-1} (42.5 and 24 kcal mol^{-1}), respectively. The appearance temperature recorded for $\text{Pb}(\text{NO}_3)_2$ and PbCl_2 is 1040 K. Below this temperature, $\text{PbO}_{(s)}$ (m.p. = 1161 K) is present as a result of decomposition of the nitrate (139): $\text{Pb}(\text{NO}_3)_2(s) \xrightarrow{925 \text{ K}} \text{PbO}_{(s)}$. Hydrolysis of lead chloride may also result in the production of the oxide. In the absence of reducing agents, $\text{PbO}_{(s)}$ is known to sublime to $\text{PbO}_{(g)}$ (140). Therefore, in the present system $\text{Pb}_{(g)}$ must be formed by the reduction of $\text{PbO}_{(s)}$. This is a favourable reaction at 1050 K (Table 45). Atomization of the lead is therefore a sequence of two processes: (the energy, in kJ mol^{-1} , associated with each process is shown above or below the lines).

Consideration of the ΔH_M and ΔH_D values for Pb suggest that there is an increase in $\text{Pb}_{2(g)}$ species with increasing temperature. The existence of $\text{Pb}_{2(g)}$ in equilibrium with $\text{Pb}_{(l)}$ has also been confirmed mass-spectrometrically (130, 131, 141, 142).

Copper. For both the nitrate and the chloride forms of copper, a single appearance temperature of 1270 K and E_a values of 320 and 180 kJ mol^{-1} (77 and 44 kcal mol^{-1}), corresponding to the heat of atomization of copper and the Cu-Cu bond energy, respectively, were obtained. Below the appearance temperature, $\text{CuO}_{(s)}$ is formed (139):

Brewer and Mastick (140) have reported that $\text{CuO}_{(g)}$ is in equilibrium with $\text{CuO}_{(s)}$ in the temperature range 873 – 1223 K. The production of $\text{Cu}_{(g)}$ may be accounted for only by a reductive decomposition of the solid oxide (m.p. 1600 K), which is a favourable reaction at 1200 K. The proposed atomization mechanism for copper is therefore:

The existence of $\text{Cu}_2(g)$ is well documented in the literature (141, 143, 144) and has been observed in emission from a King furnace (143).

Table 47 presents the results obtained for the atomization of various solid copper compounds, the average values being 360 and 180 kJ mol^{-1} . Thermogravimetric data (139) for the following compounds: Cu_2O , CuCl_2 , CuI , CuCN , CuSO_4 and $\text{Cu}(\text{NO}_3)_2$ show that $\text{CuO}_{(s)}$ is the common decomposition product below a temperature of 1250 K. It may be concluded that copper salts are also atomized as described earlier, the aqueous sampling playing no physicochemical role in the process.

Cobalt. Two E_a values have been obtained for Co, 410 and 180 kJ mol^{-1} (97 and 44 kcal mol^{-1}), corresponding to the heat of atomization of solid cobalt metal and the dissociation energy of Co-Co, respectively. These values are identical for both the nitrate and chloride forms of the analyte. Below the appearance temperature (1430 K), the nitrate and chloride are converted to the oxide (139): $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} \xrightarrow{970 \text{ K}} \text{CoO}_{(s)}$; $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}_{(s)} \xrightarrow{430 \text{ K}} \text{CoO}_{(s)}$. Reduction of $\text{CoO}_{(s)}$ to $\text{Co}_{(s)}$ is favourable at the appearance temperature. Atomization of Co is similar

Table 47

Heats of Atomization of Solid Samples

Compound	Appearance Temp./K	$E_a/\text{kJ mol}^{-1}$	Selected Literature Values	
			Intermediate ^a	Energy/ kJ mol^{-1}
CuI	1300	360/200		
CuBr ₂	1310	350/180		
CuCl ₂	1250	360/170		
Cu ₂ O	1310	370/190	Cu(s)/Cu ₂	338/195
CuSO ₄	1300	320/180		
Cu(NO ₃) ₂	1310	370/160		
CuCN	1310	360/180		
Al ₂ O ₃	2190	850/460		
Al ₂ (SO ₄) ₃	2010	810/460	-----	-----
AlCl ₃	2150	880/480		

^aSubscript (s) denotes the heat of atomization of the element from its standard state at 298 K.

to that for lead and copper:

$\text{Co}_{2(g)}$ has been observed, mass-spectrometrically, effusing from a Knudsen cell containing $\text{Co}_{(l)}$ (145).

Tin. Two sequential atomization energies have been obtained for tin, 310 and 200 kJ mol^{-1} (74 and 47 kcal mol^{-1}), irrespective of whether it is taken as the chloride or hydrous oxide. These energies correspond to the heat of atomization of the metal and the Sn-Sn bond dissociation energy, respectively. $\text{Sn}_{2(g)}$ has been widely reported to have been observed above $\text{Sn}_{(l)}$ (130, 141, 142).

Below the appearance temperature the following reactions occur (139): $\text{SnO}_2 \cdot \text{H}_2\text{O}_{(s)} \xrightarrow{1110 \text{ K}} \text{SnO}_{2(s)}$; $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}_{(s)} \xrightarrow{780 \text{ K}} \text{SnCl}_2 \cdot \text{SnO}_{(s)}$. In neutral media, over the temperature range 994 - 1166 K, $\text{SnO}_{(g)}$ is in equilibrium with $\text{SnO}_{(s)}$ (140); consequently, $\text{Sn}_{(g)}$ must be accounted for by the reductive decomposition of $\text{SnO}_{2(l)}$. The data in Table 45 show that, at the appearance temperature, reduction of the oxide by carbon is very favourable. The following mechanism for the production of $\text{Sn}_{(g)}$ is therefore postulated:

Aggett and Sprott (12) have also indicated that reduction by carbon plays a major role in the production of $\text{Sn}_{(g)}$. These authors

reported a 260 K lower appearance temperature for the atomization of tin from a graphite atomizer as compared to that from a tantalum atomizer.

Nickel. Two sequential atomization energies have been obtained for nickel, 410 and 210 kJ mol⁻¹ (99 and 50 kcal mol⁻¹), corresponding to the heat of atomization of Ni_(s) and the dissociation energy of Ni_{2(g)}, respectively. Ni_{2(g)} has been observed mass-spectrometrically (146).

Below the appearance temperature (1590 K), NiO_(s) is formed by the thermal decomposition of the nitrate (139):

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{s}) \xrightarrow{615 \text{ K}} \text{NiO}(\text{s})$. NiO_(s) must also be formed by the hydrolysis of the chloride, since no difference was observed in the appearance temperature of nickel as either the chloride or the nitrate. NiO_(s) is readily reduced at a temperature of 1600 K to produce Ni_(s). It is reasonable to conclude that Ni_(g) arises from the following reaction sequence:

It is appropriate at this point to reconsider the assumption made in the model concerning the establishment of a gas phase-condensed phase equilibrium. The activation energy for Ni reported by Torsi and Tessari (405 kJ mol⁻¹, (67)) is in agreement with that obtained in this study for the heat of atomization of the metal. Torsi and Tessari (67), however, have not obtained an energy corresponding to the dissociation

of $\text{Ni}_2(\text{g})$, the reason being that condensed phase-gas phase (dimer) equilibrium cannot be attained in their open filament system, but is established in the HGA-2100.

Molybdenum. The E_a value of 690 kJ mol^{-1} ($165 \text{ kcal mol}^{-1}$) obtained for molybdenum is in agreement with the heat of atomization of the element, 685 kJ mol^{-1} .

Unlike Pb, Cu, Co, Sn and Ni, the dimeric metal species (i.e., $\text{Mo}_{2(g)}$) written into the above atomization sequence has been enclosed in parentheses because no E_a value corresponding to the dissociation energy of $\text{Mo}_{2(g)}$ could be obtained from the high temperature region of the E_a plot (because of curvature in the plot as a result of factors discussed earlier). This, however, does not preclude the possibility of the presence of the dimer; it simply means that not all of the $\text{Mo}_{(s)}$ was vaporized within the measurement period. As a result, only the energy associated with the heat of atomization was obtained.

The magnitude of the E_a value does not rule out the formation of an involatile molybdenum carbide species over the initial temperature range studied. Runnels et al. (47) have determined, by energy-dispersive x-ray analysis, that Mo forms a carbide through surface reactions with the graphite of the furnace wall. The E_a value obtained for Mo does suggest, however, that any carbide that is formed is not dissociated to an appreciable extent throughout the temperature range used in this study ($< 2350 \text{ K}$).

1000-fold increases in sensitivity have been reported for molybdenum in graphite atomizers as compared to tantalum- and tungsten-lined atomizers (58). It is possible that in the latter cases an involatile alloy may be formed by molybdenum with tantalum or tungsten (147; 120, p. 462).

When Mo is atomized from a pyrolytic-graphite-coated tube, an atomization energy of 670 kJ mol^{-1} ($160 \text{ kcal mol}^{-1}$), is obtained. This is in agreement with the value of 690 kJ mol^{-1} obtained when Mo is atomized from an uncoated tube. It seems, therefore, that the mechanism of atomization of Mo remains unchanged when pyrolytic-graphite-coated tubes are used. It is reasonable to conclude, therefore, that the increased sensitivity obtained for Mo (and V) with pyrolytic-graphite-coated tubes is due only to the decreased porosity of the pyrolytic graphite surface, as discussed in Chapter 2.

Vanadium. Two E_a values are reported for vanadium; 640 kJ mol^{-1} ($153 \text{ kcal mol}^{-1}$) in the low temperature portion of the E_a plot (2200 - 2360 K) corresponding to the V-O bond energy, and 490 kJ mol^{-1} ($116 \text{ kcal mol}^{-1}$) above 2360 K corresponding to the heat of vaporization of the metal.

Above 2020 K, V_2O_5 is decomposed to $\text{V}_2\text{O}_3(\text{s})$ (m.p. 2240 K). On further heating, $\text{V}_2\text{O}_3(\text{s})$ is decomposed (148): $\text{V}_2\text{O}_3(\text{s}) \rightarrow 2\text{VO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$ liberating $\text{VO}(\text{g})$. Subsequent dissociation of $\text{VO}(\text{g})$ yields an E_a value equal to the V-O bond energy, as observed:

Reduction of $\text{V}_2\text{O}_3(\text{s})$ at the appearance temperature (2200 K) is a

thermodynamically favourable reaction. It would appear from the above data, however, that the kinetics of the reduction are slow. Only above 2360 K is an E_a value obtained which is in agreement with the heat of vaporization of liquid vanadium:

As in the case of Mo, an energy value corresponding to the dissociation of $\text{V}_2(\text{g})$ was not obtained because all of the condensed phase was not vaporized within the time interval of the measurement. At 2360 K the metal, if pure, should be in the liquid form (m.p. 2163 K). It is known (149), however, that small amounts of interstitial carbon can greatly increase the melting point of V (10% C increases the m.p. by approximately 1000 K). As a result, $\text{V}(\text{s})$ can just as likely (in the present circumstances) be substituted for $\text{V}(\text{l})$ in the above equation. Although this necessitates reinterpretation of the E_a value as the heat of atomization of the metal (515 kJ mol^{-1}), the uncertainty of the experimental results ($\pm 10\%$) does not rule this out.

As with molybdenum, dissociation of involatile vanadium carbide was not observed over the initial temperature range studied. This, of course, does not rule out its formation.

Iron. Two different E_a values have been obtained for the atomization of iron: 410 and 360 kJ mol^{-1} (97 and 86 kcal mol^{-1}) depending upon whether the metal is taken as the nitrate or the chloride, respectively. The atomization characteristics of the chloride will be discussed in

a later section. When iron is taken as the nitrate, the E_a value may represent either the dissociation energy of Fe-O (402 kJ mol^{-1}) or the heat of atomization of iron (415 kJ mol^{-1}). The correct choice must be based on the physicochemical behaviour of the analyte as follows. Below the appearance temperature (1500 K), $\text{Fe}(\text{NO}_3)_3$ is converted to the oxide (139): $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}(\text{s}) \xrightarrow{585 \text{ K}} \text{Fe}_3\text{O}_4(\text{s}) \equiv (\text{FeO} \cdot \text{Fe}_2\text{O}_3)$. Table 45 indicates that reduction by carbon of both FeO and Fe_3O_4 at 1500 K is very favourable. In addition, Aggett and Sprott (12) have observed at 220 K decrease in the appearance temperature of iron from a graphite atomizer as compared to that from a tantalum atomizer. These data strongly suggest that iron vapour must arise from the sublimation of solid iron, and that the observed E_a value of 410 kJ mol^{-1} corresponds to the energy of the reaction:

Because all of the iron on the surface of the furnace was not vaporized during the time taken in the measurement, no E_a value corresponding to the dissociation energy of $\text{Fe}_2(\text{g})$ was observed.

Chromium. The E_a value of 410 kJ mol^{-1} (99 kcal mol^{-1}) obtained for chromium (taken as either the chloride or nitrate) is in agreement with the heat of atomization of the element, 397 kJ mol^{-1} . Below the appearance temperature of 1660 K , $\text{Cr}_2\text{O}_3(\text{s})$ is the most stable oxide of chromium (139). Reduction of the oxide by carbon is highly favourable at the appearance temperature, hence,

As in the cases of Mo, V and Fe, no dimeric $\text{Cr}_2(\text{g})$ species was observed.

To gain greater insight into the processes being investigated and the energy values obtained from this type of measurement, the energy required to produce gaseous metal atoms in an electronic excited state was measured.

If the atomic population in an electronic excited state is studied, the measured energy should equal the sum of the energies for the formation of atomic vapour and electronic excitation. This determination may be made only with an element having a line arising from a transition from an upper electronic level of energy not less than 80 kJ above the electronic ground state (in order to reliably measure this energy difference). Such a precaution is necessary because of the $\pm 10\%$ uncertainty in the measurement. Additional requirements for the transition selected are that the line be strong in emission (from the hollow cathode lamp emission source), that it have an appreciable gf value and not be much above 80 kJ in energy, otherwise the population of the electronic excited state would be too small. Finally, elements which meet these criteria must also satisfy the temperature requirement outlined below. Atomization of the element must take place at a sufficiently high temperature such that the electronic excited state is adequately populated. Elements that have an appearance temperature of 1000 K are poor choices for this reason even though they may satisfy all other criteria. All of these criteria are satisfied by Cr, which has a line at 520.8 nm (91 kJ above the electronic ground state).

Figures 92 and 93 are E_a plots obtained from the atomization of chromium. Figure 92 represents the production of the electronic ground state atoms at 357.8 nm ($E_a = 410 \text{ kJ mol}^{-1}$), whereas Figure 93 represents the production of the electronic excited state atoms at 520.8 nm ($E_a = 500 \text{ kJ mol}^{-1}$). The observed 90 kJ mol^{-1} energy difference is in excellent agreement with the expected difference of 91 kJ mol^{-1} . This observation lends support to the credibility of the energy measurements obtained by this technique and also to the assumption that a Boltzmann distribution of population has been attained. Recently, Ottaway and Shaw (150) have described a graphite furnace atomic emission technique in which detection limits for a number of elements have been found to vary with temperature in accordance with the Boltzmann equation.

II. Dissociation of Oxides

Magnesium. The energy of atomization obtained for magnesium is 380 kJ mol^{-1} (90 kcal mol^{-1}), regardless of whether the chloride or the nitrate is taken for analysis. This value correlates well with the bond dissociation energy of Mg-O (393 kJ mol^{-1}). Thermogravimetric analysis (139) indicates that $\text{MgO}_{(s)}$ (m.p. 3073 K) is a common intermediate in the decomposition of both the chloride and the nitrate below the appearance temperature (1510 K): $\text{MgCl}_2 \cdot 5\text{H}_2\text{O}_{(s)} \xrightarrow{890 \text{ K}} \text{MgO}_{(s)}$; $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}_{(s)} \xrightarrow{750 \text{ K}} \text{MgO}_{(s)}$. Reduction of $\text{MgO}_{(s)}$ by carbon at 1500 K is very unfavourable; this suggests that $\text{Mg}_{(g)}$ is formed by thermal dissociation of the oxide in the gas phase. It is known, however, that $\text{Mg}_{(g)}$ and $\text{O}_{2(g)}$ are the principal gas phase species in equilibrium.

Figure 92: E_a plot for 2.5×10^{-12} kg Cr taken as the nitrate, together with oscillogram from which the plot was drawn. Absorbance = 0.05/scale div., time = 50 ms/scale div. Trigger delay time = 800 ms.
 $\lambda = 357.8$ nm.

Figure 93: E_a plot for 2.5×10^{-10} kg Cr taken as the nitrate, together with oscillogram from which the plot was drawn. Absorbance = 0.05/scale div., time = 50 ms/scale div. Trigger delay time = 900 ms. $\lambda = 520.8$ nm.

with $\text{MgO}_{(s)}$ (151). Dissociation upon vaporization often occurs when the heat of sublimation of the oxide is greater than its dissociation energy. To a first approximation, the bond energy of the molecule may be compared with the heat of vaporization of the substance. If the bond energy is much higher than 2/3 of its heat of vaporization, the substance may be expected to vaporize without dissociation. If the bond energy is less than the heat of vaporization, the substance will be partially or wholly dissociated in the gas phase, depending on the relative magnitudes of these two energies (152, p. 80). The high heat of sublimation of $\text{MgO}_{(s)}$, $661 \pm 16 \text{ kJ mol}^{-1}$ (151), leads to its dissociation upon vaporization. It would be reasonable, in light of the above, to expect the atomization energy to correspond to the negative of the heat of formation of $\text{MgO}_{(s)}$ at and above the appearance temperature (1510 K); i.e., 730 kJ mol^{-1} (calculated from (136) for $\text{MgO}_{(s)} \rightarrow \text{Mg}_{(g)} + \frac{1}{2}\text{O}_{2(g)}$ at 1600 K). When excessively large masses of the analyte are atomized (100-fold larger than those used to obtain the above data), an E_a value of 760 kJ mol^{-1} is obtained. A reasonable explanation for these observations involves a consideration of the equilibrium vapour pressure of MgO at and above the appearance temperature. Vapour pressure data (153) indicate that, at the appearance temperature and with the analyte masses used in this study (approximately 10^{-13} kg for Mg), all of the oxide is vaporized. As a result, magnesium atoms are formed by gas phase dissociation of $\text{MgO}_{(g)}$:

reduction of $\text{CdO}_{(s)}$ by carbon is not thermodynamically favourable. Gaseous Cd may be accounted for only by dissociation of the oxide. Brewer and Mastick (140) have reported that, in the absence of a reducing atmosphere, $\text{Cd}_{(g)}$ and $\text{O}_{2(g)}$ are the major species in equilibrium with solid CdO. Atomization of CdO is identical with that encountered for MgO. The atomization energy should correspond to the sum of the energies of the negative of the heat of formation of $\text{CdO}_{(s)}$ (at the delay temperature of 700 K) and the heat of vaporization of $\text{Cd}_{(l)}$, these being approximately 262 and 100 kJ mol^{-1} , respectively, corresponding to the reaction:

As in the case of MgO, the masses of analyte used in this study were not sufficient to yield the equilibrium partial pressure of the analyte within the graphite tube. When very large masses of analyte are introduced (500-fold larger than that normally employed) into the graphite tube, an E_a of 340 kJ mol^{-1} is obtained, corresponding to the ΔH_{700}^0 of the above reaction (362 kJ mol^{-1} , calculated from data in (136)). It is evident from such studies that at low concentrations, all of the analyte has been transferred to the gas phase below the appearance temperature. As a result, the measured E_a value corresponds to the bond dissociation energy of $\text{CdO}_{(g)}$.

Zinc. The atomization energies for zinc are 270 and 200 kJ mol^{-1} (65 and 48 kcal mol^{-1}) depending upon whether the analyte is taken as the nitrate or the chloride, respectively. These values are in

close agreement with the Zn-O and Zn-Cl bond dissociation energies, respectively. The atomization behaviour of the chloride will be presented in a later section.

Thermogravimetric analysis (139) of $\text{Zn}(\text{NO}_3)_2$ indicates that the monoxide is formed below the appearance temperature (1140 K):
 $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{s}) \xrightarrow{623 \text{ K}} \text{ZnO}(\text{s})$. Reduction of the oxide by carbon is unfavourable below the appearance temperature; $\text{Zn}(\text{g})$ must therefore result from the dissociation of $\text{ZnO}(\text{g})$. As in the case of MgO and CdO, ZnO dissociates upon vaporization. $\text{Zn}(\text{g})$ and $\text{O}_2(\text{g})$ are the major species in equilibrium with $\text{ZnO}(\text{s})$ (140, 154). The agreement between E_a and the Zn-O bond energy can be rationalized only by an argument identical with that invoked for CdO. Production of $\text{Zn}(\text{g})$ directly from $\text{ZnO}(\text{s})$ requires not only the energy equal to the negative of the heat of formation of $\text{ZnO}(\text{s})$ at 1100 K but also the heat of vaporization of $\text{Zn}(\text{l})$, i.e.,

the total of such energy, $\Delta H_{1100}^0 = 468 \text{ kJ mol}^{-1}$. Atomization of large masses of ZnO yields an E_a of 430 kJ mol^{-1} . It can be shown from vapour pressure data (153) that the masses of Zn analyte normally employed in this study are too low to yield the equilibrium partial pressure of $\text{ZnO}(\text{g})$ within the graphite tube at 1100 K. Consequently, all of the ZnO is vaporized into the gas phase where dissociation occurs.

Manganese. The atomization energy obtained for manganese is 390 kJ mol^{-1} (92 kcal mol^{-1}) and corresponds to the bond dissociation energy of MnO. Below the appearance temperature, $\text{MnO}(\text{s})$ is present on the graphite

surface irrespective of whether it has been introduced as the chloride or the nitrate (139):

Brewer and Mastick (140) have reported that, at a temperature of 1767 K, $\text{Mn}(\text{g})$ and $\text{O}_2(\text{g})$ are the major species in equilibrium with $\text{MnO}(\text{s})$ (the heat of vaporization of $\text{MnO}(\text{s})$ is 508 kJ mol^{-1} (152, p. 177)).

Consequently, the atomization energy should correlate with the sum of the energies of the negative of the heat of formation of $\text{MnO}(\text{s})$ from the elements in their standard states at 1500 K, and the heat of vaporization of the metal, i.e.,

corresponding to a ΔH_{1500}° of 611 kJ mol^{-1} . When large masses of the analyte are atomized, an E_a of 650 kJ mol^{-1} is obtained, in agreement with the above value. As has been the case with metal oxides discussed earlier, the normal masses of analyte employed in this study are too small to yield the equilibrium partial pressure of the oxide in the gas phase (153); consequently, all of the analyte is vaporized into the gas phase below the appearance temperature. Subsequent dissociation of MnO leads to the agreement between the observed E_a and the Mn-O bond

The following reaction is postulated:

(5-XXV)

At higher temperatures, when all of the CaO(s) has disappeared, E_a should correspond to the Ca-O bond energy.

Aluminium. Two sequential atomization energies have been obtained for Al, 980 and 480 kJ mol^{-1} (234 and 114 kcal mol^{-1}). Below the appearance temperature, Al_2O_3 is the common intermediate for the nitrate and the chloride (139): $\text{Al(NO}_3)_3 \cdot 9\text{H}_2\text{O(s)} \xrightarrow{1020-1270 \text{ K}} \text{Al}_2\text{O}_3\text{(s)}$; $\text{AlCl}_3 \cdot 6\text{H}_2\text{O(s)} \xrightarrow{770 \text{ K}} \text{Al}_2\text{O}_3\text{(s)}$. Since reduction of this oxide is not thermodynamically favourable at the appearance temperature, Al(g) must be formed by the thermal decomposition of an oxide(s). This conclusion is supported by the observations of Aggett and Sprott (12) that the appearance temperature for atomization of aluminium is the same from both a carbon and a tantalum atomizer. The vapour in equilibrium with $\text{Al}_2\text{O}_3\text{(s/l)}$ is a complex mixture of atomic and molecular species -- Al, AlO, Al_2O , Al_2O_2 , O_2 and O have been reported (156,157). Although no consistent mechanism for Al(g) formation that accounts for the observed E_a value can be advanced, it seems reasonable that one or more oxide species may be involved and that formation of Al(g) may arise by direct decomposition of Al_2O_3 .

The results of atomization of some selected aluminium compounds introduced into the atomizer in an oxalic acid medium are presented in Table 47. Like the chloride and the nitrate, the sulphate is also

converted to the oxide below the appearance temperature (139) :

$\text{Al}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}(\text{s}) \xrightarrow{880-1270 \text{ K}} \text{Al}_2\text{O}_3(\text{s})$. The atomization energies of the solid compounds are in agreement with those obtained using aqueous solutions of aluminium salts.

Substitution of N_2 for Ar as the sheath gas decreases the peak height and integrated sensitivities for Al by a factor of three (Figure 47). This effect has been explained, on the basis of equation 1-24, as being the result of suppression of the dissociation of AlCN formed at high temperatures. Identical atomization energies are obtained for aluminium in both Ar and N_2 sheath gases. This may be the result of the formation of an insignificant amount of AlCN over the initial 300 ms following the appearance of the Al signal or the result of an insignificant amount of dissociation of any AlCN formed.

III. Dissociation of Chlorides

Cadmium. When Cd is taken as the chloride, an E_a value of 210 kJ mol^{-1} (50 kcal mol^{-1}) is obtained, in agreement with the Cd-Cl bond energy of 209 kJ mol^{-1} . At the appearance temperature of the signal (720 K), cadmium is present as the chloride if it is introduced into the atomizer in chloride media (139): $\text{CdCl}_2 \cdot 5\text{H}_2\text{O}(\text{s}) \xrightarrow{873 \text{ K}} \text{CdO}(\text{s})$. Mass-spectrometric analysis of the vapour, above liquid CdCl_2 , over the temperature range $785-838 \text{ K}$, indicates that $\text{Cd}(\text{g})$, $\text{CdCl}_2(\text{g})$ and $\text{CdCl}(\text{g})$ are the major species (158). The formation of $\text{CdCl}(\text{g})$ was accounted for by dissociation of $\text{CdCl}_2(\text{g})$ by ion-source electron impact and, as such, was not considered to be a direct product of vaporization. The results of the present study can be rationalized only by assuming that $\text{CdCl}(\text{g})$ is a direct product of vaporization of $\text{CdCl}_2(\text{l})$ since gas phase

dissociation of $\text{CdCl}_{2(g)}$ should yield an E_a value twice as large as that obtained. No satisfactory alternative interpretation can be offered.

Zinc. When zinc is atomized from hydrochloric acid media, an appearance temperature of 940 K is obtained. The 200 K decrease in the appearance temperature, with respect to that of the nitrate, is indicative of a radical change in atomization characteristics; hence, atomization appears to proceed via thermal dissociation of the chloride. The agreement obtained between the E_a value and the Zn-Cl bond energy can only be accounted for by the gas phase dissociation of $\text{ZnCl}_{(g)}$. As in the case of CdCl_2 , this reaction presupposes the existence of $\text{ZnCl}_{(g)}$ in the vapour phase above $\text{ZnCl}_{2(l)}$. However, mass-spectrometric studies (159) have not reported $\text{ZnCl}_{(g)}$ as a major species in equilibrium with $\text{ZnCl}_{2(l)}$.

Iron. Atomization of the chloride commences at 1400 K. An E_a of 360 kJ mol^{-1} (86 kcal mol^{-1}) was obtained which is in close agreement with the reported Fe-Cl bond energy. At a temperature of approximately 590 K (160), $\text{FeCl}_{3(s)}$ is reduced to $\text{FeCl}_{2(s)}$. Above 674 K $\text{FeCl}_{2(s)}$ sublimes. It has been reported (161) that the major gaseous species in equilibrium with $\text{FeCl}_{2(s)}$ are $\text{FeCl}_{2(g)}$ and $(\text{FeCl}_2)_2(g)$. The E_a value obtained in this study could only be achieved by atomizing large masses of the analyte (i.e., above 10^{-11} kg Fe).

Relationship of the Appearance Temperature to E_a

In agreement with the findings of Johnson et al. (10), a linear relationship between the appearance temperature and the atomization energy of the analyte has been observed. The slope of such a plot, shown in Figure 94, is approximately $0.25 \text{ kJ mol}^{-1} \text{ K}^{-1}$ and is in agreement with

Figure 94: Plot of the activation energy of the atomization step versus the appearance temperature for small analyte masses.

that calculated from the data of Johnson et al. (10). No point is shown for Al in this figure because its coordinates (2080 K, 980 kJ mol⁻¹) are anomalous with respect to the linear relationship observed with the other elements. Atomization of Al occurs predominantly by solid-state decomposition. When the coordinates for Al are plotted on a graph containing the data for CdO, ZnO, MnO, MgO and CaO, which were obtained using large masses of the analytes, a straight line of slope 0.4 kJ mol⁻¹ K⁻¹ is obtained, as shown in Figure 95. The feature common to each of these oxides is that atom formation occurs as a result of solid-state decomposition of the oxide.

The linear relationship between the atomization energy and the appearance temperature may be predicted from equation 5-12. At the appearance temperature, equation 5-12 may be written as:

$$(E_a + \Delta H^0) = 2.3(A_0 - \log A_{T_{app}})T_{app}R \quad (5-15)$$

$A_{T_{app}}$ is, by definition, the minimum detectable signal and, to a first approximation, is a constant, independent of the nature of the element, its magnitude being determined by the noise level of the baseline at the point when the atomic absorption signal is first perceived to rise from the baseline noise. $A_{T_{app}}$ is also independent of temperature. Additionally, to a first approximation, A_0 is independent of temperature. If the variation in k_A (equation 5-11) for various elements is neglected, equation 5-15 predicts a linear relationship between the atomization energy and the appearance temperature. The fact that two different slopes are obtained from the plots of this relationship, as shown in Figures 94 and 95, must be the result of a substantial increase in the magnitude of A_0 for those cases where the mechanism of atom formation

Figure 95: Plot of the activation energy of the atomization step versus the appearance temperature for large analyte masses.

involves a solid-state decomposition to give gaseous products.

The major factor responsible for an increase in A_0 is the entropy change accompanying the reaction.

L'vov (56) has also rationalized the linear relationship between the atomization energy and the appearance temperature by considering that atom formation is the result of sublimation of the metal. This, however, is based on the implicit assumption that physical and chemical equilibria exist within the atomizer; additionally, consideration has not been given to those cases for which atom formation is the result of a molecular dissociation process.

Figure 94 is useful for the purposes of prediction. With a knowledge of the experimental appearance temperature of the analyte, an atomization energy may be obtained. By correlating E_a with the energy of some possible atomization processes, as outlined earlier, a reasonable guess as to the identity of the immediate precursor to analyte atoms may be made. The correlation between E_a and T_{app} also appears to be independent of the type of atomizer used (cf. reference 10).

The mechanism of atomization may be obtained from a knowledge of the appearance temperature of the element, a detailed consideration of the physicochemical properties of the analyte and/or its decomposition products below the appearance temperature, and a consideration of thermodynamic data. Treatment of the atom formation processes from the point of view of a quasi-equilibrium appears to lead to conclusions in reasonable agreement with the experimental results.

Summary

Quantitative evidence has been presented regarding the mechanism of atomization of a number of elements. The major pathways leading to gaseous atoms have been found to be thermal dissociation of the metal oxide, reduction of the oxide by carbon followed by vaporization of the free metal and thermal dissociation of the metal halide.

The energy values obtained by the methods outlined in this study provide information only as to the major suppliers of gas phase atoms over the initial stages of signal production. Generation of atoms by other species at significantly higher temperatures, not handled by this technique (e.g., carbides of Fe, Cr, Ni, Mo, V, etc., which may give rise to the characteristically long decay regions associated with these signals) cannot be investigated and, consequently, formation and decomposition of other species cannot be ruled out.

Chapter 6

Atomization Above Atmospheric Pressure in Graphite Furnace AAS

The influence of an applied pressure of inert gas on the rate of loss of atomic vapour from a heated graphite atomizer has been discussed in Chapter 4. Because diffusion of the atomic vapour is reduced under an applied pressure, it is of interest to study the effect of an applied pressure on the analytical characteristics of the absorbance signals. L'vov (11) investigated the effects of an applied pressure of inert gas on the atomization processes within an isothermal cuvette. He observed that an applied pressure broadens the absorbance-time profiles by increasing the residence time of the atomic vapour, decreases the peak absorbance, and improves the linear range of the calibration curves - a consequence of broadening of the absorption line profile (Lorentz effect). Apart from the stated theoretical independence of the integrated absorbance from the ambient pressure, no experimental data which support this statement have been published.

Commercial atomizers, such as the HGA-2100, do not function as isothermal cuvettes; consequently, many of the conclusions drawn by L'vov (11) regarding the effects of an applied pressure on the atomization characteristics of various analytes must be critically re-examined.

EXPERIMENTAL

Apparatus. The furnace and pressurizable housing have been described in Chapter 4. Besides using the commercial power supply for the furnace, a novel, laboratory-made ~~power supply~~ was also used in this study. Unlike conventional graphite furnace power supplies, this has, in addition to the usual drying and ashing stages, two high-temperature atomization stages. In addition, its power capabilities are much greater than the commercial units. A custom-wound transformer (Electrodesign Ltd., Ville Lasalle, Quebec, Canada) operating at 208 V provides 1000 amperes at 15 volts to the furnace. With conventional power supplies, the highest rate of rise of temperature requires the maximum atomization setting, resulting in the maximum temperature of the atomizer being attained. The power supply described above allows maximum rate of heating of the furnace for a short period of time with the first atomization stage while maintaining a controllable upper limit on the temperature with the second atomization stage. This flexibility allows for a wider variety of heating regimes and may be used to achieve very rapid heating to a preset temperature followed by isothermal conditions. Figure 96 shows the temperature-time profiles for the furnace when powered by both the new power supply (set at 80% power output in the first atomization stage) and the commercial HGA-2100 power supply (at an atomization setting of 2700 C). The final, upper temperatures are approximately the same but the manner in which they are achieved is radically different. The new power supply heats the furnace three times faster than the commercial HGA-2100 unit (3.5 K ms^{-1} versus 1.2 K ms^{-1} , based on a measurement of the slope of the

Figure 96: Temperature-time profile of the surface of an uncoated graphite tube.

- A. Atomizer heated by the laboratory-built power supply at 80% output power ($dT/dt = 3.5 \text{ K ms}^{-1}$).
- B. Atomizer heated by the Perkin-Elmer power supply set at 2700 C ($dT/dt = 1.2 \text{ K ms}^{-1}$).

temperature-time curve of an uncoated tube taken from its initial linear segment).

Except where stated otherwise, the furnace was operated with the Perkin-Elmer power supply. Pyrolytic-graphite-coated tubes (supplied by The Perkin-Elmer Corporation) were used throughout.

Reagents, gases and the detector-recorder system have been described in earlier chapters.

Procedure. The sequence of operations followed for sample atomization under pressure is described below. Sample volumes of $5 \times 10^{-6} \text{ dm}^3$ were introduced through the injection port of the pressure chamber with an Eppendorf pipette fitted with disposable plastic tips. The sample was subjected to the usual drying and ashing with both internal and external sheath gases flowing. The heating sequence was then interrupted before the ashing stage was completed, and the flow of both sheath gases was stopped. The injection port was then closed and the furnace was flushed once with the pressurizing gas (directly from a cylinder of the compressed gas) and then pressurized to the desired pressure (reproducibility ± 2 psig). The drying, ashing and atomization stages were then reinitiated and absorbance measurements taken. The gas pressure was then released through a separate valve, the chamber repressurized and the blank signal obtained. The sequence of operations (including the blank), as described, requires approximately two minutes for completion. In addition to the measurements taken above atmospheric pressure, runs below atmospheric pressure were made using a water aspirator.

RESULTS AND DISCUSSION

The effects of increasing pressure on the shapes of the absorbance pulses are two-fold: a reduction in the magnitude of the peak and a shift of the entire pulse to increasingly longer times. Tables 48 - 51 present the pulse characterization times as a function of applied pressure of Ar for Cd, Pb, Cu and Mo. Although the rate of heating of the furnace was varied with each of the elements, a number of conclusions may be drawn. With increasing pressure both the appearance time of the pulse and the time to reach the peak absorbance increase for each element. The display times for Cd and Pb decrease, whereas those for Mo and Cu increase. The above observations are explained below.

Effect of Pressure on the Appearance Time

The appearance time is determined by the rate of analyte evaporation. Although the mechanisms of atom formation are complex, for simplicity, evaporation may be treated as the only process responsible for the formation of atomic vapour (11, Chapter 1). The appearance time is determined by the rate of evaporation, $R(T)$, and is subject to the influence of the parameters which alter $R(T)$. The rate of analyte evaporation is exponentially dependent upon the temperature, as described by equations 1-22 and 1-23. A minimum temperature, T_{vap} , must be attained in order that $R(T)$ be rapid. Thereafter, an increase by 100 - 200 K close to T_{vap} will increase $R(T)$ by an order of magnitude. The time taken to vaporize a sample is, therefore, roughly equal to the time required to increase the temperature of the atomizer by a few

Table 48

Effect of Pressure on the Pulse Characterization

Times of Cd

$p_{Ar}/10^5 \text{ N}\cdot\text{m}^{-2}$	Characterization times/ms			
	$\tau_{\text{appearance}}$	τ_{peak}	τ_{end}	τ_{display}
1.0	240	550	1850	1610
3.1	250	580	1650	1400
5.2	280	580	1350	1070
7.2	320	620	1300	980
9.3	330	630	1250	920

Table 49.

Effect of Pressure on the Pulse Characterization
Times of Pb

$p_{Ar}/10^5 \text{ N}\cdot\text{m}^{-2}$	Characterization times/ms			
	$\tau_{\text{appearance}}$	τ_{peak}	τ_{end}	τ_{display}
1.0	770	1080	2300	1540
3.1	830	1130	2000	1180
5.2	830	1130	1800	970
7.2	840	1120	1600	760
9.3	870	1170	1500	630

Table 50

Effect of Pressure on the Pulse Characterization

Times of Cu

$P_{Ar}/10^5 \text{ N}\cdot\text{m}^{-2}$	Characterization times/ms			
	$\tau_{\text{appearance}}$	τ_{peak}	τ_{end}	τ_{display}
0.4	470	1550	3700	3230
1.0	500	1550	4400	3900
3.1	600	1680	4800	4200
5.2	600	1700	5000	4400
7.2	650	1700	5200	4550
9.3	650	1760	5300	4650
11.4	700	1780	5450	4750

Table 51

Effect of Pressure on the Pulse Characterization

Times of ^6Mo

$p_{\text{Ar}}/10^5 \text{ N}\cdot\text{m}^{-2}$	Characterization times/ms			
	$\tau_{\text{appearance}}$	τ_{peak}	τ_{end}	τ_{display}
1.0	2100	3530	10500	8400
3.1	2300	3950	10500	8200
5.2	2350	4130	10900	8550
7.2	2450	4250	11450	9000
9.3	2550	4700	12000	9450

hundred degrees close to the temperature T_{vap} .

The relationship between the rate of evaporation and the ambient pressure has been studied by a number of workers (162 - 165). Bradley et al. (165) considered the effects of an external pressure on the rate of isothermal evaporation of liquid droplets. Assuming that droplet evaporation takes place within an enclosure, the walls of which consist of an adsorbent material such as charcoal, giving an effectively zero vapour pressure at the walls, and that the molecules evaporating from the surface do not begin their diffusion processes directly from the surface of the evaporating sphere, but from an enveloping sphere of larger radius, the rate of evaporation as a function of pressure can be expressed as:

$$R(P) \propto 1/(x + yP) \quad (6-1)$$

where x and y are a collection of constants dependent upon the diffusing species, the droplet radius, the equilibrium vapour pressure at a given temperature, and the distance of the centre of the droplet from the walls of the enclosure. The function $R(P)$ approaches the vacuum rate as $P \rightarrow 0$ and asymptotically approaches 0 as $P \rightarrow \infty$. Although the evaporation of droplets has been considered, equation 6-1 should be directly applicable to evaporation of material from a plane surface (it being related to the pressure through the Kelvin equation). As the ambient pressure increases, the appearance time increases, reflecting the longer period of time required for the temperature of the analyte to increase to the point where its rate of evaporation is comparable to that at atmospheric pressure. An additional effect responsible for the increase

in the appearance time with applied pressure is the lowering of the absolute sensitivity with which the element can be determined. This effect will be further discussed in a subsequent section.

To account for the increased time necessary to attain the absorption peak, the influence of pressure on the atomization time must be considered.

Effect of Pressure on τ_1

The increase with pressure in the time required to attain the absorption peak is approximately equal to the increase in the appearance time for Cd, Pb and Cu, as is evident from the τ_1 values presented in Table 52. The atomization time for these elements is independent of the applied pressure, whereas that for Mo increases with increasing pressure; for copper, this relationship was observed over a pressure range of almost 30-fold.

Although the rate of evaporation is related to the ambient pressure (equation 6-1), its dependence on the temperature, or the rate of rise of temperature in the case of accelerated evaporation (equation 1-23), is much more pronounced. To a good approximation, therefore, τ_1 will be exponentially dependent on γ but independent of the ambient pressure, provided the furnace is heated at a constant rate during the period of analyte evaporation. Figure 97 presents the temperature-time profile of the surface of the HGA-2100 furnace superimposed on the absorbance-time profile of each element. The rate of heating of the furnace as a function of time ($\gamma = dT/dt$) is also shown. The arrows

Table 52

Effect of Pressure on τ_1

$p_{Ar}/10^5 \text{ N}\cdot\text{m}^{-2}$	τ_1/ms			
	Cd	Pb	Cu	Mo
0.4	---	---	1080	----
1.0	310	310	1050	1430
3.1	330	300	1080	1650
5.2	300	300	1100	1780
7.2	300	280	1050	1800
9.3	300	300	1110	2150
11.4	---	---	1080	----

Figure 97: Temperature and rate of heating of the atomizer as a function of time superimposed on the absorbance-time profiles of Cd, Pb, Cu and Mo.

at the top of each absorbance peak are quantitative measures of the direction and magnitude of the pressure-induced shift of each absorption pulse to longer time (higher temperature) as a result of the ambient pressure increasing from 100 to 930 $\text{kN}\cdot\text{m}^{-2}$ (1 to 9.2 atm). Atomization (the time to reach the peak absorbance) of Cd, Pb and Cu occurs over the linear portion of the temperature-time profile of the furnace (i.e., $\gamma = \text{constant}$) at all pressures, and for these elements τ_1 is independent of the applied pressure. Atomization of Mo occurs in that temperature region where γ is a decreasing function of time. As the pressure is increased, shifting the Mo pulse to higher temperature, γ is further decreased. It is clear, that as the pressure increases, the rate of heating of the atomizer decreases over the rise time of the Mo signal; consequently, τ_1 for Mo increases with pressure. Slight changes in γ over this time period produce large changes in τ_1 as these two parameters are related in an inverse exponential manner.

To verify this conclusion, Mo was atomized under pressure using the new laboratory-built power supply to power the furnace. Without reaching excessively high temperatures (Figure 96), it is possible to achieve a constant, high rate of rise of temperature over the time interval required to attain the maximum absorbance for Mo. Table 53 shows that the τ_1 values obtained for Mo are independent of the applied pressure provided that, at all pressures, the rate of heating of the furnace is constant over the rise of the absorption pulse to a maximum.

Table 53

Effect of Pressure on the Pulse Characterization

Times and τ_1 for Mo^a

Characterization times/ms					
$p_{Ar}/10^5 \text{ N}\cdot\text{m}^{-2}$	$\tau_{\text{appearance}}$	τ_{peak}	τ_{end}	τ_{display}	τ_1/ms
1.0	460	700	1750	1290	240
3.1	490	730	1800	1310	240
5.2	510	770	1900	1390	260
7.2	540	790	2000	1460	250
9.3	600	840	2100	1500	240

^a Obtained using the laboratory -built power supply for the furnace,
and a rate of heating of the furnace of 3.5 K ms^{-1} .

Effect of Pressure on the Display Time and τ_2

The variation of the display times of the elements as a function of pressure (Tables 48 - 51) may be explained by considering that the shape of the absorption pulse is determined by two opposing "rate-constants", k_1 characterizing the rate of production of atomic vapour, and k_D characterizing its rate of loss (Chapter 5). Since τ_1 for Cd, Pb and Cu is unaffected by pressure, changes in the display times for these elements as a function of applied pressure are determined solely by the tail of the pulse, which is governed by k_D . The shift of the pulses to higher temperature with increasing pressure causes a minor increase in the rate of loss of atomic vapour (i.e., rates of loss by diffusion increase according to $T^{1.5}$, equation 1-20). Whereas the rate of vapour loss due to diffusion is inversely related to the applied pressure, at high pressure convection currents mechanically expel the atomic vapour from the analytical volume as the temperature of the sheath gas within the furnace increases (11, p. 211, Chapter 4). Losses are largest for Cd and Pb because the signals for these two elements occur simultaneously with the initial rapid heating period of the furnace when expansion of the pressurizing gas and mechanical expulsion of the entrained analyte vapour is at a maximum. Correspondingly, the display times for these elements decrease rapidly with applied pressure. At higher temperatures, where Cu and Mo begin to be atomized rapidly, the initial period of rapid expansion of gas has passed, this effect becoming smaller with time. Under the conditions of minimum convectional loss, atomic vapour is removed from the analytical volume

by diffusion to the cooler extremities of the furnace where condensation occurs and also by diffusion through the sample injection port. As the ambient pressure is increased, such diffusional losses decrease, with the result that the atomic vapour remains within the analytical volume of the furnace for a longer period of time. Increases in the display times were noted for Cu and Mo as a result of these effects.

The residence times of Cd, Pb, Cu and Mo are presented in Table 54. Their variation with applied pressure parallels that of their display times. Although convectional losses are much reduced for Cu and Mo, the increase in the τ_2 values for these elements is not directly proportional to the applied pressure, contrary to the prediction of the theory (11, 56).

Effect of Pressure on the Peak Height and Integrated Absorbance

The normalized peak height and integrated absorbances for each of the elements (the amount of the analyte being held constant) as a function of applied pressure of Ar are plotted in Figures 98 and 99, respectively. In each case the sensitivity of the element decreases as the applied pressure increases. The exponential-like attenuation of each signal with increasing pressure is similar to that obtained by Nemets and Nikolàev (166) and Nemets et al. (167).

When it may be assumed that the width of the emission line in the source is much smaller than the width of the absorption line and in the general case when the absorption line is determined by Doppler and Lorentz broadening, the measured absorbance (84) is given by (without considering the hyperfine structure of the absorption line,

Table 54

Effect of Pressure on τ_2

$p_{Ar}/10^5 \text{ N}\cdot\text{m}^{-2}$	τ_2/ms			
	Cd	Pb	Cu	Mo
0.4	---	---	840	----
1.0	400	370	1050	1350
3.1	290	260	1280	1650
5.2	290	210	1410	2100
7.2	250	180	1500	2250
9.3	260	200	1560	2580
11.4	---	---	1600	----

Figure 98: Normalized peak absorbance as a function of Ar pressure.

Figure 99: Normalized integrated absorbance as a function of Ar pressure.

nor the effects of self-absorption or asymmetry and shift in wavelength which occur at high analyte concentrations):

$$A = 0.434 k_0 l H(a, 0.725a) \quad (6-2)$$

where k_0 is the Doppler absorption coefficient at the centre of the absorption line, l the path length of the absorbing vapour, $H(a, 0.725a)$ the Voigt integral describing the absorption line profile and a is the damping parameter. For a constant concentration of absorbing atoms, the sharp-line absorbance is determined by the Voigt integral, which is a single-valued function of the a -parameter. Taking into account the linear dependence of a on the applied pressure (through the Lorentz half-width) and the inverse exponential dependence of $H(a, 0.725a)$ on a (84), the absorbance should be inversely related to the applied pressure in an exponential manner. The actual ratios of the absorbance at various pressures can be represented as a ratio of Voigt functions at the corresponding a values, as follows:

$$A_{p_1}/A_{p_2} = H(\frac{a}{n}, 0.725\frac{a}{n})/H(a, 0.725a) \quad (6-3)$$

where A_{p_1} and A_{p_2} are absorbances measured at applied gas pressures p_1 and p_2 , respectively, and $n = p_2/p_1$. A plot of the normalized absorbance by Cu as a function of the applied pressure, calculated from equation 6-3, is presented in Figure 100, where curve A was calculated using a value of 0.46 (168) for the damping parameter (2480 K, $101.3 \text{ kN}\cdot\text{m}^{-2}$, $\lambda = 324.8 \text{ nm}$), and curve B using a hypothetical value of 2.0. Comparison of Figures 98 and 100 (curve A) shows that the (normalized) theoretical absorbance as a function of the pressure

Figure 100: Variation of $R = H(a/n, \omega = 0.725a/n)/H(a, \omega = 0.725a)$ with pressure.

A. $a = 0.46$

B. $a = 2.0$

does not decrease as drastically as the experimental absorbance. The combined influence of the variation of the Voigt integral with pressure and of the effects of kinetic factors (equation 1-9, mechanical expulsion) is responsible for the observed pressure dependence of the signals.

The variation of the integrated absorbance with pressure (Figure 99) is similar to that of the peak absorbance.

Effect of Pressure on Instrument Calibration

Calibration of the instrument as a function of a known sample mass is, at present, the most rapid, accurate and convenient method used in atomic absorption analysis. The principle of the method is to measure the absorption coefficient at its maximum using a monochromatic emission line whose central frequency coincides with that of the absorption line. The fact that emission lines are not monochromatic, among other factors, causes non-linearity of the calibration curve (169-171). When sample atomization occurs under high pressure, the absorption line is broadened by the Lorentz effect and, consequently, the emission line becomes effectively more monochromatic in terms of the ratio of absorption line-width to emission line-width. As a result, curvature of calibration graphs is reduced when samples are atomized under high pressure. The influence of the width of the emission line on the peak and the integrated absorbance given by Cd is shown in Figure 101. If the current passing through the hollow cathode lamp is increased, the broadening of the resonance line is increased (particularly the broadening due to self-absorption) and, at $100 \text{ kN}\cdot\text{m}^{-2}$ pressure, the absorbance decreases

Figure 101: Effect of hollow cathode lamp current on the peak and integrated absorbance by $5.0 \times 10^{-14} \text{ kg Cd}$ at Ar pressures of $1.0 \times 10^5 \text{ N.m}^{-2}$ and $9.3 \times 10^5 \text{ N.m}^{-2}$.

○ peak absorbance at $1.0 \times 10^5 \text{ N.m}^{-2} \text{ Ar}$.
 ● integrated absorbance at $1.0 \times 10^5 \text{ N.m}^{-2} \text{ Ar}$
 △ peak absorbance at $9.3 \times 10^5 \text{ N.m}^{-2} \text{ of Ar}$

rapidly. If the pressure is increased to $930 \text{ kN}\cdot\text{m}^{-2}$ (9.2 atm), however, increased broadening of the emission line has little effect on the absorbance. The reason for this is that at high pressure, the absorption line has become so broad that the broadened emission line has effectively become more monochromatic. Both the peak and the integrated absorbance behave in this manner.

The effect of pressure on the calibration curves of Cd and Cu by the peak height and the integration methods of measurement is shown in Figures 102 - 105. In all cases the increased pressure results in (in addition to reduced sensitivity) an increase in the range of linearity of the curves. Maximum advantage is realized for Cd, an element of relatively high volatility, the emission line of which is more easily broadened than that for Cu. As a result, increase in the effective monochromaticity of the emission line, relative to the pressure-broadened absorption line, is more pronounced for this element. For Cd, a 6-fold increase in the linear dynamic range of the peak height curve is observed at an applied pressure of $610 \text{ kN}\cdot\text{m}^{-2}$ (6 atm)/Ar, whereas under the same conditions, only a 2-fold increase in the linear dynamic range is observed for Cu. In all cases, the integrated absorbance is expected, and is experimentally observed, to yield greater linear dynamic ranges in calibration curves since the relative importance of the absorption pulse region having the absorbance maximum is small in comparison with the total absorption pulse area.

Summary

The effects of an applied pressure of inert gas on the analytical

Figure 102: Calibration curves for Cd drawn using peak height absorbance.

$\Delta 1.0 \times 10^5 \text{ N m}^{-2}$ $\bullet 3.1 \times 10^5 \text{ N m}^{-2}$ $\circ 6.1 \times 10^5 \text{ N m}^{-2}$

Figure 103: Calibration curves for Cd drawn using integrated absorbance.

Figure 104: Calibration curves for Cu drawn using peak absorbance.

$\Delta 1.0 \times 10^5 \text{ N m}^{-2}$ $\bullet 3.1 \times 10^5 \text{ N m}^{-2}$ $\circ 6.1 \times 10^5 \text{ N m}^{-2}$

Figure 105: Calibration curves for Cu drawn using integrated absorbance.
 $\Delta 1.0 \times 10^5 \text{ N m}^{-2}$ $\bullet 3.1 \times 10^5 \text{ N m}^{-2}$ $\circ 6.1 \times 10^5 \text{ N m}^{-2}$

characteristics of signals arising from atomization of an analyte in the HGA-2100 can be attributed to both the effect of the pressure on the rate of analyte evaporation (this causing a shift in the absorption pulse to longer times and higher temperature) and the decrease in the absorption coefficient of the atomic vapour with applied pressure (Lorentz effect). Since commercial atomizers do not function as isothermal cuvettes, atomization under pressure in these furnaces offers only the following advantages in practical analysis: (1) linearization of nonlinear calibration curves; (2) an increase in the linear dynamic range of calibration curves; (3) increased freedom from the effect of variations in discharge conditions in the emission source.

CONCLUSIONS

The objectives of this research were to study the factors governing the dynamics of growth and decay of the atom population within tube-type graphite atomizers, to assess the relative merits of the peak and integration methods of signal measurement, and to acquire a more comprehensive understanding of the mechanisms of formation of atoms in and their loss from heated graphite atomizers. With this knowledge, the design of existing and subsequent electrothermal atomizers may be optimized on the basis of theoretical principles as opposed to empirical trial and error methods.

The rates of growth and decay of the atom population are determined by the rate of heating of the atomizer, the physicochemical properties of its surface (porosity, density, permeability, chemical reactivity), the material used for its construction (graphite, pyrolytic graphite, Ta, W), its geometry (length, cross-sectional area), and the temporal and spatial non-isothermality of the atomizer.

The rôle of each of these parameters in determining the degree of influence on the measured signal by either the peak height or the integration method varies from one analyte to another. The advantages of the integration method of measurement predicted by theory were not realized with the commercial electrothermal atomizers. The reason for this is that these atomizers do not meet the requirements of correct use of the integration method, mainly because of the temporal and spatial non-isothermality of the atomizers, the inseparability of

the rate of heating and the maximum temperature attained by these atomizers, and their continuous rise in temperature throughout the duration of the entire absorption pulse.

The effect of various atomizer parameters on the absorption pulse characteristics is determined by the physicochemical properties of the analyte and/or its major products of thermal decomposition. The unique properties of each analyte determine the major mechanisms by which free atoms are formed in and lost from the atomizer. Atom formation in graphite atomizers occurs through three major pathways: thermal dissociation of the metal oxide; reduction of the oxide by carbon followed by vaporization of the reduced metal; and thermal dissociation of the metal halide. Loss of atoms from the atomizer occurs primarily by condensation of the atomic vapour at its cooler extremities, by chemical reaction to form involatile and/or undissociated species, and by expulsion and/or diffusion of vapour through the sample introduction port. The relationship of the appearance temperature of an element, T_{app} , to the temperature-time profile of the atomizer determines both the rate of atom formation and the rate of atomic vapour loss because of the effects of the magnitude of T_{app} , the rate of heating of the atomizer beyond T_{app} , and the temporal and spatial non-isothermality of the atomizer at and beyond T_{app} .

In light of the knowledge gained from this study, the following factors are considered important in the design and operation of more effective electrothermal atomizers.

1. The atomizer should be tubular in design in order to contain the atomic and molecular vapour. This would improve vapour-tube wall

thermal equilibration, and increase the vapour temperature.

2. The atomizer should be constructed of pyrolytic graphite.

This material has the desirable properties of low permeability to gases, low porosity, high purity, a high sublimation temperature, a high resistance to oxidation and a high thermal conductivity. Additionally, incandescent graphite provides a highly reducing environment which aids in the reduction of oxides to metals.

With atomizers similar in design to the CRA-63, the anisotropic properties of pyrolytic graphite may be used to advantage. The electrodes supplying the power to the heating element should be so arranged that the direction of the flow of the input current is perpendicular to the direction of the layers of graphite. The low resistance along the longitudinal axis of the atomizer (with the analytical volume of the atomizer drilled parallel to the longitudinal axis along the graphite layers) and the high resistance across the transverse cross-section in the direction of current flow allow uniform heating along the length of the graphite tube.

3. The atomizer should be capable of achieving high rates of heating. This maximizes the rate of analyte vaporization and the rate of molecular dissociation, thereby increasing the instantaneous atom population within the analytical volume, minimizing the amount of analyte lost by diffusion both as atoms and molecules, and reducing the extent of penetration of the analyte into the pores of the surface of the graphite tube.

4. The maximum temperature attained by the atomizer must be made to be independent of its rate of heating. Separation of the rate

of heating from the maximum temperature to be attained by the atomizer would allow one to set an optimum temperature for each element which should be high enough to prevent vapour condensation but low enough to prevent excessive diffusional losses from the analytical volume.

5. Temporal and spatial non-isothermality of the atomizer must be minimized, both to generate higher atomic vapour temperatures (promoting molecular dissociation), and to reduce the concentration gradient of vapour within the atomizer (hence, loss of vapour). Non-isothermality may be eliminated or reduced through proper design of the atomizer, choice of proper construction material, and with the use of high rates of heating.

6. The atomizer tube should be as long as possible, the upper limit on its length being limited by the requirements of higher electric power, of achieving rapid heating, of maintaining an isothermal condition along the tube and a reasonable throughput of the emission source radiation. The integral value of the effective length of the absorbing volume is proportional to the square of the length of the hot working zone of the atomizer tube.

7. The atomizer tube should have the minimum cross-sectional area to maximize both the effective length of the absorbing volume at the peak of the absorbance pulse and the integral value of the effective length of the absorbing volume. The minimum cross-sectional area will be determined by the throughput of the emission source radiation.

8. The atomizer tube should be of minimum mass to maximize the rate of heating. The minimum mass will be determined by the mechanical properties of a pyrolytic graphite tube of maximum length,

minimum cross-sectional area, and minimum wall thickness.

9. The option of performing analyte atomization above atmospheric pressure will provide the operator with the ability to linearize calibration curves, use the extended linear dynamic range, and allow atomization of concentrated solutions without the necessity of sample dilution (which is the usual practice) with its attendant hazards of contamination, hydrolysis of samples, dilution errors, more time required per analysis, etc.

10. The optical system must be designed for maximum throughput of the emission source radiation, and the source beam must completely illuminate the interior of the atomizer tube. For this reason, quartz plano-convex lenses of small diameter are desirable.

11. The emission source must be modulated at high frequency in order that the signals can be accurately measured at high rates of heating. Optimum modulation frequency will be governed by adequate sampling times and reasonable S/N ratio.

12. Both peak height and integration methods of signal measurement should be available.

13. Solid sampling is not only feasible but is a very desirable capability with the graphite furnace. Provision of high temperatures (upto ~ 3600 K) and adoption of the integration method of measurement would be required for the analysis of refractory solid samples. The use of long integration times requires long-term stability of the emission source radiation, the detection system, and/or provision of a double-beam optical system.

A growing problem with graphite furnace atomic absorption spectrometry is the increasing number of sampling and interference problems encountered, many of which can be attributed to the use of incorrect atomization conditions and/or improper correction for non-specific background absorption. Investigation of these physicochemical interferences by the techniques used to obtain the mechanisms of atom formation may provide information which will enable selection of methods for their elimination and/or control.

FUTURE RESEARCH

Future research in electrothermal atomization should include studies designed to improve the analytical performance of commercially available atomizers and to investigate the mechanisms of interference from concomitant species in the sample. The primary thrust of this work should be the modification of commercial atomizers in an effort to increase the efficiency of production of atomic vapour, its confinement within the analytical volume, and the elimination or reduction of interferences. In this respect, there are three aspects which must be considered, each designed to reduce the temporal and spatial non-isothermality of the atomizer: (a) changes in the physical design of the atomizer tubes; (b) the utilization of a sampling platform (56); and (c) pulse heating of the atomizer.

The simplest technique that may be used to decrease the magnitude of the thermal gradient within the furnace during sample atomization is to reduce the thickness of the wall of the tube at its ends. By cutting channels into its surface, to thin the wall, the tube will become hotter at the ends (173), increasing the effective length of the absorbing layer as well as the peak and the integrated absorbance.

L'vov (56) has illustrated the use of a sampling platform for operation with a HGA-2100. The platform, a small chip of graphite (preferably pyrolytic graphite), is placed in the centre of the atomizer in thermal contact with the wall. Because the platform will heat up more slowly than the atomizer, it is possible to achieve conditions

under which rapid vaporization of the sample is retarded until the atomizer has achieved a steady-state temperature. Under such conditions, the thermal gradient within the atomizer will be reduced during atomization of the sample, leading to increases in the integrated absorbance, and improvements in the constancy of the integrated absorbance as the sample matrix and/or the rate of heating of the atomizer is varied.

Rapid heating of the atomizer increases both the peak and the integrated absorbance, particularly for analytes of medium and low volatility. Although the laboratory-built atomizer/power supply combination described in Chapters 4 and 6 provides an order of magnitude increase in the peak height sensitivity at heating rates of $4\text{--}4.5\text{ K ms}^{-1}$ (172), more rapid heating ($30\text{--}40\text{ K ms}^{-1}$) may be achieved with the power delivered by a capacitive discharge power supply (56). With pulse heating of the atomizer (i.e., $\tau_1 \ll \tau_2$), maximum sensitivity may be achieved. The use of pulse heating for elimination or reduction of matrix interferences should be an important area of study.

The above techniques may be evaluated both by comparing the peak height and the integrated sensitivity, and by comparing the excitation temperature of the atomic vapour measured under the above conditions with that in a commercial atomizer. Provided the excitation temperature-time characteristics of the atomic vapour are determined by the thermal gradient within the atomizer, higher vapour temperatures should be attained with pulse heating, with the sampling platform, and with tubes which have had their end walls thinned.

To investigate further the phenomenon of ionization of analytes in the graphite atomizer, the time-dependent concentration of electrons

generated within the tube may be measured using microwave absorption techniques. Further studies of the mechanism of loss of atomic vapour in the HGA-2100 are required to confirm the results obtained using Mo and V as probes. In particular, a study of the distribution, after atomization, of γ -active tracer elements (Mn, Na, Cu etc.) in the individual components of the atomizer (end windows, tube extremities, interior surfaces of cones, etc.) for both pyrolytic-graphite-coated and uncoated tubes at various rates of heating of the atomizer is required. This will allow the contribution of each loss mechanism to be assessed for easy-to-volatilize elements such as Cu and Cd and a confirmation of those outlined for Mo and V to be made. Additionally, the rate of loss of atomic vapour at high pressure should be measured to determine whether mechanical expulsion of the atomic vapour occurs as the atomizer and pressurizing gas are rapidly heated. This aspect may be conveniently studied with the use of a sampling platform, for which the initial period of atomizer heating and rapid expulsion of the pressurizing gas from the graphite tube occur prior to generation of the atomic vapour.

Atomization of analytes has been determined to proceed via three major routes, i.e., thermal dissociation of the halide, thermal dissociation of the oxide, and reduction of the oxide followed by vaporization of the metal. Additional investigations are required to obtain confirmation of some of the suggested gaseous molecular species and their concentration-time profiles for correlation with atomic absorption signal-time profiles. Hutton et al. (173) have attempted such measurements by placing a graphite atomizer in the sample compartment of an infra-red

spectrophotometer. Some preliminary success on the investigation of losses of analyte as volatile molecular species in chloride media has been reported (173). The aim of such studies is the understanding of the mechanisms of interferences in the graphite atomizer and to use this information to reduce interferences by proper design of the atomizer or by their chemical elimination.

An aspect of AAS not covered in this thesis is the study of interferences in graphite atomizers. The determination of the energy of atomization in those cases where solute vaporization or chemical interferences are present will provide energy values which may serve as quantitative measures of such effects. Measurement of atomization energies may prove to be a useful tool in the characterization of interferences, their mechanism of action and methods for their removal or control. Additionally, application of a sampling platform and pulse heating of the atomizer with a view to eliminating or reducing interferences will prove interesting and rewarding.

With a more comprehensive theoretical understanding of the physicochemical processes that occur in graphite furnace atomizers, significant progress would be made in developing the IDEAL method of analysis - the absolute method of analysis, i.e., without standards (56).

Appendix I

The Relationship Between τ_1 , τ_2 , τ_1' and τ_2'

A discussion of the relationship of the experimentally calculated τ_1 and τ_2 values to the τ'_1 and τ'_2 of L'vov's model (5,25,26,27) is given below. The τ'_1 and τ'_2 values are mathematically defined by equations 1-8 and 1-13 as times when $t=\tau'_1$ and $t=\tau'_2$, respectively, provided $\tau'_1/\tau'_2 \ll 1$. Additionally, it has been assumed in L'vov's model that the decay of the signal is independent of its growth. Because instantaneous atomization of the sample is not achieved in practice with the result $\tau'_1 \approx \tau'_2$, and because of the temporal and spatial non-isothermality of the atomizer and the atomic vapour, analyte signals obtained with the commercial electrothermal atomizers cannot be accurately characterized by τ'_1 and τ'_2 . It is therefore necessary to distinguish between the experimentally observed values (called τ_1 and τ_2) obtained with the commercial atomizers, and the theoretical (L'vov's model) values (τ'_1 and τ'_2). To a good approximation, $\tau_1 \approx \tau'_1$ if the rate of formation of vapour is sufficiently rapid that little vapour escapes from the analytical volume before the bulk of the analyte is atomized. An estimate of τ'_2 may be obtained by a method of successive approximation, in which a first-order rate constant for the loss of atomic vapour is assumed and τ'_2 is measured as the time taken for the signal to decay to $1/e$ of its value; calculated from a number of points on the tail of the absorption pulse until a constant value for τ'_2 is obtained. Alternatively, τ'_2 may be calculated from the slope of a $\log(A_0/A_t)$ versus time plot, as outlined in Chapter 4 (provided a straight-line plot is obtained). These two methods are formally equivalent and, to be successful, require that the temperature of both the atomic vapour and the atomizer be constant over the time of decay of the signal.

These conditions cannot be achieved with the existing commercial electrothermal atomizers with the result that there is little hope of obtaining accurate values of τ_2 . Till such time as the commercial atomizers fulfil the conditions mentioned in this discussion, the τ_2 value will be useful only as a parameter to characterize the signal profile.

Appendix II

Activation Energy Plots

E_a plots together with oscillograms from
which the plots were drawn^a

Figure	Element	Trigger Delay Time/ms	Time Scan/ms · (scale div) ⁻¹	Page
A-1	Cd/HNO ₃	50	20	342
A-2	Cd/HCl	30	20	343
A-3	Zn/HNO ₃	400	50	344
A-4	Zn/HCl	300	50	345
A-5	Cu	450	50	346
A-6	Co	700	50	347
A-7	Mn	650	50	348
A-8	Fe/HNO ₃	700	50	349
A-9	Sn	950	50	350
A-10	Ni	800	50	351
A-11	Ca	1000	50	352
A-12	Mo	1300	100	353
A-13	V	1400	50	354
A-14	Al	1300	50	355
^b A-15	Ca	850	50	356
^b A-16	Mg	600	50	357
^b A-17	Mn	600	50	358
^b A-18	Zn	330	20	359
^b A-19	Cd	50	20	360

^aAtomization conditions: dry 100 C, ash 300 C, atomize 2700 C.

^bLarge masses of analyte (solid-state decomposition)

Figure A-1

Figure A-2

Figure A-3

Figure A-4

Figure A-5

Figure A-6

Figure A-7

Figure A-8

Figure A-9

Figure A-10

Figure A-11

Figure A-12

Figure A-13

Figure A-14

Figure A-15

Figure A-16

Figure A-17

Figure A-18

Figure A-19

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