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LA THÈSE A ÉTÉ MICROFILMÉE TELLE QUE NOUS L'AVONS RECEUE
THE EFFECT OF HEATING RATES ON THE SENSITIVITY AND SELECTIVITY OF
GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY

by

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A thesis submitted to the Faculty of
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ABSTRACT

Results of studies are presented on the effect of heating rates and (final) atomization temperatures on peak height and integrated absorbances of some elements atomized using temperature-controlled heating. The three categories of elements are: those which are of relatively high volatility (Cd and Pb); those which are of medium volatility (Cu and Al); those which are of low volatility (Mo and V), or the elements which form involatile carbides or lamellar compounds with graphite (U). This study was done using a laboratory-built graphite tube atomizer and a power supply capable of achieving a given temperature at various heating rates. This power supply allowed the heating rate and the final temperature to be set independently of each other so that the effect of heating rate could be separated from that of the temperature. The effect of the heating rate was studied using atomization surfaces as follows: pyrocoated graphite tube surface with and without metal lining. When atomized from these surfaces, sensitivity increases with increasing heating rates for relatively involatile elements or elements which form involatile compounds such as carbidies or lamellar compounds of graphite, whereas sensitivity of the relatively volatile elements increases up to certain heating rates, and then decreases with further increase in the heating rate. Atomization from
graphite surface and various metal surfaces using heating rates from 0.3 to 75 K ms⁻¹ has revealed the effect of heating rates on atomization and residence times, and has shown that the three loss mechanisms, diffusion, convection and expulsion by the rapidly expanding gases, are differently affected by the heating rates -- the diffusion being the predominant mechanism of loss at very low heating rates and convection, and especially, expulsion by the rapidly expanding gases being the predominant mechanism of loss at very high heating rates.

The effect of different atomization surfaces on the sensitivity of some elements was studied using a constant heating rate of 3.3 K ms⁻¹. It was found that the atomization surface had a significant effect on the characteristics of the atomic absorption pulse for some elements, especially those elements which formed refractory carbides with the heated graphite surface (e.g. U). The use of a metal lining in these cases considerably enhanced the sensitivity of these elements.

Use of an anisotropic pyrolytic graphite tube atomizer heated at very high heating rates by a capacitive discharge combined with maintenance of an isothermal condition by an auxiliary heating with another power supply results in much higher sensitivities for some elements than those available from commercial graphite furnaces; the former also results in absence of condensation of the analyte element at the ends of the graphite tube, and hence, absence of memory effect. In such a graphite tube atomizer, an isothermal condition results from 5000 fold greater resistance across the tube than along the tube length and 225 fold greater thermal conductivity along the tube length than across the tube, and also
by its thermal conductivity being about 10 fold greater than that of regular (isotropic) graphite. The peak height absorbance of elements increases exponentially with increasing heating rates, the low-volatility elements showing greater increase in the peak height absorbance with heating rates than the high-volatility elements. Pulse heating of an anisotropic graphite tube atomizer by capacitive discharge increases sensitivity of those elements which have as the mechanism (of atom formation) reduction of the solid metal oxide by carbon, followed by evaporation of the metal atoms, or solid-state decomposition of the metal oxide to form the metal atoms in the vapour phase. This technique offers promise of high sensitivity and relative freedom from matrix interferences.

A new analytical technique has been developed using graphite furnace atomic absorption spectrometry. The technique employs an anisotropic pyrolytic graphite tube atomizer which is heated at very high heating rates (up to 100 K ms\(^{-1}\)) by capacitive discharge to produce high temperatures (up to 3300 K) and an isothermal condition. Synthetic samples of saline water were analyzed by capacitive discharge technique and also by the conventional graphite furnace atomic absorption technique using for the latter the Perkin-Elmer Heated Graphite Atomizer 768. Recoveries by the capacitive discharge technique and the conventional graphite furnace atomic absorption technique were typically \(\sim 100\%\) with the former technique and 12-75\% with the latter technique. Using the solid-sampling technique, the capacitive discharge technique gave \(\sim 100\%\)
recoveries and large enhancements in the sensitivities of trace
elements in the National Bureau of Standards -- Standard Reference
Materials: bovine liver, oyster tissue and The United States
Geological Survey marine mud. There is also another very significant
difference -- the Background Corrector was not required nor was used
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absorbance and the sensitivity constant.
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Finally, I should like to dedicate this thesis to my wife, Muna, for her patience and encouragement throughout this work.
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CHAPTER 1
INTRODUCTION

King (1) used an electrothermal atomizer in the first decade of this century for study of atomic vapour. Many years later, L'vov (2-4) reported the first application of electrothermal atomization in a constant-temperature graphite cuvette to quantitative determination of elements by atomic absorption spectrometry. Later work reported by Massmann (5) in West Germany, Woodruff et al. (6-8) in the U.S.A., West and Williams (9) in the U.K. and Aspila et al. (10) in Canada, introduced other types of electrothermal atomizers and extended the applications of this technique.

In atomic absorption spectrometry, electrothermal atomization has several advantages over flame atomization. Among these advantages are: requirement of an extremely small sample; improvement of up to 2-3 orders of magnitude in sensitivity; better detection limits; separation of the desolvation, decomposition, and atomization process in a flame which precede the measurement of the atomic absorption signal into three distinct steps of drying, charring (pyrolysis) and atomization in a graphite furnace. If each of these processes can be fully completed before proceeding with the next, the matrix interferences which occur in flame atomization techniques can be reduced; better
efficiencies of vaporization and atomization, especially for elements which tend to form thermally stable compounds; the possibility of handling viscous liquids that are difficult to nebulize in a flame; the possibility of analyzing solid samples directly, i.e., without prior dissolution in a solvent.

Various nonflame atomizers have been developed for use in atomic absorption spectrometry. These atomizers have utilized heated graphite tubes, carbon rods and filaments, sampling boats and cups, loops, and metal filaments. Kirkbright (11), Syty (12) and Woodriff (13) have reviewed the development of these atomizers and described the more common designs. More recent developments have been reviewed by Hieftje and Copeland (14).

Commercial electrothermal atomizers which are used in atomic absorption spectrometry have two serious limitations: their low heating rates limit them to much lower sensitivity than what is achievable at much higher heating rates; and they are temporally and spatially non-isothermal, resulting in condensation of the analyte vapour at the cooler ends of the graphite tube and re-evaporation producing memory effects and erroneous results. Also, their slow heating rates, lack of isothermal conditions and the much lower vapour temperatures into which the samples are vaporized cause severe matrix interferences of various kinds: spectral, chemical and physical. Spectral interferences that are not caused by an overlap of atomic lines can be eliminated in most cases by using the background correction technique. Chemical interferences are very troublesome and may be due to formation
by the analyte of a compounds of a significantly different volatility (relative to the standard used for calibration of the measurement system). Physical interferences may be due to occlusion of the analyte in the matrix or co-volatilization of the analyte along with a more volatile matrix.

Determination of low-volatility elements requires use of high temperatures (> 3000°C). With the commercial instruments, even at the maximum available temperature (~2800°C), their evaporation and atomization are slow and incomplete. Such incomplete evaporation and atomization in a furnace reduces analytical sensitivity and produces memory effects. Sometimes, the reason for this slow evaporation and atomization of low-volatility metals in graphite furnaces is that the metals form with the graphite refractory carbides or intercalation (lamellar) metal-graphite compounds which are even more difficult to atomize than the metals themselves (15).

Various metal-based electrothermal atomizers were used as substitutes for conventional graphite-based systems during the last few years (16-46). These atomizers were heated boats, rods and filaments made of various low-volatility metals, such as tantalum, tungsten, molybdenum, platinum, etc. Some authors (47-51) tried to improve the performance of graphite atomizers for determination of carbide-forming elements by inserting a metal foil into the graphite atomizer and using the metal foil surface for atomization of the elements.
Advantages claimed for metallic electrothermal atomizers are as follows: the need for only a relatively low input power; no problems with carbide formation, long life time (depending on the kind of metal, the quality of protective atmosphere, and the sample analyzed); lower background emission from a metal surface in the 250-350 nm spectral region than that from a graphite surface at the same temperature. However, metallic atomizers suffer from several important disadvantages as follows. Compared to graphite atomizers their mechanical strength may decrease after long, extensive heating, especially at high temperatures; there is also a possibility of forming by the metal (of the atomizer) refractory inter-metallic compounds with the analyte, resulting in memory effects and decrease in sensitivity; also, their chemical resistance is lower, leading to corrosion problems.

All instrumental methods of analysis including graphite furnace atomic absorption spectrometry (GFAAS) are comparative methods in which the analytes in unknown samples are determined by means of calibration curves prepared with standards which must be of the same composition as that of the unknown samples. This is because the sensitivity of all instrumental methods of analysis is dependent on the composition of the sample; often the relationship between the sensitivity and the sample composition is too complex for simple mathematical formulation. Such relationships are best expressed by calibration curves. Moreover, the above situation is aggravated by the ever-present possibility of interferences, and also the need for analyte preconcentration because of inadequate sensitivity. Solution
of these problems often requires complicated procedures involving careful
calibration and re-calibration, and study and removal of, or compensation
for the interfering components of the sample. Such complicated procedures
usually involve considerable cost in time and money, besides bringing
in their train the serious problems of contamination and/or loss of
analytes during the sample preparation, its chemical treatment, the
separation of the interfering matrix, and the preconcentration of the
analysis. The problem of contamination and/or loss of analytes is
important by itself in all analyses, but becomes critical with
vanishingly small concentrations of analytes in trace and ultratrace
analysis.

The general objective of the research reported in this thesis is
to extend the present state of knowledge about nonflame atomic
absorption spectrometry. The specific objectives are: 1) to study
the performance and efficiency of some electrothermal atomizers;
2) to study the effects of various parameters on the sensitivity and
selectivity of graphite furnace atomic absorption spectrometry; 3) to
study the effects of heating rates on the sensitivity and on the
atomization mechanisms; 4) to develop and study a new technique-
called the capacitive discharge technique (CDT) in graphite furnace
atomic absorption spectrometry (GFAAS) -- this new technique has
shown early promise of enhancing the sensitivity and eliminating the
serious problem of matrix interferences in GFAAS.
CHAPTER 2

MEASUREMENT OF TRANSIENT SIGNALS

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 all of the studies reported in this thesis. For the study of the effect of heating rates, the spectrometer was fitted with a laboratory-made heated graphite atomizer of a design similar to that of The Perkin-Elmer Heated Graphite Atomizer (HGA) model 2100 -- this atomizer will be called the modified HGA-2100. For the studies on the capacitive discharge technique, another laboratory-made graphite tube atomizer which is described later under the title Capacitive Discharge Apparatus, was used.

The Modified HGA-2100 Atomizer

As mentioned earlier this was a laboratory-made atomizer. This atomizer was resistively heated using a constant-power program for heating the graphite tube. By maintaining the contact resistance at a preset value (22 m\(\Omega\)) power-regulated heating was achieved. The
objective was to achieve higher heating rates and an isothermal condition early in the atomization cycle so that atomization occurred in a more nearly isothermal condition (relative to the condition in commercial graphite furnaces). The atomizer was fabricated from nickel-plated brass and was of a size and design similar to that of The Perkin-Elmer HGA-2100. Commercially available graphite cones, tubes and quartz end windows were used in this atomizer. Since this atomizer had a more efficient water-cooling device, experiments requiring prolonged high-temperature (> 3000 K) atomization cycles could be done using this atomizer without the risk of melting of the atomizer housing.

Figure 1 shows a schematic diagram of the side view of the modified HGA-2100 atomizer. As with The Perkin-Elmer HGA-2100, there are two separate systems for gas flow. One flow (the purge gas) enters from both ends of the graphite tube and leaves through the sample injection port. This flow is maintained during the dry and ash stages of the heating cycle and is designed to sweep away water vapour and sample matrix components (or their decomposition products) prior to atomization of the sample. A second independent gas flow (of an inert gas -- called the sheathing gas) is maintained continuously throughout the entire heating cycle. This gas flow prevents oxidation of the graphite tubes and contact rings of the atomizer and circulates in the concentric space between the graphite tube and the contact rings.

The atomizer has been designed to provide larger water-cooling ports and channels than The Perkin-Elmer HGA-2100 and is capable of
Figure 1. Cross-section of the modified HGA-2100 atomizer.
handling currents of 1000 amperes at 15 volts. Figure 2 shows the modified HGA-2100 fitted on a stainless steel circular baseplate which serves as a mount on the optical rail and is also a support for all the service connections to and from the atomizer. The atomizer is equipped with a special high-pressure chamber to allow study of atomization under higher-than-atmospheric pressures. For this purpose, the device has been fitted with a pressure release valve and external regulator valves for each of the two gas flows. The baseplate has a flange 2 cm in width and is grooved to accept a rubber 'O' ring and 12 equally-spaced hex-head screws. The fittings allow the atomizer to be enclosed in a pressurizable chamber which is attached to the baseplate by the screw-type mount. The stainless steel pressure chamber is fitted with two demountable quartz windows to allow passage of the incident radiation, a detachable quartz observation window mounted at 90° to the optical axis, and a sample injection port with a quartz window through which the optical pyrometer can be used for measurement of the graphite surface temperature. The chamber has also a pressure gauge and a safety release valve.

The Modified HGA-2100 Atomizer Control Unit

A laboratory-made atomizer control unit supplies power to the atomizer in four discrete stages. The first stage (the lowest power stage) dries and removes all water from the sample thus eliminating the absorption of incident radiation by molecular absorption bands of water-vapour and the sputtering of wet samples during subsequent
Figure 2. Modified HGA-2100 atomizer head.
heating stages. Typically, a $5 \times 10^{-6}$ dm$^3$ sample requires a drying time of about 30 s at 373 K to ensure complete dryness of the sample. The charring (pyrolysis) stage (the second stage) is generally maintained at higher temperatures than those of the drying stage, and for varying time intervals depending on the analyte being studied and the characteristics of the sample matrix. In this stage as much of the sample matrix as possible is removed by volatilization and/or oxidation making sure of not causing any loss of the analyte. The final two stages are identical in power output characteristics and correspond to the atomization stage of commercial atomizers. The first atomization stage provides a variable initial rate of heating of the graphite tube up to some pre-determined temperature, and the second atomization stage maintains this temperature to the end of the atomization period.

Power to the control unit is provided by a custom wound transformer (Electrodesign Ltd., Ville Lasalle, P.Q., Canada) operating at 208 V. This transformer provides 1000 amperes at 15 volts to the atomizer. This power capability is approximately three times that of The Perkin-Elmer HGA-2100 atomizer control unit.

Each heating stage of the atomizer control unit is equipped with a variable timer control enabling the duration of each heating stage to be reproducibly controlled. A gas control valve and a flow meter regulate the flow of the sheathing gas and the internal purge gas to the atomizer. The modified HGA-2100 atomizer control unit and the spectrometer are shown in Figure 3.
Figure 3. HGA-2100 atomizer control unit and the spectrophotometer.
The voltage drop across the power terminals of the atomizer was measured with a rectifier-type ac meter, model Avo 8 (Avometer Inc., Plainview, New York, USA); the current passing through the power cables was measured with an Amprobe RS-34 clip-on ammeter (Amprobe Inc., Lynbrook, New York, USA), and the resistance across the workhead terminals was measured with a model 4328A milliohm meter (Hewlett-Packard Co., Ltd.).

Since the temperature-time characteristics of the atomizer are largely determined by its power consumption, the relationship between the instrument setting (in arbitrary units) and the input power to the atomization stage was determined. The results are presented in Figure 4.

The Amplifier-Integrator Assembly

A simplified schematic diagram of the amplifier-integrator assembly is shown in Figure 5. 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 x second readout) was assembled in this laboratory. The integrating voltmeter was a Dymec model 2401C (Hewlett-Packard Co. Ltd., Los Angeles, California, USA). The DVM can provide a continuous 5-digit display of either percentage transmittance or absorbance. In addition, analog display of either of these is also possible using a voltmeter incorporated into the amplifier module of the spectrometer. The operation of the unit
Figure 4. Power consumptions of the atomizer as a function of instrument setting.
*LOG AMP = logarithmic amplifier.

Figure 5. Amplifier-integrator assembly.
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 the integrating digital voltmeter, which sums up the absorbance signals over a preset time interval. The DVM shows the integrated absorbance in absorbance/s. The oscilloscope shows the shape of the absorbance pulse. The absorbance-time trace of the pulse is 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 absorbance signal can be photographed with a "Polaroid" camera (Tektronix Inc., Portland, Oregon, U.S.A.).

The amplifier assembly described above is provided with variable time constants, situated at the output of the logarithmic amplifier. The time constant of the amplifier ranges from 0.5 to 4800 ms.

To assess the effect of time constants of the measurement system on analysis signals, the absorbance-time traces obtained by the atomization of Cd, Pb and Cu using the modified HGA-2100 under increasingly damped response at a low heating rate (0.61 K ms\(^{-1}\)) and at a high heating rate (3.3 K ms\(^{-1}\)) were examined. Cd and Pb were selected for this study as they are typical of relatively high-volatility elements which yield extremely fast signals that are most difficult (for the amplifier) to follow. Cu is typical of the medium-volatility elements and was chosen for comparison. Figures 6 and 7 show the
effect of the time constant of the recording circuit on the Cd signal at heating rates of 3.3 K ms\(^{-1}\) and 0.61 K ms\(^{-1}\), respectively. Figures 8 and 9 also illustrate the effect of the time constant of the recording circuit on the Pb signal at heating rates of 3.3 K ms\(^{-1}\) and 0.61 K ms\(^{-1}\), respectively. It can be seen from these Figures that the higher the heating rate, the greater is the distortion in the Cd and Pb signals. This is because the degree of distortion in the signal depends on the rate of atom formation (which is inversely proportional to the atomization time, \(\tau_1\); assuming first-order kinetics for the atom formation -- a fairly reasonable assumption). At high heating rates, the rates of atom formation of high-volatility elements (Cd and Pb) are very high. Such high rates of atom formation yield extremely fast signals requiring use of very short time constants of the recording circuit to measure analysis signals without any distortion. For a medium-volatility element (Cu) and for low-volatility elements, the rates of atom formation even at a high heating rate are lower (than those for Cd and Pb at the same heating rate); hence, their analysis signals can be measured with less distortion than those of Cd and Pb using the same time constant. The atomization times, \(\tau_1\), for Cd and Pb at the heating rate of 3.3 K ms\(^{-1}\) are 120 ms and 140 ms, respectively (Table III, Chapter 3). Hence, at the heating rate of 3.3 K ms\(^{-1}\), the signals of Cd and Pb can be reliably recorded with the amplifier time constant of 18 ms but the signals become severely distorted with increased time constants. Figures 10 and 11 show the effect of the amplifier time constant on the signals of Cu atomized at heating rates.
Figure 6. Effect of amplifier time constant, $\tau_{RC}$, on the absorption pulse of $1 \times 10^{-13}$ kg Cd atomized at the heating rate of 3.3 K ms$^{-1}$. Absorbance = 0.1/scale division.
Time = 200 ms/scale division.
1. $\tau_{RC} = 18$ ms  2. $\tau_{RC} = 160$ ms  3. $\tau_{RC} = 300$ ms.

Figure 7. Effect of amplifier time constant on the absorption pulse of $5 \times 10^{-14}$ kg Cd atomized at the heating rate of 0.61 K ms$^{-1}$. Absorbance = 0.1/scale division.
Time = 500 ms/scale division.
1. $\tau_{RC} = 18$ ms  2. $\tau_{RC} = 160$ ms  3. $\tau_{RC} = 300$ ms.
Figure 8. Effect of amplifier time constant, $\tau_{RC}$, on the absorption pulse of $2.5 \times 10^{-12}$ kg Pb atomized at the heating rate of 3.3 K ms$^{-1}$. Absorbance = 0.2/scale division.
Time = 200 ms/scale division.
1. $\tau_{RC} = 48$ ms  2. $\tau_{RC} = 160$ ms  3. $\tau_{RC} = 300$ ms  4. $\tau_{RC} = 840$ ms.

Figure 9. Effect of amplifier time constant, $\tau_{RC}$, on the absorption pulse of $1 \times 10^{-12}$ kg Pb atomized at the heating rate of 0.61 K ms$^{-1}$. Absorbance = 0.2/scale division.
Time = 500 ms/scale division.
1. $\tau_{RC} = 18$ ms  2. $\tau_{RC} = 160$ ms  3. $\tau_{RC} = 300$ ms  4. $\tau_{RC} = 840$ ms.
Figure 10. Effect of amplifier time constant, $\tau_{RC}$, on the absorption pulse of $1 \times 10^{-12}$ kg Cu atomized at a heating rate of 3.3 K ms$^{-1}$. Absorbance = 0.2/scale division. Time = 200 ms/scale division.
1. $\tau_{RC} = 18$ ms  2. $\tau_{RC} = 160$ ms  3. $\tau_{RC} = 300$ ms  4. $\tau_{RC} = 840$ ms.

Figure 11. Effect of amplifier time constant, $\tau_{RC}$, on the absorption pulse of $1 \times 10^{-12}$ kg Cu atomized at the heating rate of 0.61 K ms$^{-1}$. Absorbance = 0.2/scale division. Time = 500 ms/scale division.
1. $\tau_{RC} = 18$ ms  2. $\tau_{RC} = 160$ ms  3. $\tau_{RC} = 300$ ms  4. $\tau_{RC} = 840$ ms.
of 3.3 K ms\(^{-1}\) and 0.61 K ms\(^{-1}\), respectively. The atomization time, \(\tau_1\), of the Cu signal is larger (260 ms) than those of Cd and Pb; the result is that in the Cu signal the distortion is less (than those of Cd and Pb) with increasing time constants. The influence of heating rates and the amplifier time constants on the degree of distortion of signals can be seen in Figures 6-9. Signals generated at low heating rates are broader, with larger atomization times, \(\tau_1\), than those generated at high heating rates. Consequently, the signals generated by the modified HGA-2100 at a heating rate of 3.3 K ms\(^{-1}\), at equivalent time constants, are subject to less distortion than the signals generated at much higher heating rates (up to 100 K ms\(^{-1}\)) by the capacitive discharge heating (Chapter 5).

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 atomizer, but also by the instrumental parameters. Undistorted signals are required for study of theoretical aspects of atomization, or else the signal measurements from which conclusions will be drawn will be influenced by instrumental parameters. Using the modified HGA-2100 and a heating rate of 3.3 K ms\(^{-1}\), the Cd and Pb signals obtained with the amplifier time constant of 18 ms have been found to be identical with those obtained with a time constant of 0.5 ms, but the noise level with the former is lower. However, at a much higher heating rate of 40 K ms\(^{-1}\), a decrease in the time constant of the amplifier (\(\tau_{RC}\)) from 18 ms
to 0.5 ms increases the peak height absorbance of Cd by 7%, and also makes the absorption pulse narrower and the peak sharper. A faster-response instrument (than that used) is needed for measurement of the peak height absorbance of high-volatility elements at very high heating rates of the capacitive discharge heating.

Temperature-time Characteristics of the Modified HGA-2100 Atomizer

The temperature of a semi-enclosed graphite tube 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 (52,53). The temperatures of the surface of the modified HGA-2100 atomizer were measured with an automatic optical pyrometer, series 1100 (Ircon Inc., Niles, Illinois, U.S.A.), which measured the intensity of blackbody radiation emitted by its interior surface through the sample injection port.

In all temperature measurements the parameter of importance is the thermal time constant of the measuring device. With electrothermal atomizers, the temperature of the graphite tube surface continuously changes with time, and it is necessary to measure these temperature changes instantaneously. For thermocouples, the response time ranges from milliseconds to seconds. Even where it may be assumed that the thermocouple is in perfect thermal contact with the graphite surface, 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. 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 the temperature-time studies has a time constant of 1 ms and therefore could be used to measure correctly the temperature of the graphite tube surface even at the highest heating rate used. The voltage-temperature calibration provided by the manufacturer of the optical pyrometer was confirmed experimentally by measuring the temperature of the modified HGA-2100 atomizer surface with thermocouples and by checking the temperature calibration with the melting points of a number of pure metals placed within the atomizer. The temperature-time curves obtained in this way have been determined to be accurate to within 30 - 40 K. This result was in good agreement with the previous calibration done in this laboratory (54). From a number of the temperature-time curves obtained, it was established that the reproducibility of the temperature measurement was ±20 K at all temperatures. This value represents the sum of the uncertainties due to variations in the optical focusing of the pyrometer on the inner surface of the graphite tube, the reproducible setting of the atomizer resistance and the atomization temperature program, the contribution due to small variations in the emissivity of the graphite surface with different tubes and with the aging of the surface. There is also a contribution to the variation in temperatures caused by variation in the flow rate and temperature of the cooling water. This
latter factor has been reported by others (55,56) 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 atomizer power circuit.

Figure 12 presents the temperature of the graphite tube surface as a function of time at different heating rates. The instrument setting used to obtain these temperature-time curves are presented in Table I. The charring (pyrolysis) temperature setting are variable as the optimum charring temperature is specific for each analyte. Much lower charring temperatures (< 500°C) should be used for relatively volatile analytes than those for the relatively involatile analytes. The duration of the second atomization stage (the last vertical column, Table I) is also variable and is dependent on the nature of the analyte. Analytes of relatively low volatility require much longer atomization times than do analytes of relatively high volatility.

The temperature-time characteristics of the drying and charring stages were measured separately using a chromel-alumel thermocouple as these temperatures were generally below the lower temperature limit of the optical pyrometer (1300 K). The 600 K intercept (Figure 12), common to each temperature-time curve, is the temperature of the atomizer at the end of the charring stage of the heating cycle. This temperature was measured with the thermocouple placed in contact with the interior surface of the atomizer, directly opposite the sample injection port; is the steady-state temperature attained after 15 seconds of heating.
Figure 12. Temperature-time characteristics of the modified HGA-2100 atomizer at various heating rates but at constant final temperatures.

○ 3.3 K ms⁻¹; ● 2.3 K ms⁻¹; △ 1.9 K ms⁻¹; ▲ 1.3 K ms⁻¹.
Table I

Instrument Settings of the Atomizer Control Unit

<table>
<thead>
<tr>
<th>$\frac{dT}{dt}$ /K ms$^{-1}$</th>
<th>Drying Stage</th>
<th>Charring Stage</th>
<th>First Atomization Stage</th>
<th>Second Atomization Stage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Setting</td>
<td>Setting</td>
<td>Setting</td>
<td>Setting</td>
</tr>
<tr>
<td></td>
<td>T/s</td>
<td>T/s</td>
<td>T/ms</td>
<td>T/s</td>
</tr>
<tr>
<td>3.3</td>
<td>5.0</td>
<td>V</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>2.3</td>
<td>5.0</td>
<td>V</td>
<td>20</td>
<td>8</td>
</tr>
<tr>
<td>1.9</td>
<td>5.0</td>
<td>V</td>
<td>20</td>
<td>7</td>
</tr>
<tr>
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<td>5.0</td>
<td>V</td>
<td>20</td>
<td>6</td>
</tr>
<tr>
<td>0.86</td>
<td>5.0</td>
<td>V</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
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<td>V</td>
<td>20</td>
<td>4</td>
</tr>
<tr>
<td>0.32</td>
<td>5.0</td>
<td>V</td>
<td>20</td>
<td>3</td>
</tr>
</tbody>
</table>

$V =$ variable
As mentioned earlier, the modified HGA-2100 atomizer control unit had the capability to supply input power sequentially to the two atomization stages. A high input power was supplied for a short period of time to the first atomization stage, which resulted in a very rapid rise in temperature of the graphite tube to some pre-selected value; this was followed by a more moderate input power supplied to the second atomization stage. The second stage maintained the final atomization temperature constant up to the end of the heating cycle. Of interest is the determination of the heating rate of the atomizer during the operation of the first atomization stage. The heating rate is defined as the slope of the initial, linear parts of the temperature-time curves (such as those presented in Figure 12). Figure 13 shows a plot of the heating rate (in K ms\(^{-1}\)) of the atomizer as a function of the voltage control setting of the first atomization stage. For the highest heating rate, the initial heating period was limited to less than 1 s to avoid overshooting of the maximum final temperature.

Figure 14 shows oscilloscopic traces of the temperature-time characteristics of the atomizer surface heated at different heating rates to the same final temperature. Figure 15 shows oscilloscopic traces of the temperature-time characteristics of the atomizer heated at the same heating rate to different final temperatures. It can be seen from these photographs that the heating rate and the final temperature of the atomizer can be set independently so that one can study effect of the heating rate and of the final temperature on the analysis signal independently of each other.
Figure 13. Initial heating rate of the atomizer surface as a function of the instrument setting.
Figure 14. Temperature-time curves of the modified HGA-2100 atomizer heated at different heating rates to the same final temperature.

Figure 15. Temperature-time curves of the modified HGA-2100 atomizer heated at the same heating rate to different final temperatures.
In all cases, the temperature-time curves rise linearly and asymptotically approach an upper study-state temperature which reflects the balance attained between the input power (i.e. the heating rate) and the rate of heat loss. 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. Therefore, at low temperatures, the rate of increase in the temperature of the atomizer is related to the input power by Equation 1:

\[ \frac{dT}{dt} = \frac{P}{mc} \]

where \( P \) is the power consumption of the atomizer (J s\(^{-1}\)), \( m \) is the mass of the graphite tube (kg) and \( c \) is the heat capacity (J kg\(^{-1}\) K\(^{-1}\)). According to Equation 1, there is a linear relationship between the initial rate of heating of the atomizer (i.e. at low temperatures) and its power consumption. This linear relationship has been confirmed experimentally and is shown graphically in Figure 16. Such a linear relationship was also observed by Johnson et al. (57) and Torsi and Tessari (58) using a filament-type atomizer.

The Capacitive Discharge Power Supply Unit

Figure 17 presents a basic circuit diagram of the capacitive discharge power supply unit which was fabricated in this laboratory. The capacitor bank contained 25 "Computamite" aluminium electrolytic
Figure 16. Initial heating rate of the atomizer surface as a function of the atomization power.
Figure 17. Basic circuit of the capacitive discharge power supply unit.  
1, diode; 2, capacitor bank, 3,5,7, silicon-controlled rectifier (SCR); 4, graphite tube atomizer, 6, 3.3 KW step-down transformer; 8, current shunt.
capacitors, each of 6000 μF capacitance and each rated at 300 V dc (Cornell-Dubilier Electric Corporation, Newark, N.J.). These capacitors were connected in parallel and provided a total capacitance of 0.15 F. High-voltage capacitors were used because fewer capacitors were needed in constructing the capacitor bank than if low-voltage capacitors were used.

To charge the capacitor bank, a Nobatron Model DCR 300 (Sorensen Co., Inc., Manchester, N.H.) 2.5-ampere constant-current dc power supply was used. A constant current dc power supply makes possible rapid charging of the capacitor bank (< 1 min), whereas a variable-decreasing current power supply would require approximately 20 min to charge the bank fully -- such a length of time would severely limit the number of determinations per working day. The voltage applied to the capacitor bank was monitored with a Model 3476 A digital multimeter (Hewlett-Packard Co., Ltd.). In this way, the voltage applied to the capacitor bank could be manually controlled to ensure reproducible setting of the atomizer heating rates. The apparatus has a temperature control unit, which uses a voltage control to set a pre-determined temperature of the atomizer.

An auxiliary power via a step-down transformer was used for the drying andcharmingcycles. However, the primary function of the auxiliary power supply was to maintain the temperature constant after the atomizer was pulse-heated by the capacitor bank. The atomizer control unit and capacitive discharge power supply are shown in Figure 18.
Figure 18. Capacitive discharge power supply and atomizer control unit.
The capacitive discharge power supply unit and the temperature control unit were mounted on a Hammond rack. A series of timing circuits controlled the sequence and the duration of each of the four heating steps. Since the time taken by the atomizer to reach the maximum temperature (from the end of the charring cycle) is 10 - 15 ms and the heating rate up to 75 K ms⁻¹ has been used, timing control with a reproducibility of ±10 μs is needed. In commercial atomizers, which use much lower heating rates, timing control to within only a fraction of a second is adequate.

The Atomizer for the Capacitive Discharge Apparatus

The atomizer head was a modified Carbon Rod Atomizer model 63 (CRA 63) workhead (Varian Techtron Pty. Ltd., Melbourne, Australia). Figure 19 shows the atomizer mounted on the optical rail of the spectrometer described earlier. The atomizer was constructed (in this laboratory) of nickel-plated brass and was mounted on the optical rail of the spectrometer. Provision was made for a flow of cooling water through the metal parts housing the graphite contact electrodes. Internal purge gas (Ar) was supplied by two ceramic-tipped copper capillary tubes positioned just above and to the side at each end of the graphite tube. To prevent air oxidation the graphite tube was continuously swept with a laminar flow of an inert gas (Ar) via a series of rectangular slots cut into the atomizer housing. The flow of the inert gas was directed from above and below the graphite tube to ensure complete containment of the graphite tube in a chemically inert atmosphere.
Figure 19. The atomizer assembly of the capacitive discharge apparatus.
An optical stop with an aperture diameter slightly smaller than the
diameter of the graphite tube was placed in the optical path between
the atomizer and the spectrometer slit to prevent the intense continuum
emitted by the incandescent graphite walls from entering the monochromator.

Heating Rates of the Capacitive Discharge Atomizer

The heating rates of the Capacitive Discharge atomizer measured
over a range of voltages applied to the capacitor bank are presented
in Table II. These rates were obtained using an anisotropic pyrolytic
graphite tube of mass of $1.4 \times 10^{-3}$ kg and of wall thickness of 1.0 mm.
All temperatures were measured with the automatic optical pyrometer
focussed onto the inner surface of the graphite tube through the sample
injection port. The heating rates of the atomizer were determined
from the slope of the initial linear part of the temperature-time
curve of the surface temperature of the graphite tube.

The relationship between energy, capacitance and voltage of
the capacitor is given by Equation 2:

$$U = CV^2/2$$  \hspace{1cm} 2

where $U$ is the energy stored in the capacitor bank, $C$ is the capacitance,
and $V$ is the applied voltage to the capacitor bank. The heating rate
of the atomizer is related to the energy of the capacitor bank as
shown by Equation 3:

$$\text{Heating rate} = \frac{U}{t}$$  \hspace{1cm} 3
<table>
<thead>
<tr>
<th>Voltage</th>
<th>Heating Rate/K ms$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>5.9</td>
</tr>
<tr>
<td>80</td>
<td>9.7</td>
</tr>
<tr>
<td>90</td>
<td>17</td>
</tr>
<tr>
<td>100</td>
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<td>140</td>
<td>59</td>
</tr>
<tr>
<td>150</td>
<td>74</td>
</tr>
</tbody>
</table>
where \( t \) is the time in ms. By substituting the value of \( U \) from Equation 2 into Equation 3, one gets

\[
\text{Heating rate} = CV^2/2t
\]

According to Equation 4, for given values of \( C \) and \( t \) the heating rate of the atomizer is proportional to the square of the applied voltage. This linear relationship between the heating rate and the square of the applied voltage was confirmed experimentally, as shown in Figure 20.

**Reagents**

All chemicals used were of certified ACS grade or of the highest purity available. Stock solutions of metal standards were prepared for each metal separately and contained 1000 \( \mu \)g/mL of that metal only. Stock solutions of Al, Cu, Mg, Mn, Ni, Pb, Sn and Zn were prepared from the metals (purity > 99.9%), and those of Cd, Mo, Se, V, Y and U were prepared from their oxides (purity > 99.9%). The above metals or their oxides were dissolved in pure acids or bases as required and diluted with ultrapure water obtained directly from a Milli-Q 2 water system (Millipore Corporation, Mississauga, Ontario, Canada). All test solutions were prepared by serial dilution of the stock solutions with ultrapure water immediately prior to determination.
Figure 20. Heating rates of the capacitive discharge atomizer as a function of the square of the applied voltage.
Gases.

High purity Argon gas (99.95% purity) was used as the external/internal sheath/purge gas throughout this study. A flow rate of $1.3 \times 10^{-3} \text{ dm}^3 \text{ s}^{-1} (0.08 \text{ L min}^{-1})$ for the internal purge gas and a rate of $1.7 \times 10^{-2} \text{ dm}^3 \text{ s}^{-1} (1.0 \text{ L min}^{-1})$ for the external sheath gas were used. Since the internal gas interrupt mode was used at all times, the gas flow rate was not critical; the only requirement being that it must be sufficient to prevent oxidation of the graphite tube.

Measurement Procedure

Test solutions of $5 \times 10^{-6} \text{ dm}^3$ volume were injected into the graphite tube with an Eppendorf syringe (Brinkmann Instruments Inc., Westbury, New York, U.S.A.) fitted with disposable plastic tips. It was possible to employ larger volumes to reduce delivery errors, but this was not attempted in order to avoid long drying time and the possibility of fogging the end windows because of condensation (in the case of the modified HGA-2100). A blank was run with every test solution, and its value was subtracted from the gross value to get the net value, which was reported.

A nominal spectral bandpass of 0.16 nm was used for all elements studied. Unless otherwise stated, the following resonance lines (wavelengths in nm) were used: Al 309.3, Cd 228.8, Cu 324.7, Mg 285.2, Mn 279.5, Mo 313.3, Ni 232.0, Pb 217, Se 196.0, Sn 224.6, U 358.5, V 318.5, Y 407.8 and Zn 213.9. The quartz plano-convex lenses were focussed for maximum throughput of the radiation from the
hollow cathode lamps at the wavelengths used. A parallel beam of radiation was obtained which illuminated completely the interior of the graphite tube.

The sequence of operations for the integration control unit of the amplifier-integrator assembly is described below. The initiation and the duration of the integration period are controlled by an automatic timing circuit activated by a trigger signal from the power supply unit. This trigger signal is synchronous with the start of the atomization stage. The absorbance pulse from analyte is displayed on a storage oscilloscope and the appearance time (defined as the time elapsed from the start of the atomization stage to the point in time at which the signal is just detectable over the baseline) is measured. This appearance time is then manually introduced into the delay cycle of the timing circuit of the integration control unit. Similarly, the duration (time) of the entire absorbance pulse is 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 50 ms preceding and following the absorption pulse. Such a precaution was taken to ensure that integration over the entire width of the absorption pulse was carried out.
CHAPTER 3

EFFECTS OF HEATING RATES AND ATOMIZATION TEMPERATURES ON THE CHARACTERISTICS OF ABSORPTION PULSE

The amplitude and shape of atomic absorption pulses generated in heated graphite atomizers depend upon the rate of introduction of analyte atoms into analysis volume and the rate of their loss from it (52, 53, 59-61). Factors affecting these two rates directly influence the atomic absorption signal. Several theories for atomization in electrothermal atomizers have been proposed (24, 52, 53, 57-73).

Assuming, for the sake of simplicity, that analyte atoms are introduced into the analysis volume simply by the vaporization of the analyte element from the graphite surface (i.e. ignoring all preceding steps of drying and charring (pyrolysis) which may involve decomposition of and other reactions with the sample, and all intermediate steps that may be involved in atom formation), the rate constant \( k \) for evaporation of an analyte element as a function of the absolute temperature may be expressed by:

\[
k = Ae^{-\Delta H/RT}
\]

where \( A \) is a frequency factor, \( \Delta H \) is the heat of vaporization of the analyte element, \( R \) is the universal gas constant and \( T \) is the
temperature in degree Kelvin. Since in commercial graphite tube atomizer vaporization of the analyte occurs simultaneously with increasing temperature of the graphite tube atomizer, Equation 5 may be expressed as a function of time:

\[ k = Ae^{-\Delta H/R(T_0 + \alpha t)} \]

where \((T_0 + \alpha t)\) defines the temperature-time characteristics of the atomizer, i.e., \(\alpha\) is the slope of the \(T\) versus \(t\) graph and is the rate of heating of the atomizer in K ms\(^{-1}\), \(t\) is the time in ms, and \(T_0\) is the intercept on the temperature axis.

Equation 6 may be expressed as

\[ \ln k = \ln A - \Delta H/R(T_0 + \alpha t) \]

Assume \(\Delta H\) is constant and independent of the temperature \(T\) (a fairly reasonable assumption over the narrow range of temperature involved). In applying Equation 6 or 7 we can recognize two cases as follows.

Case 1: \(\alpha t \gg T_0\). This is the case with capacitive discharge heating with its high heating rates (up to 100 K ms\(^{-1}\)); \(T_0\), being the temperature at the end of the charring cycle, is < 500 K in a typical case.

\(\alpha t \gg T_0\), so that \((T_0 + \alpha t) = \alpha t\)

With the above approximation, Equation 7 becomes
\[ \ln k = \ln A - \frac{\Delta H}{R \alpha t} \]

\[ k = Ae^{-\frac{\Delta H}{RT_0}} \]

Equation 9 shows that the rate constant \( k \) varies "exponentially" with \( \frac{1}{\alpha} \).

**Case 2: \( at \ll T_0 \).**

\[ \frac{1}{(T_0 + at)} = \frac{1}{T_0} \left( 1 + \frac{at}{T_0} \right) = \frac{1}{T_0} (1 + \alpha t/T_0)^{-1} = \frac{1}{T_0} (1 - \frac{at}{T_0})^{-1} \]

\[ \ln k = \ln A - \frac{\Delta H}{R} \left( \frac{1}{T_0} \right) (1 - \frac{at}{T_0}) \]

\[ \ln k = \ln A - \frac{\Delta H}{RT_0} + \frac{\Delta H}{RT_0^2} \alpha t \]

\[ k = Ae^{-\frac{\Delta H}{RT_0}} e^{\frac{\Delta H}{RT_0^2} \alpha t} \]

Equation 12 shows that the rate constant \( k \) varies exponentially with the heating rate \( \alpha \). So, the rate constant \( k \) varies exponentially with the heating rate \( \alpha \) when \( at \gg T_0 \) or \( at \ll T_0 \). For first-order kinetics at a steady-state temperature \( T \), the rate constant \( k \) is inversely proportional to the atomization time \( \tau_1 \); hence, atomization time \( \tau_1 \).
should vary exponentially with the heating rate $\alpha$ when $\alpha t >> T_0$ or $\alpha t << T_0$.

This exponential dependence of the rate constant $k$ on the heating rate $\alpha$ when $\alpha t >> T_0$ will be used to account for the exponential increase in the peak-height absorbance with increasing heating rates presented in a later section.

L'vov (59,72) and Katskov and L'vov (73) have shown that in the case of evaporation occurring from an atomizer surface whose temperature is increasing linearly with time, $t$, the variation of the atomic population in the analysis volume with time may be described by Equation 13:

$$N_t \leq \frac{2N_0 \tau_2^2}{\tau_1^2} \left( \frac{t}{\tau_2} - 1 + e^{-t/\tau_2} \right)$$

where $N_t$ is the analyte atomic population at any instant of time, $t$, $N_0$ is the total number of analyte atoms in the sample, $\tau_1$ is the atomization time (which is defined as the time elapsed from the appearance time to the time corresponding to the peak of the absorption pulse (52,53)), and $\tau_2$ is the residence time (which is defined as the time taken for any absorbance value in the right-hand part of an absorption pulse to decay to $1/e$ times its initial value (52,53), assuming first-order kinetics for the decay process). The peak-height absorbance mode is based on measuring the absorbance corresponding to the peak of the absorption pulse, i.e., at $t = \tau_1$. For the
peak-height absorbance mode, i.e., at \( t = \tau_1 \), Equation 13 may be expressed by:

\[
N_{t=\tau_1} = \frac{2N_0 \tau_2^2}{\tau_1^2} \left( \frac{\tau_1}{1 + e^{-\tau_1/\tau_2}} \right)
\]

Equation 14 shows that the peak-height absorbance, \( A_{\text{peak}} \), (which is proportional to \( N_t \)) should increase as the ratio \( \tau_1/\tau_2 \) decreases. For a constant \( \tau_2 \), \( A_{\text{peak}} \) should increase exponentially as \( \tau_1 \) decreases. As will be seen in a later section, \( \tau_1 \) decreases exponentially with the heating rate, \( \alpha \); hence, \( A_{\text{peak}} \) should increase exponentially with heating rate, \( \alpha \).

According to the L'vov model (59,72) for electrothermal atomization in an isothermal graphite cuvette, the integrated absorbance \( Q_N \), is proportional to the residence time, \( \tau_2 \), of atoms in the analysis volume, and the total number of analyte atoms in the sample, \( N_0 \), provided that the analyte is completely atomized during the time of measurement.

\[
Q_N = N_0 \tau_2
\]

However, with commercial graphite tube atomizers, complete atomization of the analyte is sometimes not achieved and the experimental \( \tau_2 \) values are sometimes different from the theoretical \( \tau_2 \) values (52,53).

Equation 15 shows that the integrated absorbance is entirely independent of the atomization time, \( \tau_1 \), i.e., independent of the
kinetics of atomization and, hence, is independent of the heating rate and the composition of the sample. Here the only requirements are complete atomization of the analyte and constant experimental conditions so that the mean length of time spent by the atoms in the analysis volume (i.e. \( \tau_2 \)) remains constant.

It has been demonstrated (52,53,73) that the above mentioned conditions are not fulfilled by commercial graphite tube atomizers and the experimental integrated absorbance may not be independent of the kinetics of atomization and the heating rate. The terms experimental atomization time and experimental residence time will be used throughout this thesis to differentiate them from theoretical atomization time and theoretical residence time of the L'沃vov model.

The effect of the heating rate of an electrothermal atomizer on the absorbance of elements has been studied by several workers (16,52,57,58,60,69,74-80). The heating rate of a graphite tube or filament atomizer has been found to have a large effect on the absorbance of elements.

For resistively-heated electrothermal devices (Joule's heating), the rate of heating is equal to \( E^2/R \), i.e., is proportional to the square of the applied voltage if the resistance of the circuit is held constant.

Sturgeon and Chakrabarti (52,60,77) have studied the effect of electrical power (i.e. the heating rate) on the peak height and integrated absorbance using Carbon Rod Atomizer 63 (CRA 63) and Heated Graphite Atomizer HGA 2100 and they have observed that the
peak height absorbances increase with increasing heating rates, whereas the integrated absorbances remain essentially constant for relatively volatile elements (Zn, Cd) and for Cu, but increase with increasing heating rates for medium volatility elements (Al and Sn). However, these authors could not study the effect of heating rates on the relatively involatile elements, Mo and V, because of the inadequate power capability of these commercial atomizers which resulted in incomplete atomization of Mo and V.

Johnson et al. (57) found a linear relationship between the peak height absorbance and the square of the input voltage, i.e. the heating rate. These authors (57) have also observed a correlation between the appearance temperature and the heat of vaporization of the metal or the bond dissociation energy of the metal oxide. Torsi and Tessari (58) have used another model to study the effect of heating rates on peak height absorbances. Their model predicts that a linear relationship should exist between the peak height absorbance and the input power, i.e., the heating rate of the atomizer. Using chromium as a probe, they have verified the predictive power of their model. However, these authors have not observed the predicted linear relationship above the heating rate of 4 K ms⁻¹.

Posma et al. (69) have studied the variation of peak height absorbance for copper with the heating rate of a CRA 63 atomizer using various time constants. These authors (69) have reported that when recording undistorted signals, the peak height absorbance increases up to a heating rate of about 0.850 K ms⁻¹, but when recording signals
under optimum signal-to-noise ratio conditions (e.g., using a time constant of 0.3 s), the measuring device can measure the signal without distortion up to about 0.400 K ms⁻¹, whereafter the peak height absorbance remains constant. Using a very slow-response system (i.e., a time constant of 3.0 s) these authors (69) have observed that the peak height absorbance increases slowly up to 0.450 K ms⁻¹, after which it decreases slowly. They have also obtained similar results with silver and copper.

Based upon the Torsi-Tessari model (58) Zsako (74) proposed another model to study the influence of heating rates and of kinetic parameters on the shape and magnitude of the signals. The Zsako model also predicts a linear increase of the peak height absorbance with the increasing heating rate of the atomizer.

Using a graphite tube atomizer Johnson et al. (75) have found that the shape of the germanium absorption pulse varies with the voltage applied to the atomizer unit. Above a certain minimum voltage the absorption pulse increases in height and decreases in width as the input power, i.e., the heating rate is increased. These authors have observed a heating rate of 1.6 K ms⁻¹ at the maximum applied voltage of 11 V. These authors have postulated that the germanium atomic vapour is formed by the gas phase dissociation of the volatile GeO species, and that high atomizer heating rates are necessary in order to reach rapidly a temperature at which the thermal decomposition of GeO(g) is thermodynamically favourable -- the time to reach the above temperature must be shorter than the time required for the GeO(g) to diffuse out of the analysis volume. A similar effect has been
observed by Donega and Burgess (16) who have determined Si in an enclosed Ta boat atomizer. These authors have also concluded that the rapid loss of gaseous SiO below a minimum input power accounts for the low sensitivity obtained at low atomizer heating rates.

Maessen and Posma (76) have studied the effect of the square of the applied voltage on the peak separation between the analyte peak and the matrix peak using a Carbon Rod Atomizer (CRA) 63. These authors have observed an initial linear relationship between the absorbance of gold and cobalt in blood plasma and the square of the applied voltage, followed by a slower increase in the absorbance with higher values of the square of the applied voltages.

In an investigation of the effect of the rate of heating in the atomization step (550 to 2000°C), Manning and Slavin (78) have shown that a heating rate of approximately 0.14 K ms⁻¹ maximizes the integrated lead signal. As the heating rate is increased the integrated lead signal becomes progressively smaller; at 700 K s⁻¹ it is reduced to 25% of the maximum value. At heating rates lower than 140 K ms⁻¹ the peaks become broad.

Gregoire et al. (79) have studied the effect of heating rates on peak height and integrated absorbances and have observed an increase in peak height absorbances with increasing heating rates. They have also found that integrated absorbances of relatively volatile elements decrease exponentially with increasing heating rates, whereas those of relatively involatile elements increase exponentially with increasing heating rates.
More recently Chakrabarti et al. (80) have achieved heating rates as high as 75 K ms$^{-1}$ by using an anisotropic pyrolytic graphite tube atomizer heated by a capacitive discharge. In an investigation of the effect of heating rates, these authors have observed an exponential increase in the peak height absorbance with the square of the applied voltage, -- the low volatility elements show a faster rate of increase in the peak height absorbance than the high volatility elements studied by these authors.

In most of the studies discussed above, the power supply is so designed that any change in the rate of heating of the atomizer also results in a change in the final temperature of the atomizer. Since the final temperature of the atomizer affects the characteristics of the absorption pulse of elements (52, 53), the effect of the heating rate cannot be separated from the effect of temperature. In the present work the effect of heating rates on the peak height and integrated absorbances of some selected elements was studied, using a laboratory-made power supply and a graphite tube atomizer -- this power supply allowed independent setting of both heating rates and final temperatures. Three categories of elements studied were: those which were atomized relatively easily (Cd, Pb); those which were atomized not so easily (Cu, Al); those which were poorly atomized such as the relatively involatile elements (V, Mo), or the elements which formed involatile carbides or lamellar compounds with graphite (U). The effect of the heating rates was studied using atomization surfaces as follows: pyrocoated graphite tubes (PCGT) and surfaces with and without linings of metals, Ta or W.
EXPERIMENTAL

The apparatus and reagents used for this study have been described in detail in Chapter 2. The following special precautions were taken to ensure reproducible experimental conditions throughout the course of this study. i) The resistance between the tube and the graphite contact rings was set at 22 mΩ for every firing. This was accomplished by turning the adjustment screw on the atomizer which regulated the contact tension exerted by the contact rings on the ends of the graphite tube. The resetting of the resistance to 22 mΩ was necessary since every firing slightly changed the porosity of the graphite tube and, hence, its resistance; also firing of the tube caused graphite to be selectively volatilized from the centre of the tube, thus reducing the mass and, hence, heat capacity of the tube. Without the above readjustment of the contact tension, and with the same experimental conditions, the rate of heating of the graphite tube would gradually change with each firing. ii) After each firing the flow rate of water passing through the atomizer was reset to 1.5 dm³/min. This was done to eliminate any variations in the atomizer temperature caused by changes in the flow rate of the cooling water. An increase in the atomizer temperature with increasing rates of water flow was observed by some workers (55,56), and was attributed by these authors to a negative temperature
coefficient of the resistance of graphite atomizer.

A volume $5.0 \times 10^{-6} \text{ dm}^3$ of the test solution was introduced into the atomizer by means of an Eppendorf microlitre syringe. Prior to the atomization step, all samples ($5.0 \times 10^{-6} \text{ dm}^3$) were dried at 370 K for a period of 30 s to drive off all water from the sample. This was followed by a charring (pyrolysis) step at 570 K, maintained for a period of 20 s.
RESULTS AND DISCUSSION

Temperature-controlled heating of the graphite tube atomizer

In graphite furnace atomic absorption technique, a semi-enclosed graphite tube is resistively heated to a temperature at which the analyte is atomized. The atomization temperature depends on the analyte; for example, in case of cadmium which is typical of relatively volatile analytes, the atomization temperature is 900°C, whereas in the case of vanadium which is typical of relatively involatile analytes, the atomization temperature is 2800°C. At these temperatures, atomization is fairly rapid but it starts much earlier; for example, the atomization of cadmium starts at a temperature less than 400°C. Therefore, it is important to reach a sufficiently high temperature before a measureable fraction of the elements disappears from the analysis volume by diffusion (the analysis volume is defined by the geometry of the incident radiation passing through the graphite tube). Also, it is important to achieve the atomization temperature very rapidly to prevent the loss of the analyte through formation of refractory compounds (e.g., involatile carbides) with graphite. However, the final temperature should not be greater than that necessary to atomize the analyte completely, because all loss processes (by diffusion, convection, and expulsion) are temperature-dependent and become more effective with increasing temperatures.
In commercial graphite furnaces, the power supplies are usually so designed as to apply a constant voltage to the atomizer. With such power supplies, temperature increases with increasing time until heat loss balances the heat gain. Figure 21 presents schematic diagrams of temperature-time curves obtained using voltage-controlled heating (the left hand curves) and temperature-controlled heating (the right hand curves). In voltage-controlled heating, higher voltages (i.e., higher heating rates) are applied to attain higher temperature; hence, with such devices temperatures cannot be set independently of the heating rate. In temperature-controlled heating the same (pre-determined) temperature can be obtained using different heating rates. Temperature-controlled (i.e., constant-temperature) heating is accomplished by using a much faster rate of heating at the initial heating stage by applying maximum power to the atomizer for a very short time to achieve a preset temperature and then to maintain that temperature constant by applying normal power to the atomizer. Temperature-controlled heating allows desirable flexibility in the choice of the operating parameters (heating rate and temperature); hence, optimum operating parameters can be selected for each analyte to yield the best analytical results. The work described in this thesis was done using temperature-controlled heating of the atomizer. Figure 22 presents temperature-time curves obtained using temperature-controlled heating of the atomizer. In Figure 22, the temperature increases rapidly until a preselected value is obtained; then, the electric power is
Figure 2.1. Schematic diagram of different ways of heating of the atomizer. The left hand figure for constant-voltage heating and the right hand figure for temperature-controlled heating.
Figure 22. Temperature-time curves of the modified HGA-2100 atomizer heated at different heating rates, but at a constant final temperature.

- 3.3 K ms\(^{-1}\);
- 2.3 K ms\(^{-1}\);
- 1.9 K ms\(^{-1}\);
- 1.3 K ms\(^{-1}\);
- 0.86 K ms\(^{-1}\);
- 0.61 K ms\(^{-1}\).
adjusted so as to hold the temperature constant (Figure 21, the right hand curves). Alternatively, different heating rates can be used to attain the same (final) temperature (Figure 22). Figure 22 shows that using this power supply the heating rate and the final temperature can be set independently of each other.

The temperatures shown in Figure 22 are those of the inside surface of the atomizer. The temperature-time curves in Figure 22 show initial linear parts, followed by shorter non-linear parts, the end of which marks the end of the first atomization stage and the beginning of the second atomization stage; finally, they show a horizontal part where the atomizer asymptotically approaches the preset (final) temperature. Each curve in Figure 22 represents a different heating rate of the graphite tube atomizer. This heating rate is determined by the input power set at the first atomization stage, and therefore, one could attain any desired (final) surface temperature at a rapid or slow heating rate. With the power supply used in this study, heating rates up to 3.3 K ms⁻¹ were attained. The fact that the rate of heating is variable and that the final temperature at each new rate of heating can be made the same, allowed the effect of the heating rate and the final temperature to be studied independently of each other.

Maximum final temperatures above 3300 K were impractical since at higher temperatures there was scattering of the incident radiation by the ejected carbon from the graphite tube surface; and also, the useful life of the graphite tube is shortened at higher temperatures.
It is interesting to compare the performance of the modified HGA 2100 with that of the commercial instrument (The Perkin-Elmer HGA 2100). There are four significant differences: i) The same final temperature can be attained with the modified HGA 2100 using different heating rates, whereas this can be attained with the commercial instrument using only one heating rate. ii) The modified HGA 2100 can heat the atomizer about three times faster (3.3 K ms⁻¹) than the maximum heating rate (1.23 K ms⁻¹) of the commercial instrument (the former is based on the measurement of the slope of the linear segment of the temperature-time curve). iii) Different (final) temperatures can be attained with the modified HGA 2100 using the same heating rate. iv) Temperature above 3300 K can be attained with the modified HGA 2100, whereas such a high temperature cannot be attained with the HGA 2100 (60), its highest temperature being limited to about 3000 K.

Effect of heating rates on absorption pulse shapes

Figure 23 presents a schematic diagram of an absorption pulse superimposed on the temperature versus time curve of a commercial graphite furnace. Figure 23 also serves to define the following characterization times: $\tau_{\text{appearance}}$ is the time elapsed from the start of the atomization cycle to the point in time at which the observed absorbance signal becomes just visible above the baseline; $\tau_{\text{peak}}$ is the time elapsed from the start of the atomization cycle to the point in time at which the absorbance maximum occurs; $\tau_{\text{end}}$
Figure 23. Absorption pulse characterization times.
is the time elapsed from the start of the atomization cycle to the point in time at which the pulse returns to the baseline; \( \tau_{\text{display}} \) is the total duration of the pulse \((\tau_{\text{end}} - \tau_{\text{appearance}})\). Additionally, the atomization time, \( \tau_1 \), and the residence time, \( \tau_2 \), are shown. The atomization time, \( \tau_1 \), is defined as the difference in time between the appearance time, \( \tau_{\text{appearance}} \), and the absorbance-maximum time, \( \tau_{\text{peak}} \). The residence time, \( \tau_2 \), is defined as the time taken for the absorbance signal to decrease from any value to \( 1/e \) times the value \((e\) is the base of the Naperian logarithm\) measured from the decay part of the absorption pulse. This definition of the residence time \( \tau_2 \) is based on the assumption that the analyte is completely atomized by \( \tau_{\text{peak}} \) and the loss of analyte atoms follow first-order kinetics -- both are fairly reasonable assumptions.

Of particular interest is the change in the shape of the absorption pulse as a function of the rate of heating. Figures 24-27 show photographs of a series of oscillographic traces for Cd, Pb, Cu and Al, respectively, atomized at different heating rates from a pyrolytic graphite surface. The following trends appear from Figures 24-27. For relatively high-volatility analytes (Pb and Cd), with increasing heating rates (starting from very low heating rates) the pulse amplitude \( (A_{\text{peak}}) \) first increases, passes through a maximum and then decreases, whereas the pulse area \( (A_{\text{int}}) \) continues to decrease. For medium-volatility analytes (Cu and Al), with increasing heating rates (starting from very low heating rates) the pulse amplitude \( (A_{\text{peak}}) \) increases and continues to increase up to the
Figure 24. Oscilloscopic traces for $5 \times 10^{-14}$ kg Cd atomized at different heating rates. Left to right: 3.3 K ms$^{-1}$, 2.3 K ms$^{-1}$, 1.9 K ms$^{-1}$, 1.3 K ms$^{-1}$, 0.86 K ms$^{-1}$, 0.61 K ms$^{-1}$, 0.32 K ms$^{-1}$, 0.16 K ms$^{-1}$. Horizontal scale: 200 ms/scale division. Vertical scale: 0.1 absorbance/scale division.

Figure 25. Oscilloscopic traces for $5 \times 10^{-13}$ kg Pb atomized at different heating rates. Left to right: 3.3 K ms$^{-1}$, 2.3 K ms$^{-1}$, 1.9 K ms$^{-1}$, 1.3 K ms$^{-1}$, 0.86 K ms$^{-1}$, 0.61 K ms$^{-1}$, 0.32 K ms$^{-1}$, 0.16 K ms$^{-1}$. Horizontal scale: 500 ms/scale division. Vertical scale: 0.1 absorbance/scale division.
Figure 26. Oscilloscopic traces for \(1 \times 10^{-12}\) kg Cu atomized at different heating rates. Left to right: 3.3 K ms\(^{-1}\), 2.3 K ms\(^{-1}\), 1.9 K ms\(^{-1}\), 1.3 K ms\(^{-1}\), 0.86 K ms\(^{-1}\), 0.61 K ms\(^{-1}\), 0.32 K ms\(^{-1}\). Horizontal scale: 500 ms/scale division. Vertical scale: 0.2 absorbance/scale division.

Figure 27. Oscilloscopic traces for \(5 \times 10^{-13}\) kg Al atomized at different heating rates. Left to right: 3.3 K ms\(^{-1}\), 2.3 K ms\(^{-1}\), 1.9 K ms\(^{-1}\), 0.86 K ms\(^{-1}\), 0.61 K ms\(^{-1}\). Horizontal scale: 200 ms/scale division. Vertical scale: 0.1 absorbance/scale division.
highest heating rates used, whereas the pulse area ($A_{int}$) remains more or less the same. The classification of elements according to their volatility does not mean that there is a necessary correlation between the volatility of elements and their atomization characteristics (e.g., appearance temperature, temperature at the absorbance maximum). But, if such a correlation is observed experimentally, it would indicate that the formation of analyte atoms in the vapour phase has occurred by evaporation or vaporization of the analyte atoms from the condensed phase. In all cases, the increasing heating rate makes the appearance time shorter as would be expected if the appearance temperature is to remain constant and independent of the heating rate (60). Increasing heating rates decrease the atomization time, $\tau_1$, and the residence time, $\tau_2$, for all the elements studied, as can be seen from Tables III and IV, respectively. The decrease in $\tau_1$ values with increasing heating rates is to be expected from the fact that atomization will be completed in shorter time with increasing heating rates (i.e., increasing temperature). The increasing $\tau_2$ values with decreasing heating rates is the result of decreasing rates of analyte loss — all the loss processes (by diffusion, convection and expulsion) are slower at lower heating rates (i.e., lower temperatures).

Attempts to shift the absorption pulses for Cd and Pb to the isothermal region of the temperature-time profile (where the loss by diffusion is constant) by increasing the heating rate up to 3.3 km s$^{-1}$ were not successful. This is because these elements are of relatively high volatility, and the entire absorption pulse
Table III

Effect of Heating Rate on Experimental Atomization Time, $\tau_i$

<table>
<thead>
<tr>
<th>$\frac{dT}{dt}$ /K ms$^{-1}$</th>
<th>Cd</th>
<th>Pb</th>
<th>Cu</th>
<th>Al</th>
<th>V</th>
<th>Mo</th>
</tr>
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<tr>
<td>3.3</td>
<td>120</td>
<td>140</td>
<td>260</td>
<td>285</td>
<td>360</td>
<td>420</td>
</tr>
<tr>
<td>2.3</td>
<td>140</td>
<td>155</td>
<td>355</td>
<td>390</td>
<td>455</td>
<td>540</td>
</tr>
<tr>
<td>1.9</td>
<td>160</td>
<td>225</td>
<td>430</td>
<td>510</td>
<td>600</td>
<td>800</td>
</tr>
<tr>
<td>1.3</td>
<td>200</td>
<td>325</td>
<td>580</td>
<td>680</td>
<td>-</td>
<td>140x10$^1$</td>
</tr>
<tr>
<td>0.86</td>
<td>280</td>
<td>420</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.61</td>
<td>540</td>
<td>640</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table IV

Effect of Heating Rate on Experimental Residence Time, $\tau_2$

<table>
<thead>
<tr>
<th>$\frac{dT}{dt}$ /K ms$^{-1}$</th>
<th>Cd</th>
<th>Pb</th>
<th>Cu</th>
<th>Al</th>
<th>V</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3</td>
<td>110</td>
<td>100</td>
<td>250</td>
<td>-</td>
<td>180</td>
<td>400</td>
</tr>
<tr>
<td>2.3</td>
<td>140</td>
<td>125</td>
<td>275</td>
<td>220</td>
<td>455</td>
<td>610</td>
</tr>
<tr>
<td>1.9</td>
<td>185</td>
<td>180</td>
<td>300</td>
<td>270</td>
<td>520</td>
<td>875</td>
</tr>
<tr>
<td>1.3</td>
<td>255</td>
<td>270</td>
<td>380</td>
<td>375</td>
<td>-</td>
<td>160x10$^1$</td>
</tr>
<tr>
<td>0.86</td>
<td>400</td>
<td>390</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.61</td>
<td>770</td>
<td>550</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
appears in the fast-rising region of the temperature-time profile when the inert gas is expanding very rapidly, expelling some of the analyte atomic vapour; hence, the lower $A_{\text{peak}}$ and $A_{\text{int}}$ values for Cd and Pb at higher heating rates. Figures 28 and 29 show the temperature-time profiles for Cd and Pb, respectively -- the temperature being that of the interior surface of the graphite tube. Figures 30-35 show that the absorption pulses for Cu, Al, V, and Mo are shifted toward the isothermal region of the temperature-time profile so that the decay region for each one of these elements appears partly in the isothermal region. The degree of this shift to the isothermal region parallels the involatilility of these elements.

At a given temperature (say, 2800 - 2900 K), the observed shift increases in the order: $\text{Cu} \sim \text{Al} < \text{Mo} \sim \text{V}$. Since the diffusion coefficient is proportional to $T^{1.5}$ (59, p. 204) shifting of the absorption pulse to the isothermal region makes the loss by diffusion constant and, hence, the residence time, $\tau_2$ constant. The dependence of the degree of the absorption pulse shift (to the isothermal region) on the heating rate is illustrated by Figures 30 and 31, which show that an increase in the heating rate from 0.86 K ms$^{-1}$ to 3.3 K ms$^{-1}$ shifts the tail of the Cu absorption pulse to the isothermal region. This shift of the absorption pulse of any element towards the isothermal region is to be expected since for a given final temperature (isothermal), the higher the heating rate the sooner will this temperature be attained. and hence, the absorption pulse of a given element will be shifted towards the isothermal region at higher heating rates and/or at
Figure 28. Absorption pulse of $5 \times 10^{-14}$ kg Cd superimposed on the (surface) temperature-time profile at heating rate of 0.86 K ms$^{-1}$. Horizontal scale: 500 ms/scale division. Vertical scale: 0.1 absorbance/scale division.

Figure 29. Absorption pulse of $5 \times 10^{-13}$ kg Pb superimposed on the (surface) temperature-time profile at heating rate of 1.3 K ms$^{-1}$. Horizontal scale: 500 ms/scale division. Vertical scale: 0.1 absorbance/scale division.
Figure 30. Absorption pulse of $1 \times 10^{-12}$ kg Cu superimposed on the (surface) temperature-time profile at heating rate of 0.86 K ms$^{-1}$. Horizontal scale: 500 ms/scale division. Vertical scale: 0.2 absorbance/scale division.

Figure 31. Absorption pulse of $1 \times 10^{-12}$ kg Cu superimposed on the temperature-time profile at a heating rate of 3.3 K ms$^{-1}$. Horizontal scale: 200 ms/scale division. Vertical scale: 0.2 absorbance/scale division.
Figure 32. Absorption pulse of $5 \times 10^{-13}$ kg Al superimposed on the temperature-time profile at heating rate of 3.3 K ms$^{-1}$. Horizontal scale: 200 ms/scale division. Vertical scale: 0.1 absorbance/scale division.
Figure 33. Absorption pulse of $5 \times 10^{-12}$ kg V superimposed on the temperature-time profile at heating rate of 1.3 K ms$^{-1}$. Horizontal scale: 500 ms/scale division. Vertical scale: 0.05 absorbance/scale division.

Figure 34. Absorption pulse of $5 \times 10^{-12}$ kg V superimposed on the temperature-time profile at heating rate of 3.3 K ms$^{-1}$. Horizontal scale: 500 ms/scale division. Vertical scale: 0.05 absorbance/scale division.
Figure 35. Absorption pulse of $1.5 \times 10^{-12}$ kg Mo superimposed on the temperature-time profile at heating rate of 3.3 K ms$^{-1}$. Horizontal scale: 500 ms/scale division. Vertical scale: 0.1 absorbance/scale division.
lower, final temperatures (isothermal). It has been recently shown by Chakrabarti et al. (80) that the absorption pulses of medium-volatility elements, Al and Ni, can be shifted almost entirely to the isothermal region using very high heating rates by capacitive discharge heating of an anisotropic pyrolytic graphite tube atomizer.

Effect of heating rates on atomization time, $\tau_1$ and peak absorbance

According to Equation 6, the rate of analyte evaporation is governed predominantly by the exponential term involving the heating rate, $\alpha$; hence, the atomization time, $\tau_1$, should be related to $\alpha$ in an inverse exponential manner. Figure 36 shows the variation of $\tau_1$, with the heating rate, $\alpha$. It can be seen from this Figure that, in general, $\tau_1$ decreases rapidly with increasing heating rate, as expected from Equation 6. However, the decrease in $\tau_1$ with increasing heating rate is greater for elements of lower volatility (Cu, Al, Mo, V) than for elements of higher volatility (Cd, Pb).

Figure 37 presents normalized peak height absorbance as a function of the graphite tube heating rate from 0.31 K ms$^{-1}$ to 3.3 K ms$^{-1}$. The peak height absorbance has been normalized by assigning the value of 100 to the highest absorbance of every element studied and expressing the absorbances measured at various heating rates in the scale of 0-100. As predicted by Equation 6, an exponential increase in the peak height absorbance with the increasing heating rate was observed for U, Mo and V, but less for Cu and Al. Relatively volatile elements (Cd and Pb) showed maxima in their curves at some low values of the
Figure 36. Atomization time, $\tau_i$, as a function of the graphite tube heating rate.

- Cd
- Pb
- Cu
- Al
- V
- Mo
Figure 37: Normalized peak height absorbance as a function of the graphite tube heating rate.

- Pb
- Cd
- Cu
- Al
- Mo
- V
- U
heating rates and had lower absorbances on both sides of the maxima. This can be explained as follows. For relatively volatile elements (Cd, Pb), at the heating rates used in Figure 37, the entire absorption pulse occurred in the period of time during which the temperature of both the atomic vapour and the diffusion medium was increasing very rapidly, resulting in extremely rapid expansion of the gas phase, and loss of the analyte atomic vapour by expulsion with the expanding gases; also, the loss of analyte atomic vapour by diffusion and convection increased with increasing heating rates (i.e. with higher temperatures) (69,71). Like all other elements, the absorbances for Cd and Pb also increase initially with increasing heating rates. However, as explained above, the loss of Cd and Pb mainly by expulsion also increases with increasing heating rates. The maxima in the curves of Cd and Pb mark the point of balance between the two rates -- at the left hand side of the maxima the atom formation process predominates, at the right hand side of the maxima the atom loss processes predominate. The greater the heating rate, the greater is the above loss and the earlier is the appearance of the absorbance maximum. Since the appearance temperature is specific for each analyte (60), at any given rate of heating the absorbance maximum which marks the point of balance between the growth and decay of the analyte atomic vapour is specific for each element in terms of the temperature at which it occurs. In the case of the elements which form atomic vapour by evaporation from the condensed phase and for which no subsequent reaction (e.g., formation of refractory carbides) depletes the free analyte atomic vapour, the position of the absorbance maximum in time (at a given
heating rate) should parallel the volatility of the analytes (melting points and boiling points are good indicators of the volatility). The above generalization can be re-phrased as follows: under the conditions mentioned above, for a group of relatively volatile elements (Cd and Pb), the absorbance maxima for the more volatile elements will occur at lower heating rates, as seen in Figure 37 in which the heating rates corresponding to the absorbance maxima for Cd and Pb are 0.86 K ms⁻¹ and 1.3 K ms⁻¹, respectively (the melting points and boiling points of Cd are 594 K and 1038 K, respectively, and of Pb are 600 K and 1998 K, respectively).

It has been shown by Sturgeon et al. (70,71) that both the magnitude and position of the peak of an absorption pulse are determined by the rates of formation and loss of atoms, the absorbance maximum marking the point of balance between these rates and that an increase in the rate of loss decreases the peak height and also shifts the absorbance maximum to an earlier point in time. Sturgeon et al. demonstrated the above fact by means of an oscilloscopic trace showing the effect of an internal purge gas (i.e., forced convection) on the peak of the absorption pulses from 4 x 10⁻¹³ kg Cu atomized in an HGA 2100; in the presence of the internal purge gas (i.e., forced convection), the peak of the absorption pulse decreased in magnitude and shifted to an earlier point in time. Since the peak of an absorption 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 peak to an earlier point in time. Like the convection in the above case, any increase in any other loss
processes, viz., expulsion due to rapid expansion of the purge gas, diffusion, formation of refractory compounds, may affect the peak of an absorption pulse both in magnitude and position in time. An increase in the pulse height can result from either an increase in the rate of atom formation (i.e. increase in the heating rate) and/or a decrease in the rate of atom loss.

It can be seen from Figure 37 that Cu and Al show an increase in the peak height absorbance with increasing heating rates, and the peak height absorbances of both show signs of levelling off at the highest heating rate (3.3 K ms⁻¹) used. Molybdenum, vanadium and uranium still show an exponential increase in the peak height absorbance at the highest heating rate of 3.3 K ms⁻¹. Since, for a given heating rate, atomization time, τ₁, decreases far more for the low volatility elements (Figure 36) than for the high volatility elements, with increasing heating rates the peak height absorbance is expected to increase more for the medium and low volatility elements (Cu, Al, Mo, V, U) than for the relatively volatile elements (Cd, Pb), as has been observed experimentally. For relatively involatile elements, increasing heating rates decreases τ₁ without corresponding decrease in τ₂, with the results that the peak height absorbance continues to increase with increasing heating rates.

It is important to attain the atomization temperature rapidly in order to achieve the following objectives: 1) One objective is to prevent the loss of analyte through formation of refractory compounds with the graphite surface at high temperatures. Runnels
et al. (81) have published evidence to show that Mo forms a refractory carbide during the atomization step. Uranium is also known to form thermally stable carbides at high temperatures (82, p. 27). The other objective is to reduce the loss of analyte due to the premature (i.e. at too low a vapour-phase temperature) vaporization of the analyte molecular species which will be partly or fully lost from the analysis volume by various loss processes before an adequate vapour-phase temperature is attained to enable extensive dissociation of the analyte molecular species to analytic atomic vapour. For example, UO$_2$(s) sublimes at temperatures above 1970 K (82, p. 75) which is below the appearance temperature of uranium (2570 K), to give UO$_2$(g) which diffuses out of the analysis volume, resulting in a low sensitivity for U.

The experimental atomization time, $\tau_1$, measured for the elements over the range of heating rates studied is presented in Table III. For each of these elements, the experimental atomization time, $\tau_1$, at first decreases rapidly with increasing heating rates and then decreases slowly at higher heating rates.

The experimental residence time, $\tau_2$, is presented in Table IV. As predicted from Equation 14, a maximum in the peak height absorbance occurs when the ratio $\tau_1/\tau_2 \ll 1$. Therefore, as the peak height absorbance increases, the experimental $\tau_1/\tau_2$ ratio is expected to decrease. The ratio $\tau_1/\tau_2$ measured for each element over a range of heating rates are presented in Table V. As predicted, in general, the ratio does in fact decrease with increasing heating rates.
Table V

Effect of Heating Rate on the Ratio of Experimental Atomization Time/Experimental Residence Time

<table>
<thead>
<tr>
<th align="left">( \frac{dT}{dt} / \text{K ms}^{-1} )</th>
<th align="left">( \tau_1/\tau_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td align="left">Cd</td>
<td align="left">Pb</td>
</tr>
<tr>
<td align="left">3.3</td>
<td align="left">1.09</td>
</tr>
<tr>
<td align="left">2.3</td>
<td align="left">1.00</td>
</tr>
<tr>
<td align="left">1.9</td>
<td align="left">0.86</td>
</tr>
<tr>
<td align="left">1.3</td>
<td align="left">0.78</td>
</tr>
<tr>
<td align="left">0.86</td>
<td align="left">0.70</td>
</tr>
<tr>
<td align="left">0.61</td>
<td align="left">0.70</td>
</tr>
</tbody>
</table>
The practical significance of the above observations is that with the commercial, semi-enclosed graphite tube atomizers, high heating rates increase the peak height sensitivity of elements; the more involatile the element, the greater, generally, is the increase in the peak height sensitivity. The greatest increase in the peak height sensitivity with increasing heating rates is found with relatively involatile elements. Heating rates higher than 4 K ms\(^{-1}\) are best accomplished by capacitive discharge heating (80).

The above discussion based solely on the relative volatility of elements is valid only in the simple case in which the atom formation and loss reactions for an analyte are not complicated by the formation of its intermediates of significantly different volatilities in the temperature range studies, and is generally valid for the above elements.

Effect of Heating Rates on Integrated Absorbance

Integrated absorbances for a number of elements as a function of the heating rates are presented in Figure 38, which show three general trends as follows. Lead and cadmium show an exponential decrease in the integrated absorbance with increasing heating rates; copper and aluminium show an increase in the integrated absorbance with increasing heating rates up to certain heating rates (1.3 K ms\(^{-1}\) for Cu and 1.9 K ms\(^{-1}\) for Al) and then they show an exponential decrease with further increase in heating rates; Mo and V show an exponential increase in the integrated absorbance with increasing heating rates, but show signs of levelling off at the maximum heating rate used (3.3 K ms\(^{-1}\)).
Figure 38. Normalized integrated absorbance as a function of the graphite tube heating rate.

- ○ Pb;
- ■ Cd;
- O Cu;
- □ Al;
- Δ Mo;
- ▲ V.
According to Equation 15, the integrated absorbance depends only on the residence time, \( \tau_2 \), of the analyte atoms in the analysis volume. This equation to be valid, however, requires the fulfilment of the following conditions: complete atomization of the analyte and a constant residence time, \( \tau_2 \). Commercial atomizers, however, do not fulfil these conditions. For example, even for relatively volatile elements where complete atomization is expected, the entire absorption pulse appears during the time when the temperature of the atomizer surface is rising very rapidly (Figures 28 and 29). A continuously changing thermal gradient across the longitudinal axis of the graphite tube greatly affects the residence time, \( \tau_2 \), of the analyte atomic vapour in the analysis volume. At high heating rates, thermal gradient across the length of the graphite tube sharply increases, and atom loss due to diffusion and convection across this thermal gradient towards the cold end-cap windows also increases. Furthermore, because of the rapid expansion of the purge gas inside the graphite tube, there is an increase in the atom loss due to mechanical expulsion of the analyte atoms through the sample injection port. At high rates of heating, there is probably also an increase in the loss by diffusion through the pyrolytic graphite tube walls although such loss is probably negligible at lower rates of heating. Therefore, as heating rate increases, the rapidly increasing temperature, and consequently, the rapid expansion of the internal purge gas together with the large thermal gradient across the longitudinal axis of the graphite tube yield an analyte atomic population which is less than the total number of analyte atoms present in the sample. Therefore, the experimental values for the
integrated absorbance are not constant and are less than the theoretical values. Furthermore, complete atomization of the analyte does not occur sometimes, as for example in the case of relatively involatile analytes or analytes which form refractory and/or undissociated compounds.

Table IV shows that the values of experimental residence time, $\tau_2$, for the elements studied are smaller and nearly constant at high heating rates, whereas they are larger and variable at low heating rates. It can be seen from Figure 38 that in the case of the volatile elements studied, with increasing heating rates, the sharp decrease in $\tau_2$ values more than cancels the rather small increase in the peak height absorbance, the net result being a rather sharp decrease in the integrated absorbance values. In case of Cu and Al, the increase in the integrated absorbance, $A_{int}$, with increasing heating rates is due to more extensive formation of analyte atoms caused by higher temperatures, the decrease in $A_{int}$ after the absorbance maximum (i.e. at still higher heating rates) is due to an increase in the rate of loss of analyte atoms from the analysis volume. In case of Mo and V, low heating rates could not be used because of lack of complete atomization at low heating rates. The curves for Mo and V at heating rates $> 1.3 \text{ K ms}^{-1}$ show an initial slight increase, followed by levelling off at higher heating rates. This can be rationalized as follows. Since the final temperature used for Mo and V in both Figures 37 and 38 is the same (2900 K), Figure 37 can be used to provide an understanding of the levelling off.
phenomenon in the curves for Mo and V. The near-constancy of $A_{\text{int}}$ for Mo and V at higher heating rates can be the result of either $N_0$ and $\tau_2$ being both constant or their products remaining constant (fortuitously). Figure 37 shows that the peak absorbances of Mo and V increase exponentially with increasing heating rates. Table IV shows that $\tau_2$ values for both Mo and V decrease greatly between the heating rates of $1.3 \text{ K ms}^{-1}$ and $3.3 \text{ K ms}^{-1}$. Therefore, the near-constancy of $A_{\text{int}}$ for Mo and V must be the result of an increase in the absorbances being balanced by a corresponding decrease in $\tau_2$ values.

Table IV also shows that the experimental $\tau_2$ values are not constant for any of the elements studied. Only for the easily-atomized elements (Cd and Pb), do the absorbance maxima mark the end of the atomization and the beginning of the loss processes. The experimental residence time, $\tau_2$, values are not equal to the theoretical $\tau_2$ values for these elements because of increase in the loss of analyte atomic vapour with increasing heating rates; this increase in the loss is partly due to expulsion of analyte atoms from the analysis volume and partly due to increasing diffusional and convectional loss with increasing heating rates. Therefore, the values of the experimental residence time, $\tau_2$, for the volatile elements (Cd and Pb) tend to be smaller than the theoretical $\tau_2$ values (the theoretical $\tau_2$ values are determined by the lower rate of loss by diffusion at a constant temperature). For the medium-volatility elements and the low-volatility elements, the absorbance maximum simply marks the point of balance between the rates of formation and loss of analyte atoms. Hence, the experimental $\tau_2$
values of these elements contain contributions from the continuing atomization of the analyte beyond the point of the absorbance maximum, and the experimental $\tau_2$ values for these elements tend to be greater than the theoretical $\tau_2$ values. The less easily the elements are atomized, the greater will be the effect of this continuing atomization on the experimental $\tau_2$ values; hence, the effect will be greatest for Mo and V and much less for Cu and Al. This agrees with the results in Table IV. The effect of heating rates on the integrated absorbance of uranium could not be studied because of incomplete atomization and severe memory effect -- the latter was probably due to formation of refractory carbide by uranium with the graphite surface at high temperature (82, p. 27).

Effect of Heating Rates on the Shape of the Absorption Pulse from Metal-lined Surfaces of Pyrocoated Graphite Tube Atomizer

Figures 39-44 show the effect of heating rates on the shapes of absorption pulses of Cd, Pb, Cu and Al when they are atomized from Ta-metal-lined or W-metal-lined surfaces of pyrocoated graphite tube atomizers. Cd and Pb show an increase in the peak height absorbance with increasing heating rates up to certain heating rates (this heating rate will be called the optimum heating rate and is specific for each element), and thereafter, they show a decrease in the peak height absorbance with further increase in the heating rate. These trends are the same as those found when they are atomized from pyrocoated graphite surface. This agreement may suggest that the heating rate has the same effect on the
Figure 39. Oscilloscopic traces of $5 \times 10^{-14}$ kg Cd atomized from a Ta-lined surface at different heating rates. Left to right: 3.3 K ms$^{-1}$, 2.3 K ms$^{-1}$, 1.9 K ms$^{-1}$, 1.3 K ms$^{-1}$, 0.86 K ms$^{-1}$, 0.61 K ms$^{-1}$, 0.32 K ms$^{-1}$. Horizontal scale: 200 ms/scale division. Vertical scale: 0.1 absorbance/scale division.

Figure 40. Oscilloscopic traces of $5 \times 10^{-14}$ kg Cd atomized from a W-lined surface at different heating rates. Left to right: 3.3 K ms$^{-1}$, 2.3 K ms$^{-1}$, 1.9 K ms$^{-1}$, 1.3 K ms$^{-1}$, 0.86 K ms$^{-1}$, 0.61 K ms$^{-1}$, 0.32 K ms$^{-1}$. Horizontal scale: 200 ms/scale division. Vertical scale: 0.1 absorbance/scale division.
Figure 41. Oscilloscopic traces of $5 \times 10^{-13}$ kg Pb atomized from a Ta-lined surface at different heating rates. Left to right: 3.3 K ms$^{-1}$, 2.3 K ms$^{-1}$, 1.9 K ms$^{-1}$, 1.3 K ms$^{-1}$, 0.86 K ms$^{-1}$, 0.61 K ms$^{-1}$, 0.32 K ms$^{-1}$. Horizontal scale: 500 ms/scale division. Vertical scale: 0.1 absorbance/scale division.

Figure 42. Oscilloscopic traces of $5 \times 10^{-13}$ kg Pb atomized from a W-lined surface at different heating rates. Left to right: 3.3 K ms$^{-1}$, 2.3 K ms$^{-1}$, 1.9 K ms$^{-1}$, 1.3 K ms$^{-1}$, 0.86 K ms$^{-1}$, 0.61 K ms$^{-1}$, 0.32 K ms$^{-1}$. Horizontal scale: 500 ms/scale division. Vertical scale: 0.1 absorbance/scale division.
Figure 43. Oscilloscopic traces of $5 \times 10^{-13}$ kg Cu atomized from a Ta-lined surface at different heating rates. Left to right: 3.3 K ms$^{-1}$, 2.3 K ms$^{-1}$, 1.9 K ms$^{-1}$, 1.3 K ms$^{-1}$, 0.86 K ms$^{-1}$, 0.61 K ms$^{-1}$. Horizontal scale: 500 ms/scale division. Vertical scale: 0.2 absorbance/scale division.

Figure 44. Oscilloscopic traces of $1.5 \times 10^{-12}$ kg Al atomized from a W-lined surface at different heating rates. Left to right: 3.3 K ms$^{-1}$, 2.3 K ms$^{-1}$, 1.9 K ms$^{-1}$, 1.3 K ms$^{-1}$. Horizontal scale: 200 ms/scale division. Vertical scale: 0.2 absorbance/scale division.
mechanisms of atom formation and loss for these elements from all these surfaces (pyrocoated graphite, Ta-lined pyrocoated graphite, and W-lined pyrocoated graphite). The effects of heating rates on the absorption pulse shape of Cu from both Ta-lined or W-lined surfaces, and of Al from a W-lined surface show the same trend as those when they are atomized from a pyrocoated graphite surface. Figure 43 shows the effect of heating rates on the absorption pulse shape of Cu atomized from a Ta-lined surface. The trend is the same as that for the atomization of Cu from a pyrocoated graphite surface, but the sensitivity is different. Figure 44 shows the effect of heating rates on the absorption pulse shape and height of Al when atomized from a W-lined surface. The trend for Al is the same as when it is atomized from a pyrocoated graphite surface.

Effect of Maximum, Final Temperature on the Peak Height Sensitivity

Figure 45 presents peak-height absorbance of copper as a function of atomization temperature. The temperature settings are shown in the centigrade scale in accordance with that on the meter of the HGA 76B power supply. The curve has a sigmoid shape characterized by an initial, exponential growth with increasing temperatures, followed by smaller growth, and, finally, a levelling of the growth at still higher temperatures. The above growth pattern can be explained on the basis of the exponentially increasing difference between the rate of atom formation and that of atom loss below the inflection point of the curve, and of the exponentially decreasing difference between the rate of atom formation and that of
Figure 45. Peak height absorbance of Cu as a function of atomization temperature.
Cu λ 324.7 nm.

The temperature setting has been shown in the centigrade scale in accordance with the meter of the power supply of HGA 76B.
atom loss above the inflection point. The final part of the curve is determined by the rate of change in the temperature of the vapour phase. For elements of medium volatility, such as Cu and Al, and of low volatility, such as U and Y, the final part of the curve occurs when the atomizer has attained an isothermal condition, in which the loss of analyte atoms is predominantly by diffusion with a constant rate of diffusional loss, and hence, a constant $\tau_2$. In the region of constant temperature, the absorbance maximum marking the point of balance between the rate of atom formation and that of atom loss reaches a constant value because the total population of analyte atoms in the analysis volume has attained a steady state. For relatively involatile elements, such as U and Y, the highest available temperature ($2800^\circ$C) is too low even to reach the inflection point, as can be seen from Figures 46 and 47. For relatively volatile elements, such as Cd and Pb (Figures 48 and 49), the high-temperature part of the curve beyond the inflection point occurs much earlier ($1000^\circ$C - $1600^\circ$C) at a time when the temperature of the vapour phase is increasing very rapidly, causing an extremely rapid expansion of the vapour phase. This results in expulsion of the analyte atoms along with the expanding gases and lower $\tau_2$ values. The atomization curves for Cd and Pb show a decrease in the absorbance values at high temperatures, as can be seen from Figures 48 and 49 for Cd and Pb, respectively. The optimum atomization temperature is defined as the minimum temperature in the plateau of the atomization curve that gives the maximum absorbance. The practical importance of selecting the
Figure 46. Peak height absorbance of U as a function of atomization temperature. U \( \lambda \) 358.5 nm.

*The temperature setting has been shown in the centigrade scale in accordance with the meter of the power supply of HGA 768.*
Figure 47. Peak height absorbance of $1 \times 10^{-10}$ kg Y as a function of atomization temperature. Y $\lambda$ 407.8 nm.

The temperature setting has been shown in the centigrade scale in accordance with the meter of the power supply of HGA 76B.
Figure 48. Peak height absorbance of Cd as a function of atomization temperature. Cd \( \lambda \) 228.8 nm.

\(^a\)The temperature setting has been shown in the centigrade scale in accordance with the meter of the power supply of HGA 76B.
Figure 49. Peak height absorbance of Pb as a function of atomization temperature. Pb λ 283.3 nm.

The temperature setting has been shown in the centigrade scale in accordance with the meter of the power supply of HGA 76B.
optimum atomization temperature from the plateau of the atomization curve is that the alternative would be the setting of temperature at the edge of a rising or falling part of the curve, for which the uncertainty would be intolerably high. The optimum atomization temperature for Cu is $2000^\circ$C, for Al is $2500^\circ$C, for Cd is $1600^\circ$C and for Pb is $2000^\circ$C, whereas for U and Y it is the maximum available temperature, $2800^\circ$C (higher temperatures are not available with the apparatus used) which gives the maximum absorbances since their atomization curves (Figures 46 and 47) have not reached the plateau of maximum absorbance. The atomization curves of U reflects its high boiling point ($4091$ K) and is consistent with the report in the literature that it forms thermally stable carbides at temperatures above $1520$ K (82, p. 27) and this carbide is stable up to a temperature of $2830$ K (82, p. 170). Temperatures above $2830$ K would be expected to lead to thermal decomposition of the carbide and, hence, an increase in the absorbance; such an increase has been observed experimentally. Since the decomposition reaction is endothermic, an increase in the temperature even beyond the maximum temperature ($2800^\circ$C) used would be expected to make the decomposition reaction still more extensive and, hence, to increase the absorbance. The atomization curve for Y (Figure 47) shows an exponential increase in peak height absorbance with increasing atomization temperature. Yttrium (boiling point $3200$ K) has been reported (51, 83, p. 166) to form stable carbides at high temperature ($1600 - 2100^\circ$C). Temperatures above $2100^\circ$C will result in thermal dissociation of the carbides and, hence, in an increase in the peak height absorbance. Such an
increase in the peak height absorbance has been observed experimentally up to a temperature of 2800°C.

Figures 50 and 51 show oscilloscopic traces of Cu and Al, respectively, as a function of atomization temperature using a constant heating rate of 3.3 K ms⁻¹. The importance of the optimum atomization temperature will be brought out by a comparison of these Figures. At the heating rate of 3.3 K ms⁻¹, the optimum atomization temperatures for Cu and Al have been found to be 2000°C and 2500°C, respectively. Figure 50 shows five almost completely overlapping curves for Cu with identical peak height absorbances (Aₚₑᵃᵏ) and equal areas under the curves (A₀) at the five temperatures from 2150°C to 2600°C used. Thus, in the case of Cu, the optimum atomization temperature can be any temperature from 2000°C to at least 2600°C, and both the peak height absorbance mode and the integrated absorbance mode of measurements will give correct results for Cu, and the sensitivity of the two modes will be independent of the atomization temperature. Figure 51 shows five curves for Al (including two fully overlapping curves) -- the curves show diminishing peak height absorbances with decreasing temperatures, with the exception that the curves for the highest temperature (2600°C) and the next highest temperature (2500°C) have identical peak height absorbances. Hence, the peak height sensitivity for Al is temperature dependent, and the maximum peak height sensitivity for Al is obtained at a temperature of 2500°C. However, the areas under the curves are about the same, and hence, the integrated absorbance sensitivity for Al
Figure 50. Effect of atomization temperature on the peak height and shape of $1 \times 10^{-12}$ kg Cu atomized at constant heating rate of 3.3 K ms$^{-1}$. Horizontal scale: 200 ms/scale division. Vertical scale: 0.2 absorbance/scale division. Temperatures from left to right: 2600°C, 2500°C, 2400°C, 2300°C and 2150°C (the five curves are almost fully overlapping).

Figure 51. Effect of atomization temperature on the peak height and shape of $1.5 \times 10^{-12}$ kg Al atomized at constant heating rate of 3.3 K ms$^{-1}$. Horizontal scale: 200 ms/scale division. Vertical scale: 0.2 absorbance/scale division. Temperatures from left to right: 2600°C, 2500°C (curves for 2600°C and 2500°C are fully overlapping) 2400°C, 2300°C and 2150°C.
is independent of the temperature at least in the temperature range of 2150 - 2600°C. Also, both the modes of measurement should give correct results for Al.
CONCLUSIONS

The factors responsible for low efficiencies of commercial semi-enclosed tube-type atomizers are: their low heating rates and absence of an isothermal (both spatial and temporal) condition throughout the atomization cycle. The chemical composition of the atomizing surface also plays an important role in determining the sensitivity of many elements.

The peak height and integrated absorbances as well as the time required to atomize a sample are very dependent on the heating rate. In general, relatively involatile elements benefit greatly from increased heating rates. Even faster heating rates than are currently available are required to obtain high peak-height sensitivities for refractory analytes, such as Mo, V and U.

The residence time of atoms in the atomizers depends not only on the heating rate, but also on the physicochemical properties of the analyte species. The primary reason for the short residence time of relatively volatile analytes is the expulsion of the analyte species from the analysis volume by the rapidly expanding gases at the initial part of the atomization cycle when the temperature rises very rapidly, causing an extremely rapid expansion of the inert gas which carries with it any analyte species that may be present in the vapour phase.
For elements of low volatility (i.e. with high boiling points), the principal mechanism of analyte atom loss is by condensation of the vaporized analyte onto the cooler end-parts of the atomizer. Subsequent re-evaporation of the condensed analyte produces memory effect and erroneous results.

Both the heating rate and the atomization temperature affect the characteristics of the atomic absorption pulse. In the peak-height mode of measurement, one should use the highest heating rate and the minimum atomization temperature that ensure complete atomization of the analyte and highest sensitivity. In the integrated mode of measurement, one should use a heating rate (not necessarily the highest, but the highest if necessary) and an atomization temperature that ensures complete atomization of the analyte (to attain \( N_0 \)) and isothermal atomization (to achieve a constant \( \tau_2 \) -- i.e., the mechanism for atom loss should be predominantly by diffusion at a constant temperature).

High heating rates and an isothermal (both spatial and temporal) condition throughout the atomization cycle are essential requirements for high sensitivity and high selectivity for both modes of measurement.
CHAPTER 4

EFFECT OF ATOMIZATION SURFACE ON THE SENSITIVITY

Although in recent years the use of pyrocoated graphite tube atomizers in atomic absorption spectrometry has been popular, pyrocoated graphite tube atomizers could not be used successfully for the determination of elements which are refractory or form refractory carbides by reaction with the graphite surface at high temperatures. Formation of involatile carbides, intercalation metal-graphite compounds and/or penetration of the analyte into the pores of the graphite tube is responsible for incomplete vaporization of the analyte (60).

Several approaches have been used to eliminate the above-mentioned problems. One approach has been the pretreatment of graphite tubes with compounds of metals that easily form high-temperature carbides (51, 81, 84-91). In the pretreatment procedure, a layer of metal carbide is formed over the graphite surface inside the graphite tube. This surface layer of metal carbide prevents interactions between the analyte and the graphite surface. Other workers completely avoided the use of graphite as an atomization surface and used atomizers made entirely of a metal such as Pt (25,31,92), W (16,23,25,45,46), Mo (26,33,45), or Ta (18,20,28,33).

An alternative to atomizers made totally of a metal has been the atomizer containing a metal foil placed inside the graphite tube.
This metal foil is placed in such a way that the sample is contained on the metal surface and is isolated from the graphite surface (47-51).

In the present work, the effect of lining the pyrocoated graphite tube with Ta or W on the sensitivity of some elements (Cd, Pb, Cu, Al and U) was investigated using the modified heated graphite atomizer HGA 2100 which was heated at a constant heating rate of 3.3 K ms⁻¹.
EXPERIMENTAL

The apparatus and sampling procedure used are as described in Chapter 2. Linings of tantalum or tungsten metal (A.D. Mackay, Darien, Connecticut, U.S.A.) were cut from metal foils of purity 99.95% and of thickness 0.1 and 0.05 mm, respectively. Rectangular strips 15 x 18 mm were rolled into cylindrical shapes and fitted tightly onto the inside surface of the graphite tube, making sure of complete coverage of the surface area that lay between the grooved end portions of the graphite tube. The inserted metal will be called the metal foil. A sample introduction port 2.0 mm in diameter was drilled at the centre of the metal foil. The graphite tubes were lined with metal foil by first forming the metal strip around a glass mandrel whose diameter was slightly less than that of the graphite tube. After insertion of the metal foil inside the graphite tube, care was taken to adjust the position of the foil such that the sampling hole in the foil coincided exactly with the sample injection port of the graphite tube. The metal-lined tubes were used for analysis only after several high-temperature (2800 K) firings has been done -- these firings expanded the metal foil and formed a tight fit. The tube fitted with the metal foil was heated at a rate of 3.3 K ms$^{-1}$. 
RESULTS AND DISCUSSION

Figures 52-55 present the results of Scanning Electron Microscopy (SEM) of the inside surfaces and edges of used and unused pyrocoated graphite tubes. It can be seen from Figure 52 that the inside surface of the pyrocoated graphite tube has porous sponge-like structure, and the porosity increases with increasing temperature (Figure 53) and with increasing number of firings. Increasing porosity due to high-temperature atomization causes increasing penetration of the analyte into the pores, resulting in formation of lamellar compounds in which the analyte atoms, molecules, etc. are trapped or intercalated between the graphite layers. Besides this, increasing porosity increases the resistance of the graphite tube, resulting in an increase in the heating rate which, if the resistance of the circuit is not reset to a fixed value at the beginning of each firing, will produce variable analytical results. It can be seen from Figure 55 that the separation between the pyrolytic graphite layers increases with increased number of heating cycles (firings) completed by the graphite tube. This effect may be due to the increased weakening of the loose, layered structure of the pyrolytic graphite caused by thermal stress. Once the analyte has penetrated between the layers of pyrolytic graphite, atomization becomes difficult and incomplete, resulting in memory effect and loss in analytical sensitivity. The more involatile the element is the more severe will be the memory effect and the greater
Figure 52. Electron micrograph (x 1000) of the inside surface of an unused pyrocoated graphite tube.

Figure 53. Electron micrograph (x 1500) of the inside surface of a pyrocoated graphite tube after six atomization cycles at 2700°C.
Figure 54. Electron micrograph (x 1500) of the fracture edge of an unused pyrocoated graphite tube.

Figure 55. Electron micrograph (x 1500) of the fracture edge of a pyrocoated graphite tube after six atomization cycles at 2700°C.
will be the loss in analytical sensitivity. Memory effect makes the analytical results of the whole series of samples involved erroneous and is thus a more serious problem than a partial loss in sensitivity, which is sometimes tolerable.

Table VI presents the absolute sensitivities of Cd, Pb, Cu, Al and U atomized from various atomization surfaces. Cd and Pb showed very little enhancement (≈ 1.1 fold) in sensitivity from a Ta-lined or W-lined surface. Cu on the other hand showed an increase in sensitivity from both Ta-lined and W-lined surfaces (≈ 1.7 fold from Ta-lined and 1.5 fold from W-lined surfaces). Fuller (63) reported a similar enhancement for Cu when atomized from a Ta liner using The Perkin-Elmer HGA-70 graphite furnace. Fuller has postulated the following reaction mechanism consistent with the observed first-order kinetics.

\[
\text{Cu}_2\text{O} + \text{C or Ta} \xrightarrow{\text{Slow}} \text{Cu(sℓ)} + \text{CO}
\]

\[
\text{Cu(sℓ)} \xrightarrow{\text{Fast}} \text{Cu(g)}
\]

where the subscripts s, ℓ and g represent the solid, liquid and gas phases, respectively. As the concentration of carbon or tantalum is virtually constant throughout and in very large excess over the amounts of copper present, reaction 16 will reduce to pseudo-first-order kinetics. Fuller has proposed that the enhancement in sensitivity given by the foil may be due in part to the greater free energy change involved for the tantalum reduction of copper oxide, but ultimately
Table VI

<table>
<thead>
<tr>
<th>Atomization surface/Element</th>
<th>Cd, kg</th>
<th>Pb, kg</th>
<th>Cu, kg</th>
<th>Al, kg</th>
<th>U, kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrocoated graphite tube (PCGT)</td>
<td>5.5x10^-16</td>
<td>4.2x10^-15</td>
<td>3.1x10^-15</td>
<td>4.6x10^-15</td>
<td>5.6x10^-8</td>
</tr>
<tr>
<td>PCGT lined with Ta</td>
<td>5.1x10^-16</td>
<td>3.4x10^-15</td>
<td>1.8x10^-15</td>
<td>1.5x10^-14</td>
<td>3.8x10^-9</td>
</tr>
<tr>
<td>PCGT lined with W</td>
<td>5.2x10^-16</td>
<td>3.6x10^-15</td>
<td>2.1x10^-15</td>
<td>4.0x10^-15</td>
<td>4.3x10^-9</td>
</tr>
</tbody>
</table>

*Defined as the mass of the element in kg that gives a peak height absorbance of 0.0044.*
will depend on a more favourable rate of reaction. The above proposal seems reasonable and can be extended to tungsten reduction with a slight modification in the sensitivity.

Another factor which may have contributed to the enhancement in sensitivity by the Ta- or W-lining is that the metal foil of 0.1 mm thickness presents an impermeable barrier to the sample solution to penetrate into the graphite pores and soaking the walls of the graphite tube, or to the graphite atoms diffusing through the metal foil. In the absence of the metal lining, penetration of the sample solution into the graphite pores and soaking the walls of the graphite tube may result in analyte atoms being trapped inside the pores of the graphite wall and diffusing out of the graphite tube through the tube wall.

The above explanation is consistent with the decrease (10%) in the sensitivity obtained using a Ta-foil of 0.05 mm thickness, i.e. of half the above-mentioned thickness (Figures 56 and 57), which suggests that the loss of analyte atoms by diffusion through thinner metal foil is distinctly a possibility and is probably a contributory factor in lower sensitivity. Since the graphite tubes used with both the metal foil of 0.1 mm and 0.05 mm thickness were uncoated, the analyte atomic vapour could diffuse through the tube wall if the atomic vapour could pass through the metal foil which separated it from the tube wall.

The difference in enhancement in the sensitivity of Cu from Ta-lined (1.7 fold) and W-lined surface (1.5 fold) may be due to the difference in thickness of the foil (0.1 mm for the Ta foil and 0.05 mm for the W foil). Figure 56 and 57 present oscillographic traces for
Figure 56: Oscilloscopic trace of $2.5 \times 10^{-13}$ kg Cu (taken as nitrate) atomized from Ta-lined (0.1 mm thick) graphite tube at heating rate of 3.3 K ms$^{-1}$. Horizontal scale: 200 ms/scale division. Vertical scale: 0.1 absorbance/scale division.

Figure 57. Oscilloscopic trace of $2.5 \times 10^{-13}$ kg Cu (taken as nitrate) atomized from Ta-lined (0.05 ms thick) graphite tube at heating rate of 3.3 K ms$^{-1}$. Horizontal scale: 200 ms/scale division. Vertical scale: 0.1 absorbance/scale division.
2.5 x 10^{-13} \text{ kg Cu} \text{ atomized from Ta-lined uncoated graphite tube using 0.1 mm and 0.05 mm thick foil, respectively. It can be seen from these photographs that the 0.1 mm thick foil gives 2 fold greater sensitivity than the 0.05 mm thick foil. This difference may be due to the diffusion of the analyte atomic vapour through the thinner foil -- the uncoated graphite being permeable to atomic vapour will allow diffusion through the graphite wall.}

Aluminium showed a 1.5 fold enhancement in sensitivity when atomized from a W-lined surface and 3.3 fold decrease in sensitivity from a Ta-lined surface. Figures 58 and 59 show oscilloscopic traces of Al atomized from a pyrocoated graphite surface and a Ta-lined surface, respectively. The decrease in sensitivity of Al from a Ta-lined surface may be due to formation of a refractory intermetallic compound of Al and Ta (93) -- the shallow, long-drawn-out absorption pulse in Figure 59 is characteristic of an absorption pulse of an analyte species that is refractory. Since the temperature (2600°C) used was the optimum atomization temperature for Al, and the heating rate (3.3 K ms^{-1}) used was the highest available and the heating rate of 3.3 K ms^{-1} should and does provide high sensitivity for Al in Figure 58, the long-drawn-out absorption pulse in Figure 59 is most probably due to a refractory intermetallic compound of Al and Ta.

Table VI also shows that the use of a tantalum or tungsten foil considerably enhances the absolute sensitivity of uranium (15 fold from a Ta-lined surface and 13 fold from a W-lined surface). The lower sensitivity of uranium from pyrocoated graphite
Figure 58. Oscilloscopic trace of $5 \times 10^{-13}$ kg Al (taken as chloride) atomized from a pyrocoated graphite surface at heating rate of 3.3 K ms$^{-1}$ and temperature of 2600°C. Horizontal scale: 200 ms/scale division. Vertical scale: 0.1 absorbance/scale division.

Figure 59. Oscilloscopic trace of $5 \times 10^{-13}$ kg Al (taken as chloride) atomized from a Ta-lined surface at heating rate of 3.3 K ms$^{-1}$ and temperature of 2600°C. Horizontal scale: 200 ms/scale division. Vertical scale: 0.1 absorbance/scale division.
surface can be rationalized as follows. Thermogravimetric analysis (94) indicates that for U, taken as nitrate, the UO$_2$\textsuperscript{(s)} (m.p. 3070 K) is present at its appearance temperature (2570 K).

\[
\text{UO}_2(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}(s) \xrightarrow{570 \text{ K}} \text{UO}_3(s) \xrightarrow{1030 \text{ K}} \text{U}_3\text{O}_8(s) \xrightarrow{1570 \text{ K}} \text{UO}_2(s)
\]

The reduction of UO$_2$\textsuperscript{(s)} by carbon to uranium metal is thermodynamically favourable above 2400 K (82). However, the uranium produced dissolves carbon rapidly and forms a thermally stable carbide which is easily produced at temperatures above 1520 K (82, p. 27) and is stable up to a temperature of 2830 K (82, p. 170). At temperatures below 2830 K, a substantial fraction of the U atoms produced by carbon reduction is therefore lost by carbide formation and is not transferred to the vapour phase until higher temperatures are reached. Lining of a graphite tube with a metal foil not only prevents the penetration of the analyte solution into the pores of the graphite tube, but also, and more importantly, prevents the above reaction between uranium and graphite at high temperatures.

Gregoire (95) proposed the following mechanisms for the atomization of uranium from a graphite or a tantalum surface.

i) Pyrocoated Graphite Surface.

\[
\text{UO}_2(s) \xrightarrow{1598 \text{ K mol}^{-1}} \text{U}(\ell) + \text{O}_2(g) \rightarrow \text{U}(g)
\]
ii) Tantalum Surface.

\[ \text{UO}_2(g) \xrightarrow{1508 \text{ kJ mol}^{-1}} \text{U}(g) + 2 \text{O} \]

Figure 60 shows decomposition/atomization curves for uranium atomized from a pyrocoated graphite surface. The left-hand curve of Figure 60 represents absorbance values plotted as a function of the charring (pyrolysis) temperature -- the absorbance values being obtained using the atomization temperature of 2800°C (higher temperatures are not available with this instrument). The right-hand curve of Figure 60 represents absorbance values plotted as a function of atomization temperature using the optimum charring temperature (1400°C) for uranium -- the optimum charring temperature had been determined earlier. It can be seen from this Figure that above a temperature of 1600°C, a sharp decrease in the absorbance begins. However, no atomic absorption signal of U is detectable until a temperature of 2300°C is reached. Hence, the above decrease in the absorbance at the charring stage between the temperature of 1600°C and 2300°C is due to the loss of uranium, not as uranium atoms but as uranium molecular species which is not dissociated in the temperature range 1600°C - 2300°C. Uranium has been reported (94) to form \( \text{UO}_2^2(s) \) at temperatures above 1570 K, and \( \text{UO}_2^2(s) \) is known to sublime at temperatures above 1970 K (82, p. 75) to give \( \text{UO}_2(g) \), which diffuses out of the analysis volume, thereby causing a decrease in the absorbance. In determination of uranium, it is therefore advisable to use a charring temperature < 1600°C and to use a very high rate of
Figure 60. Decomposition curve (left) and atomization curve (right) for uranium taken as nitrate in aqueous solution using a pyrocoated graphite tube.

The temperature setting has been shown in the centigrade scale in accordance with the meter of the power supply of HGA 76B.
heating so that the temperature change from 1600°C to 2300°C occurs over so short a time as to offer very little time for the above loss of uranium as undissociated UO$_2^-$ species to occur. Moreover, use of a very high rate of heating and a final temperature $\geq 2800^\circ$C will give high sensitivity.
CONCLUSIONS

The atomization surface has a significant effect on the characteristics of the atomic absorption pulse for some elements, especially those elements which form refractory carbides with the heated graphite surface -- the use of metal lining in these cases considerably enhances the sensitivity of these elements.
CHAPTER 5

CAPACITIVE DISCHARGE HEATING OF AN ANISOTROPIC PYROLYTIC GRAPHITE SEMI-ENCLOSED TUBE ATOMIZER

Commercial electrothermal graphite tube atomizers have two limitations: they give relatively low sensitivities because of their relatively low rates of heating; they are not isothermal (both spatial and temporal), which results in condensation of the analyte vapour at the cooler ends of the graphite tube and its subsequent re-evaporation producing memory effects and erroneous results (52-54,60,70,71,77,96, 97). The above two limitations can be removed by using much faster heating rates with a capacitive discharge power supply and an anisotropic pyrolytic graphite tube atomizer. The effect of heating rates in graphite furnace atomic absorption spectrometry has been reported by several workers (16,52,57,58,69,74-79,98); the heating rate of a graphite tube or filament atomizer has been reported to have a large effect on the absorbance of elements.

Cresser and Mullins (55) have suggested the use of a large electrolytic capacitor for rapidly heating metal filament atomizers. A practical device for capacitive discharge heating has been recently patented (99). More recently L'vov (15) has reported the use of a capacitor bank as a source of electrothermal energy for heating graphite tube atomizers, and also that rates of heating of \(40 \text{ K ms}^{-1}\)
can be achieved. However, no publication has yet appeared on the application of this technique to determination of elements by electrothermal atomization in graphite tube atomizers.
MECHANISM FOR ATOMIZATION OF ELEMENTS

Chakrabarti et al. (60,70) have proposed the following mechanism for atomization of elements in graphite furnace atomic absorption spectrometry.

Mechanism I. Reduction of Solid Oxide by Graphite Surface.

\[ \text{MO}(s) \xrightarrow{\text{reduction by } C} \text{M}(\ell) \xrightarrow{\text{C}} \text{M}_2(\ell) \xrightarrow{\text{C}} \text{M}(g) \]

where \( M = \text{Pb, Cu, Co, Sn, Ni, Mo, V, Cr, Fe} \). For example,

\[ \text{PbO}(s) \xrightarrow{\text{reduction by } C} \text{Pb}(\ell) \xrightarrow{\text{C}} \text{Pb}_2(\ell) \xrightarrow{\text{C}} \text{Pb}(g) \]

Mechanism II. Thermal Decomposition of Solid Oxide.

\[ \text{MO}(s) \xrightarrow{\text{thermal decomposition}} \text{M}(g) + \frac{1}{2} \text{O}_2(g) \]

where \( M = \text{Al, Cd, Zn} \). For example,

\[ \text{CdO}(s) \xrightarrow{\text{thermal}} \frac{1}{2} \text{O}_2(g) + \text{Cd}(\ell) \xrightarrow{\text{C}} \text{Cd}(g) \]
Mechanism III. Dissociation of Oxide Vapour.

\[ \text{MO}_s \xleftrightarrow{\text{MO}_g} \text{MO}_g \xrightarrow{\text{O}_g} \text{M}_g \]

where \( \text{M} = \text{Mg}, \text{Mn}, \text{Cd}, \text{Zn} \). For example,

\[ \text{MgO}_s \xleftrightarrow{\text{MgO}_g} \text{MgO}_g \xrightarrow{\text{O}_g} \text{M}_g \xrightarrow{\text{O}_2(g)} \]

Mechanism IV. Dissociation of Halide Vapour.

\[ \text{MX}_2(g) \xrightarrow{\text{MX}_2(l)} \text{MX}(g) \xrightarrow{\text{M}(g)} \text{X}(g) \]

where \( \text{M} = \text{Cd}, \text{Zn}, \text{Fe}; \text{X} = \text{Cl} \). For example,

\[ \text{CdCl}_2(g) \xrightarrow{\text{CdCl}_2(l)} \text{CdCl}_1(g) \xrightarrow{\text{Cd}(g)} \text{Cl}(g) \]
Mechanisms I and II involve the condensed-phase reduction by carbon or thermal decomposition of the analyte compound while it is in intimate physical contact with the graphite surface, whereas mechanisms III and IV involve the vapour-phase dissociation of the analyte oxide or halide vapour. It is important to consider the significance of the above mechanisms in the case of electrothermal heating by capacitive discharge. At the high rate of heating by capacitive discharge (up to 100 K ms\(^{-1}\) compared to about 2 K ms\(^{-1}\) by a conventional power supply), the vapour-phase temperature lags behind the surface temperature -- the higher the heating rate, the greater the lag in the vapour-phase temperature. Therefore, one can conclude that, other things being equal, the analytes which follow mechanisms I or II should show an enhancement in sensitivity with increasing heating rates of the graphite tube surface (and the condensed phase which is in intimate physical contact with the graphite surface), whereas the analytes which follow mechanisms III or IV should yield smaller enhancements in their sensitivity because of the slower rate of increase in the vapour-phase temperature.

It is also important to realize that high-volatility analytes are atomized during the fast-rising initial stage of the atomization cycle when the temperature of the graphite surface is rising very rapidly. The high-volatility elements, e.g., Cd, Zn, Pb, are vaporized at low temperatures (the appearance temperatures for these elements as nitrates are < 1100 K) at a time when the extremely rapid expansion of the gas inside the graphite tube causes expulsion of the atomic
vapour of relatively volatile elements. This reduces the peak height absorbance of the following relatively volatile elements regardless of their atomization mechanisms: Pb (mechanism I), Cd, Zn (as oxides, mechanism II), Mg (mechanism III), Cd, Zn (as chlorides, mechanism IV).

In summary, high rates of heating by capacitive discharge are expected to affect the sensitivity as follows: (1) larger increase for relatively low-volatility elements, especially those which follow atomization mechanism I or II; (2) smaller increase for relatively high-volatility elements regardless of their atomization mechanisms.
EXPERIMENTAL

Apparatus

Details of the spectrophotometer, the capacitive discharge power supply unit, and the atomizer for the capacitive discharge technique have been given in Chapter 2.

Anisotropic Pyrolytic Graphite Tubes

A major difficulty is encountered when resistively heating conventional, isotropic graphite tubes at very high input power levels. The low resistance of the graphite tube (~ 0.02 Ω) limits the voltage of the power supply unit to about 20 volts. At this voltage, currents of the order of 100 to 1000 amperes result. The large power level needed to heat graphite tube atomizers at very rapid rates requires very large step-down transformers and the use of electrical components designed to function at even higher current. In practice, the power output of the step-down transformer is limited by the maximum current capability of the ac line supply (~0 A) to the primary of the transformer.

This problem was overcome by constructing the graphite tubes from highly oriented, anisotropic pyrolytic graphite. Pyrolytic graphite is a vapour-deposited form of carbon having a high degree of preferred crystalline orientation. This material is produced (100) by the
decomposition of a hydrocarbon gas (methane) on a hot surface and deposits in such a way that the lamellar planes of graphite in the bulk material are oriented parallel to the plane of deposition. The resulting material has physical and electrical properties that differ greatly if these are measured in a direction parallel (a-direction) and perpendicular (c-direction) to the plane of deposition. Figure 61 shows the diagram of a block of anisotropic pyrolytic graphite, its crystallographic axes, a, b and c, the lamellas in the ab plane, and a graphite tube bored through the block. Figures 62 and 63 show diagrams of the graphite tube and the graphite contact electrodes. The graphite tubes and the graphite coated electrodes were fabricated in this laboratory.

Table VII lists some of the anisotropic properties of pyrolytic graphite that are of importance to the present discussion. The electrical resistivity in the c-direction is approximately 5000 fold greater than that in the a-direction at room temperature. This means that in the a-direction pyrolytic graphite is a good electrical conductor and that in the c-direction it acts more like an electrical insulator. The high resistance offered in the c-direction allows the use of high-voltage capacitors. Because of low resistivity in the direction of the current, the current density along each part of the graphite tube length, and consequently, the temperature throughout the graphite tube is essentially constant regardless of the point where the current is applied, the shape of the graphite contact electrodes, and the length of the graphite tube.
Figure 61. An anisotropic pyrolytic graphite block showing the crystallographic axes: a, b and c. Solid lines show the direction of the lamellas in the ab plane. The circle and dashed line show the tube bored through the block.

Figure 62. End-on view of the graphite tube atomizer: (a) graphite tube atomizer made of anisotropic pyrolytic graphite; the solid lines indicate the direction of lamellas; dotted lines indicate 1-mm diameter injection port; (b) contact electrodes made of standard spectrographic graphite - only two of the three electrodes used are shown.
Figure 63. Top view of the graphite tube atomizer; (a) graphite tube atomizer; (b) three-contact electrodes.
<table>
<thead>
<tr>
<th>Property</th>
<th>a-direction</th>
<th>c-direction</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical resistivity/Ω cm</td>
<td>4.0±0.5x10^{-5}</td>
<td>0.20±0.05</td>
<td>101, 102</td>
</tr>
<tr>
<td>Thermal conductivity/W cm^{-1} K^{-1}</td>
<td>18±2</td>
<td>0.08±0.01</td>
<td>103, 104</td>
</tr>
<tr>
<td>Thermal expansion b/K^{-1}</td>
<td>-1x10^{-6}</td>
<td>25x10^{-6}</td>
<td>105</td>
</tr>
</tbody>
</table>

\(^{a}\) Measured at 298 K.

\(^{b}\) Measured between 290 and 370 K.
A problem associated with commercial electrothermal graphite tube atomizers are that they are not isothermal (both spatially and temporally, except towards the end of the heating cycle). Even at a time when the atomizer surface has attained a steady-state temperature, the difference in the temperature between the centre and the cooler ends of the graphite tube is in excess of 500 K (15,70). This temperature gradient is very detrimental to vapour confinement in graphite atomizers and often results in condensation of the analyte atoms in the cooler ends of the graphite tube, thereby reducing the residence time of analyte atomic vapour in the analysis volume.

The use of highly oriented, anisotropic pyrolytic graphite promises to solve this problem. The thermal conductivity of pyrolytic graphite in the a-direction is 225 fold greater (at 298 K) than that in the c-direction and approximately 10 fold greater than that of regular (isotropic) graphite (106). This high thermal conductivity in the a-direction (in the direction along the graphite tube length) promotes rapid distribution of heat uniformly along the graphite tube length.

Graphite tubes containing a cylindrical atomizer cavity bored parallel to the graphite layers (Figure 61) provides the proper configuration necessary to take advantage of the high thermal conductivity in the a-direction. However, the thermal conductivity in the a-direction is very temperature-dependent; upon heating the graphite tube from room temperature to approximately 1400 K, one finds that the thermal
conductivity drops to about 15 percent of its original value. Further increase in the temperature cause no appreciable changes in thermal conductivity (100). In the c-direction, the thermal conductivity is nearly independent of temperature and decreases only slightly upon heating from room temperature to 1400 K (100). At room temperature, in the a-direction, pyrolytic graphite is one of the best heat conductors among elementary materials.

Anisotropic pyrolytic graphite (Super-Temp Co., Santa Fe Springs, California) (107) was obtained in blocks 102 mm in length, 31 mm in breadth and 10 mm in thickness. Tubes cut from these blocks were 28 mm in length and had an internal diameter of about 6 mm. The thickness of the tube wall varied from 0.5 to 1.5 mm. To take advantage of the high thermal conductivity in the a-direction, the cylindrical cavity was cut in a direction parallel to the planes of deposition of the pyrolytic graphite. A sample injection port 1 mm in diameter was drilled into the tube.

Graphite tubes fabricated in this way had a mass that varied from $0.7 \times 10^{-3}$ to $1.4 \times 10^{-3}$ kg. The contact electrodes used to support the pyrolytic graphite tube were made of regular, high-purity graphite. The end of the electrode in contact with the graphite tube was cut so as to fit exactly the shape of the graphite tube. Poor contact at this point causes excessive arcing which results in great loss in electrical energy supplied to the atomizer by the capacitor bank and can also cause serious damage to the metal part of the atomizer.
Procedure

The sequence of steps making up the heating program is as follows: The sample was dried at 370 K for 15 s and ashed at 570 K for 20 s. During this time, the capacitor bank was charged to the desired voltage. The time to reach the maximum surface temperature (starting from the temperature at the end of the charring stage) was 10 - 15 ms. The capacitor bank and the atomization stage of the temperature control unit were fired sequentially, with a minimum resolution of one μs. The atomizer temperature was set by adjusting the voltage of the temperature control unit. The electrical energy from the capacitor bank was used for extremely fast heating of the atomizer to its maximum temperature; the atomization stage of the temperature control unit was used to maintain the temperature of the atomizer constant at some pre-selected value.
RESULTS AND DISCUSSION

Table VIII presents a comparison of the absolute sensitivities obtained with the Perkin-Elmer HGA 76B, the modified HGA-2100, and the capacitive discharge apparatus. The sensitivities were determined under optimum experimental conditions for each element, using the commercially available pyrolytically-coated graphite tubes for the HGA 76B and the modified HGA-2100 instruments, and the laboratory-made anisotropic pyrolytic graphite tubes with the capacitive discharge instrument. The higher heating rates available with the capacitive discharge and modified HGA-2100 instruments enhances the sensitivity of elements, the former instrument enhancing the sensitivity of Cu 27 fold, Al 20 fold and Ni 24 fold.

Table VIII shows that high heating rates of the capacitive discharge instrument results in larger enhancements in the sensitivity for Cu, Al and Ni, and smaller enhancements in the sensitivity for Sn, Se, Pb, Zn, Cd, Mn and Mg. Both the larger and smaller enhancements in the sensitivity show correlation with the different mechanisms for atom formation proposed earlier for these elements. One group of elements includes Cu, Ni and Sn which form metal atoms by mechanism I involving reduction of the metal oxide by carbon, followed by evaporation of metal atoms. The second group includes Al which follows mechanism II for atom formation involved solid-state decomposition.
## Table VIII

Comparison of the Absolute Sensitivity

Peak Height Sensitivity in kg/0.0044 Absorbance

<table>
<thead>
<tr>
<th>The Perkin-Elmer HGA 76B</th>
<th>Enhancement(^a) at heating rate 4.3 K ms(^{-1})</th>
<th>Enhancement(^a) by capacitive discharge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb (217.0 nm)</td>
<td>2.0 \times 10^{-14}</td>
<td>4.2 \times 10^{-15}(^c) (4.8-fold)</td>
</tr>
<tr>
<td>Cu (324.7 nm)</td>
<td>3.0 \times 10^{-14}</td>
<td>3.0 \times 10^{-15}(^d) (10-fold)</td>
</tr>
<tr>
<td>Zn (213.9 nm)</td>
<td>5.0 \times 10^{-16}(^b)</td>
<td>2.6 \times 10^{-16} (2.0-fold)</td>
</tr>
<tr>
<td>Cd (228.8 nm)</td>
<td>1.0 \times 10^{-15}</td>
<td>5.5 \times 10^{-16}(^e) (1.8-fold)</td>
</tr>
<tr>
<td>Al (309.3 nm)</td>
<td>4.0 \times 10^{-14}</td>
<td>4.6 \times 10^{-15}(^d) (8.7-fold)</td>
</tr>
<tr>
<td>Ni (232.0 nm)</td>
<td>9.0 \times 10^{-14}</td>
<td>1.3 \times 10^{-14} (7.0-fold)</td>
</tr>
<tr>
<td>Mo (313.3 nm)</td>
<td>1.0 \times 10^{-14}</td>
<td>4.6 \times 10^{-15} (2.2-fold)</td>
</tr>
<tr>
<td>V (318.4 nm)</td>
<td>3.5 \times 10^{-13}</td>
<td>2.5 \times 10^{-14} (14-fold)</td>
</tr>
<tr>
<td>Mg (285.2 nm)</td>
<td>3.0 \times 10^{-16}(^b)</td>
<td></td>
</tr>
<tr>
<td>Se (196.0 nm)</td>
<td>5.0 \times 10^{-14}(^b)</td>
<td></td>
</tr>
<tr>
<td>Sn (286.3 nm)</td>
<td>1.0 \times 10^{-13}(^b)</td>
<td></td>
</tr>
<tr>
<td>Mn (279.5 nm)</td>
<td>2.0 \times 10^{-15}</td>
<td></td>
</tr>
</tbody>
</table>

(continued)
Table VIII

(continued)

a. Enhancement shown in parentheses alongside the sensitivity values are relative to the sensitivity obtained using HGA 76B (The Perkin-Elmer). Except where stated to be otherwise, used graphite tubes of dimensions: length 28 mm, external diameter 8 mm, internal diameter 6 mm, and wall thickness 1 mm.

b. Data for HGA 2100 (The Perkin-Elmer).

c. Used the optimum heating rate of 1.3 K ms$^{-1}$.

d. Used the heating rate of 3.3 K ms$^{-1}$.

e. Used the optimum heating rate of 0.86 K ms$^{-1}$.

f. Used a heating rate of 47 K ms$^{-1}$, a temperature 2870 K and graphite tubes of dimensions: length 28 mm, external diameter 8 mm, internal diameter 6.4 mm, wall thickness 0.8 mm; mass 1.09 g and resistance 850 mΩ.

g. Used graphite tubes of dimensions: length 15 mm, external diameter 6 mm, internal diameter 3 mm, wall thickness 1.5 mm, mass 0.67 g and resistance 720 mΩ.

h. Used the heating rate of 40 K ms$^{-1}$ and temperature of 2300 K for Pb, Zn and Cd, and temperature of 2820 K for Mn, Mg and Se.

i. Used the heating rate of 75 K ms$^{-1}$ and temperature of 3000 K.
of aluminium oxide(s) to form \( \text{Al}_2 \text{(g)} \) in the vapour phase among other species. The third group includes Mg, Zn and Cd when taken as oxides or when they form oxides and which form metal atoms by mechanism III involving vapour-phase dissociation of the metal oxide. The fourth group includes Cd and Zn when they are taken as chlorides (only chlorides among the halides have been studied) and which form analyte metal atoms by mechanism IV involving vapour-phase dissociation of metal chlorides. In the present context, the important distinction between mechanisms I and II on the one hand and mechanisms III and IV on the other hand, is that in the former case the atom formation reaction occurs at the graphite-analyte (monolayer) interface where the temperature of the graphite surface determines the rate of the reaction, whereas in the latter case the atom formation reaction occurs in the vapour-phase where the analyte vapour is no longer in intimate contact with the graphite surface. The above distinction is crucial as will be shown later in this section.

In mechanism I, both reduction of the metal oxide in the condensed phase and the evaporation of the metal formed occur while the analyte is in intimate physical contact with the heated graphite surface. At the very high rates of heating by capacitive discharge, the graphite surface temperature rises rapidly but the vapour-phase temperature lags behind the surface temperature. In earlier publications (53, 60, 96) from this laboratory, it was reported that the rate at which this difference in the temperature increases is
proportional to the rate of heating of the atomizer. Thus, at the very high rates of heating by capacitive discharge, the vapour-phase temperature at the initial stage of heating and at the initial higher rate of heating would be very much lower than the surface temperature during the very short time required to attain the absorbance maximum. The results is that very high heating rates, by increasing very rapidly the graphite surface temperature, would favour mechanisms I and II which depend on the condensed-phase reactions occurring at the graphite-analyte (monolayer) interface, and to less extent, mechanisms III and IV which depend on the much lower vapour-phase temperature. Also, in mechanisms III and IV, the vapour-phase analyte metal atoms are subject to greater loss (60,71) through expulsion by the fast-expanding inert gas, and by convection (due to temperature gradient), resulting in smaller residence time and smaller enhancements in the sensitivity. It is significant that the enhancements given by the modified HGA-2100 using the heating rate of 4.3 K ms⁻¹ parallel those given by the capacitive discharge apparatus -- larger enhancements for Pb, Cu, Ni and V (mechanism I) and Al (mechanism II) and smaller enhancements for Zn and Cd (mechanism III or IV). The small (2.2 fold) enhancement for Mo (mechanism I) is an anomaly and is probably due to formation of refractory carbides by Mo (84) with the heated graphite surface. On the basis of the above observations, one can predict that other elements that have been reported (60,70) to follow mechanisms I or II, viz., Co, Fe (as oxides) and Cr (there may be other
elements) would be expected to show larger enhancements in the sensitivity, whereas other elements that have been reported (60,70) to follow mechanisms III or IV, viz., Ca and Fe (as a chloride) (there may be other elements) would be expected to show smaller enhancements in the sensitivity at high rates of heating by capacitive discharge. Se is expected to follow mechanism I or II.

Figure 64 shows the oscillographic traces from a dual-trace oscilloscope -- the left trace is that of the dc current from the capacitor bank and the right trace is that of the graphite surface temperature. The oscillating trace at the right is that of the ac current from the auxiliary power supply. The capacitor bank was charged to 165 V. The capacitor discharge was switched off at 150 ms simultaneously with the switching on of the auxiliary power supply. As can be seen from Figure 64, the 150 ms was too long a time to elapse before the heating by the auxiliary supply to commence. The surface temperature of the graphite tube atomizer started decreasing after 100 ms, i.e. 50 ms before the commencement of heating with the auxiliary power supply, and this decrease could not be arrested by subsequent heating with the auxiliary power supply. The temperature curve steadily went downward and at no time did an isothermal condition prevail.

Figure 65 shows similar dual oscillographic traces as in Figure 64 but with an important difference -- the capacitive discharge was switched off at 100 ms (instead of 150 ms as in Figure 64) simultaneously with the switching on of the auxiliary power supply.
Figure 64. Oscilloscopic traces from a dual-trace oscilloscope. The capacitor bank was charged to 165 V. The capacitive discharge was switched off at 150 ms.

Figure 65. Oscilloscopic traces from a dual-trace oscilloscope. The capacitor bank was charged to 140 V. The capacitive discharge was switched off at 100 ms.
unit. In this case, the temperature from the capacitive discharge was still increasing when the capacitive discharge was switched off simultaneously with the switching on of the auxiliary power supply unit. The result was that the temperature eventually became almost constant and an isothermal condition prevailed.

Figure 66 shows an oscilloscopic trace of the graphite surface temperature. The capacitor bank was charged to 105 V and the auxiliary power supply was switched on "almost simultaneously" (i.e. after 100 μs) with the switching on of the capacitive discharge, and the simultaneous heating by both the power supplies was continued right to the end of the atomization cycle. The temperature became nearly constant -- the highest and the lowest temperatures in the plateau region were 2550 and 2500 K, respectively. In view of the experimental uncertainty of ±25 K in the temperature measurements, the above temperatures mean an almost isothermal condition which prevailed over a relatively long time.

One of the most important advantages of capacitive discharge heating of graphite tube atomizer is to shift the absorption pulse of the analyte element to the isothermal region of the temperature profile, by applying very high heating rates. Under isothermal condition the diffusional loss of the analyte atoms from the analysis volume becomes constant. The temperature dependence of the diffusion coefficient, \( D \), is given by the following equation:

\[
D = D_0 \left(\frac{T}{T_0}\right)^n \frac{P_0}{P} \quad \text{(in cm}^2/\text{s)}
\]
Figure 66. Oscilloscopic trace of the graphite surface temperature. The capacitor bank was charged to 105 V. Heating was done by both power supplies in the "almost simultaneous" mode.
where \( D \) is the diffusion coefficient at a pressure \( P \) and at a temperature \( T \) and is expressed in terms of the diffusion coefficient \( D_0 \) at the standard state of one atmosphere \( (P_0) \) and temperature 273 K. The values of \( n \) varies from 1.5 to 2.0 for different combination of gases (59, p. 204). The residence time, \( \tau_2 \), is inversely proportional to the diffusion coefficient, \( D \), of the analyte species in the analysis volume (59, p. 205) and is given by:

\[
\tau_2 = \frac{L^2}{8D}
\]

where \( L \) is the effective length (the hot part) of the graphite tube.

If atomization of the analyte occurs in an isothermal condition under which the diffusional loss of the analyte atoms from the analysis volume is constant, then the mean residence time, \( \tau_2 \), is a constant.

Figure 67 shows oscillographic traces of the surface temperature (left trace) and the absorbance signal (right trace) from 2.5 x 10^{-12} kg of Al (taken as aluminium chloride in an aqueous solution) using the Al 309.2 nm line. It can be seen that the absorption pulse is located entirely within the isothermal region. In Figure 67, a temperature of 2470 K which was considerably below the optimum temperature for Al was employed.

Figure 68 shows oscillographic traces of the surface temperatures (left trace) and the absorbance signal (right trace) from 2.5 x 10^{-12} kg of Ni (taken as nickel nitrate in an aqueous solution) using the Ni 232.0 nm line. A temperature of 2570 K (which was also
Figure 67. Oscillographic traces of the surface temperature (left trace) and the absorption signal (right trace) from $2.5 \times 10^{-12}$ kg of Al (added as chloride in an aqueous solution). Al 309.2-nm line. The capacitor bank was charged to 100 V. Horizontal scale: 50 ms/scale division; vertical scale: 0.1 absorbance/scale division.
Figure 68. Oscilloscopic traces of the surface temperature (left trace) and the absorption signal (right trace) from $2.5 \times 10^{-12}$ kg of Ni (added as nitrate in an aqueous solution). Ni 232.0-nm line. The capacitor bank was charged to 115 V. Horizontal scale: 100 ms/scale division; vertical scale: 0.1 absorbance/scale division.
below the optimum temperature) was employed. The capacitor bank was charged to 115 V. In Figure 68, only a small fraction of the auxiliary power was employed -- the result was a drop of only 50 K (from 2620 to 2570 K) in the temperature from the beginning to the end of the absorption pulse. Because of the uncertainty of ±25 K involved in the temperature measurement, the entire absorption pulse of Ni can be considered to lie within the nearly isothermal region. Had the full heating of the auxiliary power supply been employed (as was usual), the above drop in temperature would not have occurred.

Figure 69 shows oscillographic traces of the surface temperature (right trace) and the absorbance signal (left trace) from 1 x 10^{-13} kg of Cd (taken as cadmium nitrate in an aqueous solution) using the cadmium 228.8 nm line -- the final (isothermal) temperature was 2500 K. As can be seen from Figure 69, only the decay part of the absorption pulse was mostly in the isothermal region of the heating curve -- the remaining part of the absorption pulse also would have been in the isothermal region had the final (isothermal) temperature been set much lower, say at 1000 K (which is sufficient for its complete atomization) (cf. Figures 70 and 71).

In order to shift the entire absorption pulse of the volatile elements to the isothermal region of the temperature profile, one should use the minimum temperature that assures complete atomization of the analyte together with a very fast heating rate. The use of the minimum temperature and a very fast heating rate mean early attainment of an isothermal condition. Figure 70 shows
Figure 69. Oscilloscopic traces of the surface temperature (right trace) and the absorption signal (left trace) from $1 \times 10^{-13}$ kg of Cd (added as nitrate in an aqueous solution). Cd 228.8-nm line. The capacitor bank was charged to 105 V. Horizontal scale: 50 ms/scale division; vertical scale: 0.1 absorbance/scale division. Surface temperature 2500 K.
Figure 70. Oscilloscopic traces of the surface temperature (upper trace) and absorption signal (lower trace) from $5 \times 10^{-13}$ kg of Pb. Heating rate = 60 K ms$^{-1}$. Temperature = 2750 K. Vertical scale: 0.1 absorbance/scale division. Horizontal scale: 50 ms/scale division.

Figure 71. Oscilloscopic traces of the surface temperature (left trace) and absorption signal (right trace) from $5 \times 10^{-13}$ kg of Pb. Heating rate = 60 K ms$^{-1}$. Temperature = 2300 K. Vertical scale: 0.1 absorbance/scale division. Horizontal scale: 50 ms/scale division.
oscilloscopic traces of the surface temperature and absorbance signal from $5 \times 10^{-13}$ kg of Pb atomized at a heating rate of 60 K ms$^{-1}$ and a temperature of 2750 K. Figure 71 shows oscilloscopic traces of the surface temperature and absorbance signal from $5 \times 10^{-13}$ kg of Pb atomized at a heating rate of 60 K ms$^{-1}$ and a temperature of 2300 K. As can be seen from Figure 70 about 25% of the absorption pulse is located within the isothermal region when a heating rate of 60 K ms$^{-1}$ and temperature of 2750 K are used, whereas in Figure 71 about 75% of the absorption pulse appears within the isothermal region when the same heating rate (60 K) but a lower temperature (2300 K) are used. Therefore, a very fast heating rate combined with a minimum (isothermal) atomization temperature that yields complete atomization should be used.

In summary, by proper adjustment of the duration of the capacitor bank discharge and using an optimum combination of both the power supplies -- either in the sequential or "almost-simultaneous" mode of heat -- an isothermal condition can be created and maintained. Also, by a proper choice of the heating rate and the final temperature (isothermal), the absorption pulse of all analytes can be made to occur entirely within the isothermal region of the heating curve of the graphite surface.

Figures 72 and 73 show the temperature-time curves of the surface temperature of two anisotropic graphite tubes of different mass and wall thickness. Since an optical pyrometer (52,53) based on blackbody radiation was used for measuring the surface temperature, temperatures lower than about 1300 K could not be reliably measured.
Figure 72. Temperature of the graphite tube surface as a function of the time of heating by capacitive discharge. The capacitor bank was charged to 120 V. Mass of the graphite tube $1.05 \times 10^{-3}$ kg. Thickness of the graphite tube wall 0.5 mm.
Figure 73. Temperature of the graphite tube surface as a function of the time of heating by capacitive discharge. The capacitor bank was charged to 120 V. Mass of the graphite tube $1.4 \times 10^{-3}$ kg. Thickness of the graphite tube wall 1.0 mm.
All temperatures were measured with the automatic optical pyrometer focused onto the inner surface of the graphite tube through the sample injection port. The heating rate of the atomizer was determined from the initial, linear part of the temperature-time curve of the surface temperature of the graphite tubes. The heating rates measured from Figures 72 and 73 were 57 and 38 K ms\(^{-1}\), respectively. Still higher heating rates could be obtained by using higher voltages and/or lower masses of the graphite tubes. The power supplied to the atomizer is dissipated by radiation, conduction, convection and in raising the temperature of the atomizer. At relatively low temperatures, and at the center of the interior surface of the atomizer (where the temperature was measured), heat losses due to radiation, conduction and convection should be small and the rate of increase in the temperature of the atomizer is related to the input power by Equation 1.

\[
\frac{dT}{dt} = \frac{P}{mc}
\]

where P is the power consumption of the atomizer (J s\(^{-1}\)), m is the mass of the graphite tube (kg), and c is its heat capacity (J kg\(^{-1}\) K\(^{-1}\)). According to Equation 1, the initial rate of heating of the atomizer should be inversely proportional to the mass of the atomizer, as has been observed experimentally. On comparing Figures 72 and 73, one finds that the rate of heating in Figure 73 is lower than one would expect from Equation 1 -- the 33% increase in the mass in Figure 73 from that in Figure 72 should have given a 33% decrease
in the rate of heating. However, the decrease in the heating rate was somewhat greater than 33%. This can be explained on the basis of greater loss of heat at the lower rate of heating in Figure 73.

Equation 1 does not have any term for the thickness of the graphite tube wall. However, wall thickness can affect the rate of heat distribution across the transverse cross-section of an anisotropic pyrolytic graphite tube, because this is the direction in which both electrical resistivity is very high and thermal conductivity is low. The smaller the wall thickness, the more rapid is the attainment of uniform distribution of heat across the wall thickness.

Figure 74 presents the relationship between the (voltage)$^2$ applied to the capacitor bank and the heating rates with the charring (pyrolysis) temperature as a parameter. The charring temperature represents the temperature at the initiation of the atomization cycle. Figure 74 shows that a linear relationship exists between the (voltage)$^2$ and the heating rates. The slopes of the three curves are the same (within the experimental error) indicating that the heating rate is proportional to the (voltage)$^2$ as predicted by the theory of capacitive discharge technique (Equation 4, Chapter 2) -- a higher charring temperature allowing the setting of a lower applied voltage to attain the same heating rate as the setting of a higher applied voltage together with a lower charring temperature.

Figure 75 shows the variation in peak height absorbance as a function of the square of the voltage applied to the capacitor bank ($V^2$) i.e., with the heating rate. As predicted by Equation 14,
Figure 74. Relationship between heating rate and square of the applied voltage at different charring temperatures.

○ charring temperature 1000°C;  □ charring temperature 600°C;  △ charring temperature 300°C.
Figure 75. Peak height absorbance as a function of the square of the applied voltage on the capacitor bank. △ Pb; ○ Cd; ■ Mg; ● Cu; ▲ Ni; □ Al; ○ Se; ○ Sn.
an exponential increase in the peak height absorbance with increasing values of $V^2$ was observed for Cu, Ni, Al and Sn, but less for Pb, Cd, Mg, and Se. This difference in behaviour can be explained as follows. The high-volatility elements are atomized at a time when the temperature of the atomizer is rising very rapidly, resulting in the expulsion of the analyte vapour with the rapidly expanding gases -- the greater the heating rate, the greater the loss of the analyte vapour. Obviously, the above loss of analyte vapour reduces considerably the otherwise exponential increase in the analyte atomic vapour, especially at higher heating rates, with the result that the curves for the high-volatility elements bend toward the abscissa with increasing heating rates. At higher heating rates (not shown for Cd, Mg and Se in Figure 75), the curves for the high-volatility elements show a maximum in the peak height absorbance (this maximum is specific for each element) and show continuously decreasing peak height absorbances on both sides of the optimum heating rate (the heating rate corresponding to the absorbance maximum will be called the optimum heating rate). These optimum heating rates are rather low and their values are determined by the rates of the following two opposing processes occurring simultaneously: the rate of production of analyte atomic vapour which is dependent on the volatility of the analyte, and the rate of loss of analyte atomic vapour which is due to expulsion by the rapidly expanding inert gas and convection, and to a lesser extent to diffusion. Since both the above rates are strongly dependent on temperature, for every element there is a specific temperature (hence, a specific heating rate) at which the balance between these two opposing rates reaches a maximum. Hence,
the existence of optimum heating rates for relatively volatile elements. Since for a given energy $U$, atomization time $\tau_1$ decreases far more for the low-volatility elements than for the high-volatility elements, the peak height absorbance is expected to increase more for the low-volatility elements (Cu, Ni, Al, and Sn) than for the high-volatility elements (Pb, Cd, Mg, and Se), as has been observed experimentally. This agreement between the theory (Chapter 3) and the experimental results support the theory and also indicates that the assumption of a constant $\tau_2$ in the theory (Chapter 3) is valid, lending further support for the existence of an isothermal condition during the atomization of all elements.

In Figure 75, there is also an instrumental contribution to the bending of the curves of the high-volatility elements toward the abscissa, especially at high heating rates. Because the transient signals for the high-volatility elements are too fast for the time constant ($\tau_{RC}$) 18 ms of the amplifier used in the measurement of the signals, a part of the bending of the curves at high heating rates is due to the slow response of the amplifier, as can be seen from the results of the following experiment. Because of limitation of the instrument response time ($\tau_{RC}$), we could increase the instrument response by reducing $\tau_{RC}$ from 18 ms to only 0.5 ms -- the latter increased by 7% the peak height absorbance of Cd and also made the peak sharper and the appearance time ($\tau_{appearance}$) shorter (Chapter 2). The above results gave an indication of the distortion in the signals due to
the time constant \( \tau_{RC} \) 18 ms used in this study. A faster-response instrument is needed for the measurement of peak height absorbances (and temperatures) of high-volatility elements at very high heating rates.

Figure 76 shows oscillographic traces of Cu (324.7 nm line) found as an impurity in the specially-prepared anisotropic pyrolytic graphite used for fabricating this particular graphite tube. The copper impurity gave an absorbance signal that diminished very slowly with successive firings of the graphite tube probably because of the formation of a refractory copper carbide. After 12 consecutive firings, the nonzero baseline shown by the bottom curve (obtained at 13th firing) became constant.

Figure 77 shows again the nonzero baseline (lower trace) for Cu. Using the above graphite tube with its copper impurity absorbance signal brought to a constant level after several firings, copper (added as nitrate in an aqueous solution) was atomized. The peak height absorbance of Cu at 324.7 nm line was recorded with the oscilloscope as the upper trace.
Figure 76. Oscillographic traces for Cu found as an impurity. Cu 324.7-nm line. The capacitor bank was charged to 150 V. The horizontal scale: 500 ms/scale division; vertical scale: 0.2 absorbance/scale division.

Figure 77. Oscillographic traces for Cu at 324.7-nm line. Lower trace is for Cu impurity. Upper trace is for 5 x 10^{-2} kg of Cu (added as nitrate in an aqueous solution). The capacitor bank was charged to 160 V. Horizontal scale: 500 ms/scale division; vertical scale: 0.1 absorbance/scale division.
CONCLUSIONS.

Based on this study, the following conclusions on the effects of capacitive discharge heating of anisotropic pyrolytic graphite tube atomizers may be drawn.

i) High-heating rates give greater enhancement in sensitivity for those analytes which form atoms by solid-phase decomposition or reduction at the graphite surface than for those which form atoms by vapour-phase dissociation.

ii) High heating rates give greater enhancement in sensitivity for low-volatility analytes (which remain longer on the graphite surface) and less enhancement in sensitivity for high-volatility analytes.

iii) Expulsion of the atomic vapour of high-volatility analytes by the rapidly expanding gases at the initial heating stage of the atomization cycle when the temperature increases very rapidly, decreases their $\tau_2$ and, hence, gives lower enhancements in their sensitivity.

iv) The appearance temperatures for low-volatility analytes are high enough for their evaporation to occur when the temperature has attained a steady state, thus eliminating loss of the analyte atomic vapour by expulsion and convection. Therefore, $\tau_2$ values.
for low-volatility analytes are much greater, resulting in a much lower $\tau_1/\tau_2$ ratio and, hence, in a higher sensitivity at high heating rates.

v) The capacitive discharge apparatus provides the unique advantage of setting the heating rates independently of the final temperature of the graphite surface. The same final temperature (isothermal condition) can be attained using different heating rates, or different final temperatures (isothermal conditions) can be attained using the same heating rate. This is accomplished by a combination of the voltage and the timing controls.

This technique, which combines very high heating rates of capacitive discharge with an isothermal condition of an anisotropic pyrolytic graphite tube atomizer offers great promise of enhancement in the sensitivity of the low-volatility elements, especially difficult-to-atomize elements which show poor sensitivity with conventional graphite furnace atomic absorption spectrometry. However, another extremely important advantage of this technique is elimination of matrix effect by using high heating rates and by the creation and maintenance of a high-temperature, isothermal condition.
CHAPTER 6

A NEW METHOD OF ANALYSIS BY THE CAPACITIVE DISCHARGE TECHNIQUE IN GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY

INTRODUCTION

Numerous workers (108-122) have reported matrix interferences in graphite furnace atomic absorption spectrometry (GFAAS). Slavin et al. (78, 123, 124) have reported various ways of reducing interferences especially with lead. Matrix interferences can be classified into three groups: spectral, chemical and physical interferences. Spectral interferences that are not caused by an overlap of atomic lines may be eliminated by the use of background correction technique suggested by Kiortyohann and Piókett (109-111). Chemical interferences may be caused by reaction either on the surface of the graphite atomizer (condensed-phase interference), or in the vapour phase inside the analysis volume (vapour-phase interference). The slow release of an element in the atomic form from graphite atomizers is sometimes ascribed to the formation of stable carbide species (15, 50) in the condensed phase. Vapour-phase interferences have been reported by West et al. (112-115) and by Matousek (116, 117). Physical interferences may be caused by either occlusion of the analyte element in the matrix, which has been proposed by Smeyers-Verbeke et al. (118), Cruz and
Van Loon (119), Krasowski and Copeland (108), and Churella and Copeland (120), or by covolatilization of the analyte element along with a more volatile matrix as proposed by Hutton et al. (121).

In order to overcome the matrix problem, several procedures involving separation of the trace metals from the salt matrix before atomization have been reported. These include extraction of the trace elements as chelates (125-130), separation of the trace elements by a column of ion-exchange-resin (131-134), and separation of trace elements by coprecipitation (135,136). However, in trace and ultratrace analysis, these preconcentration and pretreatment procedures are not desirable since they invariably lead to contamination, loss or change in nature of species, in addition to being laborious, time-consuming and costly.

Ediger (137,138) has introduced the matrix modification technique which transforms the matrix components into different chemical compounds of significantly different volatilities -- this is done by letting the matrix react with appropriate chemical reagents which are added to the sample before analysis. Chakrabarti et al. (139,140) introduced a variation of the above technique and called it the analyte modification technique, which differs from the matrix modification technique (137,138) in that the former modifies the analyte species by forming with an added chemical reagent a new analyte species of significantly different volatility than the original analyte species present in the sample. In both the above techniques the goal is to increase the difference between the volatilities of the matrix and the analyte element so much so that a clean separation between the matrix and the
analyte element and quantitative determination of the analyte element can be readily done by a single operation using temperature-programmed, selective volatilization and atomization (141,142).

Commercial electrothermal atomizers which are used in graphite furnace atomic absorption spectrometry have two serious limitations -- their low heating rates limit them to much lower sensitivity than are achievable at much higher heating rates, and they are spatially and temporally non-isothermal. The result of the latter is that samples which are vaporized from hot central parts condense at the cold ends of the graphite tube resulting in much lower residence times, hence, lower sensitivities; also, the condensed analytes may be revaporized in the next analysis producing memory effects and erroneous results (52-54, 60, 70, 71, 77, 96, 97). Also, their slow heating rates, non-isothermal conditions and the much lower vapour temperatures into which the samples are vaporized cause severe matrix interferences of various kinds: spectral, chemical and physical interferences which have plagued graphite furnace atomic absorption spectrometry. The effects of heating rates in graphite furnace atomic absorption spectrometry have been reported in Chapters 3 and 5. A breakthrough in graphite furnace atomic absorption spectrometry is the capacitive discharge technique (15,80) which has made graphite furnace atomic absorption spectrometry relatively free from matrix interferences (143,144). This relative freedom from matrix interferences has been accomplished by using an anisotropic pyrolytic graphite tube atomizer which is heated at very high heating rates (up to 100 K ms⁻¹) by capacitive discharge producing
isothermal conditions and high temperatures.

Conventional instrumental analytical techniques require careful calibration of the instrument with chemically analyzed standards or synthetic standards of known composition (145). When analyses of miscellaneous materials are required, the task of providing the required range of standards becomes insurmountable and instrumental techniques then lose their accuracy, since accurate analyses generally necessitate the use of standards which are closely similar in composition to the sample for analysis. The reasons for such close matching of standards and samples in their composition is that the analytical sensitivity of conventional instrumental techniques depends on the samples' composition, often in a complicated way. The necessity of preparing standards of the same composition as that of the unknown samples involves prior knowledge of the sample composition and chemical treatment or modification of the standards and/or samples, thereby exposing them to the risk of contamination and/or loss; the consequence is questionable results, especially in trace and ultra-trace analysis. The capacitive discharge technique employs electrothermal heating of an anisotropic pyrolytic graphite tube atomizer in atomic absorption spectrometry producing very fast rates of heating (up to 100 K ms\(^{-1}\)) and an isothermal condition, both spatial and temporal (15,80). This technique dispenses with the calibration curve and yields analytical results directly from the absorbance of the unknown sample and the use of a simple equation relating the absorbance to the mass of the analyte element. By simplifying and
shortening the analytical procedure, this technique often eliminates
the sample preparation stage with its attendant risk of contamination
and/or loss of analyte elements, and gives accurate and precise results
at a small fraction of the time and cost of the conventional graphite
furnace atomic absorption spectrometry (143,144).

Equation 20 is a modified version of that given by B.V. L'vov
(59).

\[ A_{\text{peak}} = C_1(T^{0.7}/SP)M = C'_1 M \]

where \( A_{\text{peak}} \) is the peak absorbance, \( C_1 \) is a coefficient determined by
atomic and spectroscopic constants and by experimental conditions, \( T \)
is the absolute temperature, \( S \) is the cross-sectional area of the
graphite tube, \( P \) is the pressure inside the graphite tube, and
\( C'_1 = C_1(T^{0.7}/SP) \). Equation 20 is used for analysis as follows.
The proportionality constant \( C'_1 \) is evaluated for a given analysis
line and experimental conditions using a standard made of the
analyte element (salt) dissolved in ultrapure water. The mass of
analyte element \( M \) in an unknown sample is evaluated from its \( A_{\text{peak}} \)
values and the proportionality constant \( C'_1 \) of Equation 20.

This technique has been found to be relatively free from
matrix interferences. This relative freedom from interferences
results from a combination of factors: high heating rates, isothermal
condition and high temperatures into which samples are vaporized.
The extremely fast heating rates and high temperatures dissociate
the analyte molecular species before they have a chance to be lost
from the analysis volume, resulting in complete atomization of the
analyte element and also in complete dissociation of the matrix
molecular species that would otherwise cause severe background absorption interference. Also, the extremely high heating rates and high temperatures of the new technique ensure complete vaporization of the sample, thereby eliminating also scattering of the incident radiation. The result of high heating rates combined with high temperatures is large enhancements in the analytical sensitivities of many analyte elements and elimination of all matrix interferences including background absorption and scattering of the incident radiation. Also, the sensitivity is independent of the matrix.

Although this method does not need nor use calibration curves, it uses a single-point calibration, and is not an absolute method of analysis, but is the closest approach to an absolute method of instrumental analysis that has been successfully made. With continuing improvement in the capacitive discharge technique and in the design of the tube atomizer, it is confidently expected that even closer approach to an absolute method of analysis by the capacitive discharge technique will be possible. This method of analysis gives accurate and precise results at a small fraction of the time and cost required by the conventional methods of analysis by graphite furnace atomic-absorption spectrometry.
EXPERIMENTAL

Apparatus

The details of the apparatus and accessories and their operation have been reported in Chapter 2.

Reagents

Stock solutions of Pb, Cd and Mn were prepared separately by dissolving the appropriate mass of pure metals (> 99.9% pure) in pure nitric acid and the solutions made up to 1000 µg/mL with ultrapure water of resistivity 18.4 megohm-cm obtained directly from a Milli-Q water purification system (Millipore Corporation, Mississauga, Ontario, Canada). Stock solutions of NaCl, MgCl₂ and CaCl₂ were prepared separately by dissolving the appropriate mass of the pure salts (ACS reagent grade purity) in ultrapure water containing 1% (v/v) nitric acid. These solutions were then diluted with ultrapure water to make the solutions contain 5% (w/v) of the salts in 1% (v/v) nitric acid. All test solutions were prepared by serial dilution of the above stock solutions with ultrapure water immediately prior to determination.
Solution Sampling Procedure

Sample solutions \(5.0 \times 10^{-6} \text{ dm}^3\) are injected into the atomizer by means of an Eppendorf syringe fitted with disposable plastic tips.

Solid Sampling Procedure

A solid sample weighing from 0.2 to 2 mg is delivered to the central part of the graphite tube and the loaded graphite tube is then re-weighed to determine the weight of the solid sample.

The sequence of steps making up the heating program is as follows: the sample is dried at 370 K for 10 s. During this time, the capacitor bank is charged to the desired voltage. The time to reach the maximum surface temperature of the atomizer is 10-15 ms. The capacitor bank and the atomization stage of the temperature control unit are fired sequentially, with a minimum resolution of 1 \(\mu\)s. The atomizer temperature is set by adjusting the voltage of the temperature control unit. The electrical energy from the capacitor bank is used for extremely fast heating of the atomizer to its maximum (isothermal) temperature; the atomization stage of the temperature control unit is used to maintain the temperature of the atomizer constant at some preselected value.

Absorption pulses are recorded with a model 549 storage oscilloscope (Techtronix, Inc., Portland, Ore.) fitted with a type 1A7A high-gain differential plug-in. The signal trace is photographed with a Polaroid camera (Tektronix, Inc.).
In the case of elements which were present in the materials in relatively higher concentrations, their less sensitive analysis lines were employed. Using the analysis line of the desired sensitivity and optimizing the operating conditions, the proportionality constant of Equation 20 was evaluated as follows. Three standard solutions of the analyte element of varying concentrations were employed. Each of the standard solution was analyzed in triplicate and the arithmetic mean of these triplicate determinations for each of the three solutions was averaged to provide the value for the proportionality constant. The concentrations of the unknown samples were determined from their absorbance values obtained using the above conditions and suitable mass of solid samples or 5.0 x 10^{-6} \text{dm}^3 volume of the dissolved (aqueous) samples as the cases might be and solving Equation 20 for the unknown mass of the analyte element.
RESULTS AND DISCUSSION

Table IX presents the experimental conditions used, and also, the precision of the proportionality constant for Equation 20. It can be seen from Table IX that precision of the mean varied from 2.5 to 7.6% R.S.D. These relatively low values of the % R.S.D. is a measure of the validity of the proportionality expressed by Equation 20. Since Table IX has established the constancy (within ±7.6% R.S.D.) of the proportionality constant of Equation 20, considerable savings in time can be achieved by using a single standard in place of three standards. Further savings in time can be achieved by running the single standard and each sample in duplicate in place of larger number of replicates. In actual analysis of samples, such economy of measures will mean much faster turn-around of samples without any appreciable loss of accuracy. Tables X - XIV present the results of analysis of various materials. Table XIII shows a comparison of the analytical results obtained by employing the new technique with the results of the conventional graphite furnace atomic absorption spectrometry, using The Perkin-Elmer Heated Graphite Atomizer HGA 76B, which is widely regarded as one of the best equipment commercially available. Optimized experimental conditions were used in both cases. Tables X - XIV show that recoveries of 100 ± 12% are generally obtainable. Table XIII also shows that the results of the conventional graphite furnace atomic absorption spectrometry suffer from extremely severe depression by the matrix, whereas the
### Table IX

Experimental Conditions and the Precision of the Proportionality Constant for Eq. 20

<table>
<thead>
<tr>
<th>Day No.</th>
<th>Element</th>
<th>Analysis line, nm</th>
<th>Atomization temperature, K</th>
<th>Proportionality constant of Eq. 20</th>
<th>Relative standard deviation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pb</td>
<td>283.3</td>
<td>2670</td>
<td>$5.85 \times 10^{11}$</td>
<td>4.3</td>
</tr>
<tr>
<td>2</td>
<td>Pb</td>
<td>283.3</td>
<td>2670</td>
<td>$7.43 \times 10^{11}$</td>
<td>6.6</td>
</tr>
<tr>
<td>1</td>
<td>Mn</td>
<td>279.5</td>
<td>2820</td>
<td>$7.90 \times 10^{12}$</td>
<td>7.6</td>
</tr>
<tr>
<td>2</td>
<td>Mn</td>
<td>403.1</td>
<td>2820</td>
<td>$8.89 \times 10^{10}$</td>
<td>4.0</td>
</tr>
<tr>
<td>3</td>
<td>Mn</td>
<td>403.1</td>
<td>2820</td>
<td>$1.21 \times 10^{11}$</td>
<td>2.5</td>
</tr>
<tr>
<td>1</td>
<td>Ni</td>
<td>232.0</td>
<td>2970</td>
<td>$1.65 \times 10^{11}$</td>
<td>3.0</td>
</tr>
<tr>
<td>1</td>
<td>Cd</td>
<td>228.8</td>
<td>2300</td>
<td>$2.30 \times 10^{13}$</td>
<td>3.5</td>
</tr>
<tr>
<td>2</td>
<td>Cd</td>
<td>228.8</td>
<td>2300</td>
<td>$9.90 \times 10^{13}$</td>
<td>7.6</td>
</tr>
</tbody>
</table>

*Three different concentrations -- each concentration was determined in triplicate, making a total of nine determinations. The value represents % R.S.D. of the mean of three determinations.*
### Table X

Analytical Recoveries - Solution Sampling

United States Geological Survey Marine Mud, MAG-1

<table>
<thead>
<tr>
<th>Element</th>
<th>Analysis line, nm</th>
<th>Most probable value, kg/kg</th>
<th>Recovered value, kg/kg*</th>
<th>Analytical recoveries, %$^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>283.3</td>
<td>$(2.04\pm0.13)\times10^{-5}$</td>
<td>$(2.01\pm0.13)\times10^{-5}$</td>
<td>98.5</td>
</tr>
<tr>
<td>Ni</td>
<td>232.0</td>
<td>$(7.02\pm0.66)\times10^{-5}$</td>
<td>$(6.97\pm0.23)\times10^{-5}$</td>
<td>99.3</td>
</tr>
<tr>
<td>Mn</td>
<td>403.1</td>
<td>$(1.02\pm0.04)\times10^{-3}$</td>
<td>$(0.978\pm0.21)\times10^{-3}$</td>
<td>95.9</td>
</tr>
</tbody>
</table>

*$^*$The ± values represent one standard deviation of five successive replicate determinations.

$^5$Arithmetic means of five successive replicate determination.
Table XI

Analytical Recoveries - Solid Sampling

National Bureau of Standards Oyster Tissue, SRM 1566

<table>
<thead>
<tr>
<th>Element</th>
<th>Analysis line, nm</th>
<th>Certified value, kg/kg</th>
<th>Recovered value, kg/kg*</th>
<th>Analytical recoveries, %$^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>283.3</td>
<td>(4.8±0.3)×10$^{-7}$</td>
<td>(4.7±0.10)×10$^{-7}$</td>
<td>98.5</td>
</tr>
<tr>
<td>Cd</td>
<td>326.1</td>
<td>(3.2±0.4)×10$^{-6}$</td>
<td>(3.4±0.22)×10$^{-6}$</td>
<td>105</td>
</tr>
<tr>
<td>Mn</td>
<td>403.1</td>
<td>(1.75±0.06)×10$^{-5}$</td>
<td>(1.72±0.06)×10$^{-5}$</td>
<td>98.3</td>
</tr>
</tbody>
</table>

*The ± values represent one standard deviation of five successive replicate determinations.

$^6$Arithmetic means of five-successive replicate determinations.
Table XII

Analytical Recoveries - Solid Sampling
National Bureau of Standards Bovine Liver, SRM 1577

<table>
<thead>
<tr>
<th>Element</th>
<th>Analysis line, nm</th>
<th>Certified value, kg/kg</th>
<th>Recovered value, kg/kg*</th>
<th>Analytical recoveries, %$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>283.3</td>
<td>(3.4±0.8)x10^{-7}</td>
<td>(3.5±0.15)x10^{-7}</td>
<td>102</td>
</tr>
<tr>
<td>Mn</td>
<td>403.1</td>
<td>(1.03±0.10)x10^{-5}</td>
<td>(1.10±0.04)x10^{-5}</td>
<td>107</td>
</tr>
<tr>
<td>Fe</td>
<td>305.9</td>
<td>(2.68±0.08)x10^{-4}</td>
<td>(2.73±0.09)x10^{-4}</td>
<td>102</td>
</tr>
</tbody>
</table>

*The ± values represent one standard deviation of five successive replicate determinations.

$Arithmetic means of five successive replicate determinations.
### Table XIII

**Analytical Recoveries - Solution Sampling**

**Synthetic Aqueous Samples**

<table>
<thead>
<tr>
<th>Element</th>
<th>Analysis line, nm</th>
<th>Mass of analyte</th>
<th>Matrix in excess over the analyte</th>
<th>Analytical recoveries expressed as % of the amount of analyte taken</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Conventional GFAAS technique using HGA 76B*</td>
</tr>
<tr>
<td>Cd</td>
<td>228.8</td>
<td>1.0x10⁻¹⁴ kg</td>
<td>NaCl 70000 fold</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>+MgCl₂ 84000 fold</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>+CaCl₂ 28000 fold</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>217.0</td>
<td>5.0x10⁻¹³ kg</td>
<td>NaCl -30000 fold</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>+MgCl₂ 3600 fold</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>+CaCl₂ 12000 fold</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>279.5</td>
<td>2.0x10⁻¹³ kg</td>
<td>NaCl 25000 fold</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>+MgCl₂ 3000 fold</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>+CaCl₂ 10000 fold</td>
<td></td>
</tr>
</tbody>
</table>

HGA 76B is Heated Graphite Atomizer 76B (which is the European version of the North American model 2200), used with an atomic absorption spectrophotometer, model 603 (The Perkin-Elmer Corporation, Norwalk, Conn., U.S.A.).

*The relative standard deviation (R.S.D.) of the mean of five replicate determinations = ±8% for the conventional GFAAS using HGA 76B.

5 The relative standard deviation (R.S.D.) of the mean of five replicate determinations = ±12% for the new technique.
Table XIV

Analytical Recoveries - Solution Sampling

<table>
<thead>
<tr>
<th>Analysis line, nm</th>
<th>Mass of analyte taken</th>
<th>Matrix in excess over the analyte</th>
<th>Analytical recoveries expressed as % of the amount of analyte taken*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd 228.8</td>
<td>Cd (2.0\times10^{-14}) kg taken as nitrate</td>
<td>Ultrapure water</td>
<td>104</td>
</tr>
<tr>
<td></td>
<td>Cd (1.0\times10^{-14}) kg taken as nitrate</td>
<td>Ultrapure water +NaCl (600000) fold +MgCl (72000) fold +CaCl (24000) fold</td>
<td>105</td>
</tr>
<tr>
<td>Mn 279.5</td>
<td>Mn (1.5\times10^{-14}) kg taken as nitrate</td>
<td>Ultrapure water</td>
<td>(88.2)</td>
</tr>
<tr>
<td></td>
<td>Mn (1.5\times10^{-14}) kg taken as nitrate</td>
<td>Ultrapure water +NaCl (100000) fold +MgCl (12000) fold +CaCl (4000) fold</td>
<td>98.5</td>
</tr>
<tr>
<td>Pb 283.3</td>
<td>Pb (2.0\times10^{-13}) kg taken as nitrate</td>
<td>Ultrapure water</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td>Pb (2.0\times10^{-13}) kg taken as nitrate</td>
<td>Ultrapure water +NaCl (25000) fold +MgCl (3000) fold +CaCl (1000) fold</td>
<td>100</td>
</tr>
</tbody>
</table>

*The relative standard deviation (R.S.D.) of the mean of five replicate determinations = \(\pm 12\%\).
matrix interferences have been almost completely eliminated by the new technique. The significance of these results is that matrix interferences are mostly eliminated by this technique and the analytical sensitivity is mostly independent of the matrix. This is of great practical and theoretical importance since analysis by graphite furnace atomic absorption spectrometry has all along been characterized by matrix interferences. There is also another very significant difference — background correction was not required, nor employed with the new technique, whereas background correction was required and was employed with the conventional graphite furnace atomic absorption spectrometry. Background correction in the conventional graphite furnace atomic absorption spectrometry is usually done with a continuum-source background correction technique, which has some limitations (146,147). These include the need for several continuum sources to cover both the UV and visible wavelengths regions; some degradation in the signal-to-noise ratio due to the additional light sources; possibility of inaccurate correction if the background is structured; limitations in the ability to match the intensities of the source and continuum lamps; and the need to have very good alignment between the optical beams of the source and continuum lamps. The combined effect of these limitations is that in analytical situations involving high background levels, errors can occur due to under- or overcompensation for the background signal (146,147). Since analysis of complex materials (e.g., seawater) by the conventional graphite furnace atomic absorption spectrometry usually requires
the removal of interfering matrices (including those that give extremely intense background absorption) from the sample prior to the determination of the analyte elements, background correction represents a serious limiting factor in the speed and accuracy of analysis by the conventional graphite furnace atomic absorption spectrometry. Even removal of the bulk of the interfering matrices in the charring (pyrolysis) stage of the heating cycle of the conventional graphite furnace atomic absorption spectrometry by employing the time-resolved selective volatilization and atomization technique (139-142) requires precise determination of the heating program that is required to remove the bulk of the matrix without any loss of the analyte elements, and correction for the residual background absorption by the background correction technique. Since the background absorption is eliminated by this new technique, large economy of operation results from greatly simplified and shortened analytical procedures of this technique permitted by the absence of matrix interferences including background absorption. However, this technique does not eliminate interferences from overlapping atomic lines, which is also a spectral interference but of rare occurrence. Elimination of the background absorption by the new technique results in better accuracy. Using the solid-sampling technique in conjunction with the new technique, 100 ± 12% recoveries were obtained; also, the problem of soaking of the sample solutions into the graphite tube and the effect of such soaking on the peak absorbance values were eliminated. The solid-sampling technique with the conventional graphite furnace atomic absorption
spectrometry is even more subject to interferences than the solution-sampling technique. The solid-sampling technique, applied in conjunction with the new technique, eliminates the enormous dilution factor involved in the solution-sampling technique, and thereby enhances greatly the relative analytical sensitivity. This is in addition to the large enhancements in the absolute sensitivity of this technique, e.g., for Cu, Ni and Al, the enhancements are 27-fold, 24-fold and 20-fold, respectively (80).

Matrix Interferences

In Table XIII the chloride interference in graphite furnace atomic absorption spectrometry can be explained by using Pb as an example (similar explanation is also valid for Cd and Mn since these metals and their chlorides have volatilities similar to those of Pb). Loss of volatile chlorides of Pb apparently occurs at the moment of vaporization of the bulk of NaCl, MgCl₂ and CaCl₂, i.e., when the surface temperature of the graphite tube is 900°-1000°C. This effect can be explained by the "carrier effect" or "carrier distillation" as known in emission spectroscopy (148), which is also called co-volatilization by some other workers. It is reasonable to expect that evaporation of the salts would cause simultaneous introduction of lead into the vapour phase as chlorides. Sturgeon et al. (60, 96) have reported that the vapour phase temperature lags considerably behind the surface temperature in the conventional graphite furnace atomic absorption spectrometry. At the above temperature the lead chlorides are only partly dissociated and are
partly lost. The earlier the lead chlorides are vaporized the longer is the time they have for the loss process to deplete the analyte-containing compounds. However, in the above case, the primary mechanism for the loss of analyte-containing compounds is by expulsion with the rapidly expanding inert gas at the initial phase of heating in the atomization cycle when the graphite-surface temperature is rising very rapidly; the loss is also partly due to convection and diffusion.

It would be instructive to investigate the specific roles of the capacitive discharge technique in removing matrix interferences which plague the conventional graphite furnace atomic absorption spectrometry. It is unquestionable that the capacitive discharge technique produces isothermal atomization, whereas the conventional graphite furnace atomic absorption spectrometry does not. Figure 78 shows oscillographic traces for the surface temperature (left trace) and absorbance signal (right trace) of $4.0 \times 10^{-13}$ kg of Pb atomized at a heating rate of $60 \text{ K ms}^{-1}$ and final (isothermal) temperature of 1900 K using the capacitive discharge technique. It can be seen from this Figure that the absorption pulse is located almost entirely within the isothermal region of the heating curve. Had a lower, final (isothermal) temperature (say, 1700 K) been selected (which, like 1900 K, must ensure complete atomization) together with the heating rate of $60 \text{ K ms}^{-1}$, the entire absorption pulse would have been located within the isothermal region of the heating curve. The effect of isothermal atomization is mainly in eliminating memory effect, and in increasing sensitivity as a result of an increase in the residence time.
Figure 78. Oscilloscopic traces of the surface temperature (left trace) and the absorbance signal (right trace) for $4.0 \times 10^{-13}$ kg of Pb (taken as lead nitrate in aqueous solution). Heating rate = 60 K ms$^{-1}$. Temperature = 1900 K. Vertical scale: 0.1 absorbance/scale division. Horizontal scale: 50 ms/scale division.
The effect of very high heating rates on isothermal atomization is seen from Figure 79, which shows oscillographic traces of \(5 \times 10^{-13}\) kg of Pb atomized at a heating rate of 1.3 K ms\(^{-1}\) and an atomization temperature of 2200 K, using the conventional graphite furnace atomic absorption spectrometry, but with an anisotropic pyrolytic graphite tube. The left trace is for Pb (taken as nitrate in an aqueous solution) in a 0.5% NaCl aqueous solution, and the right trace is for the lead nitrate alone. It can be seen from this Figure that in the presence of the chloride matrix the lead appearance time is shorter and, hence, the lead appearance temperature is lower; also, the pulse amplitude is lower than those of the lead nitrate alone. In this case, the peak height mode of measurement would give a lower result (relative to the lead standard) and a decrease in the lead sensitivity. However, since the areas under both the absorption pulses are about the same, the integrated absorbance mode of measurement would give more correct results than the peak height absorbance mode. Figure 80 shows oscillographic traces for the above systems using the capacitive discharge technique, a heating rate of 40 K ms\(^{-1}\), and isothermal atomization at a final (isothermal) temperature of 2200 K (same as that of Figure 79).

It is seen from Figure 80 that the two absorption pulses are identical in both amplitudes and areas; and the matrix effects have been completely eliminated. It can also be seen from Figure 80 that the appearance time for lead and, hence, the appearance temperature for lead are considerably higher (by ca. 400 K) than those in Figure 79. The considerably high appearance temperature for Pb in Figure 80 is crucial for eliminating chloride matrix interferences, as will
Figure 79. Oscillographic traces for 5.0 x 10^{-13} kg of Pb atomized at
heating rate of 1.3 K ms^{-1} and temperature of 2200 K. Left
trace is for lead in 0.5% NaCl solution and right trace is
for lead in aqueous solution. Vertical scale: 0.1 absorbance/scale
division. Horizontal scale: 500 ms/scale division.

Figure 80. Oscillographic traces for 2.5 x 10^{-13} kg of Pb atomized at
heating rate of 40 K ms^{-1} and temperature of 2200 K. There
is a complete overlap between lead signals both in aqueous
solution and 0.5% NaCl solution. Vertical scale: 0.1 absorbance/
scale division. Horizontal scale: 100 ms/scale division.
be seen from later discussion. In Figure 80, both the peak height absorbance mode and the integrated absorbance mode of measurement would give correct results. Since the same anisotropic pyrolytic graphite tube was used in both Figures 79 and 80, equilibration of the surface temperature throughout the graphite tube was very fast in both cases. However, in Figure 79, atomization of lead occurred under non-isothermal conditions at a temperature which was lower than that in Figure 80 and at a time when the temperature of the atomizer was increasing at a very rapid rate with consequent rapid expansion of the inert gas which resulted in partial expulsion of the lead chlorides vapour — also the extent of dissociation of lead chlorides to lead was less at the lower temperature. The conclusion is that the elimination of the matrix effect in Figure 80 was mostly due to atomization at a constant temperature and a much faster rate of heating with the capacitive discharge technique.

It has been reported in the literature (117, 149, 150) that the chloride interference is a vapour phase type of interference, caused by inadequate heat delivery to the analyte element as it moves out of the atomizer surface. This kind of interference includes either a recombination of analyte atoms with interferent species, or a lack of dissociation of volatile analyte-containing compounds before atomization temperature is achieved. This kind of interference is generally a suppression, since it involves a depletion of the observable analyte atomic population. Also, the amount of chloride interference is dependent upon the cation with which the chloride is associated; those metal chlorides which vaporize and dissociate to provide chlorine at the temperature at which the analyte element is normally atomized show the greatest interference. Czobik and Matousek (117) using time-resolved studies have shown that the degree of lead signal suppression depends upon
the availability of atomic chlorine for recombination in the vapour phase at the time of lead atomization. L'vov (15) has theoretically and experimentally illustrated the effects of chlorine as a vapour phase interferent and its suppression by the addition of excess LiNO₃, thereby binding excess Cl through formation of thermally stable LiCl. Frech and Cedergren (150) also attribute chloride interferences in lead determination to the thermodynamic stability of gaseous PbCl₂ and PbCl species at the low vapour phase temperature at which they are vaporized. From thermodynamic calculations these authors (150) have found that the amount of lead chlorides decreases with increasing temperature in the ashing step. Therefore, in the atomization step, the temperature of the furnace has to be raised from a relatively low temperature to a high preset atomization temperature, thereby scanning part of the temperature range in which lead chlorides are vaporized as mentioned above. The time required to reach the final temperature is important in determining the distribution of lead among various lead compounds. If the temperature is raised slowly, the formation of volatile lead chlorides will be more probable than when rapid heating is employed. The above findings of Frech and Cedergren (150) fully agree with those of the present study, which emphasizes the crucial role of very high heating rates in determining the extent of chloride matrix interferences with lead determination. Cadmium and manganese and their chlorides are similar to lead and lead chlorides in their volatilities, and a similar situation has been demonstrated for chloride interference with manganese determination (151). The above explanation is valid also
for the chloride interferences with determination of Cd and Mn.

The effect of heating rates on chloride interferences is presented in Figure 81 which shows the recoveries of lead from a MgCl₂ matrix as a function of the heating rate. It is seen from Figure 81 that a severe depression in the signal is caused by the matrix at lower heating rates. The depression in the signal becomes progressively smaller with increasing heating rates till the heating rate of about 16 K ms⁻¹ is reached or exceeded, when the analytical recovery becomes and remains 100%. Figure 82 shows the recoveries of cadmium from an aqueous solution of salt matrices as a function of heating rates at the fixed atomization temperature of 1900 K. This Figure shows that even at the highest heating rate used (63 K ms⁻¹), the recovery curve is still rising (although very slowly), indicating a need for still higher heating rates for greater recoveries since the atomization temperature of 1900 K used is adequate for complete atomization. The importance of the heating rate on the matrix interferences in the conventional graphite furnace atomic absorption spectrometry and the relative freedom from matrix interference which is provided by the new technique is illustrated by Figures 83-94. It is clear from Figures 83-94 that the conventional graphite furnace atomic absorption spectrometry with its much lower heating rates suffers from severe matrix interferences even at relatively low concentrations of the matrix, whereas the new technique with its much higher heating rates is relatively free from chloride matrix interferences, and probably other interferences as shown in Tables X - XIV. The relative
Figure 81. Analytical recoveries of lead from an aqueous solution containing magnesium chloride at the matrix. $\text{Pb} \lambda = 217.0 \text{ nm}$. $\text{Pb} = 1.0 \times 10^{-12} \text{ kg}; \text{MgCl}_2 = 2.5 \times 10^{-5} \text{ kg}$. 
Figure 82. Analytical recoveries of cadmium from an aqueous solution containing sodium chloride + magnesium chloride + calcium chloride as the matrix. Cd λ = 228.8 nm. Cd = 4.0 x 10^{-1} kg. NaCl = 1.0 x 10^{-1} kg; MgCl₂ = 1.2 x 10^{-9} kg; CaCl₂ = 4.0 x 10^{-10} kg.

○ capacitive discharge, temperature = 1900 K; △ HGA 76B, temperature = 1900 K.
Analytical recoveries of lead as a function of the mass of the matrix, sodium chloride. Pb λ = 217.0 nm. Pb = 1.0 \times 10^{-12} \, \text{kg},
\begin{itemize}
  \item Capacitive discharge, temperature = 2300 K and heating rate = 17 \, \text{K ms}^{-1}.
  \item HGA 768, temperature = 2300 K and heating rate = 1.25 \, \text{K ms}^{-1}.
\end{itemize}
Figure 84. Analytical recoveries of lead as a function of the mass of the matrix, magnesium chloride.

Pb λ = 217.0 nm. Pb = 1.0 x 10^{-12} kg.

○ Capacitive discharge, temperature = 2300 K and heating rate = 17 K ms^{-1}.

△ HGA 76B, temperature = 2300 K and heating rate = 1.25 K ms^{-1}. 
Figure 6. Analytical recovery of lead as a function of the mass of the matrix, calcium chloride, Pb/\lambda = 2.7 \times 10^{-12} \text{ kg}, \text{ capacitive discharge, temperature } = 2300 \text{ K} \text{ and heating rate } = 17 \text{ K ms}^{-1}.

HGA 76B, temperature = 2300 K and heating rate = 1.25 K ms^{-1}. 
Figure 86. Analytical recoveries of lead as a function of the mass of matrix: sodium chloride + magnesium chloride + calcium chloride. Pb \cdot \lambda = 217.0 \text{ nm}. Pb = 5.0 \times 10^{-13} \text{ kg}.

- Capacitive discharge, temperature = 2550 K and heating rate = 40 K ms\(^{-1}\).
- HGA 76B, temperature = 2550 K and heating rate = 1.25 K ms\(^{-1}\).
Figure 87. Analytical recoveries of cadmium as a function of the mass of the matrix, sodium chloride. Cd λ = 228.8 nm. Cdₐ = 1.0 x 10⁻¹³ kg.

- Capacitive discharge, temperature = 2000 K and heating rate = 17 K ms⁻¹
- HGA 76B, temperature = 2000 K and heating rate = 1.25 K ms⁻¹.
Figure 88. Analytical recoveries of cadmium as a function of the mass of the matrix, magnesium chloride. Cd λ = 228.8 nm. Cd = 1.0 x 10^{-13} kg.
- ○ capacitive discharge, temperature = 2000 K and heating rate = 17 K ms$^{-1}$
- △ HGA 76B, temperature = 2000 K and heating rate = 1.25 K ms$^{-1}$.
Figure 89. Analytical recoveries of cadmium as a function of the mass of the matrix, calcium chloride. Cd λ = 228.8 nm. Cd = $1.0 \times 10^{-13}$ kg.

- Capacitive discharge, temperature = 2000 K and heating rate = 17 K ms$^{-1}$
- HGA 76B, temperature = 2000 K and heating rate = 1.25 K ms$^{-1}$. 

RECOVERY, %

MASS OF CaCl$_2$ x $10^8$/kg
Figure 90. Analytical recoveries of cadmium as a function of the mass of the matrix: sodium chloride + magnesium chloride + calcium chloride. Cd λ = 228.8 nm. Cd = 1.0 x 10^{-14} kg.

○ capacitive discharge, temperature = 2000 K and heating rate = 40 K ms^{-1}
△ HGA 76B, temperature = 2000 K and heating rate = 1.25 K ms^{-1}.
Figure 91. Analytical recoveries of manganese as a function of the mass of the matrix, sodium chloride.

$Mn \lambda 279.5 \text{ nm, } Mn = 1.0 \times 10^{-12} \text{ kg.}$

- Capacitive discharge, temperature = 2750 K and heating rate = 32 K ms$^{-1}$
- HGA 768, temperature = 2750 K and heating rate = 1.25 K ms$^{-1}$.
Figure 92. Analytical recoveries of manganese as a function of the mass of the matrix, magnesium chloride.

Mn $\lambda = 279.5$ nm. Mn $= 1.0 \times 10^{-12}$ kg.

○ capacitive discharge, temperature = 2750 K and heating rate = 32 K ms$^{-1}$

△ HGA 76B, temperature = 2750 K and heating rate = 1.25 K ms$^{-1}$. 
Figure 93. Analytical recoveries of manganese as a function of the mass of the matrix, calcium chloride.

\[ M_n \lambda = 279.5 \text{ nm.} \quad M_n = 1.0 \times 10^{-12} \text{ kg.} \]

- ○ capacitive discharge, temperature = 2750 K and heating rate = 32 K ms\(^{-1}\)
- △ HGA 76B, temperature = 2750 K and heating rate = 1.25 K ms\(^{-1}\).
Figure 94. Analytical recoveries of manganese as a function of the mass of the matrix: sodium chloride + magnesium chloride + calcium chloride. Mn λ = 279.5 nm. Mn ~ 2.0 x 10^{-13} kg.

○ Capacitive discharge, temperature = 2820 K and heating rate = 40 K ms^{-1}
△ HGA 76B, temperature = 2820 K and heating rate = 1.25 K ms^{-1}. 

MASS OF MATRIX x 10^8/kg
freedom from matrix interferences provided by this new technique is primarily due to its high rate of heating and the higher temperature of both the analyte-containing compounds and the vapour phase at the moment of their vaporization from the graphite surface. Both of the above-mentioned higher temperatures are due to the much faster achievement of a constant temperature of the graphite surface, and also to the smaller difference between the vapour phase temperature (lower) and the graphite surface temperature (higher). The smaller difference is due to the smaller internal diameter (3 mm) of the graphite tube used in the new technique (compared to 6 mm in the conventional graphite furnace atomic absorption technique), and faster attainment of a constant temperature of the graphite surface because of high anisotropy of the graphite used in the construction of the graphite tube for the new technique. Another, but secondary, cause for the relative freedom from the matrix interferences is isothermal condition during the atomization of the analyte element.

Figures 86, 90 and 94 show that there is a slight decrease in the analyte signals given by the new technique at high concentrations of the matrix. The matrix (NaCl + MgCl₂ + CaCl₂) used in Figures 86, 90 and 94 are major components of seawater but the highest concentrations of the above components used represent 1.2 - 5 fold dilution of their concentrations in seawater. Even the heating rate of 63 K ms⁻¹ used in Figure 82 was unable to yield 100% recoveries of the analytes when the above three components of the matrix were present together in high enough concentrations. It is possible that a combination of higher heating rates and optimum atomization
temperatures together with an optimum atomizer configuration (which will allow higher heating rates and higher temperatures to be used without arcing or delamination of the graphite) may give higher recoveries. Optimum atomizer configuration will include the shape, the tube wall thickness, and the internal diameter of the graphite tube, which determine the speed with which the temperature is equilibrated throughout the graphite tube and the vapour phase. It may be stated that direct determination of trace elements in seawater presents the ultimate challenge in handling one of the most difficult matrices (inorganic salts) present in an overwhelming excess compared to most other matrices (in the usual solution-sampling technique) encountered in real samples. The reason for selecting a matrix similar to saltwater for testing this new technique in its infancy was to determine its ability to handle one of the most difficult matrices; but, as turned out, the effort met with rather limited success at the present stage of development of this technique.

This work supports the vapour-phase mechanism as the primary mechanism for chloride interferences in the determination of Pb, Cd and Mn in chloride matrices. This mechanism is illustrated by lead chlorides as follows (150).

\[
PbCl_2(s) \xrightarrow{1220 \, K} PbCl_2(g) \rightarrow PbCl(g) + \frac{1}{2} Cl_2(g)
\]
CONCLUSIONS

The following conclusions may be drawn from the above studies.

1. This technique is relatively free from matrix interferences and gives accurate and precise results -- its sensitivity is in general independent of the matrix.

2. It dispenses with calibration curves and greatly simplifies the analytical procedure, thus reducing considerably the risk of contamination and/or loss involved in the chemical treatment of samples and standards.

3. It allows solid-sampling with its much greater relative sensitivity, and much less risk of contamination and/or loss. Also, since the solution-sampling is avoided, there can be no problem of soaking of the solution into the graphite tube and, hence, no effect of such soaking on the peak absorbance value.

4. Because of the greatly simplified and shortened analytical procedure of this technique, the cost and time per analysis are much less than those of the conventional graphite furnace atomic absorption spectrometry. Adoption of this technique for large-scale routine analysis would result in great savings in expenses and time.

5. The significance of this work is perhaps that it has opened the way toward the absolute method of analysis by developing a new technique the sensitivity of which is in general independent of the matrix.
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