Peak profile and appearance times using totally pyrolytic cuvettes in graphite furnace atomic absorption spectrometry

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Peakprofil und Erscheinungszeit bei Verwendung vollständig pyrolytischer Küvetten in der Graphitofen-AAS

Zusammenfassung. Peakprofile und Erscheinungszeiten verschiedener flüchtiger (Cd, Pb), mittelflüchtiger (Al, Cr, Mn) und nichtflüchtiger Elemente (Mo, Pt, Ti, V) wurden mit drei verschiedenen Graphitrohrtypen untersucht (Elektrographit, pyrolytisch überzogener Elektrographit und vollständig pyrolytischer Graphit). Der zuletzt genannte Rohrtyp zeigte im Vergleich zu den beiden anderen eine höhere Aufheizgeschwindigkeit und demnach eine bessere Empfindlichkeit für mittel- und nichtflüchtige Elemente. Durch die höhere Aufheizgeschwindigkeit ergab sich eine wesentlich reduzierte Erscheinungszeit, wodurch es möglich war, eine kürzere Atomisierungszeit zu benutzen und dadurch eine höhere Lebensdauer der Rohre zu erreichen.

Summary. Peak profiles and appearance times of various elements representing volatile (Cd, Pb), medium-volatile (Al, Cr, Mn), and refractory (Mo, Pt, Ti, V) elements are presented using 3 different types of graphite tube in graphite furnace atomic absorption spectrometry. The 3 tubes compared were made from electrographite, pyrolytically coated electrographite, and tubes made totally from pyrolytic graphite (TPCs). The TPCs exhibited an increased heating rate compared to the other tubes and consequently an improved sensitivity for the medium-volatile and refractory elements. The faster heating rate of the TPCs substantially reduced the appearance time for these elements and hence it was possible to use shorter atomisation times with a corresponding further increase in tube lifetime.

Introduction

The technique of graphite furnace atomic absorption spectrometry (GFAAS) is now a firmly established analytical technique in the majority of analytical laboratories with an interest in trace element (ng ml^{-1}) analyses. The inherent advantage of this technique is the selectivity of the atomic absorption (AA) measurement and the high sensitivity obtained by the atomisation of analyte elements in the

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graphite furnace (GF). Since the initial introduction of commercially available graphite furnace systems in 1969, the technique has undergone radical developments. In general these fall into two categories. These are (1) methods to increase the sensitivity of the GFAAS technique and (2) methods to reduce chemical/vapour phase interferences.

The first major development was the introduction of a practical method of achieving high heating rates of the graphite tube at low final set temperatures [1]. This is more generally known as 'temperature control' or 'maximum power heating'. The major advantage achieved by this development was a higher sensitivity for medium-volatile and refractory elements. The other major development which increased the sensitivity for medium-volatile and refractory elements was the introduction of pyrolytically coated electrographite tubes, first suggested by L'vov [2]. The pyrolytic-graphite coating reduces the carbide formation problem associated with refractory elements such as Ti, V, Mo etc., and also increases the lifetime of the graphite tube.

The concept of matrix modification procedures was first suggested in 1973 by Ediger [3]. These procedures help reduce interferences in the graphite furnace. The technique is used to alter the chemical environment/nature of either the sample matrix, or the analyte element.

Thus, nickel can be employed to stabilise selenium thus enabling a higher ashing temperature to be used, whereas nitric acid or ammonium nitrate can be used to eliminate chloride from the sample matrix during the ashing phase of the graphite furnace cycle [4]. Further developments in interference control include platform atomisation [5], probe atomisation [6], capacitive discharge heating [7] and atomisation of analyte elements into a constant temperature environment [8, 9].

Recently, there has been a resurgence of interest in the actual material used for construction of the furnace tube.

Tungsten has been used reasonably successfully by Sychra et al. [10]. Tubes made from glassy carbon have been investigated by De Galan et al. [11, 12]. Tubes made totally from pyrolytic graphite (TPCs) have been described by Lersmacher and Knippenberg [13] and evaluated by Dymott et al. [14].

This paper presents the most recent data on the analytical performance of graphite tubes made totally from pyrolytic graphite. In particular, peak profiles and appearances times for various elements are compared using conventional electrographite tubes, pyrolytically coated electrographite tubes and TPCs.

Experimental

Apparatus

A Philips Analytical PU9000 spectrometer was used with the PU9095 Graphite Furnace System and the PU9007 Data Station. Time-resolved GFAAS signals were stored on floppy disc for subsequent processing. Argon was used as the purge gas in all cases. The analytical wavelengths chosen for the tests were typically those that produced the highest sensitivity, except for lead when the 283.3 nm atomic line was used.

A Nicolet IIIA digital storage oscilloscope was used to monitor the voltage applied to the graphite tube and also the output of the silicon photo-diode which is related to the temperature of the graphite tube. These signals were used to compare the heating rates of the three different types of graphite tube investigated.

Reagents

All acids were of Aristar grade (BDH Chemicals). Doubly de-ionised water was used throughout. Trace element stock solutions were supplied by BDH Chemicals as 1,000 mg l^{-1} solutions.

Procedure

Graphite furnace AAS signals were recorded from a given weight of analyte for each of the three types of graphite tube tested (electrographite, pyrolytically coated electrographite and TPC). To obtain an accurate comparison between the three tubes, one solution was prepared and was used to generate GFAAS signals in each tube. Therefore, an electrographite tube was inserted into the graphite furnace and cleaned by preheating 3 times at 3,000°C for 5 s. Peaks were then obtained for the given weight of analyte. The electrographite tube was then taken out of the furnace and a pyrolytically coated electrographite tube, inserted. This tube was then cleaned and tested for analyte response. Finally, a TPC was inserted, cleaned, and tested for analyte response. This procedure was repeated for each analyte tested. The volume added to the graphite furnace was typically 10 µl.

All peaks were processed by the PU9007 data station and stored on floppy disc. The transient peaks from each tube type were then rescaled to give the same absorbance/time axes. The three signals were then superimposed upon the same absorbance/time axes and printed by the PU9000 printer.

To obtain accurate temperature risetimes for each graphite tube a novel, previously unpublished, method was devised. The procedure was based on two facts.

(1) The actual power supplied to the graphite tube for heating purposes is derived directly from the mains. Therefore, the waveform is a.c. at a frequency of 50 Hz (or 60 Hz). The power is controlled by thyristors and then applied to the primary input of the power transformer. The secondary coil of the transformer then supplies the low voltage wave-form with a maximum voltage of 10.5 V, to the graphite tube.

(2) The temperature control system of the PU9095 uses a silicon photo-diode to continuously monitor the temperature of the graphite tube. In the temperature control mode of operation the maximum voltage is applied to the graphite
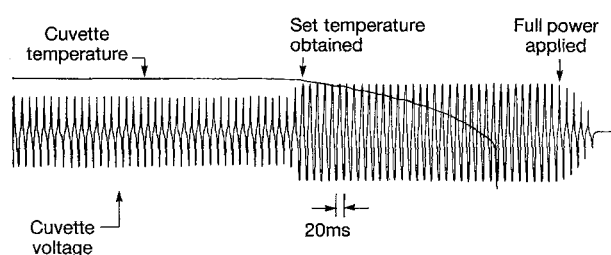

Fig. 1. Typical output from the photo-diode in the graphite furnace and the a. c. waveform of the applied voltage
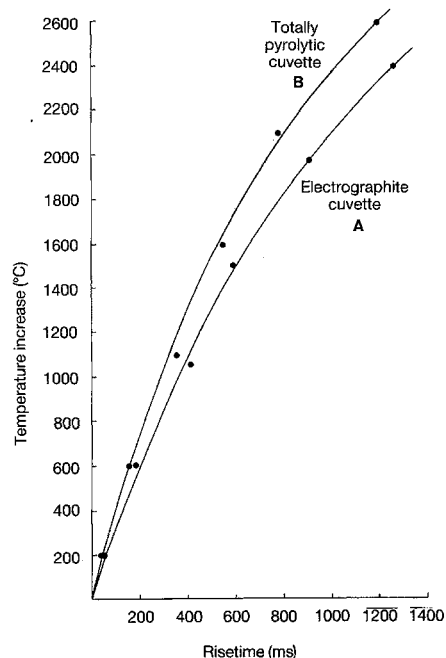

Fig. 2. Temperature risetimes for an electrographite tube (A) and TPC (B)

tube until the pre-set temperature, as measured by the photo-diode, has been obtained. At this point the voltage is reduced to such a level as to maintain the pre-set temperature as measured by the silicon photo-diode.

It is possible, therefore, to monitor simultaneously the applied voltage to the graphite tube (a.c. waveform) and the output from the silicon photo-diode (which is related to temperature). These two signals can then be fed directly into a two-channel digital oscilloscope (see Experimental section). A typical trace is shown in Fig. 1. The temperature risetime can simply be measured by counting the number of individual a. c. wave-forms, which occur every 20 ms, from the time at which the maximum power is applied, to the time at which the maximum temperature has been obtained. For other commercially available graphite furnace systems without this form of temperature control it would be necessary to use an optical pyrometer to measure the temperature increase.

Results and discussion

Temperature risetimes

Figure 2 shows a plot of temperature increase (°C) versus the time taken (ms) to reach the pre-set temperature. The

actual starting temperature in each case was 400°C. Therefore, the time taken for a temperature increase of 2,600°C is actually the time for the graphite tube to heat from 400°C to 3,000°C.

Comparison of curves A and B in Fig. 2 shows that the TPC has a 15−20% faster heating rate, compared to that of the electrographite tube, throughout the temperature range studied. The main reason for this is that pyrolytic graphite has a much higher strength to weight ratio compared to electrographite, permitting thinner wall thicknesses to be used with TPCs. A typical electrographite tube has a wall-thickness of 0.75 mm and a weight of approximately 1.1 g whereas a typical TPC has a wall-thickness of 0.5 mm with a weight of only 0.6 g. The reduced thermal mass of the TPC is responsible for the faster heating rate compared to electrographite tubes or pyrolytically coated electrographite tubes.

It is of interest to note also that the risetimes in °C s^{-1} (calculated from curve B) vary from 2,181°C s^{-1} (at a temperature increase of 2,600°C) to 4,167°C s^{-1} (at a temperature increase of 200°C). Thus, the temperature risetime in °C s^{-1} is completely variable, depending on the actual increase in temperature upon which it was calculated. The most probable explanation for this is that at high temperatures the main form of heat-loss is due to radiative losses from the graphite tube surface. At low temperatures this is not a problem. Therefore, due to the radiative losses at high temperatures there is an additional time required to achieve the pre-set temperature, and consequently a lower average temperature risetime is obtained. This data confirms the fact that temperature risetime in °C s^{-1} is not a linear function.

The problem still remains, however, as to what heating rate to quote for TPCs. To quote a heating rate of 4,167°C s^{-1} is, to say the least, ambiguous. However, over a 200°C increase in temperature (from 400°C to 600°C) this is indeed the case. For future reference, therefore, it is suggested that when a temperature risetime or heating rate is quoted in the scientific literature, the method of measurement and the temperature increase upon which the measurement was made should also be quoted. Further, it may benefit the scientific community to define a set of criteria/conditions by which temperature risetimes or heating rates of the GF can be universally compared. The procedure described in this paper may provide some advantages over alternative methods of measurement, at least for comparative purposes.

Peak profiles and appearance times

The results from this study are shown in Fig. 3 and Table 1. The elements studied were chosen to represent volatile (Cd, Pb), medium-volatile (Cr, Mn), and refractory (Mo, Pt, Ti, V) elements.

Refractory elements (Mo, Pt, Ti, V). For these elements it is obvious why the electrographite tube is not recommended. Substantial increases in sensitivity are observed, however, when a pyrolytically coated tube is used. From the appearance time data (Table 1) it is evident that there is not really a substantial difference between the electrographite tube and the pyrolytically coated tube. It may be concluded, therefore, that the heating rates are similar, the difference in sensitivity being attributed to the inert nature of the pyrolytic coating. The benefits obtained by the use of TPCs are clearly

Table 1. Appearance times for various elements using electro-graphite, pyrolytically coated electrographite and TPCs

Element	Appearance time/s.		
	Uncoated	Pyro. coated	TPC
Volatile			
Cd	0.07	0.09	0.05
Pb	0.17	0.17	0.11
Medium-Volatile			
Mn	0.42	0.42	0.27
Cr	0.56	0.52	0.33
Al	0.73	0.75	0.35
Refractory			
V	0.86	0.72	0.48
Pt	0.84	0.86	0.54
Ti	1.04	0.89	0.57
Mo	0.88	0.88	0.58

illustrated. Firstly, the appearance times for these elements are shortened by about a factor of 2. Secondly, the sensitivity is increased between 1.5 to 2.0 times (Fig. 3 and Table 1). Both of these observations can be attributed to the faster heating rates of TPCs over both electrographite and pyrolytically coated tubes. In a previous publication Dymott et al. [14] showed the increase in tube life-time of TPCs over electrographite and pyrolytically coated tubes. In that study atomisation temperatures and times were kept constant between each of the tube types. As a general principle, however, it should be possible to reduce the atomisation time when using TPCs compared to pyrolytically coated tubes. At the high temperatures required for the refractory elements the reduction in atomisation time afforded by TPCs may further increase the analytical lifetimes of these cuvettes.

Medium-volatile elements (Cr, Mn). As the volatility of the elements increases and the reactivity of the elements with graphite decreases, the response from an electrographite tube becomes more favourable. It is still apparent, however, that pyrolytically coated tubes perform much better than electrographite tubes with respect to both sensitivity and tube lifetime. The appearance times for electrographite and pyrolytically coated tubes are still similar, suggesting again, similar heating rates. Appearance times and sensitivity are again improved when TPCs are used. It would be possible to atomise for 1 second for Mn and Cr using the TPC, whereas, with the pyrolytically coated tube the times would be 1.5 and 2.0 s, respectively. This saving in atomisation time would again offer further improved tube lifetime.

Volatile elements (Cd, Pb). As shown by Chakrabarti et al. [15] the optimum heating rate for Cd and Pb is about 2,000°C s^{-1}. Any increase in heating rate above this value does not significantly increase the sensitivity for these elements. This is also confirmed by the results shown in Fig. 3. In this case there are no real differences between electrographite, pyrolytically coated electrographite and TPC tubes. For Pb there is a slightly earlier appearance time which can be attributed to the faster heating rate of TPCs.
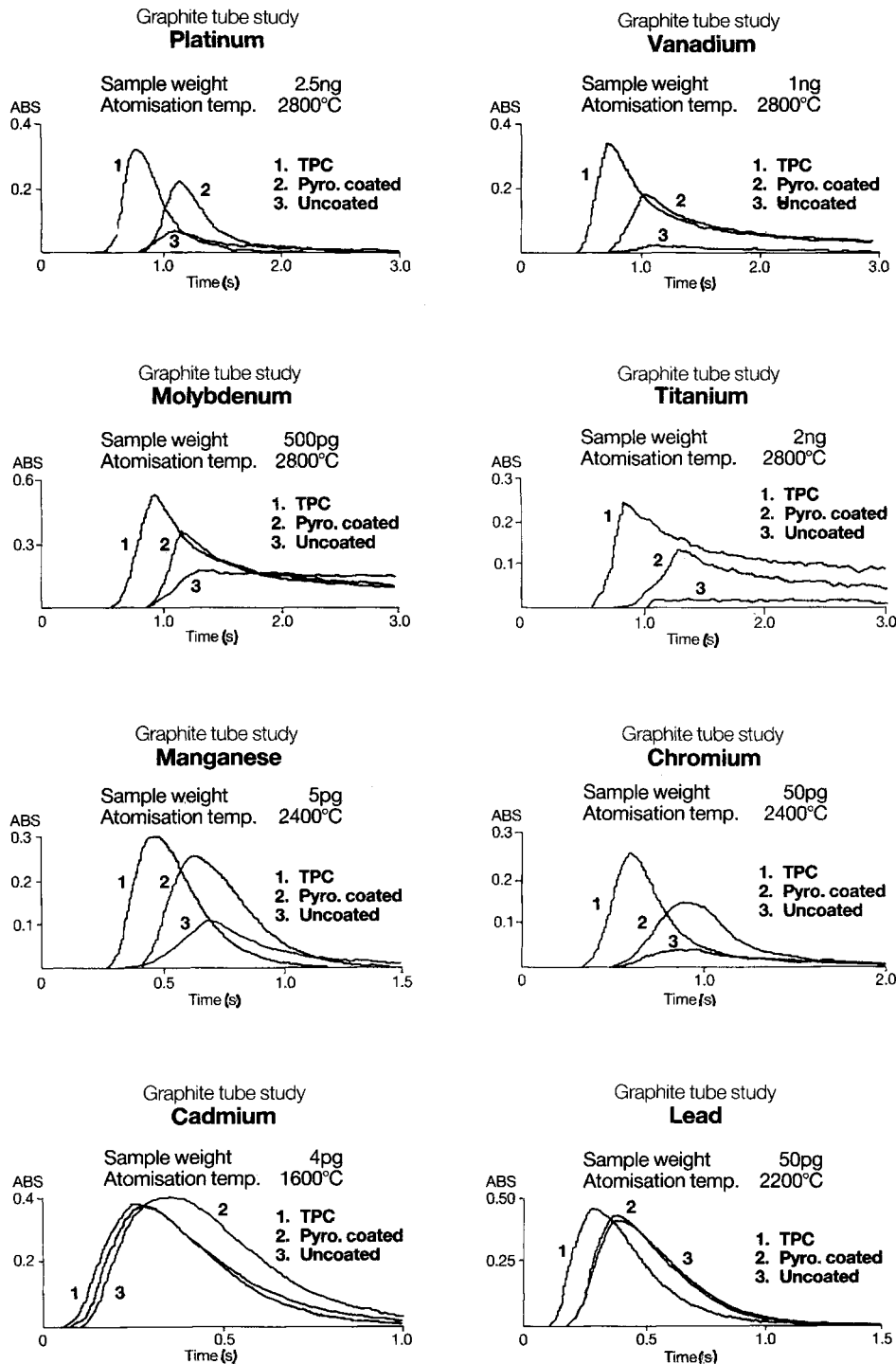
Graphite tube study
Platinum

Sample weight   2.5ng
Atomisation temp. 2800°C

1. TPC
2. Pyro. coated
3. Uncoated

Graphite tube study
Vanadium

Sample weight   1ng
Atomisation temp. 2800°C

1. TPC
2. Pyro. coated
3. Uncoated

Graphite tube study
Molybdenum

Sample weight   500pg
Atomisation temp. 2800°C

1. TPC
2. Pyro. coated
3. Uncoated

Graphite tube study
Titanium

Sample weight   2ng
Atomisation temp. 2800°C

1. TPC
2. Pyro. coated
3. Uncoated

Graphite tube study
Manganese

Sample weight   5pg
Atomisation temp. 2400°C

1. TPC
2. Pyro. coated
3. Uncoated

Graphite tube study
Chromium

Sample weight   50pg
Atomisation temp. 2400°C

1. TPC
2. Pyro. coated
3. Uncoated

Graphite tube study
Cadmium

Sample weight   4pg
Atomisation temp. 1600°C

1. TPC
2. Pyro. coated
3. Uncoated

Graphite tube study
Lead

Sample weight   50pg
Atomisation temp. 2200°C

1. TPC
2. Pyro. coated
3. Uncoated

Fig. 3
Peak profiles for various elements
using *1* TPCs, *2* pyrolytically
coated electrographite tubes and
3 electrographite tubes

However, the sensitivity remains constant between the 3 types of tube. Although there is not an actual increase in sensitivity with TPCs for the volatile elements, neither is there a decrease. It was considered possible [16] that the inert nature of the TPC surface may reduce the atomisation efficiency for certain volatile elements which are thought to be atomised via a carbon-reduction mechanism. This does not seem to be the case.

Sensitivities

The analytical sensitivity data for a number of elements are shown in Table 2. Again, the elements tested were chosen to represent volatile (Ag, Cd, Pb, Zn), medium-volatile (Al, Cr, Co, Cu, Fe, Mn, Ni) and refractory (Mo, Pt, Ti and V) elements. The ratios between electrographite tubes to TPC and pyrolytically coated electrographite tubes to TPC are also given. Of the 4 refractory elements tested the mean sensitivity increase of TPCs over pyrolytically coated tubes is 1.63 times. The mean for the medium-volatile elements is 1.38. For the volatile elements there are no significant sensitivity increases. The sensitivity increases, especially for the refractory elements, can be attributed to the faster heating rate of TPC tubes compared to pyrolytically coated electrographite tubes.

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Table 2
Comparison of sensitivities obtained using electrographite, pyrolytically coated electrographite and TPCs

Element	Characteristic mass/pg[b]			Ratio	
	Electro-graphite	Pyro. coated electro-graphite	TPC	Electro-graphite/ TPC	Pyro. coated electro-graphite/ TPC
Volatile					
Ag[a]	—	—	—	1.36	0.94
Cd	0.48	0.43	0.47	1.02	0.92
Pb	5.3	5.3	5.1	1.04	1.04
Zn[a]	—	—	—	1.44	0.97
Medium-Volatile					
Al	5.0	3.0	1.6	3.13	1.88
Cr	4.7	1.5	0.85	5.53	1.76
Co[a]	—	—	—	4.58	1.19
Cu[a]	—	—	—	4.33	1.28
Fe[a]	—	—	—	3.37	1.23
Mn	2.0	0.86	0.71	2.82	1.21
Ni[a]	—	—	—	7.37	1.13
Refractory					
Mo	12	6	4	3.00	1.50
Pt	175	48	35	5.00	1.37
Ti	550	63	35	15.7	1.80
V	88	24	13	6.77	1.85

[a] Results from Philips Research Laboratories, Eindhoven, Holland
[b] Mass of analyte equivalent to 0.0044 A

Future developments with total pyrolytic-graphite cuvettes

There are two relatively interesting ideas which may warrant further development in the future. The two ideas are based on the anisotropic nature of pyrolytic graphite. In the direction parallel to the tube surface (the 'a − b' direction), pyrolytic graphite is one of the best conductors among elementary materials, whereas, in the direction vertical to the surface (the 'c' direction), it is 300 times lower.

It is possible, therefore, to mount cuvettes in such a way as to form the electrical contact to the inner surface. In such a configuration the electrical current would flow preferentially along the inner layers of the cuvette and hence the inner surface would heat up more rapidly, and to higher temperature, than the outer layers. In addition, because of the low thermal conductivity in the radial direction, the cuvette layers would act as insulators, enhancing the temperature drop across the cuvette wall.

There are two main advantages to this configuration. Firstly, the sample is generally placed on the inner wall of the cuvette and hence, it would be heated in the shortest possible time, leading to an improvement in sensitivity compared to conventional heating. Secondly, since the outer cuvette surface would be at a significantly lower temperature than the inner surface, and heat losses at elevated temperatures are predominately governed by radiative losses (as previously discussed), the actual power required to maintain a given inner cuvette temperature would be significantly reduced.

Such a cuvette configuration has been built experimentally in the authors laboratory and temperature differences between corresponding points on the inner and outer walls, of the order of 400°C, have been measured at sample site temperatures up to 3,000°C.

The second idea, again exploits the fact that pyrolytic graphite, depending on its growth/manufacture (see reference [14]), can be chosen in such a way as to have varying resistance with respect to electrical conductivity. The current method of mounting a TPC into the Philips Analytical PU9095 graphite furnace employs the use of electrographite 'C'-rings. The choice of this configuration was based on the problems of delamination experienced by Littlejohn et al. [17] and Chakrabarti et al. [7] when the TPC tubes were mounted in a graphite furnace system which employed electrical contact to the cuvette via end-loading of the cuvette, in the crystal 'a − b' direction.

If, however, the 'C'-rings are made from pyrolytic graphite, with the 'C'-axis in a radial direction, they will present a relatively high resistance to the flow of electrical current. Hence, heating will occur predominately from the ends of the cuvette inward, unlike the normal performance of a graphite cuvette which heats from the central portion around the sample injection hole outwards.

The basic advantage of such a configuration would be that when the sample eventually atomises from the centre of the cuvette, it will atomise into a more constant temperature environment. Hence, isothermal atomisation of analyte with the corresponding reduction in vapour phase interferences, would be more fully realised.

Such cuvettes have undergone preliminary investigation in the authors laboratory and the predicted heating properties have been confirmed. Chemical interference effects have, however, yet to be investigated in detail.

Conclusions

The use of graphite tubes made totally from pyrolytic graphite in GFAAS has been shown to provide certain advantages

over conventional electrographite or pyrolytically coated electrographite tubes. The advantages discussed in this paper include increased heating rate of TPC cuvettes with a corresponding sensitivity increase for the medium-volatile and refractory elements. Also, the increased heating rate reduces the appearance time for these elements and consequently it is possible to reduce the atomisation time, further increasing tube lifetime.

The full potential of pyrolytic graphite as a material for graphite furnace cuvettes has only partially been realised and future developments may improve, yet further, on the usefulness of this material for GFAAS.

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