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Laser-excited Atomic Fluorescence Spectrometry as a Practical Analytical Method

Part I. Design of a Graphite Tube Atomiser for the Determination of Trace Amounts of Lead

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Tube atomiser designs for the laser-excited atomic fluorescence spectrometric (LAFS) technique were investigated. Commercially available cuvettes of the Beckman 1268 type and Perkin-Elmer HGA-500 - EA 3 type that had been modified for use with LAFS were used. The fluorescence was measured within the tube. These tube atomisers were tested and compared with a home-made rod atomiser by measuring the fluorescence of lead. The detection limits, sensitivities and reproducibility obtained by tube atomisation were greatly improved compared with rod atomisation. The influence of some metal nitrates and sodium sulphate on the fluorescence intensity of lead was investigated. With tube atomisation the interferences were reduced.

Keywords: *Laser-excited atomic fluorescence spectrometry; lead determination; graphite tube atomiser; trace analysis*

It has been shown that laser-excited atomic fluorescence spectrometry (LAFS) is potentially a very sensitive and selective analytical technique.[1-4] Detection limits at the femtogram level have been obtained (in most instances by extrapolation) using pulsed dye-laser excitation.

Falk[5] has shown theoretically that the detection limits in LAFS can be 10^8 times better than those obtained with AFS using conventional light sources, such as hollow-cathode or electrodeless discharge lamps. Such low detection limits have not so far been obtained in practice. We can conclude therefore that LAFS is the most sensitive method of optical atomic spectroscopy. However, the sensitivity of the method depends not only on the laser power, but also on the efficiency of atom production. Using flames for atomisation, the result is a very high atom dilution in the dynamic flame plasma, leading to poor detection limits. Hence it is better to employ electrothermal atomisers, which provide higher free atom concentrations in the vapour phase. Some workers have used graphite rod atomisers, because of the convenience of the optical geometry for implementing the fluorescence technique.[1-4,6,7] As shown in a previous paper,[7] we obtained good sensitivities for some metal ions using a carbon rod atomiser and conventional light sources (laboratory-made EDLs).

Such a system does, however, have some disadvantages, principally the strongly negative correlation between plasma temperature and the distance from the top of the carbon rod. This means that after a short time the free atoms combine to form molecules and condensate. This leads to poor excessive vapour-phase interferences and poor analytical performance.[2,6] Recently, Human[4] used a Mini-Massman graphite-tube atomiser for AFS measurements, but the tube was used only as an atom generator, the LAFS being measured outside the tube. In this work we have attempted to combine the established analytical advantages of tube atomisers with the potential sensitivity of the LAFS technique.

Experimental

Apparatus

A schematic diagram of the equipment used is shown in Fig. 1. Because the details are important, a description of some of the component parts will be given.

Nitrogen laser

The primary light source was a pulsed nitrogen laser operating at 337.13 nm (Model No. IGT 300, Central Institute of Scientific Instruments, Academy of Science, Berlin, GDR).

The pulse frequency could be varied between 0.3 and 25 Hz and the pulse duration was 8 ns. Pulse frequency and pulse energy are inversely related and, taking account of the atomisation period, an optimum frequency of 6–7 Hz was chosen. The laser power supply voltage was variable between 14 and 20 kV but, in the interests of laser lifetime, an operating voltage of 15 kV was selected, which gave a pulse energy of 2 mJ and a power of 250 kW.

Dye laser

A tunable dye laser (Model No. FLGR-2, Carl Zeiss, Jena, GDR) of the Hansch type was used to excite the Pb direct-line fluorescence. The laser was equipped with a 2600 line mm^{-1} grating and with appropriate dyes could be tuned over the
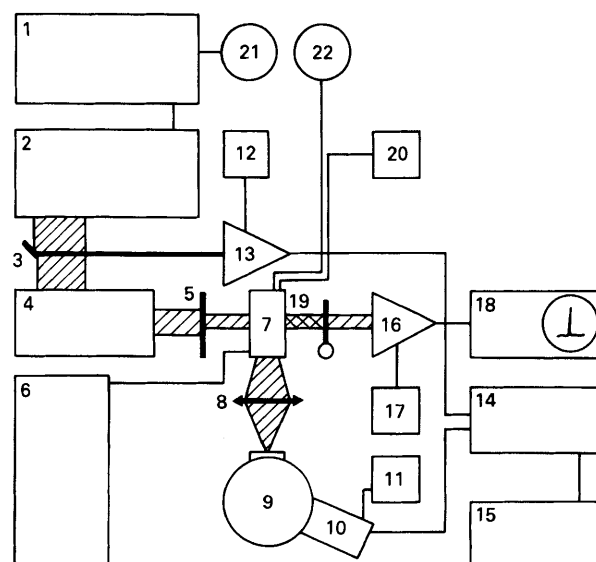

Fig. 1. Schematic diagram of the atomic fluorescence spectrometer with laser excitation. 1, Power supply for pulsed nitrogen laser; 2, pulsed nitrogen laser; 3, mirror for the light triggering the measurement; 4, dye laser with generation of secondary harmonic (SHG); 5, filter for visible part of laser light; 6, power supply for atomiser; 7, atomiser (carbon tube or carbon rod type); 8, condenser lens; 9, monochromator for fluorescent light; 10, photomultiplier (PM) tube; 11, power supply for PM tube; 12, power supply for trigger element; 13, trigger element for boxcar integrator; 14, boxcar integrator; 15, X - Y recorder; 16, pyroelectric joule meter for laser light; 17, power supply for joule meter; 18, oscilloscope for joule meter; 19, mirror for reflection of laser light; 20, thermostat; 21, nitrogen cylinder; and 22, argon cylinder

range 400–900 nm. A coumarine type dye (C462) was used to produce output in the range 525–590 nm with a maximum at 560 nm, yielding 107 μJ with a pulse duration of 6 ns. The line half-width was 40 pm. KDP crystals were used to frequency-double the laser first harmonic, achieving a 5–10% conversion efficiency with a line width of 20 pm and the pulse duration of 4 ns. The power in the second harmonic is sufficient to saturate only a few spectral transitions.

Energy meter

For controlling and measuring the pulse energy of the dye laser, a pyroelectric joule meter was used. The registration of the pulse was carried out with an oscilloscope. The maximum sensitivity of the system was 10 mV μJ^{-1} and 0.1 μJ can be measured with this device.

Detection system

The fluoresced light was focused by a quartz lens ($f = 40$ mm; diameter = 38 mm, aperture = 1 : 1.05) on to the entrance slit of an SPM 1 monochromator (Carl Zeiss) with an aperture of 1 : 6.7. Depending on the prisms used (glass, quartz or sodium chloride) different wavelength regions can be utilised.

For our purpose (direct-line fluorescence of lead at 405 nm), the glass prism has the best resolution (about 5 nm mm^{-1}). The maximum slit width of 3 mm was used, giving a spectral band width of about 15 nm. This type of monochromator was suitable for measuring atomic fluorescence. The slit height was optimum for all atomisation systems at 1 mm (rod, Beckman tube and EA 3 tube).

The intensity of the light was measured with a type M 11 FVC 520 photomultiplier (VEB Werk für Fernsehelektronik, Berlin, GDR). The cathode of the photomultiplier is sensitive between 185 and 1200 nm. High voltages of up to 1.5 kV can be used. The optimum signal to background ratio was obtained at 1.3 kV. To improve the signal to noise ratio, the output pulse from the PMT was filtered and stretched from 80 to 800 ns. The signal was measured with a BCI 280 boxcar integrator (ZWG, AdW der DDR, Berlin, GDR). Triggering of this instrument by part of the nitrogen laser light was effected by a photodetector. The signal delay was corrected. The minimum gate duration of the integrator was 10 ns, but in following a prolonged signal a gate duration of 400 ns was optimal.

Signals were recorded with an X - Y recorder (Model 620.01, Messgerätewerk Schlotheim, GDR). The best sensitivity of the recorder in relation to noise problems was 100 mV cm^{-1}.

Atomiser systems

A laboratory-constructed device described previously[7] was used as the graphite rod atomiser. The design of the atomiser is shown in Fig. 2 and the graphite rods used are shown in Fig. 3. The lower hole guarantees a high electrical resistance and a rapid heating rate of about 400 K s^{-1}. The maximum final temperature is 2800 °C. The top of the rod was pyrolytically coated with graphite. As base material, graphite of TO quality (VEB Elektrokohle, Berlin, GDR) was used.

Two different modified commercial systems were used as graphite tube atomisers.

1. Type 1268 (Beckman Instruments, USA). The design of the modified system and of the tube is shown in Fig. 4. The hole for entry of the exciting laser beam was varied in distance from the central dosage point to establish the best position. The tube length was also varied and a length of 50 mm was found to be best compared with the original length of 68 mm.

2. Modified HGA type (Perkin-Elmer, USA)/EA system (Carl Zeiss) (Fig. 5). In this instance the maximum distance between the centre of the tube and the centre of the entrance hole is 2 mm. In the outer graphite ring a third hole was bored.
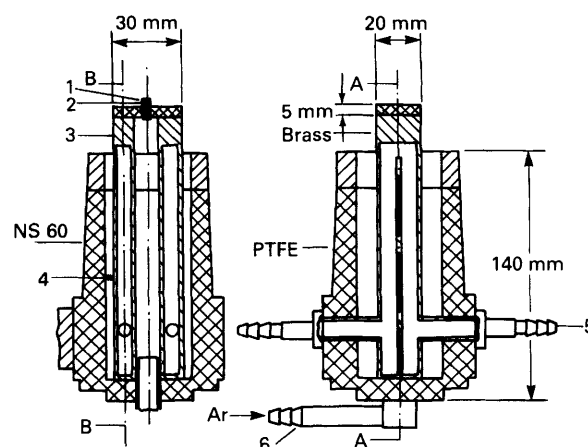

Fig. 2. Carbon rod atomiser. 1, Sample holder; 2, contacts for sample holder (graphite); 3, contacts for power supply (brass) (5, water cooled); 4, spring for holding the graphite rod; and 6, argon inlet
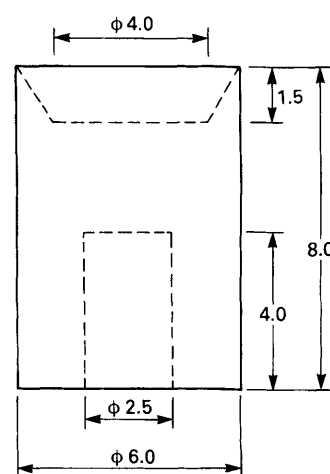

Fig. 3. Schematic diagram of graphite rods used for AFS. All dimensions in millimetres. Upper depression (diameter 4 mm) for the sample solution; lower depression (diameter 2.5 mm) for enhancement of the electrical resistance and faster heating

The graphite tube in the modified Perkin-Elmer atomiser has two holes. However, it has an outer graphite ring to shield the graphite tube from air. This ring normally has two holes, one for sample introduction and the other for temperature measurement. In our modified atomiser we have no temperature control system. For geometric reasons we used one hole (originally for temperature measurement) for sample introduction, the second hole (originally for sample introduction) as the laser inlet and a new third hole as the laser outlet (Fig. 6).

Table 1 gives some parameters of the atomisers. In all instances pyrolytically coated tubes were used. The first results showed that the best type of tube atomiser was the HGA/EA 3 type, which was used in most instances.

Procedure

A 10–20 μl volume of the analyte was placed on top of the rod or into the tube. Using programmed heating, the sample was dried, ashed and atomised, the laser beginning to operate in the ash phase. The system was excited at 283.307 nm and the direct-line atomic fluorescence at 405.782 nm was measured.

Reagents

Lead(II) stock solution, 0.2 mg ml^{-1} *in* 1 M *nitric acid* (*Suprapur*). The solution was diluted with 0.01 M nitric acid.
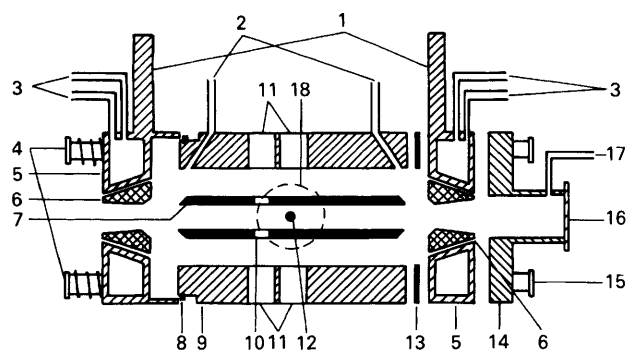
Fig. 4. Modified Beckman tube atomiser (type 1268). 1, Contacts for power supply; 2, inlet holes for outer argon shielding gas stream; 3, inlet and outlet for water cooling; 4, screws and springs for holding tube; 5, tube holder; 6, cone for direct tube holding (copper); 7, graphite tube; 8, gasket; 9, copper tube for shielding; 10, holes for entrance of laser light through the wall; 11, holes for entrance of laser light through 10 and outlet for outer argon shielding stream; 12, hole for sample introduction; 13 and 14, isolators; 15, screws for mechanical stabilisation; 16, quartz windows; and 17, inlet for inner argon gas stream
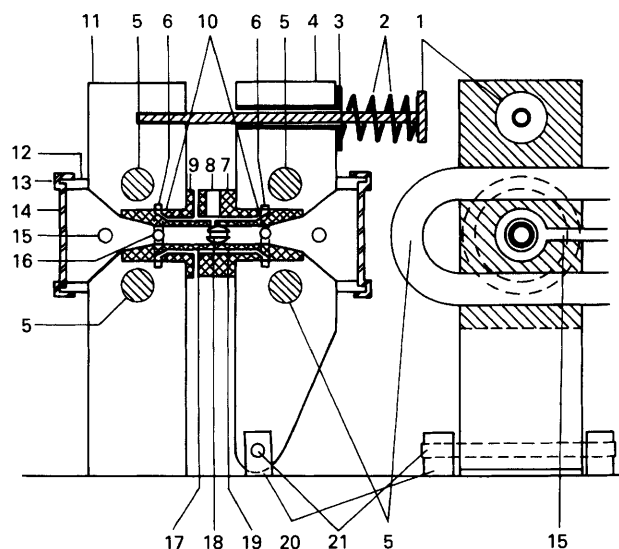

Fig. 5. Modified HGA/EA 3 atomiser. Left, side view; right, front view. 1, Screw and 2, spring for mechanical holding; 3, isolator; 4 and 11, tube holding system (brass); 5, inlets and outlets for water cooling; 6 and 10, inlet holes for outer argon shielding gas stream; 7 and 9, graphite shielding rings; 8, hole for sample introduction; 12 and 13, window holders; 14, quartz windows; 15 and 16, inlet holes for inner argon shielding gas stream; 17, graphite tube (normal dimensions); 18 and 19, asymmetric entrance hole for exciting laser light in the graphite tube and in the graphite ring (7); and 20 and 21, holder and screw for moving 4
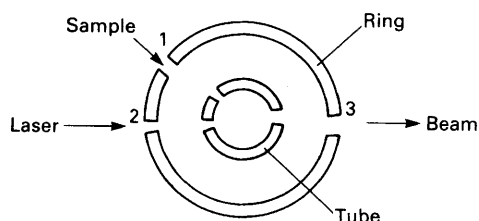

Fig. 6. Principle of the modified atomiser

Interferents. For studying matrix interferences the following salts of analytical-reagent grade were used: $NaNO_3$, KNO_3, $RbNO_3$, $Cd(NO_3)_2$, $AgNO_3$, $Cu(NO_3)_2$, $Mg(NO_3)_2$, $Al(NO_3)_3$ and Na_2SO_4.

Results and Discussion

Optimisation of the Geometry of Excitation and of the Gas System

Depending on the type of atomiser there are different parameters that can influence the fluorescence signal intensity. For the carbon rod atomiser these are (a) height of the excitation zone above the top of the rod, (b) diameter of the beam in relation to the top surface of the rod, (c) gas stream velocity and (d) heating rate.

A minimum distance from the surface of the top of the rod gave the best results because at this point the atom concentration is highest. At greater distances the plasma temperature is lower and thus the atom concentration is smaller owing to condensation and dilution processes.

The geometry of the laser beam is about 0.5×3 mm (height × width). Depending on the distance from the dye laser, the laser beam diverges. The best results were obtained with a width of 6 mm (identical with the rod diameter) because with such a small distance from the top the atom-containing plasma is cylindrical. The argon flow-rate was varied between 40 and 200 l h⁻¹ and no influence was observed. We used a flow-rate of 80 l h⁻¹ as previously.[7] The maximum heating rate gave the best fluorescence signals (peak height). We found no background, because the lead evaporation was very fast, and no stray light, because we used direct-line fluorescence.

For carbon tube atomisers similar and other parameters exist: (a) excitation geometry and fluorescence light measurement; (b) position of the hole in the tube for laser excitation; (c) gas flow-rate; (d) dimensions of the carbon tube; and (e) heating rate of the tube.

With tube atomisers two measurement geometries are possible: excitation perpendicular to the tube axis and measurement along the tube axis, and the opposite conditions. In both instances equal sensitivities were obtained. In spite of this, we used excitation perpendicular to the axis and measured the atomic fluorescence along the tube axis. The reason was that additional holes for laser beam excitation of the appropriate size can be formed and the diameter can be very small. This means that there are only small losses of atoms through the tube holes, because the atomiser tube is more efficient in a closed form. For the energy absorption, a transition with high oscillator strength was used, and strong absorption in all parts of the atom cloud was therefore obtained. Excitation along the tube axis leads to large pre-filter effects, which results in a loss of fluorescence intensity. Excitation perpendicular to the axis does not give pre-filter effects. Because in most instances direct-line fluorescence was used, for practical purposes no post-filter effects along the tube axis were observed.

The position of the access port for the exciting beam can be in the centre or displaced from the centre. With the large tube (Beckman type) a distance of 9 mm from the centre was chosen (hole diameter = 4 mm). For lead the central position gave only 50% of the sensitivity obtained with the other position, because in the central position there are atom losses as a result of convection and diffusion processes.

With small tubes (HGA/EA 3 type) the same tendency was found. However, the distance between the central sampling port and the hole for laser excitation can be varied only up to 2 mm. The dimensions of the hole are height 1.5 mm and width 4 mm. The inner gas stream was directed to the monochromator (the holes for the laser beam also lie in this direction). The gas flow-rate was optimised to 20 l h⁻¹. Up to 5 l h⁻¹ no changes were observed but at higher flow-rates smaller signals were obtained.

With the small atomiser (HGA/EA 3 type) measurements were carried out with and without quartz windows at the end of the tube axis. There are three possibilities, as follows.

(a) Both quartz windows are in place. Using a gas stream from both sides of the tube the influence of the gas flow-rate is

Table 1. Optimum conditions of some atomisers in LAFS

Type of atomiser	Final temperature/ °C	Heating rate/ K s⁻¹	Tube diameter/ mm	Tube length/ mm	Inner tube volume/ mm³	Heated mass of graphite/ mg
Rod atomiser	2800	400	—	—	—	300
1268 type (Beckman)	3000	300	8.6	68	3950	8000
Modified 1268 type (Beckman)	3000	800	8.6	50	2900	6000
HGA/EA 3 type	3000	6000	5.5	28	665	1000

Table 2. Results of the determination of trace amounts of lead by LAFS

Type of atomiser	Reciprocal sensitivity per 100 mV/ fg	Improvement factor	Detection limit (3σ)/ fg	Improvement factor
Carbon rod	10300	—	1450	—
Carbon tube (HGA/EA 3)	118	87	68	21
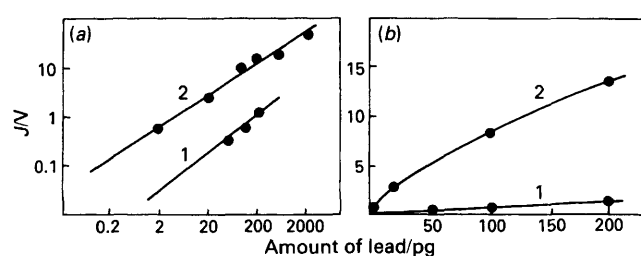
Fig. 7. Calibration graphs for trace determination of lead with (1) carbon rod and (2) carbon tube (HGA/EA 3 type) atomisation. (*a*) Logarithmic transformation; and (*b*) direct signal *versus* concentration dependence

very high (Fig. 5). The lifetime of the atoms in the tube will be shortened by closed windows and a high velocity of the gas streams. However, in the gas-stop regime during atomisation the most sensitive results were obtained.

(b) Only the opposite position (in relation to the monochromator) is closed. The sensitivity obtained with this system was good [about 90% of the sensitivity in (a) under gas-stop conditions]. The gas flow-rate in the direction of the monochromator has no significant influence on the fluorescence intensity up to 5 l h⁻¹. Higher gas flow-rates decrease the peak-height fluorescence signal because of rapid losses of atoms in the fluorescence zone by convection.

(c) Without windows present the sensitivity was poor because atmospheric N_2 and O_2 diffused into the atomiser, causing severe quenching of the fluorescence. The maximum heating rate (see Table 1) is advantageous and the best analytical results are obtained with the HGA/EA 3 type atomiser.

Summarising the investigations, it can be concluded that the following tube atomiser design is the best for the determination of lead: tubes of the HGA/EA 3 type, pyrolytically coated with carbon; two slits of length 4 mm and height 1.5 mm for the exciting laser beam; distance between the centre of the tube and the centre of the slits 2 mm in the direction of the monochromator; both ends of the cuvette closed by quartz windows; gas stop during the atomisation step; and measurement of fluorescence radiation along the tube axis.

Comparison of Sensitivities of Carbon Rod and Carbon Tube Atomisers

The dependences of the atomic fluorescence signal intensities on lead concentration in solutions were measured under comparable excitation conditions (excitation energy 8 μJ) and atomisation parameters. Two types of calibration graph were obtained: a linear dependence of signal intensity on lead concentration [Fig. 7(*b*)] and a logarithmic dependence [Fig.

7(*a*)]. Fig. 7(*b*) shows that a real linear relationship between fluorescence intensity and concentration exists only for small parts of the calibration graph. Therefore, it is better to use the logarithmic function for a wide concentration range. It can be seen from Fig. 7(*b*) that the sensitivity of the determination of lead in the carbon tube atomiser is higher but the curvature of the calibration graph is greater for tubes than for rods. The reason may be pre-filter effects in the more concentrated plasma or recording problems.

For the recording system used, 3σ was equivalent to 100 mV and therefore to facilitate comparison of sensitivities, reciprocal sensitivities relative to 100 mV are given in Table 2.

Measurements were carried out at lead concentrations up to 2 pg per 10 μl with the tube atomiser and up to 50 pg per 10 μl with the rod atomiser. Although the sensitivity for the tube was better than that for for the rod, the absolute noise level was 3.5 times lower for the rod system. The detection limits, calculated from these values are shown in Table 2. The reasons for the lower noise with the rod atomiser are the plasma dilution and the greater possibility of avoiding stray and continuum light.

It can be concluded from these results that the carbon tube atomiser is a better atom reservoir for LAFS than the carbon rod atomiser. The reasons for this conclusion with respect to the carbon tube atomiser are as follows: higher heating rate; more homogeneous temperature in the plasma; higher atomisation efficiency; longer lifetime; and higher concentration of atoms in the plasma (smaller plasma volume).

Comparison of Reproducibilities of Carbon Rod and Carbon Tube Atomisers

To compare the reproducibilities of the two atomisers, 80 measurements on each were carried out, the relative standard deviation (RSD) being determined five times each on sixteen different volumes (lead concentration 200 pg per 10 μl). For the carbon rod the RSDs were 17.2, 14.6, 9.8, 14.6 and 15.6% (mean 15%) and for the HGA/EA 3 carbon tube the RSDs were 3.1, 3.7, 3.0, 8.7 and 12.6% (mean 6%). In contrast to the results at low concentration (see the previous section), the reproducibility at higher concentration is better for the carbon tube, owing to the more homogeneous temperature of the generated plasma and of the longer lifetime of the excited atoms in this plasma in comparison with the open rod system.

Interferences

The influence of some metal nitrates and sodium sulphate on the fluorescence intensity of lead was investigated. It was found that the use of nitrate media resulted in negative

interferences, probably caused by quenching of the fluorescence by NO_x molecules. It was found that thermally stable nitrates, such as sodium and potassium nitrate, cause a stronger signal depression compared with less stable nitrates, such as aluminium and cadmium nitrate. When using graphite rods, interference from nitrates was greater than that from carbonates.

Conclusions

It has been shown that the sensitivity of LAFS measurements of lead is higher using a carbon tube atomiser instead of a carbon rod atomiser, owing to the more homogeneous temperature in tubes and the greater atom concentration.

In electrothermal atomisation atomic absorption spectrometry nitrate media are preferred in order to avoid vapour-phase interferences from metal chlorides. However, it was noted in this study that negative interferences were obtained from the nitrate anion and it is believed that these were caused by quenching of the fluorescence by NO_x molecules. More details on this and other interferences will be given in a subsequent paper.

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