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Determination of Beryllium and Lithium in Coal Ash by Inductively Coupled Plasma Atomic Emission Spectroscopy

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The use of graphite furnace atomic absorption spectroscopy for the direct determination of traces of beryllium in coal ash is shown to be difficult due to matrix interferences.

The determination of beryllium and lithium in coal ash by inductively coupled plasma atomic emission spectroscopy (ICP-AES) is discussed. Samples were prepared in Parr acid digestion bombs using a mixture of nitric and hydrofluoric acids. Results for the concentrations of the above elements in some South African coal ash samples are presented.

KEY WORDS: Beryllium, lithium, inductively coupled plasma atomic emission spectroscopy, coal ash.

INTRODUCTION

Huge tonnages of coal are burnt in South Africa each year for electric power generation, industrial use and for producing liquid fuels. Much concern has been expressed about the release of toxic elements into the environment during these processes. It is therefore imperative to acquire more knowledge of the amounts of these elements in the coal used and in the ashes produced from which elements may be released by natural leaching processes.

The concentrations of many trace elements (e.g. Be, Li, B and Cd) in South African coals and coal ashes are virtually unknown and we have undertaken their determinations in a large number of samples.

Beryllium has been shown to be very toxic to humans even in small quantities. A number of techniques including ICP-AES¹⁻¹⁰ have been used for determining this element in environmental samples. Because of the very low concentrations usually encountered and due to the complex nature of the matrix (e.g. coal and coal ash), direct determination is frequently difficult. Pre-treatment is used both for concentrating the analyte and to separate it from interfering elements. Methods used include extraction by acetylacetone into chloroform or carbon tetrachloride, and ion-exchange separation.^{2,4,5,6} Graphite furnace atomic absorption spectroscopy (GFAAS) has considerable advantages in sensitivity over many techniques and it has been the most extensively used method for trace beryllium determination.¹⁰ Direct determination of Be in coal by a solid sampling technique has been reported by Gladney,¹ and Geladi and Adams¹¹ determined Be in a National Bureau of Standards Standard Reference Material Fly ash (NBS-SRM 1633).

However, the determination of Be by GFAAS is subject to matrix interferences⁷ which therefore requires the use of matrix modifiers and careful choice of atomisation conditions (e.g. fast modes of heating and atomisation and the use of L'Vov platforms).¹²

ICP-AES offers many advantages over atomic absorption spectroscopy and its multielement capability facilitates fast analysis at both major and trace levels.

In this paper we report the use of ICP-AES for the determination of Be and Li in fly ash samples. A parallel investigation of the uses of GFAAS for Be determination proved unsuitable for routine analysis of a large number of samples due to variations in matrix interferences. Some of the problems encountered in developing methods for Be and Li determination by ICP-AES are also reported and data for about 30 South African fly ash samples are presented.

EXPERIMENTAL

Apparatus

The samples were analysed with an IL Plasma-100 spectrometer

coupled to a line printer (IL) and a video printer (Axiom Ex-850). Details of the instrument are given in Table I. Atomic absorption measurements were made with a Perkin-Elmer Model 5000 Spectrophotometer and a HGA-500 graphite atomiser. A Perkin-Elmer Model 56 chart recorder was used to study and record signal peaks.

TABLE I
ICP operating conditions.

RF power supply	27.12 MHz, 950–1750 W, selectable in seven steps (0 to 6)
Optical system	2 Double monochromators, channels A and B
Primary monochromator	$\frac{1}{3}$ m Erbert–Fastie design
Premonochromator	$\frac{1}{6}$ m Erbert–Fastie design
Resolution	0.02 nm
1st Order	190–365 nm
2nd Order	365–900 nm
Peak search window size	0.033, 0.067, 0.1 nm (user selectable)
Computer system	Intel 8080A μ P, FORTH language
Sample introduction system	Polypropylene cross-flow nebuliser with synthetic sapphire capillaries and concentric quartz tube torch
Nebuliser driving pressure	20 to 50 psi
Sample flow rate	Peristaltic pump, 0.1 to 2.2 ml/min
Plasma gas flow	15 to 20 l/min
Torch observation height	0 to 48 mm above RF coil (2 mm increments)

Reagents

High purity water from a Milli-Q system (Millipore Corp.) was used for all preparations and the washing of apparatus. The beryllium standard used was obtained from BDH (United Kingdom), Spectrosol, for atomic absorption spectroscopy. A 1000 ppm lithium standard was prepared by dissolving the contents of a Titrisol (Merck) ampoule in 1 l of water.

All acids used (HNO_3 , HF) were of high purity (Aristar, BDH).

The surfactant Triton X-100 (Tx-100) was obtained from BDH

and was used in the preparation of standards and samples for ICP-AES measurements.

Methods

1) *Beryllium determination by GFAAS.* Preliminary investigations with aqueous Be standards showed pyrolytically coated graphite tubes to be unsuitable for analysis due to the extremely poor reproducibility of atomisation signals.

Use of the stabilised temperature platform furnace to reduce or eliminate interferences in GFAAS was discussed by L'Vov¹² and consequently many authors have made use of this technique. "Home-made" platforms were constructed by cutting pyrolytically coated graphite tubes into small pieces (about 7×4 mm) and inserting them under the sample introduction port. After optimisation of the ashing and atomisation conditions, the precision obtained with aqueous standards was greatly improved.

It was then decided to test the accuracy of the method by analysing the NBS-SRM 1633a fly ash.¹⁶ Although the beryllium concentration in this reference material is not certified, an uncertified value of $12 \mu\text{g/g}$ is supplied by NBS. This was the only reference material available to us for this investigation.

NBS-SRM 1633a was dissolved in Parr acid digestion bombs (Parr Instruments Catalogue No. 4745). Approximately 0.02 g sample aliquots were weighed accurately into the teflon cups then 1 ml HNO_3 and 3 ml HF were added. The bombs were sealed and heated at 115°C for 4 hours. After cooling, the samples were quantitatively transferred to 50 ml polypropylene flasks for dilution. The samples were analysed by the standard addition method using aqueous standards. The instrumental conditions are outlined in Table II.

The concentrations for Be in the samples were found to be 12.5, 11.8, and $13.3 \mu\text{g/g}$ for three separate determinations.

Even though satisfactory results were obtained, the method was not suitable for routine analysis. Problems were experienced with manually dispensing the samples ($20 \mu\text{l}$) on the platforms, it was found difficult to place the drop on the platform in a reproducible way. Although the use of an automatic sampler should solve this problem, this facility was not used. Furthermore, widely differing drying and ashing conditions were necessary for each individual platform. This is related to the geometry of the platforms and their

TABLE II

Instrumental conditions for the analyses of Be using
GFAAS.

Spectrophotometer:

wavelength :238.7 nm

slit width :0.7 nm

lamp current:8 mA (background corrector lamp on)

HGA-500 programme:

dry :180°C

ash :1000°C for 20 seconds

atomise:2700°C for 5 seconds

clean :2700°C for 3 seconds

positioning inside the graphite tube. Commercial platforms are available but these were not available to us during this investigation.

A method involving the direct analysis of slurries in the graphite furnace with the use of a matrix modifier ($\text{Mg}(\text{NO}_3)_2$) was then investigated. We have used this technique to determine trace elements in coal and fly ash including V, Ni, Co, Mo, Mn and Cd. The advantage of this technique is that it is rapid and simple since very little sample preparation is required apart from grinding samples into a fine powder.

The slurries were prepared in the following way: approximately 0.02 g fly ash aliquots were weighed into sample tubes and 5 ml 0.005% Tx-100 containing 500 ppm Mg (as $\text{Mg}(\text{NO}_3)_2$) added. These were stirred vigorously with magnetic stirrer bars while pipetting 20 μl aliquots for dispensing into the graphite tube. The presence of $\text{Mg}(\text{NO}_3)_2$ in the sample and standards allowed elevated ashing temperatures without loss in sensitivity. The optimum ashing and atomising temperatures were determined for the slurries and aqueous standards; the optimum atomisation temperature was found to be 2500°C and the ashing temperature was 1600°C. Non-pyrolytically coated tubes were used. Again poor reproducibility was obtained. The difficulty is thought to be due to some matrix interferences that are not reduced even by using the above precaution. Furthermore with ageing of the tube and building-up of unvolatilised material in the graphite tube, the situation deteriorated. The exact mechanism of

this interference has not yet been fully investigated. These difficulties led us to investigate the determination of Be by ICP-AES.

2) *Beryllium determination by ICP-AES.* When an analytical programme for ICP-AES analysis is prepared, an interference study is usually required, especially when determining trace elements in complex matrices like coal or fly ash where the numbers of potential interferences may be large.

Interference studies involve the preparation of test solutions containing both the analyte and the possible interferent which is a very tedious procedure. To facilitate this task we have constructed a device for mixing two solutions prior to nebulisation and introduction into the ICP torch. A schematic diagram illustrating the components is shown in Figure 1.

The peristaltic pump drum has space for two rubber windings. Different designs and sizes of the mixing chamber were tried and the one described in Figure 2 was found to perform the best. However, mixing of two solutions was not "quantitative", i.e. the flow rates

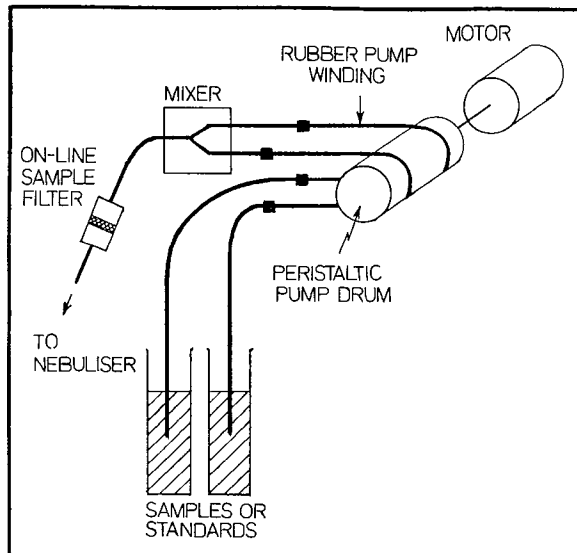


FIGURE 1 Operation of the mixing device.

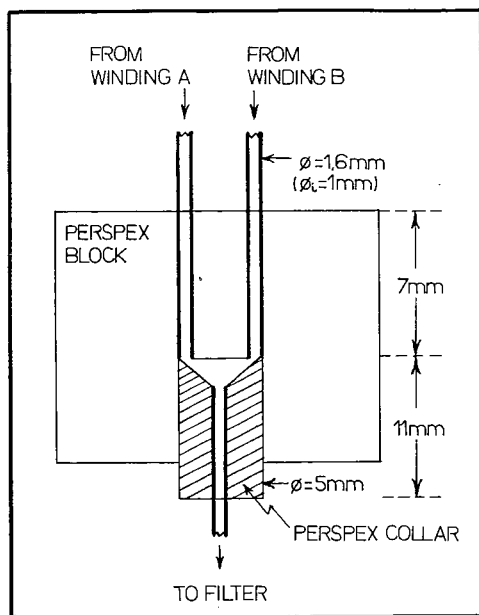


FIGURE 2 Diagram of mixing unit.

were not the same for the two windings but the difference is small enough for qualitative work. The technique also allows the standard addition technique to be used without prior spiking of samples, however, correction for non-quantitative mixing (which is nevertheless constant) must be applied. The advantages of using this technique are:

- i) Rapid analysis, since little preparation is required.
- ii) No need to matrix match the standards and blanks with the samples.
- iii) There is no waste of standard solutions or samples especially when very small volumes are available.
- iv) Possibility of fast multielement standard addition measurements.

Standard solutions were used to optimize the conditions for beryllium determination. Four spectral lines were selected and their

sensitivities and detection limits, C_L , (3σ) calculated. The results are shown in Table III. I_N/I_B is the net intensity to background intensity ratio for a 1 ppm Be standard and a water blank (note: the background intensities here are taken as blank emissions at those wavelengths). These were calculated from 10 readings of 5 seconds each.

The first two lines are close to each other but are sufficiently well resolved by the IL Plasma-100 optical system. From Table III, the Be 313.04 nm and 234.86 nm are the two lines of choice because of their higher sensitivities. The 249.47 nm line is not sensitive enough for low level determinations. An interference study was carried out for the first three lines listed in Table III.

TABLE III
Be spectral lines.

Spectral line (nm)	I_N/I_B (1 ppm Be)	C_L (ppm)
313.04(II)	46	0.00014
313.11(II)	25	0.00040
234.86(I)	45	0.00022
249.47(I)	2	0.0048

Serious interference by an iron line near the 234.86 nm Be line makes the use of this line difficult since the ratios of Fe to Be in fly ash samples are very large.

This interference is shown in Figure 3.

Vanadium interferes with the Be 313.04 nm line and a titanium line lies between the two Be lines. These are illustrated in Figure 4.

Figure 5 shows wavelength scans for a 0.01 ppm Be standard and a water blank at the Be doublet. The high blank at about 313.04 nm is caused by OH emission bands situated in this region. This appears to be two poorly resolved peaks that cannot be seen at high Be concentrations but causes a broadening of the Be peak.¹⁰

Scans of emission intensities versus observation heights in the plasma showed that near 313.04 nm, emission from the blank and titanium are stronger at higher observation heights. Therefore under

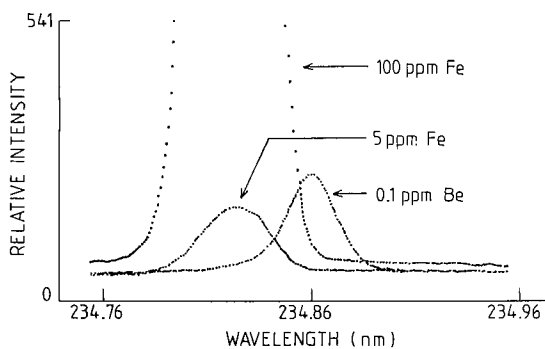


FIGURE 3 Interferences by Fe at Be 234.86 nm.

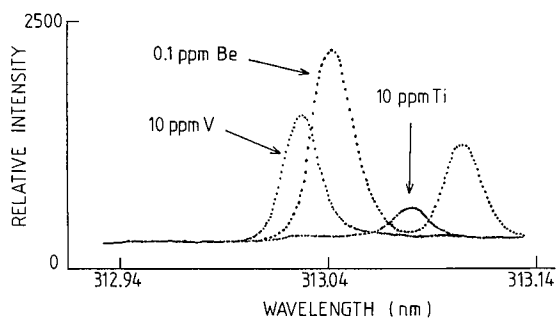


FIGURE 4 Interferences by V and Ti at Be 313.04 nm and 313.11 nm.

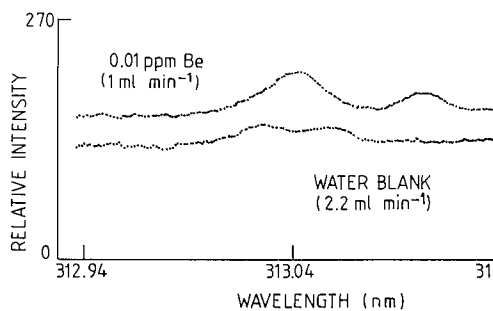


FIGURE 5 OH emission at 313.04 nm.

the experimental conditions, lower observation heights can be used to decrease interferences by Ti and OH band emissions.

Correction factors (CF) were calculated for the spectral interferences using:

$$CF = \frac{\text{Measured concentration (ppm) at Be wavelength}}{\text{Concentration of interferent (pp)}}.$$

The CF for Ti at 313.11 nm and V at 313.04 nm were 0.00015 and 0.00043 respectively. The interferent concentration in the sample C_I is measured using a sensitive interferent emission line and the correction applied to the measured Be concentration:

$$\text{Corrected } C_{Be} = \text{measured } C_{Be} - (CF \times C_I).$$

Interference by Ti in fly ash samples at the 313.04 nm line under the experimental conditions was found to be negligible.

Four aliquots of the NBS-SRM 1633a were prepared in the digestion bombs as described previously. The blank and standards were prepared similarly. All solutions were made to contain about 0.05% Tx-100. The presence of the surfactant improves the precision of measurements in ICP-AES analysis, possibly by enhancement of the nebulisation efficiency. Furthermore, we have noted a reduction in memory effects in the case of boron determination, thus it is a routine practice for us to add Tx-100 to all solutions being aspirated in the ICP. The ICP was calibrated with four Be standards (0.5, 0.1, 0.01 and 0.001 ppm) and a blank. The 313.04 nm spectral line was used and the result was as follows: $13.5(3) \pm 0.75 \mu\text{g/g}$ (5.5% RSD) which agrees reasonably well with the data obtained by FAAS analysis $12.5(3) \pm 0.75 \mu\text{g/g}$ (5.6% RSD), however, this is higher by about 10%. One of the samples was also analyzed by the standard addition method with ICP-AES. Net intensity values were plotted against Be concentrations spiked into sample aliquots. The correlation coefficient for 3 additions was 0.9987 and the concentration of Be was calculated to be $13.4(9) \mu\text{g/g}$, which agrees with the value obtained above.

The samples were analysed again by ICP-AES using the 313.04 nm line and applying the correction for vanadium interference. The V

310.23 nm line was used with background correction on one side of the peak since aluminium was found to cause large background shifts at this wavelength. The other sensitive vanadium line at 309.31 nm suffers from spectral interference by high Al concentrations (Al 309.28 nm) and the V 292.40 nm line is interfered with by an iron line.

Since the 313.11 nm line is less sensitive than the 313.04 nm line, more concentrated samples were prepared for investigating its uses for trace Be determination. The interference by titanium at this wavelength was corrected for by determining the levels of titanium in the samples using the Ti 334.94 nm line with a low observation height of 8 mm to reduce its sensitivity.

The results (mean) were 12.16 and 12.36 $\mu\text{g/g}$ Be using the 313.04 and 313.11 nm lines respectively. The difference (about 10%) between the results obtained with and without correction for spectral interference emphasize the necessity for proper investigation and correction of interferences. In conclusion, both Be lines can be used for trace analysis of fly ash and which is used depends on the Be, Ti and V concentrations in the samples.

Twenty-nine South African ash samples were prepared in the digestion bombs as described above and analysed using the 313.4 nm line with correction for vanadium and with background correction on the low wavelength side of the peak (about 0.05 nm from the centre of the Be peak).

3) *Lithium determination by ICP-AES.* The possibilities of determining this element at low levels by ICP-AES were investigated. Several spectral lines were available for analysis and these are listed in Table IV. The estimated detection limits for these lines are also listed.

For this work the most sensitive line at 670.78 nm was investigated. Standard solutions were used to optimize the ICP parameters. A remarkable dependence of the stability of the signal (precision) with (i) the nebulizer driving pressure and (ii) the observation height above the torch coil was experienced. This is illustrated in Figure 6. Each % RSD value was calculated using 10 readings of three seconds each while aspirating a 10 ppm Li aqueous standard. The best precisions were obtained at low pressures and an observation height of about 14 mm. At low observation heights, an

TABLE IV
Lithium spectral lines.

Spectral line 'nm)	C_L (ppm)
670.78(I)	0.013(13)
610.36(I)	0.043(13)
460.29(I)	1.35 (13)
323.26(I)	1.1 (14)
274.12(I)	1.6 (14)

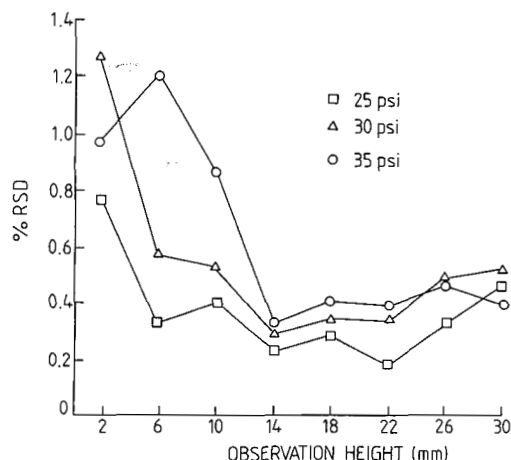


FIGURE 6 Effects of nebuliser driving pressure and observation height on precision of measurements.

increase of the nebulizer pressure was found to enhance the emission signal. This is illustrated in Figure 7.

The close dependence between the signal characteristics and ICP parameters for this element indicates that the mechanism by which emission occurs is very sensitive to small changes in plasma conditions. The effect of changing other parameters such as the sample flow rate, the torch power and the plasma gas flow rate was also investigated. The instrumental parameters outlined in Table V were

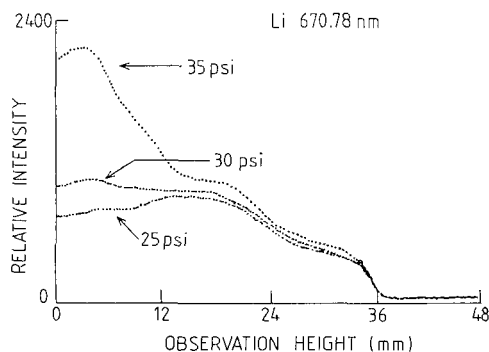


FIGURE 7 Effect of nebuliser driving pressure on Li emission.

TABLE V
Instrumental parameters for Li determination.

Power (IL power settings):	3
Nebuliser driving pressure:	27 psi
Observation height:	14 mm
Sample flow rate:	1 ml min ⁻¹

found to be optimum for the determination of Li. Under those conditions, the detection limit for this element was found to be 0.008 ppm.³

An interference study was undertaken; the effects of high concentrations of the major elements in coal and coal ash (e.g. Li, Al, Ca, Fe, Na, K) on lithium emission were investigated. No interferences were noted except that a high concentration of sodium (500 ppm Na to 10 ppm Li) was found to enhance the Li signal at low observation heights. However, the enhancement was negligible at heights of more than about 14 mm. This led us to investigate the determination of Li in sea water directly using the above instrumental parameters. A background shift between the sea water sample and aqueous standards was noted, therefore, background correction was done on the short wavelength side of the Li line. The sea water sample collected in the Cape Town region (South Africa) was filtered

through a fritted glass funnel and spiked with Tx-100. The instrument was calibrated with a water blank and two aqueous Li standards (2 and 0.5 ppm). The value obtained for two analyses of 5 readings for 5 seconds each was $0.177 \pm 0.008 \mu\text{g/ml}$ (4.6% RSD) which is in agreement with reported values, e.g. $173 \mu\text{g/l}$.¹⁵

Lithium was determined in 31 South African fly ash samples using the digestion bomb for sample preparation.

RESULTS AND DISCUSSION

The concentrations of beryllium and lithium in the South African samples are listed in Table VI, the nature of the samples (e.g., pulverized fly ash-PFA, boiler ash-BA or bituminous ash-BIA) and the names of the power stations where these were collected are also listed (e.g. Arnot, Camden, Kriel and Matla).

The Be concentrations in the samples ranged from 4.2 to $15.4 \mu\text{g/g}$ ash with a mean value of $7 \mu\text{g/g}$ (19% RSD) except for the samples from Camden power station which contained more, $9 \mu\text{g/g}$. The concentration of Li in the samples ranged from 65 to $287 \mu\text{g/g}$ with a mean value of $206 \mu\text{g/g}$ (23% RSD). The samples from Camden power station contained less than $86 \mu\text{g/g}$. The higher Be concentrations and lower Li concentrations found in those samples from Camden power station seems to indicate that this power station might be burning coals with different Be and Li concentrations from the others or operating under different conditions as the volatilisation of elements is dependent upon the operating conditions of the burners. The Be and Li concentrations in the South African coals used in those power stations have not yet been determined and more data is required for a better understanding of the distribution of these elements during combustion of coal.

ICP-AES has proved to be an excellent technique for the determination of Be and Li in fly ash samples. These two elements cannot be determined by X-ray fluorescence spectrometry, a technique which has been widely used for the determination of major elements and many trace elements in South African coal and fly ash samples.¹⁷ Although lithium can be determined easily by AAS, the aim of our investigation (to determine this element by ICP-AES) is to broaden our multielement programme whereby major elements

TABLE VI
Analytical results.

Samples	Concentrations ($\mu\text{g/g}$)	
	Beryllium	Lithium
4 PFA (Arnot)	5.6	84
6 PFA (Camden)	—	137
8 PFA (Camden)	10.2	75
10 PFA (Camden)	14.3	76
13 PFA (Camden)	11.3	65
14 PFA (Camden)	15.4	86
15 PFA (Camden)	9.2	66
40 PFA (Kriel)	6.7	207
41 PFA (Kriel)	4.2	164
42 PFA (Kriel)	6.0	216
43 PFA (Kriel)	6.7	273
44 PFA (Kriel)	7.3	220
45 PFA (Matla)	5.6	287
46 PFA (Matla)	5.8	191
47 PFA (Matla)	6.2	175
48 PFA (Matla)	8.0	185
49 PFA (Matla)	5.5	233
53 PFA (Matla)	6.7	214
54 PFA (Matla)	6.6	221
57 PFA (Matla)	7.3	—
58 PFA (Matla)	6.8	173
59 PFA (Matla)	7.0	200
60 PFA (Matla)	7.6	190
62 BIA (Matla)	—	271
65 BA (Matla)	—	288
66 PFA (Matla)	6.0	206
67 PFA (Matla)	7.4	160
68 PFA (Matla)	8.7	245
69 PFA (Matla)	9.2	248
70 BA (Matla)	4.5	153
71 PFA (Matla)	5.6	194
73 PFA (Matla)	8.8	244

and trace elements can be determined together in the same samples prepared by one method, for example acid digestion in the pressure bombs as described above. Beryllium is one of the most sensitive elements by ICP-AES and compared with GFAAS, ICP-AES analysis is much faster. The lithium 670.78 nm spectral line is very

sensitive and is interference free. The less sensitive 610.36 nm line could probably also be used satisfactorily.

Compared to developing ICP-AES programmes for major element determination in coal and fly ash, trace determination requires a more thorough investigation of the choice of instrumental parameters, spectral lines and of possible interferences due to the large ratios of major to trace elements in the samples. For trace element determinations a properly optimized system is essential in order to increase the sensitivity and to obtain accurate and precise results. One major problem we have encountered in trace element analysis is instrumental drift. Drift of the calibration curve cannot be avoided and monitoring of the drift and recalibration of the instrument is essential.

Since the levels of many trace elements in South African environmental samples are largely unknown, we feel that the use of ICP-AES can be put to good use here.

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