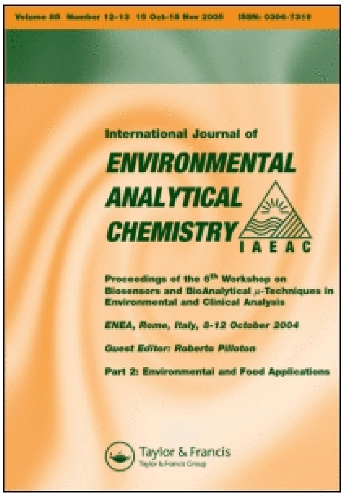

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

The Determination of Boron by Inductively Coupled Plasma Atomic Emission Spectroscopy. Part 2. Applications to South African Environmental Samples

M. A. B. Pougnet[a b]; M. J. Orren[a]
[a] Department of Analytical Science, University of Cape Town, Rondebosch, Republic of South Africa [b] CSIR, National Accelerator Centre, Faure, USA

To cite this Article Pougnet, M. A. B. and Orren, M. J.(1986) 'The Determination of Boron by Inductively Coupled Plasma Atomic Emission Spectroscopy. Part 2. Applications to South African Environmental Samples', International Journal of Environmental Analytical Chemistry, 24: 4, 267 — 282

To link to this Article: DOI: 10.1080/03067318608076477

URL: http://dx.doi.org/10.1080/03067318608076477

Intern. J. Environ. Anal. Chem., 1986, Vol. 24, pp. 267–282
0306-7319/86/2404-0267 $18.50/0

Printed in Great Britain

The Determination of Boron by Inductively Coupled Plasma Atomic Emission Spectroscopy. Part 2. Applications to South African Environmental Samples

M. A. B. POUGNET† and M. J. ORREN
Department of Analytical Science, University of Cape Town, Rondebosch, 7700, Republic of South Africa

(*Received July 1, 1985; in final form October 9, 1985*)

The use of inductively coupled plasma atomic emission spectroscopy (ICP-AES) for trace determination of boron in a variety of samples is illustrated. The sample preparation method for the analysis of coal and fly ash is described and data for boron levels in South African samples are presented. ICP-AES is also used to investigate the leaching of boron from fly ash by water and to analyze waters, including lake water, sea water and water samples collected at a coal burning plant.

KEY WORDS: Boron, inductively coupled plasma atomic emission spectroscopy, environmental samples.

INTRODUCTION

During the past decade the determination of boron in environmental samples has been widely investigated. One reason for this is the concern expressed about the distribution of this element in the environment through the ever increasing utilization of coal for the generation of power. Boron is an essential element in plant metabol-

---

†Present address: CSIR, National Accelerator Centre, Van de Graaff Group, P.O. Box 72, Faure 7131, RSA.

ism, however, many plants can only tolerate a very narrow range of boron concentrations in the soil.[1] Since boron is concentrated in the ashes during combustion of coal, leaching of this element from ash dumps by rain and ground water could well affect plant growth in the viscinity of these disposal areas. Another problem is the transfer of this element to the environment through small fly ash particles escaping from the stacks of coal burning plants. Coal is a major source of energy in South Africa and as a consequence, about 10 million tons of fly ash are currently produced per annum. The levels of boron in South African coals and ashes are largely unknown and the aim of this study was to develop suitable analytical techniques for the determination of boron in these environmental samples. The preliminary investigation done on boron determination by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and the instrumentation used have been described previously.[2]

In this study sample preparations for coal and coal ash were investigated and the data obtained for South African samples is presented. The suitability of ICP-AES for the investigation of boron leaching from South African coal ash was evaluated. Boron as well as other elements were also determined in waste water from a coal burning plant. These samples are in contact with coal ash and leaching of elements is expected to occur. Finally ICP-AES was used to measure boron concentrations in sea and lake water.

EXPERIMENTAL

Reagents

High purity water from a Milli-Q-system (Millipore Corporation) was used throughout for all preparations and washing of the equipment. The reagents used were: concentrated nitric acid (70%) and hydrofluoric acid (48%): "Aristar" grade, BDH Chemicals Ltd., England;

A $1000\,\mu\mathrm{g\,ml^{-1}}$ boron standard solution was prepared by dissolving boric acid (Aristar, BDH) in water;

All other reagents were of Analytical grade; standard solutions for other elements were supplied by BDH ("Spectrosol" standards for atomic absorption Spectroscopy), as was surfactant Triton-X-100.

Coal and coal ash analysis

Several methods for dissolution before analysis by atomic absorption and emission spectroscopy have been developed.[3] Both dissolution by acid attack and fusion techniques have been widely used for atomic absorption spectroscopic analyses of coal and ashes as well as minerals. Similar methods are adaptable for ICP-AES analyses. Nitric, perchloric and hydrochloric acids or combinations of these (e.g., aqua regia) are used to oxidize the organic (carbonaceous) matter especially in coal, and dissolution of the inorganic material (e.g. silicates) is accomplished by hydrofluoric acid. The acid attacks are more efficiently accomplished at high temperatures but losses of certain elements occur e.g., boron especially on evaporating to dryness.[4] Hence the use of closed vessels (e.g., Teflon lined Acid Digestion Pressure Bombs) at high temperatures where high pressures are obtained have been found to be efficient.[4] Attack by hydrofluoric acid results in solutions with high fluoride concentrations and therefore laboratory glassware cannot be used. To avoid this an excess of boric acid (H_3BO_3) is commonly added.[4] This complexes with fluoride to form fluoroboric acid.

In our laboratories this technique has been used for the major element and trace element (e.g., Li, and Be) ICP-AES analysis of coal and coal ashes. But since boric acid cannot be added to samples for boron determination, these solutions are aspirated directly into the hydrofluric acid resistant nebulizer and torch system for ICP-AES analysis. The use of the "digestion bombs" is limited by the amounts of sample and reagent that can be used. Therefore for trace boron determination in coal and coal ashes the capacities of these vessels might not always suffice since too dilute samples may result. This has led us to investigate the use of a "larger scale" procedure described below. The National Bureau of Standards Standards Reference Material (NBS-SRM) coal and fly ash were used for the investigation and the South African samples were taken through the same procedure.

The method used for sample preparation of coal and fly ash is relatively lengthy and we have also investigated a fusion procedure using sodium hydroxide. For this method pure nickel crucibles can be used and fusions are carried out over Bunsen burner flames. About 10 g NaOH and 1.5 g KNO_3 (as oxidizing agent) are fused over a gentle flame and after cooling, about 1 g sample aliquots are sprinkled evenly over the fused cake. Ethanol is used to wash all samples from the weighing bottles into the crucibles (ethanol has been found to help prevent violent spattering when heating is started). Then the crucibles are closed and heated gently at first and after complete fusion for about 15 minutes. After cooling, water is added and the melts are dissolved over the flame. The cold solutions are then transferred to polypropylene flasks for neutralization by HCl (about 35 ml) and 2 ml of HF are added. Solutions are diluted to 250 ml with water and Triton X-100. Some residues were always present and these were filtered off. Recovery tests using aqueous boron standards in the fusion showed no loss of boron during the procedure. Some South African fly ash samples were prepared and analysed. Although reasonable agreement with the results obtained by the method described below were obtained, problems with measurements were experienced. The high concentrations of dissolved solids caused very noisy signals affecting the precision of measurements. Other work is being done to investigate possible steps to reduce the concentrations of dissolved material e.g. by further dilution or reduction in the amount of NaOH used. The method is fast and does not require any special equipment apart from pure nickel crucibles.

Procedure for sample preparation

About 0.5 g dry sample aliquots were placed in polypropylene flasks and 5 ml concentrated HNO_3, 10 ml water and 10 ml HF (48%) were added. The flasks were sealed and shaken gently in a water bath at 70°C for about 15 hours. After cooling, 25 ml of water and 2 ml of 1% Triton X-100 (surfactant) were added and the flasks shaken for a few minutes. Residues were present after digestion and these were filtered off before analysis using Whatman filter paper (No. 541, ashless hardened). Under these experimental conditions, the boron is completely leached out of the samples as shown by the results obtained with Standard Reference Materials (Table I). The solutions are stable and can be stored in plastic bottles. Blanks were prepared in the same way. Working standards were prepared by spiking the blank solutions with 1000 $\mu g\,ml^{-1}$ standard solutions. The calibration of the spectrometer was done using 5, 2, 0.5 $\mu g\,ml^{-1}$ standards and a blank. Two wavelength scans of samples of a boron standard are shown in Figures 1 and 2. Figure 1 shows a background shift caused by large iron concentrations, less obvious is direct spectral interference by iron[2] which would require line overlap correction as well as background correction. Therefore the spectral line at 208.96 nm (Figure 2) was used instead. Due to background shift by the presence of aluminium, a two point background correction was performed (positions in Figure 2).

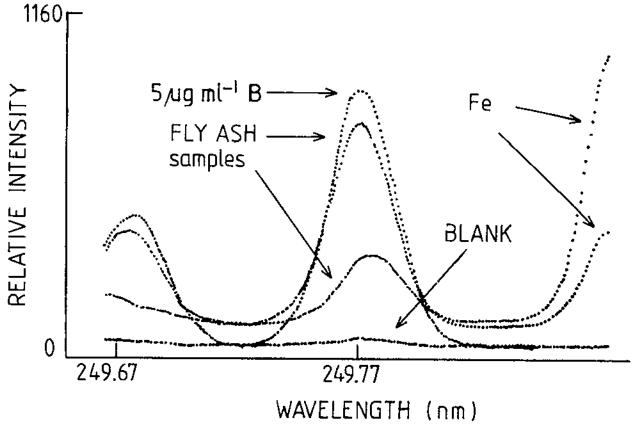

FIGURE 1 Wavelength scans of samples and a boron standard in the vicinity of the B 249.77 nm line.

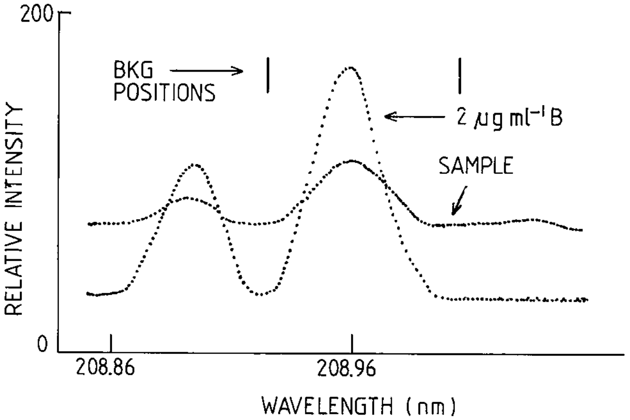

FIGURE 2 Wavelength scans of a sample and a boron standard in the vicinity of the B 208.96 nm line.

The measured B concentrations (triplicate determinations) in the NBS-SRM are listed in Table I together with available published data. Good agreement was obtained.

TABLE I

Boron concentrations in NBS-SRM, mean of triplicate analyses

	Concentrations $\mu g\,g^{-1}$			
		Reported values (References)		
Sample	This study	6	7	8
Fly ash 1633a	40.0 ± 1.5	39.2	39 ± 1	39.2 ± 0.7
Bituminous coal 1632a	53.3 ± 2	53	—	52.7 ± 1.8
Sub-bituminous coal 1635	107 ± 5	105	—	104.5 ± 2.6

The South African coal and coal ash samples were collected from the Matla power station. Coal and ashes (bituminous or boiler ash) samples were crushed and ground to fine powders. The fly ash samples collected at different electrostatic precipitators were used without grinding. All the samples were dried in a vacuum desiccator before weighing. The boron concentrations measured are shown in Table II. Because of the large numbers of samples to be prepared and analysed for B as well as the major and other trace elements, duplicate analysis for all the samples was not possible. Several analyses of a few samples yielded better than 5% RSD e.g., 4.7% for the NBS-SRM coal 1635.

The boron concentrations in fly ash samples range from 123 to 513 $\mu g\,g^{-1}$. In bituminous and boiler ashes the concentrations are usually lower (about 100 $\mu g\,g^{-1}$), showing that boron is enriched to a larger extent on fly ash particles. More interesting is the variation in B concentration with particle size fraction of the sample collected in the two sets of four precipitators: LH1, LH2, LH3, LH4, and RH1, RH2, RH3, RH4. In most cases the concentrations increase systematically between the first and last precipitators where smaller particle size fractions are collected. From these results boron is

TABLE II

Measured concentration of boron in South African coal and ash samples (Matla power station)

Sample	Concentration $\mu g\,g^{-1}$
Coal 1	60
Coal 2	53
Coal 3	60
Bituminous ash 1	118
Bituminous ash 2	108
Boiler ash 1	97
Boiler ash 2	97
Fly ash 1 LH 1	123
Fly ash 1 LH 2	300
Fly ash 1 LH 3	407
Fly ash 1 LH 4	513
Fly ash 1 LH 5	209
Fly ash 1 LH 6	343
Fly ash 1 LH 7	369
Fly ash 1 LH 8	522
Fly ash 1 RH 1	218
Fly ash 1 RH 2	186
Fly ash 1 RH 4	406
Fly ash 1 RH 5	158
Fly ash 1 RH 6	248
Fly ash 1 RH 7	352
Fly ash 1 RH 8	410
Fly ash 2 RH 1	215
Fly ash 2 RH 2	347
Fly ash 2 RH 3	436
Fly ash 2 RH 4	473
Fly ash 4 LH 1	214
Fly ash 4 LH 2	422
Fly ash 4 LH 3	517
Fly ash 4 LH 4	488

LH and RH: left hand and right hand side precipitators respectively.

found to behave like many other trace elements whereby enrichment occurs in the smaller particles.[9,10,11] This is of significance since the smaller particles are not efficiently trapped by the collection devices and are emitted and they have the highest mobilities in the atmosphere. Using the above data (i.e. B concentrations in the incoming coal, the bottom ash and the fly ash collected in the precipitators), a mass balance was calculated to estimate the amount of boron released to the atmosphere during the combustion of coal.[12] About 10–15% of the boron was lost to the atmosphere. For a power station the size of Matla, this represents an annual emission of about 60 tons of boron to the environment. The environmental impact of this is currently unknown.

Water leaching of boron from fly ash

The leaching of boron from coal ash by water as well as its retention on various solids (ash, soil and minerals) has been investigated.[13-19] Using ICP-AES, we conducted a series of experiments of South African samples; some results are presented here. A 3 kg sample of fly ash was collected at the Sasol I plant (power station II) and subsamples were used for the leaching experiments. The total boron concentration was found to be 450 $\mu g\,g^{-1}$ (triplicate determination by the method described above). The results (in duplicate) from simple shaking (flask shaker) of 10 g ash in 200 ml of water for periods of time between 15 mins and 20 hours are shown in Figure 3. Leaching of the boron is rapid and after about 3 hours all the leachable boron is freed. Concentrations tend to decrease after longer shaking times (10 to 20 hours), which might suggest that readsorption of some of the boron in solution on the fly ash could be occurring with time. The pH of all the solutions, even after a few minutes of shaking was found to be 12 for the fly ash sample from the Sasol I plant. In a parallel study leaching of boron was investigated when the fly ash is left standing in water (Figure 3), the same ratio of fly ash to water as above was used. After 15 minutes about 4% of the boron was leached out and 10% was present in the solution after 20 hours.

The effect of ash to water ratio on the availability of boron was investigated. The results are shown in Figure 4 where samples of different fly ash to water ratio (10 to 100 $g\,l^{-1}$) were shaken for 2

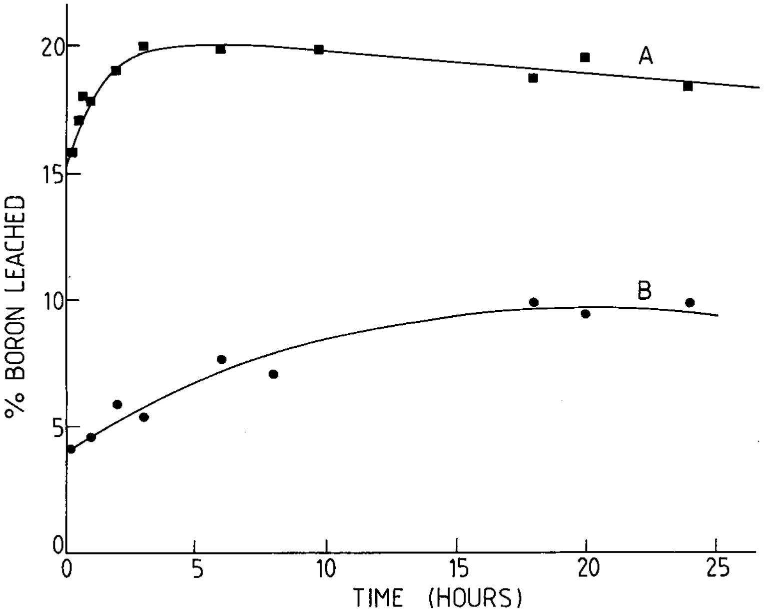

FIGURE 3 Boron leached as a function of time: (a) shaking; (b) standing.

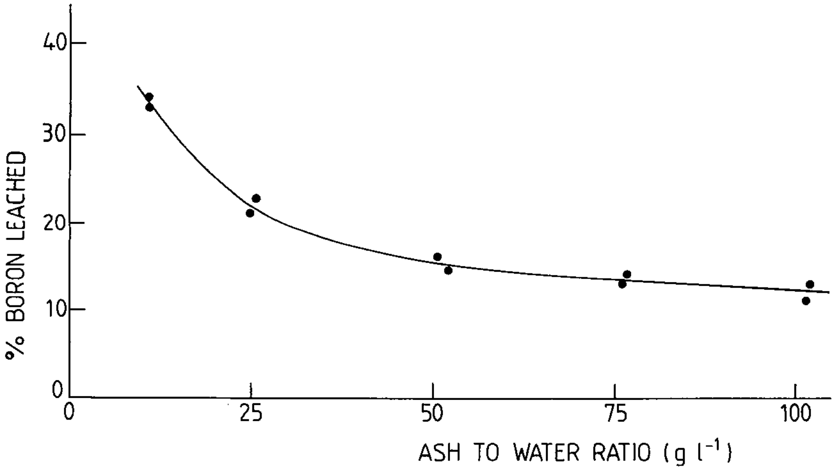

FIGURE 4 Boron leached as a function of fly ash to water ratio.

hours. The decrease of boron present into solution with increasing ash to water ratios tend to support the argument whereby the high concentrations of other soluble species into solution suppress boron transfer into solution or cause boron into solution to be adsorbed back on the solid particles.

Boron leaching from nine samples (Matla power station, Table II) was investigated, by shaking 1 g ash with 100 ml of water for 20 hours. The results are tabulated in Table III. One would expect the amounts leached to increase with samples collected in precipitators 1 to 4 and 5 to 8 respectively since increasingly larger fractions of small particles are collected in these but this is not observed. The % boron leached in samples from the first three precipitators decrease followed by an increase in the fourth one. No satisfactory explanation can be given for this behaviour, more fundamental studies are required to clarify these findings.

TABLE III

Leaching of boron from Matla power station fly ash (duplicate analyses)

Sample	Total B $\mu g\,g^{-1}$	% B leached
1 LH 1	123	33.0
1 LH 2	300	12.0
1 LH 3	407	1.5
1 LH 4	513	20.0
1 LH 5	209	15.0
1 LH 6	343	2.4
1 LH 7	396	1.8
1 LH 8	522	19.0
4 LH 4	488	23.0

The study of boron leaching from fly ash is not easy due to the many processes involved. The release of boron from fly ash by water is dependent upon (i) contact time, (ii) pH of the water, (iii) ash particle size, (iv) ratio of ash to leachate water.[19] Boron in fly ash is expected to be present in several forms, for example, more soluble species like borates that are located on the surface of the particles and depending on the temperatures at which coal burning plants are operating, less soluble species like metal borates and borosilicates. Finally the type of coal used (variation in elemental compositions) will also determine the availability of boron from fly ash.

Water analysis

Water is a suitable sample type for analysis by ICP-EAS and very little sample preparation is usually required. Some examples of water analyses are given below.

a) Lake water: 4 samples from 3 different lakes near Cape Town were collected at different periods. After collection these were frozen (at −20°C) and stored in plastic bottles. Since these samples contain relatively small concentrations of other elements e.g. Ca, Fe, no interferences at the most sensitive boron spectral line (249.77 nm) was experienced. However, due to the low analyte concentrations in these samples, maximum sensitivity was required for accurate results and the instrumental parameters were carefully optimized. Boron concentrations in the 12 samples varied from 0.05 to 0.19 $\mu g\,ml^{-1}$, these levels being only 10 to 20 times the detection limit for the boron 249.77 nm line. Great care was taken to monitor any instrumental drift which would yield large errors. Between each sample analysis, a water blank was analysed. Relative standard deviations for 3 readings of 8 seconds each ranged from 0.5 to 4%, showing that good precision can be achieved even at these low levels.

b) Sea water: The direct analysis of trace elements in sea water is often difficult because of the high dissolved salt concentrations which causes matrix interferences and poor precision.

High concentrations of sodium were found to enhance boron emission (Figure 5). The enhancement is greater at low plasma observation heights. At heights above 22 mm, the effect is negligible, however, the sensitivity decreases rapidly with increase in observation height in the plasma. Aqueous standards containing 10, 2 and 0.5 $\mu g\,ml^{-1}$ B and a water standard was used for calibration. Due to small background shifts, background correction was made on the high wavelength side of the analyte peak. A mean value of 4.51 $\mu g\,ml^{-1}$ (RSD 0.8%) was obtained for 10 readings of 6 seconds each. This value is in good agreement with the reported level of 4450 $\mu g\,l^{-1}$ boron in sea water.[20]

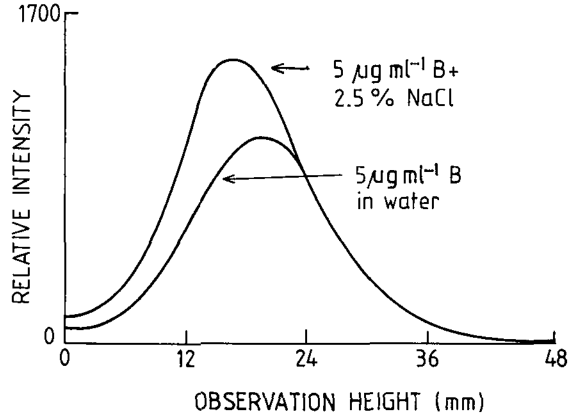

FIGURE 5 Variation of the boron signal at 249.77 nm as a function of the observation height in absence and in the presence of NaCl.

c) Analysis of water samples collected at a coal burning plant.

Water samples were collected at two different times (I and II) at various locations of the Sasol I plant (Table IV). The pH of the water was measured and samples were filtered through Whatman No. 541 filter paper. Boron and other elements were determined by ICP-AES using aqueous standards. Some trace elements in samples I were also determined by standard graphite furnace atomic absorption spectroscopy techniques, the concentrations ranged from 9 to 343 $\mu g\,l^{-1}$ for V, 17 to 103 $\mu g\,l^{-1}$ for Ni, 0.6 to 3.1 $\mu g\,l^{-1}$ for Co and 4 to 69 $\mu g\,l^{-1}$ for Mo. In samples II other elements determined by ICP-AES were: Al (2–5 $\mu g\,ml^{-1}$), Ba (0.1–0.5 $\mu g\,ml^{-1}$), C (448–1950 $\mu g\,ml^{-1}$), Fe (0.05–0.8 $\mu g\,ml^{-1}$), Li (0.2–0.5 $\mu g\,ml^{-1}$), Na (100–226 $\mu g\,ml^{-1}$), P (0.3–1 $\mu g\,ml^{-1}$), S (157–185 $\mu g\,ml^{-1}$) and Ti (0.02–0.2 $\mu g\,ml^{-1}$). Elements such as As, Cd, Cu, Pb, Se and Zn were at levels too low to be determined accurately by ICP-AES. Data for B, Ca, Mg and Si are shown in Table IV. The effect of pH on elemental concentration was studied by plotting elemental concentrations against pH on elemental concentrations against pH of the water samples. Calcium concentrations are found to be larger in the samples with higher pH values (Figure 6), Mo and Ni seem to follow the same trend while Mg and Co showed the reverse. For the other

TABLE IV

Analyses of water samples, concentrations in $\mu g\,ml^{-1}$

Samples	pH	B	Ca	Mg	Si
I					
Sewage storm water fed to holding dam	6	2.5	112	20.6	18.5
Underflow from thickener (AB) to slimes dam	9	7.6	116	0.7	9.7
Overflow for thickener (AB) to holding dam	5	3.2	112	12.6	11.1
Gas liquor to water treatment pits	6	—	5.2	2.7	7.4
Underflow for thickener (C) to slimes dam	12	0.6	813	<0.5	1.2
Overflow from thickener (C) to water treatment pits	11	7.0	359	<0.5	5.9
From classifier to thickener C	12	3.0	556	<0.5	0.7
Underflow from precipitator (CO_2) to slimes dam	6	16.0	89	42.3	2.6
Into holding dam	5	4.6	96	7.0	5.6
Overflow for precipitator (CO_2)	7	7.1	84	<0.5	4.9
II					
Water draining from newest ash heap	10	7.8	229	<0.5	5.0
Thickener input (channel A)	7	4.6	133	17.3	27.7
Thickener input (channel B)	11	6.9	235	<0.5	6.3
Collected at middle of slimes dam	6	4.4	125	14.9	24.1
Collected at edge of slimes dam	6	5.0	83	9.8	20.1

elements, no definite trends can be found except for samples II where carbon contents were definitely larger in the samples having lower pH. The study, however, shows that elements are leached out of the ashes by water over a wide range of pH. pH values are increased at certain locations of the plant due to leaching of the soluble oxides (Ca, Na, K), simple shaking of fly ash and bottom ash in water causes a rapid increase of pH to 11 and 12.

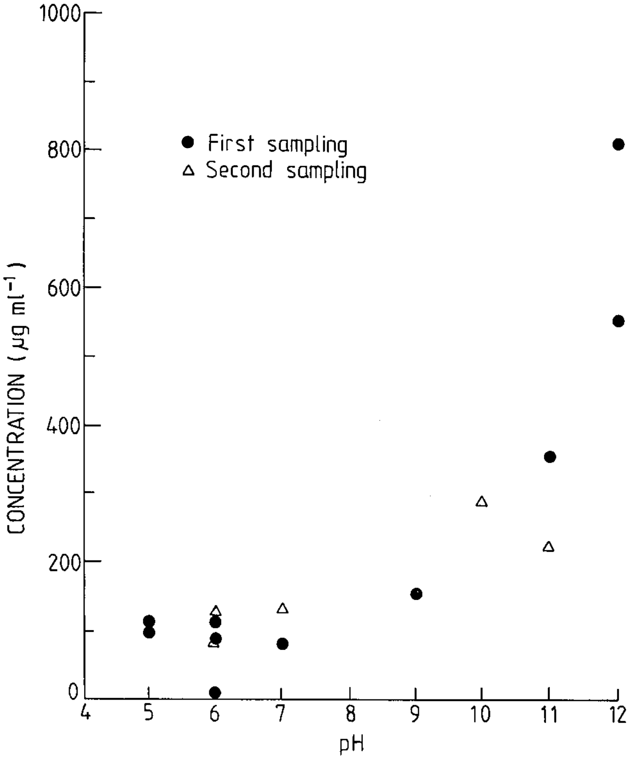

FIGURE 6 Variation of calcium concentrations with pH of water samples.

CONCLUSION

This study has demonstrated the suitability of ICP-AES for trace boron determinations. Accurate and precise results can be obtained in complex matrices like coal and coal ash provided great care is taken to fully investigate interferences. For all our analyses until now, we have used aqueous standards for the calibration of the spectrometer. The reason for this is the lack of availability of adequate standard materials. However, for trace boron analyses in coal and fly ash the NBS-SRM materials are useful calibration standards but the levels of boron is much lower in the fly ash than those in South African samples. Once we have characterized and measured elemental concentrations accurately in the South African samples, these will be used for calibration.

Insufficient data were available to make a comparison between the levels of boron in South African ashes and those produced in other countries. Concentrations measured in ashes from 19 power stations in the United States varied from 172 to 1480 $\mu g\,g^{-1}$' Similar leaching experiments were conducted on these ashes and the water leachable boron was found to vary from 17 to 64% which is higher than we have observed with South African samples. It is expected that the final concentrations of boron enriched in ashes and the water leachable fractions will differ with the origin of the coal and the operating conditions of the power plant.

The ease with which boron is leached out from fly ash is shown by the relatively high concentration of this element in waters collected at a power station. Lower pH conditions may increase the availability of boron from ashes and could cause higher than expected release of boron from ash heaps. We have shown that ICP-AES is a sensitive technique and suitable for studying possible release of boron in the environment through both fly ash particles escaping in the atmosphere and leaching processes. A more accurate way to estimate the boron released through the stacks would be to collect emissions (by filtering) but this has not been done yet. More work is being done to better understand the distribution of boron in the vicinity of coal burning plants.

Acknowledgements

We thank the Council for Scientific and Industrial Research for financial support and Miss K. Ketelby for preparing many samples.

References

1. W. D. James, C. C. Graham, M. D. Glascock and A. S. G. Hanna, *Environ. Sci. Technol.* **16,** 195 (1982).
2. M. J. Orren and M. A. B. Pougnet, *Intern. J. Environ. Chem.*, submitted.
3. J. C. Mills and C. B. Belcher, *Prog. Analyt. Atom. Spectrosc.* **4,** 49 (1981).
4. R. Bock, *A Handbook of Decomposition Methods in Analytical Chemistry* (International Textbook Company, 1979), 58.
5. M. A. B. Pougnet, M. J. Orren and L. Haraldsen, *Intern. J. Environ. Anal. Chem.*, in press.
6. E. S. Gladney, *Anal. Chim. Acta* **118,** 385 (1980).
7. J. W. Owens, E. S. Gladney and D. Knab, *Anal. Chim. Acta* **135,** 169 (1982).

8. M. P. Failey, D. L. Anderson, W. H. Zoller, G. E. Gordon and R. M. Lindstrom, *Anal. Chem.* **51,** 2209 (1979).
9. R. D. Smith, J. A. Campbell and K. K. Nielson, *Environ. Sci. Technol.* **13,** 553 (1979).
10. D. G. Coles, R. C. Ragaini, J. M. Ondov, G. L. Fisher, D. Silberman and B. A. Prentice, *Environ. Sci. Technol.* **13,** 455 (1979).
11. E. S. Gladney, L. E. Wanger, D. B. Curtis and E. T. Jurney, *Environ. Sci. Technol.* **12,** 1084 (1978).
12. R. A. Kruger, *Cooperative Scientific Programmes*, Council for Scientific and Industrial Research, PFA Steering Committee Meeting, August 1983 (unpublished).
13. J. A. Cox, G. L. Lundquist, A. Przyjazny and C. D. Schmulbach, *Environ. Sci. Technol.* **12,** 722 (1978).
14. E. B. Schalscha, F. T. Bingham, G. G. Galindo and H. P. Galvan, *Soil. Sci.* **116,** 70 (1973).
15. W. W. Choi and K. Y. Chen, *Environ. Sci. Technol.* **13,** 189 (1979).
16. A. S. Halligan and G. K. Pagenkopf, *Environ. Sci. Technol.* **14,** 995 (1980).
17. R. Keren and R. G. Gast, *Soil Sci. Soc. Am. J.* **45,** 478 (1981).
18. U. Mezuman and R. Keren, *Soil Sci. Am. J.* **45,** 722 (1981).
19. G. K. Pagenkoft and J. M. Conolly, *Environ. Sci. Technol.* **16,** 609 (1982).
20. F. Culkin. *The Major Constituents of Sea Water, Chemical Oceanography* (Riley, 1965) Volume 1.