

This article was downloaded by:

On: 18 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713640455>

The Boron and Lithium Content of South African Coals and Coal Ashes

M. A. B. Pougnet^a; J. M. Wyrley-birch^a; M. J. Orren^{ab}

^a Department of Analytical Science, University of Cape Town, Rondebosch, Republic of South Africa ^b

Department of Oceanography, University College, Galway, Ireland

To cite this Article Pougnet, M. A. B. , Wyrley-birch, J. M. and Orren, M. J.(1990) 'The Boron and Lithium Content of South African Coals and Coal Ashes', International Journal of Environmental Analytical Chemistry, 38: 4, 539 – 549

To link to this Article: DOI: 10.1080/03067319008026956

URL: <http://dx.doi.org/10.1080/03067319008026956>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

THE BORON AND LITHIUM CONTENT OF SOUTH AFRICAN COALS AND COAL ASHES

M. A. B. POUGET, J. M. WYRLEY-BIRCH and M. J. ORREN*

Department of Analytical Science, University of Cape Town, Rondebosch 7700, Republic of South Africa

(Received 12 December 1988; in final form 10 March 1989)

Boron and lithium were determined in over a hundred coals and power station ashes by inductively coupled plasma atomic emission spectroscopy. The levels of boron in coals and fly ashes range from 15 to 83 $\mu\text{g.g}^{-1}$ and from 23 to 600 $\mu\text{g.g}^{-1}$, respectively, while lithium occurred at levels of between 45 and 81 $\mu\text{g.g}^{-1}$ in coals and 77 and 359 $\mu\text{g.g}^{-1}$ in fly ashes. Both elements were found to vary considerably between different coals and ashes produced. In most cases the boron concentration was found to increase systematically between the first and last precipitators where smaller particle size fractions are collected. The availability of boron from the leaching of fly ashes by water was investigated. Leachabilities were found to vary for ashes produced at different power stations.

KEY WORDS: Boron, lithium, South Africa, coal, coal ashes, leaching.

INTRODUCTION

A national programme of the Council for Scientific and Industrial Research (CSIR) investigates the economical utilization of fly ash for example, in road building, brick making, for soil beneficiation in agriculture and possible recovery of certain metals.¹ For a number of years, a few laboratories in South Africa have been actively involved in the characterization of local coals and ashes produced at the major power stations.

X-ray fluorescence spectrometry (XRF) has been the most routinely used technique for the determination of both the major and trace elements in coals and coal ashes.^{2,3} Earlier work^{4,5} showed that ICP-AES was particularly sensitive for some light elements namely boron, lithium and beryllium that cannot be determined routinely by XRF or NAA.

One of the trace components in fly ash which is of special concern, is boron. While boron is an essential element for plant growth and development, when present and available above 5 ppm in various soils, toxicity may occur.^{6,7} Given the high concentrations of boron in some South African fly ashes,⁸ it is important to study further the occurrence of this element and its availability by leaching with water. This is particularly relevant to the evaluation studies of fly ashes to be used for soil beneficiation. In a preliminary study,⁸ the water leaching of boron from power station fly ashes was studied. It was shown that the release of boron was dependent upon contact time and ratio of ash to leachate water.

*Present address: Department of Oceanography, University College, Galway, Ireland.

Generally very little information is available on the levels of lithium in environmental materials. This is probably due to the fact that this element is classified as non-essential. The lithium content of plants has been reported to be in the range $0.1\text{--}0.3\ \mu\text{g.g}^{-1}$ and in soils between 8 and $40\ \mu\text{g.g}^{-1}$. In two recent investigations, a close correlation between the lithium content of plants and the levels in the soils was found,¹⁰ while crop responses to lithium were recorded.¹¹

Since South African fly ashes have been found to contain lithium at considerable levels, it is of interest to study the distributions of this element in the different coals and power station ashes. In this paper we report on the levels of boron and lithium in South African coals and power station ashes.

EXPERIMENTAL

Instrumentation

The samples were analysed with an IL plasma-200 ICP spectrometer fitted with two scanning monochromators, the standard air path and a vacuum one. This instrument has been described previously.⁵

Sample Preparation and ICP-AES Analyses

Coal and bottom ash samples were crushed and ground to fine powders (-300 mesh) in a Siebtechnik swing mill. Fly ash samples were used as received. All samples were dried in an oven at 110°C overnight.

Samples for boron determinations were prepared as follows: To about 0.5 g dry powders in polypropylene flasks, 5 ml concentrated HNO_3 (Aristar, BDH) 10 ml water and 10 ml 40% HF (Aristar, BDH) were accurately added. The flasks were sealed and shaken gently in a water bath kept at 70°C for about 15 h. After cooling, 23 ml of water and 2 ml of 1% Triton X-100 (BDH) were added and the flasks shaken for a few minutes. Residues present were filtered off before analysis. The development and applications of this method have been described previously.^{5,8}

For lithium determinations, coals and ashes were dissolved in Parr acid digestion bombs (catalogue No. 4745). About 0.05 g sample aliquots were heated with 2 ml concentrated HNO_3 and 3 ml 48% HF at 130°C for 4 hours. After cooling, the samples were quantitatively transferred with 25 ml saturated boric acid solution into 50 ml polypropylene flasks containing 2 ml of 1% Triton X-100 for dilution with water. These solutions were also used for the determination of major and other trace elements. The method development and instrumental parameters have been described previously.⁴

All samples were prepared and analysed in duplicate.

Leaching of Boron

1 g fly ash samples (as collected from the precipitators) were shaken with 100 ml of

water (from a Milli-Q-system, Millipore Corp.) in 250 ml polypropylene flasks on a flat bed shaker (Labotec (Pty)) for 20 h. The slurries were then immediately filtered into 50 ml volumetric flasks which contained 1 ml of 1% Triton X-100 solution and 1 ml of concentrated HNO₃. The pH of the solutions were also measured after filtration.

Coal and Ash Samples

One hundred and ten samples were collected from 11 major South African power stations. Abbreviations used in the figures and tables are as follows:

Power Stations:	ARN	Arnot
	CAM	Camden
	DUV	Duvha
	HEN	Hendrina
	KOM	Komati
	KRI	Kriel
	MAT	Matla
	TAA	Taaibos
	WIL	Wilge
	GRO	Grootvlei
	LET	Lethabo

Other abbreviations:

LH/RH	Left/Right hand precipitator
B	Boiler
BA	Bottom ash
F	Field
P	Precipitator
LHE/RHE	Left/Right hand economiser
LHF/RHF	Left/Right hand final precipitator

RESULTS AND DISCUSSION

Boron in Coals and Fly Ashes

Boron levels in coals vary between 15 and 83 $\mu\text{g.g}^{-1}$. A comparison between mean boron levels measured in coals used at various power stations appear in Figure 1. As can be seen from the figure, there is a large variation in the boron content of the different coals. Coals used at the Lethabo power station contain higher concentrations of boron than any other South African coals analysed so far. This power station has come into operation only recently and is designed to burn coals with very high ash contents.

Boron levels in fly ashes range from 23 to 600 $\mu\text{g.g}^{-1}$ and are summarized in Figure 2. Fly ashes from power stations Arnot, Duvha, Komati and Wilge contain lower levels of boron than those from the other power stations and this is clearly

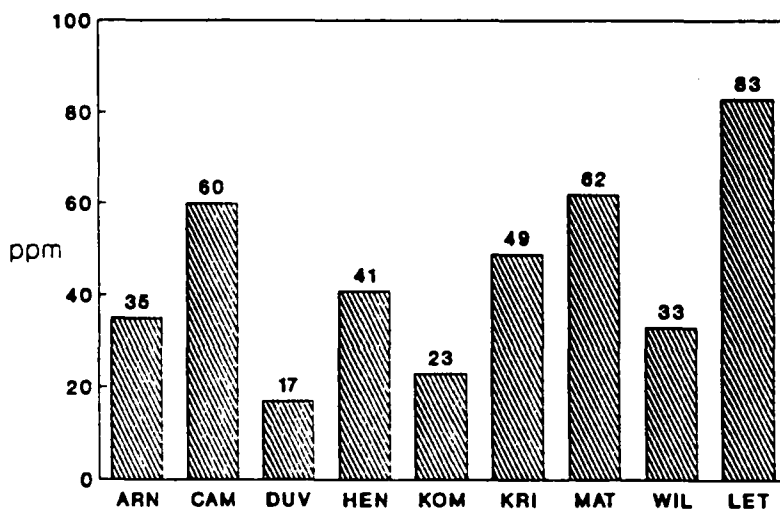


Figure 1 Boron in coals.

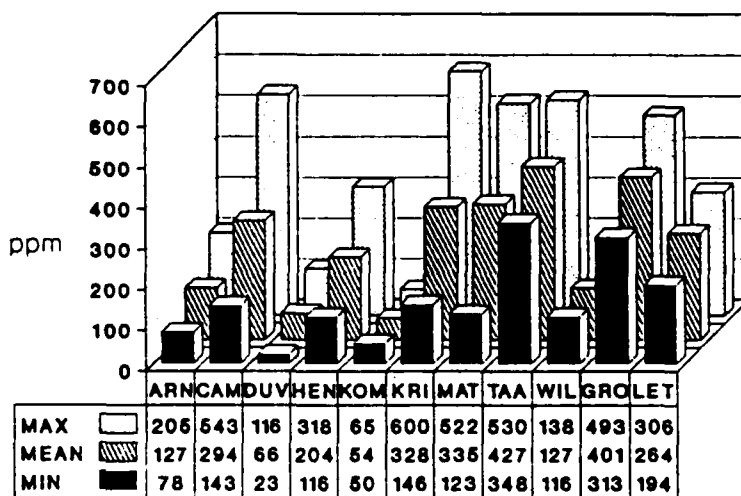
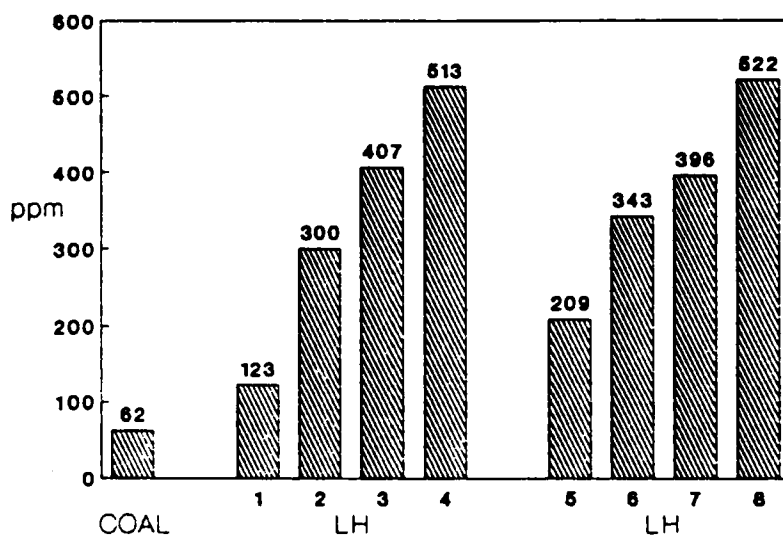


Figure 2 Boron in fly ashes.

related to the lower boron contents of the coals burnt at these power stations. Detailed results obtained for selected individual power stations appear in Table 1. These provide a comparison between firstly, the boron levels in the coals and in their respective ashes and secondly, boron levels in fly ashes collected from various precipitators at a power station (see also Table 2). The enrichment of boron in fly ashes from all the power stations can be clearly seen. Generally, ratios of boron in ash to boron in coal range from 1.4 to 12, with the highest values found for ashes collected in precipitators containing smaller particles. For most power stations, where fly ash samples were available for rows of precipitators (average particle size decreases with increasing precipitator number, e.g., RH1, RH2, RH3; P1, P2, P3) enrichment of boron in the smaller particles was found to occur (Figure 3).

Table 1 Boron in coals and fly ashes

Power Station	Boiler	Precipitator	Concentrations ($\mu\text{g.g}^{-1}$)	
			Coal	Fly ash
ARNOT	4	LH1	35	87
		LH2		205
		RH1		78
		RH2		138
DUVHA	1	LH1	17	23
		LH2		58
		LH3		94
		LH4		116
		RH1		26
		RH2		48
HENDRINA	5	F1	41	115
		F2		174
		F3		247
	6	F1	40	116
		F2		255
		F3		255
KRIEL	1	P1	43	146
		P2		213
		P3		325
	6	P1	54	173
		P2		342
		P3		496
		P4		600

**Figure 3** Boron in fly ashes from rows of precipitators showing the increase in concentration (Matla power station, boiler 1).

Only a few bottom ashes (slag) were analysed and generally the boron concentrations are lower than in the fly ashes produced from the same coals. For example, mean values ($\mu\text{g.g}^{-1}$) obtained for (i) Hendrina power station were coal 41, bottom ash 139, fly ash 204; (ii) Lethabo power station: coal 83, bottom ash 97, fly ash 264; (iii) Matla power station: coal 62, bottom ash 97, fly ash 335.

Water Leaching of Boron from Fly Ash

The experimental conditions (e.g. ash/water ratio and shaking time) were based on previous experience concerning the already mentioned dependence of the leaching characteristics on these parameters.

A total of 31 different ashes from 8 power stations were treated as previously described. All experiments were done in duplicate. The average deviation from the mean was 4% (for 31 samples) and 85% of the duplicate data yielded better than 5% deviation. The % boron leached (boron in solution/total boron \times 100) was calculated for each ash sample. Overall % boron leached ranged from 11 to 39. Detailed results for each power station appear in Table 2.

From the experiment several observations can be made. There does not appear to be any relationship between the total boron content of the fly ashes and the percentage boron leached, e.g., the % boron leached does not increase systematically with total boron content. It would appear that certain power stations' ashes have higher boron availability; for example, compare the percentage boron leached for the Hendrina, Taaibos and Grootvlei power stations to that of the Matla and Komati power stations where the mean percentage boron leached for these power stations is 33, 35.4, 29.7 and 16.5, 14, respectively.

The boron release from coal ash by leaching has been subject to many studies.^{7,12,13,14} Cox *et al.*¹² leached 0.5 g of fly ashes and one bottom ash with 200 ml of water by shaking for 2 h. The percentage boron leached was 34 and 45% for the fly ash samples and 0.1% for the bottom ash. James *et al.*⁷ used a similar ash to water ratio (0.25%) to study the release of boron from 19 ash samples from various power stations in the USA. Leachabilities in these ashes varied between 17 and 64% (mean: 43%) after 24 h shaking. In the present study, the ash/water ratios were four times higher than those used in the above studies. That factor may be responsible for the generally lower percentage boron leached measured in the South African samples. The effect of ash to water ratio on the availability of boron has been established^{8,13,14} but other factors such as pH, contact times and particle size of the ash will also determine the leachability. The pH of all leachate solutions were between 11 and 12. The very small variation in pH after leaching cannot therefore be expected to account for the variation in % boron leached from fly ashes produced at the different power stations.

It was found that the percentage boron leached is fairly constant for all the precipitators fed from the same boiler within a particular power station. Illustrative of this are the two power stations Kriel: mean value of 19.8 ± 0.7 for three precipitators P1, P2, P3 from boiler 1; Matla: 16.2 ± 2.3 for four precipitators from boiler 2 and 16.8 ± 1.4 for four precipitators from boiler 4. In a previous study⁸ it

Table 2 Leaching of boron from fly ashes

<i>Power station</i>	<i>Boiler</i>	<i>Precipitator</i>	<i>Total boron ($\mu\text{g.g}^{-1}$)</i>	<i>% Boron leached</i>
KOMATI	2	PFA	54	13.7
		PFA	52	17.7
		PFA	50	13.9
		PFA	65	11.0
MATLA	2	RH1	215	19.7
		RH2	347	15.5
		RH3	436	14.6
		RH4	473	15.2
	4	LH1	214	17.7
		LH2	422	16.6
		LH3	517	14.9
		LH4	488	17.9
KRIEL	1	P1	146	19.0
		P2	213	20.0
		P3	325	20.4
	6	P1	173	27.6
		P2	342	27.2
ARNOT	4	LH1	87	24.8
		LH2	205	21.6
DUVHA	1	LH1	23	20.1
		LH2	58	34.8
		LH3	94	28.8
GROOTVLEI		P1	313	30.5
		P2	398	27.4
		P3	493	31.3
TAAIBOS		P1	348	36.4
		P2	474	33.8
		P3	530	35.9
HENDRINA	5	F1	115	28.4
		F2	174	31.7
		F3	247	38.9

was found that the leachability varied in a row of four precipitators and was much lower in the two middle precipitators. We have found no suitable explanation for the discrepancy between the two results and this will be investigated further.

Lithium in Coals and Fly Ashes

Lithium levels in the coals analysed range from 45 to 81 $\mu\text{g.g}^{-1}$. Mean values for the different power stations coals are shown in Figure 4. Results for the corresponding fly ashes appear in Figure 5 and are between 77 and 359 $\mu\text{g.g}^{-1}$. As for boron, lithium concentrations in fly ashes are found to vary between power stations. Fly ashes generally contain between 1.5 and 5.2 times more lithium than the coals. Data for some power stations are shown in Table 3. Compared with boron, increasing lithium concentration with precipitator number is not as marked and for some power stations, no trends were obtained, for example Matla fly ashes from boiler 1.

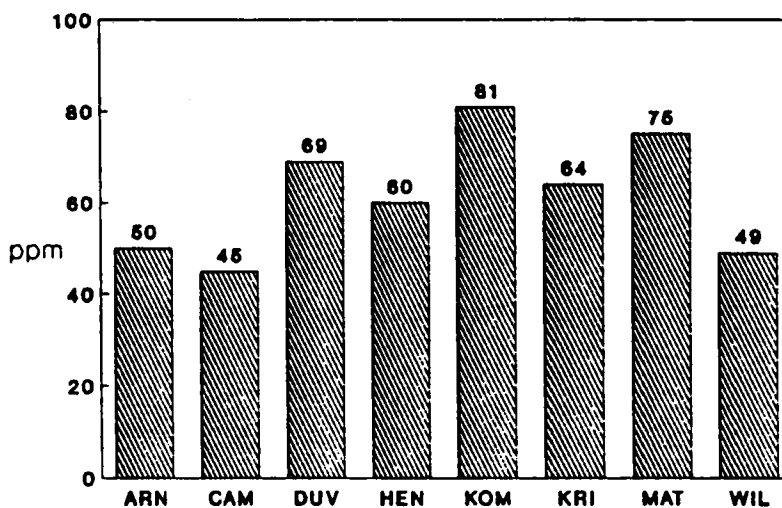


Figure 4 Lithium in coals.

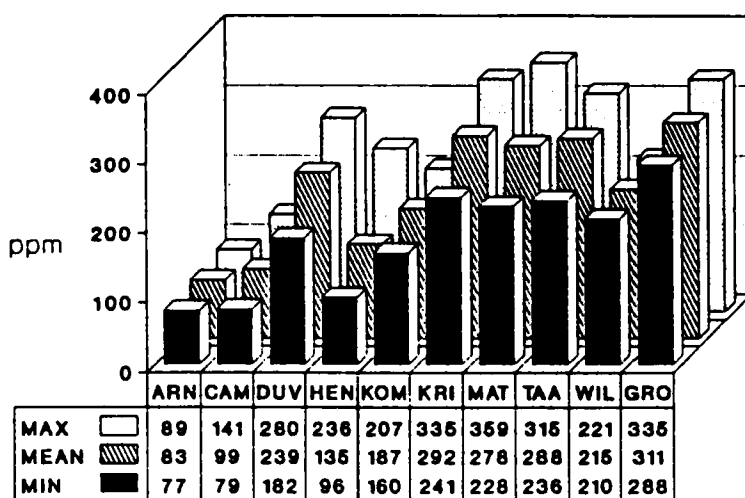


Figure 5 Lithium in fly ashes.

Very little data were available on the concentrations of boron and lithium in coals and ashes produced in other countries, for comparison with those from South African samples. In the case of lithium it would appear that no interest has been shown in measuring the levels of this element in coals and ashes. Some data on boron include Western Canadian coal ashes ($3\text{--}500\ \mu\text{g.g}^{-1}$)¹⁵ and in the USA between 172 and $1480\ \mu\text{g.g}^{-1}$ ⁷ and up to $1900\ \mu\text{g.g}^{-1}$ in Southern Illinois fly ash while in coal the concentration was $170\ \mu\text{g.g}^{-1}$.¹² Some USA fly ashes appear to contain more boron than South African samples. No definite conclusions, however, can be drawn from the limited data available.

Table 3 Lithium in coals and fly ashes

Power station	Boiler	Precipitator	Concentrations ($\mu\text{g}\cdot\text{g}^{-1}$)			
			Coal	Fly ash		
ARNOT	4	RH1	50	86		
		RH2		80		
		LH1		89		
		LH2		77		
CAMDEN	4	LH1	36	117		
		LH2		115		
		LHE		95		
		RHE		79		
	6	LHF	54	85		
		RHF		85		
		LH2		84		
		LH3		141		
		LHE		83		
		RHE		107		
DUVHA	1	LH1	69	182		
		LH2		256		
		LH3		250		
		LH4		270		
		RH1		197		
		RH2		236		
		RH3		280		
HENDRINA	5	F1	60	108		
		F2		103		
		F3		142		
	6	F1	59	96		
		F2		123		
		PFA		198		
KOMATI	2		81	198		
	6		92	207		
	7		74	180		
	8		76	160		
	9		74	190		
KRIEL	1	P1	64	318		
		P2		299		
		P3		306		
	6	P1	63	241		
		P2		247		
		P3		296		
		P4		335		
MATLA	1	LH1	83	359		
		LH2		259		
		LH3		228		
		LH4		255		
		RH1		329		
		RH2		290		
		RH3		280		
		RH4		287		
		2		RH1	265	265
				RH2		258
				RH3		313
				RH4		340
	4	LH1	249	249		
		LH2		252		
		LH3		333		
		LH4		346		

CONCLUSION

This study has provided vital information about the levels of boron and lithium in South African coals and ashes as well as their distribution in the various ash fractions within power stations. These data complement the comprehensive chemical characterization of South African coals and ashes. Other elements such as cadmium and beryllium are still under study and will be completed in the near future. Monitoring the concentration of all of these elements in both coals and power station ashes will continue since the levels are expected to change as different coals are mined and new power stations are commissioned. Such a case is the Lethabo power station whose ashes have not yet been fully characterized. From the limited data available, boron levels are higher than in other coals.

The variation in the amount of boron leached from ashes of different stations is related to the type of coal burnt and the combustion conditions. While the leaching procedure will have a strong influence on the amount of boron released, it is not possible to vary all the experimental parameters for every sample. It is however, felt that a "standard test" should be developed for checking the availability of this element from fly ashes and soil/fly ash mixtures that are used to study the uptake of elements by plants.^{16,17} While the uptake of boron as well as many other elements by crops grown on fly ash/soil mixtures is presently being investigated, lithium has not been included in the programme. In future work, lithium will be determined in the soil mixture and plants. Leaching experiments as for boron might also help understand the role played by this element on plants grown on fly ash amended soils.

Acknowledgements

We thank the Council for Scientific and Industrial Research for financial support and L J Barbour for the preparation of the figures. MABP thanks the University of Cape Town for the University Research Committee grant.

References

1. *Proceedings of International Symposium, Ash – A valuable Resource*, Pretoria 2–6 February, 1987, Vol. 1–4.
2. J. P. Willis, *Spec. Publ. Geol. Soc. S. Afr.* **7**, 129 (1983).
3. J. P. Willis and R. J. Hart, *J. Trace Microprobe Tech.* **3**(1 & 2), 109 (1985).
4. M. A. B. Pougnet, M. J. Orren and L. Haraldsen, *Intern. J. Environ. Anal. Chem.* **21**, 213 (1985).
5. M. A. B. Pougnet and M. J. Orren, *Intern. J. Environ. Anal. Chem.* **24**, 253 (1986).
6. B. E. Davies (ed.), *Applied Soil Trace Elements* (John Wiley and Sons, New York, 1980), Chap. 5, p. 169.
7. W. D. James, C. C. Graham, M. D. Glascock and A. G. Hanna, *Environ. Sci. Technol.* **16**, 195 (1982).
8. M. A. B. Pougnet and M. J. Orren, *Intern. J. Environ. Anal. Chem.* **24**, 267 (1986).
9. B. E. Davies (ed.) *Applied Soil Trace Elements* (John Wiley and Sons, New York, 1980), Chap. 11, pp. 414–415.
10. A. Regius-Mocsenyi, M. Anke and S. Szentmihalyi, *Acta Agrom. Hung.* **36**, 325 (1987).
11. B. A. Yagodin and G. A. Stupakova, *Agrokhimiya* **5**, 81 (1988).

12. J. A. Cox, G. L. Lundquist, A. Przyjazny and C. D. Schmulbach, *Environ. Sci. Technol.* **12** (6), 722 (1978).
13. G. K. Pagenkopf and J. M. Connolly, *Environ. Sci. Technol.* **16** (9), 609 (1982).
14. A. S. Halligan and G. K. Pagenkopf, *Environ. Sci. Technol.* **14** (8), 995, (1980).
15. B. I. Kronberg, J. R. Brown, W. S. Fyfe, M. Peirce and C. G. Winder, *Fuel* **68**, 59 (1981).
16. J. M. Wyrley-Birch, M. J. Orren and P. C. J. Maree, *Proceedings of International Symposium, Ash-A Valuable Resource*, Pretoria, 2-6 February (1987), Vol. 3.
17. P. C. J. Maree and J. M. Wyrley-Birch, *Proceedings of 7th International Congress on Soilless Culture*, Flevohof, Netherlands, 13-21 May (1988).