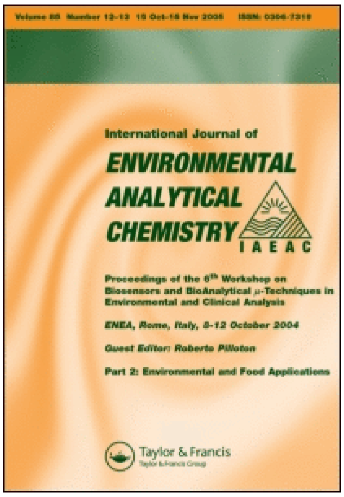

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Speciation of Aerosols by Combining Bulk Ion Chromatography and Thin-Window Electron Probe Micro Analysis

Kurt Eyckmans[a]; Johan De Hoog[a]; Ludo Van der Auwera[b]; René Van Grieken[a]
[a] Department of Chemistry, University of Antwerp, Antwerpen, Belgium [b] Royal Meteorological Institute, Brussels, Belgium

To cite this Article Eyckmans, Kurt , De Hoog, Johan , Van der Auwera, Ludo and Van Grieken, René(2003) 'Speciation of Aerosols by Combining Bulk Ion Chromatography and Thin-Window Electron Probe Micro Analysis', International Journal of Environmental Analytical Chemistry, 83: 9, 777 — 786

To link to this Article: DOI: 10.1080/0306731031000118934

URL: http://dx.doi.org/10.1080/0306731031000118934

Intern. J. Environ. Anal. Chem.
Vol. 83, No. 9, pp. 777–786, September 2003

Taylor & Francis
Taylor & Francis Group

SPECIATION OF AEROSOLS BY COMBINING BULK ION CHROMATOGRAPHY AND THIN-WINDOW ELECTRON PROBE MICRO ANALYSIS

KURT EYCKMANS[a], JOHAN DE HOOG[a],
LUDO VAN DER AUWERA[b] and RENÉ VAN GRIEKEN[a,*]

[a]*Department of Chemistry, University of Antwerp, Universiteitsplein 1, B-2610 Antwerpen, Belgium;*
[b]*Royal Meteorological Institute, Ringlaan 3, B-1180 Brussels, Belgium*

(Received 12 December 2002; in final form 3 March 2003)

Size-fractionated aerosol samples were collected at De Panne, a coastal village east of the French industrial area of Dunkerque. The samples were treated and analysed with conventional ion chromatography (IC) analysis and with the relatively new and promising thin-window electron probe microanalysis (EPMA) technique. The output data of the chromatographic bulk analysis technique were compared with the results from the individual particle analysis technique after statistical processing. Both methods give specific and complementary information concerning the aerosol composition. Statistically interpreted information on the single particle scale can give a more qualitative interpretation of the quantitative bulk analysis data. In fact, it becomes possible to define and quantify a certain compound as a constituent of different aerosol types. On the other hand, the quantitative data of the bulk analysis helps the interpretation, validation and quantification of the output from the single particle technique. Especially in the case of coagulated aerosols, the IC technique is able to define and to quantify irresolvable clusters.

Keywords: Ion chromatography; Thin-window EPMA; Aerosol; Atmospheric particles

INTRODUCTION

The most common technique for atmospheric aerosol analysis involves the collection of filter samples for subsequent bulk analysis [1]. However, no information is then obtained about the size distribution of the particles. Size-segregating impactor sampling may offer a broader insight concerning the sources, the transformation and the transportation of the aerosol particles. For this study, the airborne particulate phase was sampled with different impactors (May and Berner types) [2,3]. Compared to

---

*Corresponding author. E-mail: rene.vangrieken@ua.ac.be

ISSN 0306-7319 print: ISSN 1029-0397 online
DOI: 10.1080/0306731031000118934

bulk analysis, individual particle analysis can also provide more detailed information concerning the origin, formation, transport, reactivity, transformation reactions and environmental impact of particles, and it is therefore valuable as a complement to conventional bulk analysis [4–6]. However, quantification in single particle analysis is often difficult, because of uncertainties in the determination of the analytical interaction volume and because of the absence of suitable standards [7,8]. Also, a large number of particles needs to be analysed to ensure the statistical relevance of the measurements [5,9]. Over the years, much effort has been invested in automation and computerization of single particle analysis by, for example, electron probe microanalysis (EPMA). Also, the loss of particles, due to the operation of the microanalytical technique under vacuum, can now be avoided by working with a nitrogen-cooled sample holder. And, while the determination of light elements, such as carbon, nitrogen and oxygen, was earlier not possible when using conventional X-ray detectors with beryllium windows, nowadays many detectors are equipped with an ultra-thin polymer foil, offering the possibility to analyse these light elements also [10–16]. Thin-window EPMA (TW-EPMA) is a very promising analytical technique, providing some speciation information at the level of individual particles.

It would be very interesting to compare the results of a bulk analysis technique, such as ion chromatography (IC) with the statistically evaluated data for a large number of analysed single particles derived from a microanalysis technique like TW-EPMA.

IC analysis of the different samples offers quantitative results for different ionic compounds. But when evaluating and interpreting the results, it is not possible to draw any conclusion concerning the total composition with respect to speciation from single particle composition. It offers the possibility to quantify a certain cationic or anionic fraction, but, unfortunately, it is not possible to deduce which cationic fraction belongs to which anionic fraction in the individual particles, and certainly not in a quantitative way.

EXPERIMENTAL

Sampling Site

The sampling campaign was organized at Adinkerke (51°04′45″NW, 2°35′45″EL), De Panne, Belgium, 3 km from the French border and 2 km from the coast. The sampling point is positioned in a rural environment, east of the nearby Belgian nature reserve Westhoek and of the French industrial area of Dunkerque. Like the whole border region, the sampling point is frequently influenced by the industrial area owing to the prevailing west-southwesterly wind. Samples were taken on two different days (6/6/01 and 12/6/01), with almost identical meteorological conditions. The temperatures were comparable, between 9°C and 19°C. During these days, there was a westerly wind with an average wind speed of about 18 km/h and there was no precipitation during the sampling period. The air mass backward trajectory plots are presented in Fig. 1a, b. The air mass had a clearly marine origin with an obvious continental influence from over France for the 6 June sample and from over the UK and Ireland for the 12 June sample. The sampling was started each day in the morning at 9.00 h and was terminated around 16.00 h.

FIGURE 1 Air-mass backward trajectories for the campaigns on: a, 6 June; b, 12 June.

Sampling and Measurement Methods

For the bulk analysis with IC, the air was sampled with a May impactor (cut-off for the different stages: 0.25, 0.5, 1, 2, 4, 8 and 20 µm). Every stage consists of a glass support, covered with a Nuclepore filter as a collection substrate. The airflow is limited by the impactor to 20 Lpm, resulting in a collection of 28.8 m^3 per day. After sampling, the Nuclepore filter was removed from the glass plate, subsequently immersed in 3 mL of Milli-Q water and treated ultrasonically for 10 min [17]. After filtering by a Millex 0.22 µm filter the solution was ready for IC analysis (Dionex, DX 120, equipped with an AS 14 anion and a CS 12 cation column).

Sampling for the single particle analysis with TW-EPMA was done with a Berner impactor using stages 3–9, which have cut-offs of 0.25, 0.5, 1, 2, 4, 8 and 16 µm, respectively. The impaction substrates used were silicon for stages 3 and 4 and a polished silver foil for Stages 5 to 8. Three different sets were sampled per day, with a sampling duration of 2 min for Stage 3, 10 min for Stage 4, 45 min for Stage 5, 90 min for Stage 6, and 150 min each for Stages 7 and 8. Afterwards, the samples were analysed with a JEOL 733-JXA electron microprobe, equipped with an Oxford Link Pentafet EDS thin-window detector and a liquid nitrogen cooling stage to prevent evaporation of volatile particles. The optimization of the applied sample preparation and analysis techniques are described elsewhere [12,15]. For Stages 3 and 4, 100 particles were analysed manually, while for the large-size stages, 150 particles were analysed automatically. After analysis, the different spectra for the particles on each stage of both samples were statistically interpreted using IDAS software for hierarchical clustering [18]. The data interpretation provides, for both samples and for each stage, an insight into the presence of the different particle types and their abundance in the sampled aerosol.

RESULTS AND DISCUSSION

Bulk Analysis Results

When comparing the results of the IC analysis shown in Figs 2a and 3a, one could conclude that the concentration profiles are quite similar for both samples. The highest concentrations were collected in the smallest size fraction, with much lower and

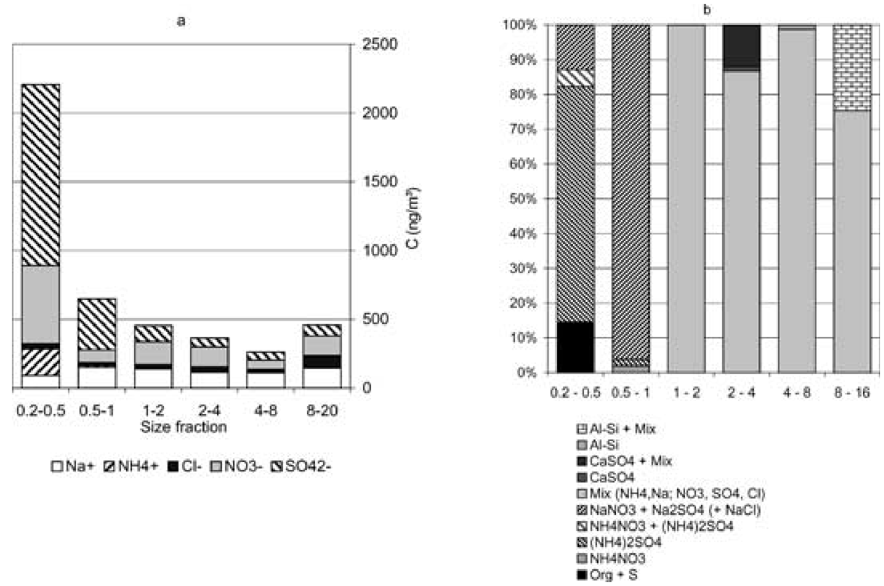

FIGURE 2 Results of the June 6 samples: a, IC; b, TW-EPMA.

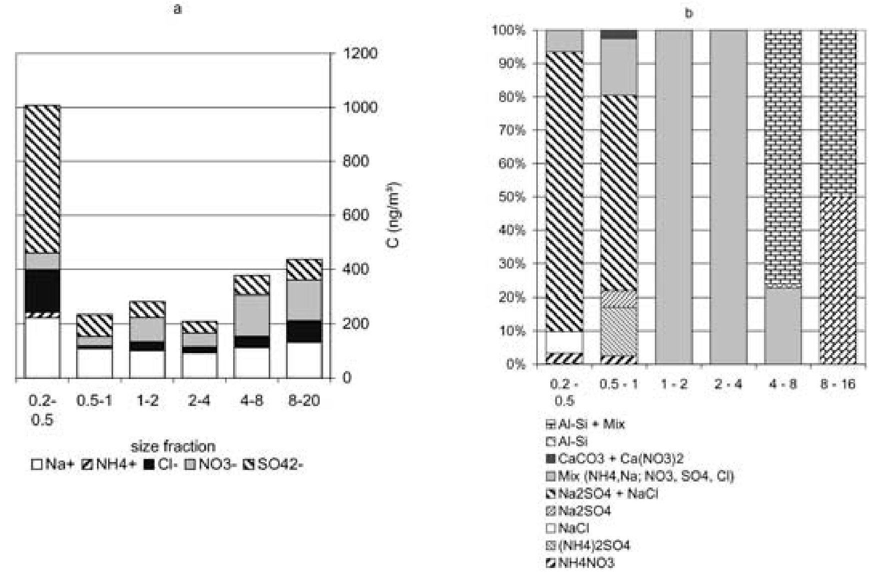

FIGURE 3 Results of the 12 June samples: a, IC; b, TW-EPMA.

comparable concentrations for the remaining size fractions. Sulphate is the dominating ion for the smallest aerosols. For particles larger than 1 μm, nitrate and sodium compounds are the most important fractions. Except for the smallest size fraction, the chloride concentration increases with the particle size, especially on 12 June.

For the smallest particles of the 6 June sample, it could be concluded that a large amount of sodium or ammonium sulphate is present, but it is very difficult, or even impossible, to define the other particle compositions. The ammonium fraction could originate from ammonium sulphate, ammonium nitrate, ammonium chloride or from a mixture of these compounds. Similar uncertainties exist on the origin of the nitrate fraction. This fraction could be coming from sodium nitrate particles, or from ammonium nitrate particles, etc. For the stage with particles between 1 and 0.5 µm, it is also impossible to conclude which components originate from which particles. In the larger size fractions, a mixture with high nitrate and sodium concentrations suggests a large sodium nitrate fraction. The higher sodium and chloride concentrations for the largest size fractions indicate the growing influence of coarse sea-salt particles.

Comparable limited conclusions can be drawn from the 12 June sample. The high sulphate concentrations for the smallest size fraction probably originate from sodium sulphate. The high chloride fraction is probably an indication of some primary sea-salt. For the larger particles, there is again a higher nitrate and sodium concentration for the sizes between 1 and 8 µm and an increasing importance of the sea-salt particles in the largest size fractions.

Single Particle Analysis Results

Figures 2b and 3b show the results of the data interpretation after hierarchical clustering on the single particle analysis by TW-EPMA by way of two stacked-bar graphs. To discuss the results in more detail, the same data are also given in Tables I and II, which show the different particle types (clusters) and their abundance for each impactor stage.

On the stages with the smallest particles in the 6 June sample, typical clusters for fine particles can be found (organic compounds, ammonium nitrate and sulphate, sodium nitrate and sulphate). On the stages with larger particles, aluminosilicates (Al-Si) and calcium sulphate are more abundant. Importantly on Stages 5–8, mostly irresolvable clusters ("Mix") were found, i.e., they could not be split up into different, smaller clusters. These clusters consist of a mixture of elements (N, O, Na, S and Cl), making it impossible to determine exactly which compounds are present. These elements could suggest the presence of unquantified mixtures of ammonium nitrates or sulphates, sodium nitrates or sulphates, and sodium chloride. Statistical classification of the analysed particles could not resolve these mixtures, which might be an indication that the particles in these statistical clusters are indeed clusters of chemical compounds in the atmosphere. Atmospheric particles react with each other or with gases to form new compounds, resulting in internally mixed particles, e.g., sodium chloride particles might be transformed to mixed particles consisting of sodium chloride, nitrate and sulphate. It should also be noted that the X-ray spectra of almost all analysed particles contained a small carbon peak, suggesting that some soot or organic compounds might be present in small quantities (maybe as adsorbed layers on the outside of the particle). In Stages 3 and 4, clusters of ammonium, nitrate and sulphate compounds can be clearly identified, while mixed clusters are more abundant in the larger particle fractions (Stages 5–6). This tendency might be explained by the fact that very small particles are often generated by primary reactions between gases, e.g., ammonium nitrate and sulphate. Larger particles are mostly secondary particles, i.e., formed by secondary reactions of particles with other particles or gases. For example, chlorine was only detected in the mixed particles at the stages with particle sizes > 1 µm, probably due to the remaining chloride of reacted sea-salt aerosols. The mixed clusters might also be formed by coagulated aerosols, consisting of different smaller aerosols from different origins and with a different composition. For example, this might be confirmed by the

TABLE I Relative abundance of the different clusters (%) of the 6 June sample

Stage	*Size fraction* (μm)	*Analysis*										
		Organic + S	NH_4NO_3	$(NH_4)_2SO_4$	Na_2SO_4	$NH_4NO_3 + (NH_4)_2SO_4$	$NaNO_3 + Na_2SO_4$	*Mix* (NH_4, *Na*, NO_3, SO_4, *Cl*)	$CaSO_4$	$CaSO_4$ + *Mix*	*Al-Si*	*Al-Si + Mix*
3	0.2–0.5	14.5	–	67.7	–	4.8	12.9	–	–	–	–	–
4	0.5–1	–	1.64	1.64	13.1	–	83.6	–	–	–	–	–
5	1–2	–	–	–	–	–	–	100.0	–	–	–	–
6	2–4	–	–	–	–	–	–	86.6	1.33	12.0	–	–
7	4–8	–	–	–	–	–	–	98.7	–	–	1.33	–
8	8–16	–	–	–	–	–	–	75.3	–	–	–	24.7

TABLE II Relative abundance of the different clusters (%) of the 12 June sample

Stage	*Size fraction* (μm)	*Analysis*								
		NH_4NO_3	$(NH_4)_2SO_4$	*NaCl*	Na_2SO_4	Na_2SO_4+NaCl	*Mix* (NH_4, *Na*, NO_3, SO_4, *Cl*)	$CaCO_3+Ca(NO_3)_2$	*Al-Si*	*Al-Si* + *Mix*
3	0.2–0.5	3.28	–	6.56	–	83.6	6.56	–	–	–
4	0.5–1	2.44	14.6	–	4.82	58.5	17.1	2.44	–	–
5	1–2	–	–	–	–	–	100.0	–	–	–
6	2–4	–	–	–	–	–	100.0	–	–	–
7	4–8	–	–	–	–	–	22.7	–	1.33	76.0
8	8–16	–	–	–	–	–	–	–	50.0	50.0

presence of an irresolvable mixed cluster of aluminosilicates, coming from soil dust, with a mix similar to the mixtures found on the other stages.

For the sample from June 12, the same conclusions can be drawn. In Table II, we can see clear clusters of ammonium, nitrate and sulphate particles; however, the presence of nitrate and ammonium compounds in the smallest size fraction is less pronounced. A higher concentration of nitrate and sodium compounds can be found for the particles between 1 and 8 µm. Again, a very important fraction could only be defined as a mix, with limited qualitative and quantitative information for those particle sizes as a result. The only additional information could be found in the fact that the abundance of chlorine in the mixtures increased with increasing particle size. This again confirms that the mixture might partly originate from reacted sea-salt particles, with a higher chlorine content for the largest sea-salt particles.

Combining Bulk and Single Particle Results

The results for both analytical techniques were combined in an attempt to obtain additional information, which could not be obtained with only one of the two methods. For comparison and evaluation of the different outputs, the relative abundances of the determined species (ions or particle types) are shown in Tables III and IV. In our attempt to link the results of IC and TW-EPMA, we paid special attention to the following questions.

- Are the results obtained for the different analytical techniques indeed comparable?
- What kind of qualitative information could TW-EPMA add to the quantitative IC bulk analysis method?
- Would it be possible to calculate atmospheric concentrations (in µg/m^3) for the semi-quantitative TW-EPMA output (in percentage for each particle type), by using the ion concentrations of the IC bulk technique?

TABLE III Comparison of the relative abundance (%) of the different compounds per stage for both analysis methods (6 June sample)

Size fraction (µm)	*IC*					*TW-EPMA*		
	Na^+	NH_4^+	Cl^-	NO_3^-	SO_4^{2-}	*mix*	$CaSO_4$ + *mix*	*Al-Si* + *mix*
1–2	31	1	5	37	26	100	0	0
2–4	32	1	10	40	18	87	12	0
4–8	43	1	8	26	22	90	0	0
8–16	32	1	19	31	17	75	0	25

TABLE IV Comparison of the relative abundance (%) of the different compounds per stage for both analysis methods (12 June sample)

Size fraction (µm)	*IC*					*TW-EPMA*	
	Na^+	NH_4^+	Cl^-	NO_3^-	SO_4^{2-}	*mix*	*Al-Si*+ *mix*
1–2	35	1	10	32	20	100	0
2–4	44	1	9	25	20	100	0
4–8	30	1	10	40	19	23	76
8–16	30	1	17	34	18	0	50

For the 6 June sample, the relative amounts for all the stages are very similar for the different techniques, with high ammonium and sulphate concentrations in the smallest stage, high sodium and sulphate concentrations in Stage 4 and important amounts of sulphate, nitrate, sodium and chloride for the remaining stages.

For Stage 3 (0.2–0.5 µm), the large amount of sulphate in the IC results (1.3 µg/m^3) seems to originate from ammonium sulphate aerosols and to a lesser extent from sodium sulphate (fraction of the mixed clusters in the TW-EPMA results, see Table I). This also implies that the ammonium fraction originates from the ammonium sulphate, and that the nitrate fraction originates from the sodium nitrate particles. The sulphate fraction of Stage 4 (0.5–1 µm) could almost exclusively be linked to the sodium sulphate fraction (small ammonium sulphate cluster, 1.64%). The rest of the sodium comes from sodium nitrate and sodium chloride. A qualitative interpretation of the IC results for the larger size fractions is not possible, because they are dominated by the mixed clusters for the TW-EPMA analysis.

However, using the IC results, it is possible to determine the qualitative and quantitative composition of the indefinable TW-EPMA mixtures. The 100% and 99% mix for Stages 5 and 7, respectively, can directly be quantified out of the IC output (see Table III). For Stages 6 and 8, there is an 87% and 75% mix, respectively, combined with a second cluster which contains also a part of the mix itself. In the case of Stage 6 there is an uncertainty concerning the quantification since the calcium sulphate interferes with the mix composition (mix also contains sulphate). For Stage 8, however, the aluminosilicate (crustal dust) fraction does not interfere and again we can quantify this stage to 100% (see Table III).

When we compare the results of the 12 June samples, we can deduce very similar relationships between the two techniques. The smallest particles (Stages 3 and 4) are mainly sodium sulphate particles. The rest of the size fractions show a mix of the various compounds, with a clear influence of soil dust in the largest fractions.

The smallest particle fraction on Stage 3 apparently consists mostly of a mixture of sodium sulphate and sodium chloride. The amount of sea-salt becomes less important on Stage 4, while the sodium sulphate fraction increases. Stages 5 and 6 again contain mixed particles, while the largest particles contain a large fraction of crustal dust (aluminium silicates).

The comparison between the two techniques again provides direct quantification of the mix on Stages 5 and 6 (see Table IV). For Stages 7 and 8, the soil-dust fraction is not expected to interfere with the mixture fraction, and thus it does not cause any problems for the quantification of the mix, also shown in Table IV.

CONCLUSIONS

When considering our three questions again, we can conclude that the application of the combination of both techniques is quite rewarding.

Both techniques give their own specific interpretation of the composition, but the results are unambiguous. Both techniques show the same trends for the particle compositions. The outputs of the bulk and individual particle analysis techniques are very complementary. Both techniques show different types of analytical results and, therefore, the interpretation of these results is done on a different level for each method. This might seem a limitation for the two techniques separately, but it could be turned into an advantage when both methods are combined. Owing to their different approaches, we have been able to make a more detailed interpretation of the aerosols in the air mass.

Combining the IC results with the TW-EPMA output, we were able to determine which inorganic compounds were present in the most important size fractions, for which IC only provided quantitative ion concentrations.

Before the interpretation of TW-EPMA with the IC output, some irresolvable, undefined clusters could only be seen as a mixture of different compounds. In the present case, the TW-EPMA technique was very limited in offering adequate information, but the combination with the IC data made it possible to quantify these mixed clusters.

Using IC and TW-EPMA, one gains clearer insights into the contribution of the different aerosol fractions. In the near future, it will be possible to give more precise information about the air mass history (marine and continental), a better definition of the pollution sources (speciation) and a better insight into the different atmospheric interactions of the pollutants (primary, secondary or coagulated particles). The combination of both methods could be most helpful in the study of processes such as sea-salt ageing, for example.

Acknowledgements

This work was partially prepared in the framework of the programme Sustainable Management of the North Sea, supported by the Belgian State – Prime Minister's Service – Services for Scientific, Technical and Cultural Affairs (contract MN/DD/10), of the Interreg II project AEROSOL, supported by the European Union, The Flemish Government and the province of West Flanders (contract NF2.2.1), and of a project by the Flemish National Science Foundation.

References

[1] W.C. Hinds, *Aerosol Technology: Properties, Behavior and Measurement of Airborne Particles*. John Wiley and Sons, New York (1982).
[2] K.R. May, *J. Aerosol Sci.*, **6**, 413–427 (1975).
[3] A. Berner, C. Lurzer, F. Pohl, O. Preining and P. Wagner, *Sci. Total Environ.*, **13**, 245–261 (1979).
[4] W. Jambers, L. De Bock and R. Van Grieken, *Fresenius J. Anal. Chem.*, **355**, 521–527 (1996).
[5] L. De Bock, B. Treiger, L. Van der Auwera and R. Van Grieken, *Mikrochim. Acta*, **128**, 191–200 (1998).
[6] P.R. Buseck and M. Posfai, *Proc. Natl. Acad. Sci. USA.*, **96**, 3372–3379 (1999).
[7] R. Zeisler, *Fresenius J. Anal. Chem.*, **360**, 376–379 (1998).
[8] J.A. Small, In: R.E. Van Grieken and A.A. Markowicz (Eds.), *Handbook of X-Ray Spectrometry*, pp. 583–656. Marcel Dekker, New York (1993).
[9] D.A. Saucy, J.R. Anderson and P.R. Buseck, *J. Geophys. Res.*, **96**, 7407–7414 (1991).
[10] A. Laskin and J.P. Cowin, *Anal. Chem.*, **73**, 1023–1029 (2001).
[11] D.E. Newbury, *Scanning*, **22**, 345–351 (2000).
[12] J. Osan, I. Szaloki, C.-U. Ro and R. Van Grieken, *Mikrochim. Acta*, **132**, 349–355 (2000).
[13] L. Paoletti, M. Diociaiuti, B. De Berardis, S. Santucci, L. Lozzi and P. Picozzi, *Atmos. Environ.*, **33**, 3603–3611 (1999).
[14] C.-U. Ro, J. Osan, I. Szaloki, K.-Y. Ho, H. Kim and R. Van Grieken, *Environ. Sci. Tech.*, **34**, 3023–3030 (2000).
[15] I. Szalóki, J.A. Worobiec, J. de Hoog and R. Van Grieken, *X-ray Spectrom.*, **30**, 143–155 (2001).
[16] M. Posfai, J.R. Anderson and P. Buseck, *J. Geophys. Res.*, **100**, 23063–23074 (1995).
[17] K. Eyckmans, J. Zhang, J. de Hoog, P. Joos and R. Van Grieken, *Intern. J. Environ. Anal. Chem.*, **80**, 227–243 (2000).
[18] I. Bondarenko, B. Treiger, R. Van Grieken and P. Van Espen, *Spectrochimica Acta*, **51**, 441–456 (1996).