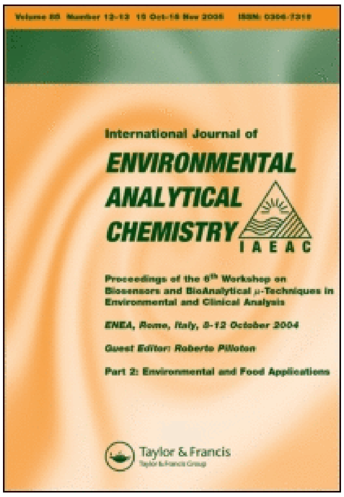

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Laser Microprobe Mass Analysis for Source Identification of Air Particulate Mattert

P. Surkyn[a]; J. De Waele[a]; F. Adams[a]
[a] Department of Chemistry, University of Antwerp (U.I.A.), Wilrijk, Belgium

To cite this Article Surkyn, P. , De Waele, J. and Adams, F.(1983) 'Laser Microprobe Mass Analysis for Source Identification of Air Particulate Mattert', International Journal of Environmental Analytical Chemistry, 13: 4, 257 — 274
To link to this Article: DOI: 10.1080/03067318308071598
URL: http://dx.doi.org/10.1080/03067318308071598

Intern. J. Environ. Anal. Chem., 1983, Vol. 13, pp. 257–274
0306-7319/83/1304-0257 $06.50/0

Printed in Great Britain

Laser Microprobe Mass Analysis for Source Identification of Air Particulate Matter†

P. SURKYN, J. DE WAELE and F. ADAMS
Department of Chemistry, University of Antwerp (U.I.A.), B-2610 Wilrijk, Belgium

Laser microprobe mass analysis with the LAMMA instrument as developed by Leybold–Heraeus, FRG is in principle an interesting new method whose applications lie in the following areas:

- qualitative and semiquantitative analysis for identifying and estimating both the matrix and trace-level constituents
- as a means of establishing a fingerprint to recognize sources of particulates
- as a means for detecting inorganic and organic molecular constituents.

A number of examples will be given to illustrate the advantages and the shortcomings of the methodology. They are selected in the following areas:

1) Source tracing of the constituents of unpolluted aerosols and estimating the extent to which long-range transport of pollutants from anthropogenic sources affect the results
2) Obtaining information on the inorganic composition of aerosol particles for the elucidation of sources of anomalous enrichment of trace elements in the unpolluted continental aerosols.
3) Identification of asbestos fibers in environmental samples and making a distinction between the mineralogical form from the characteristic mass spectrum.

KEY WORDS: Laser microprobe mass analysis, air particulates.

INTRODUCTION

A rapidly increasing number of publications illustrate the usefulness of laser microprobe mass analysis (LAMMA) in single particle analysis.[1–3] The primary advantage of the method in this application appears to lie in the areas of quick routine qualitative and semiquantita-

---

†Presented at the 12th Annual Symposium on the Analytical Chemistry of Pollutants, Amsterdam, April, 1982.

tive analysis of individual particles of micrometer size for minor and in some conditions trace level inorganic constituents.[4] At the same time there is evidence that using the technique as a variable ionisation source for mass spectrometry, information can be gained regarding the presence of molecular inorganic and organic species present in individual particles of microscopical size.

In this paper we want to report results which show that laser microprobe mass analysis can to some extent be used to quickly recognize individual particles in environmental samples and that in a number of cases, it can discriminate particles of different origin. Also, we will show that inorganic and organic constituents can be detected sensitively.

INSTRUMENTATION

The commercially available laser microprobe mass analyser (LAMMA-500, Leybold–Heraeus, Cologne, Germany) is exhaustibly described in the literature.[5,6] A frequency quadrupled Q-switched neodynium: YAG laser is focused onto the thin sample using an optical microscope with a magnification of 400 x or 1250 x. Particulate samples are held onto a Formvar film fixed to a standard copper electron microscope grid. These grids can be directly mounted for sampling into a Batelle cascade impactor.[7] Bulk samples are transferred to the grids by bringing the material in contact with the Formvar coated side.

Laser pulse energy on the sample can be varied with a set of optical filters. It is adjusted to provide either complete vaporisation of a particle of μm dimensions, or else to the lowest energy which allows recording of a mass spectrum. In the second case considerable amounts of molecular information can be derived. Organic impurities adsorbed onto the surface of the particles can sometimes be detetced at low laser irradiance.[8,9]

One of the major attractive features of LAMMA resides in the extreme speed with which particles can be analysed (1 ca every 10–15 seconds). A fast data acquisition and processing system is hence highly desirable. A Digital MINC laboratory computer is used with the instrument employed here. It is part of a laboratory automation network which is based on a VAX-VMS central computer.

EXPERIMENTAL

A number of merits and shortcomings of the LAMMA instrument in air pollution and air chemistry research will now be discussed. The topics selected include the study of aerosol particles in a remote environment and the feasibility of identification of asbestos particles (fibres).

Aerosol particles from the unpolluted atmosphere

Attempts to assess pollution transport, have indicated a need for established reference levels of aerosol composition in remote areas of the world. In order to understand long-range transport processes and to identify sources responsible for anomalous enrichment of trace elements, base-line measurements must be made in marine and continental regions. When selecting background monitoring stations, the question arises whether the site is affected by pollutants from anthropogenic sources. Also, there is a need to confirm whether at continental and marine sites, there is a significant influx from respectively sea derived or continentally generated particles. The anomalous enrichment of a number of elements in the remote atmosphere is well documented,[10] but hitherto there is, in general a lack of understanding of the sources involved in it.[11] Bulk analysis assisted by LAMMA could be instructive in answering a number of such questions.

Samples collected at several remote locations in the Southern Hemisphere were studied:

1) Chacaltaya Cosmic Physics Laboratory near La Paz (Bolivia). The laboratory is situated at 5,300 m altitude in the Eastern Cordillera. Particulate matter sampled at this location was analysed with several sensitive trace analytical techniques.[12,13] Results indicate seasonally fluctuating enrichment of a number of elements, and the absence of significant anthropogenic sources of particulates.[13]

2) Chapiquina hydropower Station, 150 km East of Arica, Chile, on the slope of the Western Cordillera. The site is separated from Arica and the Pacific Ocean by the Atacama desert, which is one of the dryest regions in the world, with virtually no precipitation year round. The site is only ca 400 km South-West from Chacaltaya but it may be affected by sources originating in the desert and in the salt lakes and salt flats on the Western altiplano.

3) Cape Grim Baseline Monitoring Station (Tasmania). With winds from West and South, particulates should reflect a purely marine aerosol, but long range transport from Australia may be the cause of a continentally derived component of variable importance during the year.

Chacaltaya

Samples of air particulate matter were obtained systematically for consecutive 14 day periods with a high-volume sampler, later with a cascade impactor, during several years starting from 1975. A limited number of samples obtained with the latter instrument were selected for investigation with LAMMA. Table I summarises elemental ratios in stages 6 (aerodynamic equivalent diameter (AED) 0.5 to 1 μm) and 5 (AED 1 to 2 μm) obtained with proton induced X-ray emission (PIXE) and energy-dispersive X-ray fluorescence analysis. The average concentration ratios for 34 samples collected over slightly more than one year are shown for comparison. Also, the concentration ratio in the earth crust as compiled by Mason[14] is shown.

TABLE I

Relative concentration to iron in stage 5 and 6 for a number of samples obtained in Chacaltaya

		Concentration ratio in sample					
Element	In crust	9	17	18	31	36	1–36[a]
Na	0.57	3.4	0.8	4.5	2.2	0.7	1.7 ± 0.9
		0.7	0.6	0.6	0.2	0.35	0.3 ± 0.15
K	0.52	1.3	0.62	0.98	7.9	0.62	1.55 ± 1.4
		0.52	0.57	0.57	0.83	0.57	0.62 ± 0.05
Ca	0.73	0.39	0.58	2.8	0.41	0.33	0.58 ± 0.58
		0.41	0.80	3.8	0.44	0.41	0.64 ± 0.58
S	5.2×10^{-3}						
		37	11.3	70	16.5	5.0	17 ±13
		3.1	3.6	6.4	0.7	2.1	2.0 ± .1.2
Pb	2.6×10^{-4}						
		0.22	0.28	1.65	0.18	0.23	0.28 ± 0.28
		0.057	0.067	0.22	0.049	0.047	0.067+0.042

[a] Arithmetic mean.

Systematic LAMMA-analyses of stage 6 of these samples were performed to investigate whether the method is able to supply evidence which might explain some of the data in Table I. A minimum of 50, and in some cases up to 100 randomly selected particles were analysed in the positive and the negative operation mode of the instrument.

Results confirm the prominence of soil-derived particles with a high concentration of Al, Si, Na, K, Ca and Fe, a variable concentration of Mg, Mn, S, Cu, Pb, Ba, and exceptionally Sb, Sn, Sr, Rb, Cs and P. Figure 1 shows three representative examples of the positive mass spectra obtained. The high abundance of this class of particles and the absence of abnormal enrichment of typical anthropogenically produced elements as e.g. Ni and V, which follows from bulk analysis,[13] indicates that they have a natural origin in wind blown dust.

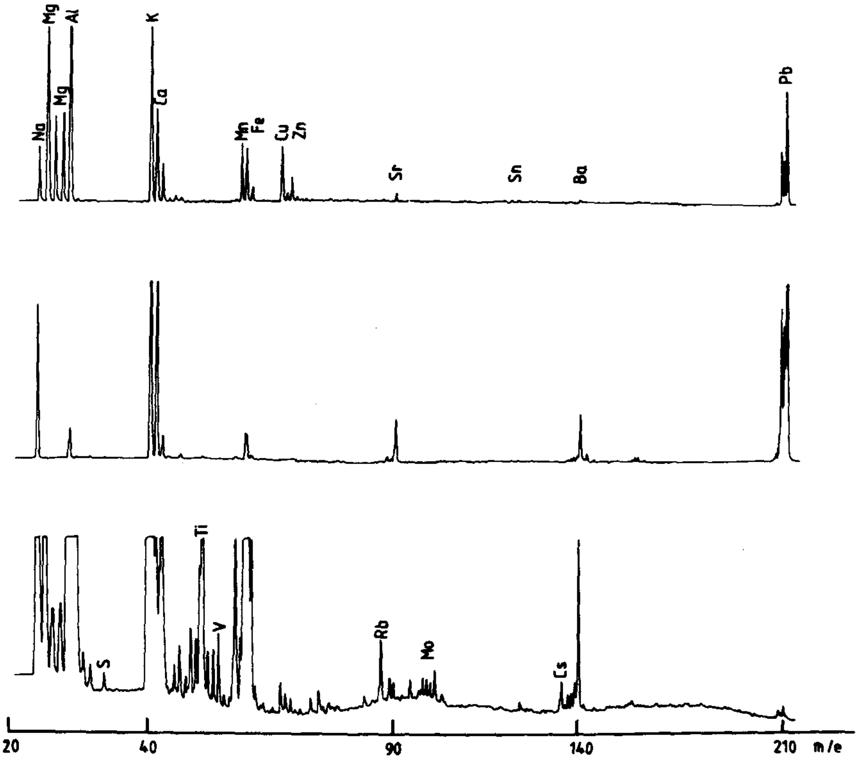

FIGURE 1 Positive mass spectra of dispersion produced particles from Chacaltaya.

A second major category are particles which contain a significant concentration of sulfate, as follows from the negative mass spectrum, Figure 2. It corresponds closely with the one obtained for $(NH_4)_2SO_4$ shown in Figure 3b. Positive mass spectra of these particles are consistently complexer than the fingerprint of $(NH_4)_2SO_4$ shown in Figure 3a. The presence of NH_4^+ follows from the characteristic peaks at $m/e = 17$ (NH_3^+) and 18 (NH_4^+).

The difference in the three positive spectra of sulfate containing particles in Figure 4 can be readily explained with the data in Table I: the spectrum in Figure 4c is a representative example of the particles present in sample 31, which has an exceptionally high K/Na concentration ratio. The other spectra are typical (Figure 4a) and more exceptional (Figure 4b) for sample 9, which contains considerably more Na than K.

A source for S and K in the continental South American fine particle aerosol has been observed previously,[16] and it was postulated that they

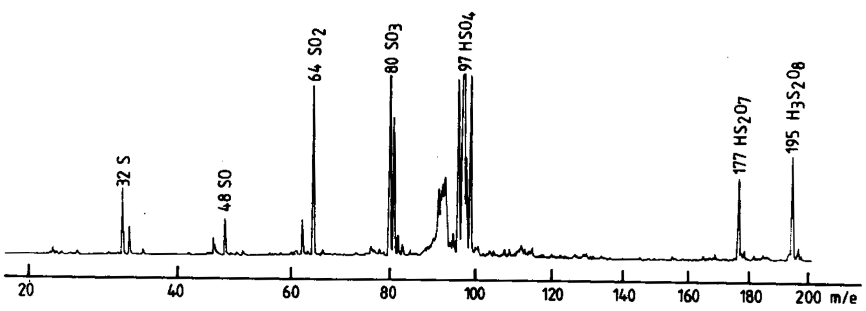

FIGURE 2 Negative mass spectrum of a typical sulfate particle.

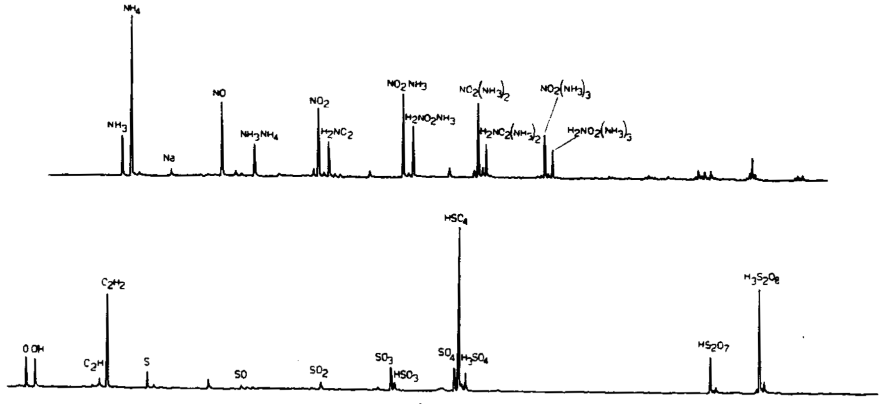

FIGURE 3 Positive (top) and negative (bottom) mass spectra of $(NH_4)_2SO_4$ crystals.

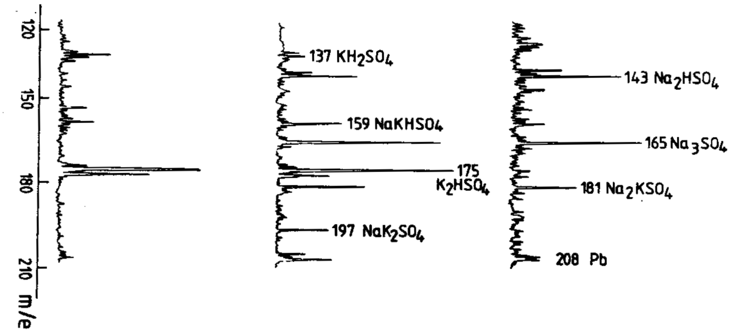

FIGURE 4 Part of the positive mass spectrum of sulfate particles in impactor stage 6. Top: typical fingerprint for sample 9; middle: less abundant fingerprint for sample 9; bottom: typical fingerprint for sample 31.

have a common origin involving gaseous precursors, possibly in forest burning activities. We then can expect carbonaceous particles in the samples which contain a high K-concentration in the small-size particle fractions. Indeed, LAMMA allowed the identification of carbon-rich particles with the typical C_n-fragmentation pattern. These C-particles also contain a high concentration of K. These particles were absent or quite uncommon in the other samples.

The relatively high concentration of Ca in sample 18 can readily be explained from the LAMMA spectra. It contains particles with a positive spectrum as shown in Figure 5. Ca is here associated with $SO_4^=$ (see e.g. the peaks at m/e = 137, 154, 193), which suggests that they are rich in $CaSO_4$. The enrichment of Ca persists in the large particles, which indicates that a common source for Ca and part of the $SO_4^=$ may be due

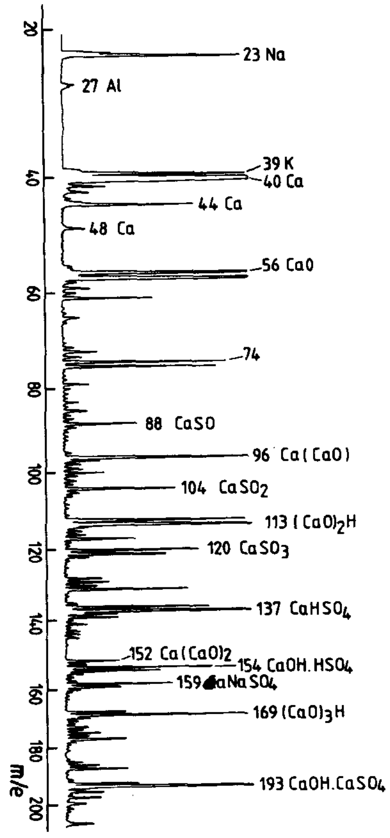

FIGURE 5 Positive fingerprint spectrum of Ca and $SO_4^=$ containing particle.

to soil derived gypsum or anhydrite from deposits in the region of sampling. However, the spectra are much more complex than the pure $CaSO_4$ fingerprint.

From the stoichiometry of $CaSO_4$ it follows that only part of the $SO_4^=$ can be due to this material. The earlier discussed condensation SO_4 aerosol is indeed abundantly present in the sample. Samples obtained in the Namib desert, which contains extensive outcrops of limestone and gypscrete ($CaSO_4$) also showed considerable enrichment of Ca[17]. Moreover, in that work direct evidence of $CaSO_4$ particles was obtained by scanning electron microscopy. Also, statistical treatment of the analyses indicates the presence of a Ca-containing aerosol component.[15] The molecular ions detected in the Ca-SO_4 and the Na/K-SO_4 particles are summarised in Figure 6 and 7 respectively.

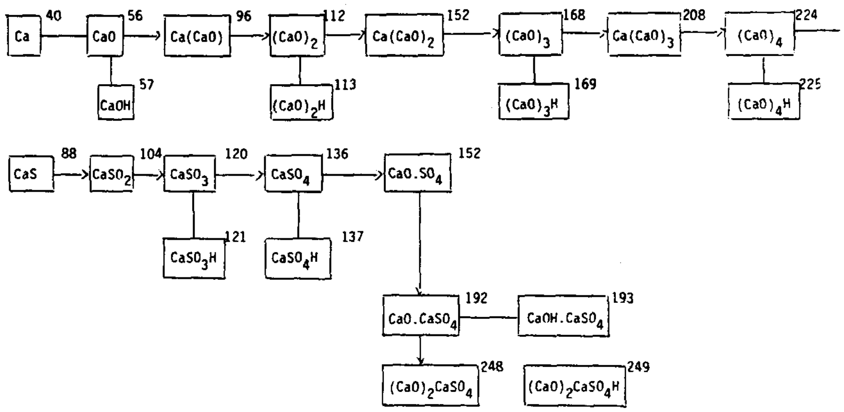

FIGURE 6 Molecular fragments commonly present in Ca and $SO_4^=$ containing particles.

The consistent presence of Pb in the spectra of the fine particulate sulfate suggests that the element has a gaseous precursor. Other atmospherically enriched elements (As, Cu, Zn,...) were not detected in the same particles probably as a result of inferior detection sensitivity.

No NaCl particles could be detected in the Chacaltaya aerosol, which indicates that the aerosol is not affected by any marine influence.

Chapiquina

Soil-derived particles obtained at this site are quite different from those obtained at Chacaltaya in minor element composition: Rb, Sr, and Ba

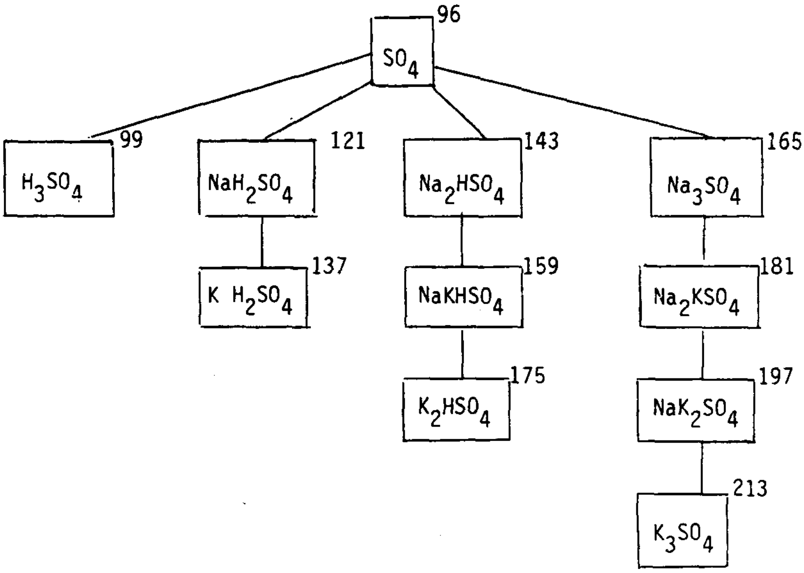

FIGURE 7 Molecular fragments detectable in sulfate particles.

containing particles are more abundant and exceptionally Zr, Ca and Ce can be detected. Sulfate containing particles are again abundant but they are systematically neutralised with *K* (as in Figure 4c). Lead is again detectable in nearly all the sulfate particles.

Sodium chloride particles can be clearly distinguished as a further component of the aerosol. The mass spectra contain the elemental ion mass of Na and molecular ions with the general composition $(Na_nCl_{n-1})^+$ in the positive spectra.[18] From the spectra it was not possible to trace their origin to sea spray derived material or material originating in salt lakes or salt flats.

The presence of a further Na-containing particulate component is clearly detected. Morphologically it is characterized by needle-like particles with the mass spectrum shown in Figure 8a and 9a. Comparison with the fingerprint of pure $NaNO_3$ (Figure 8b and 9b) gives sufficient evidence for their origin: $NaNO_3$ as wind blown dust from deposits of this material in the area. Both the NaCl and the $NaNO_3$ particles provide an explanation for the high enrichment of Na in the coarse particle fraction of the aerosol.

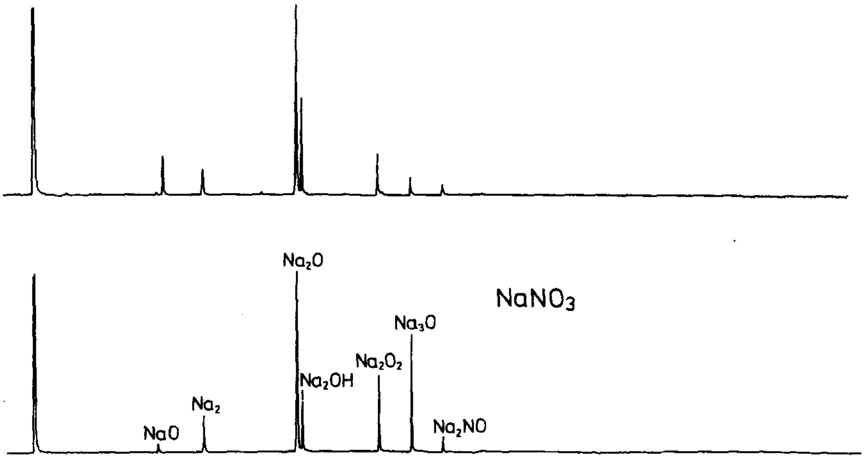

FIGURE 8 Positive mass spectrum of a typical particle from Chapiquina (top) and positive fingerprint mass spectrum of $NaNO_3$ crystals (bottom).

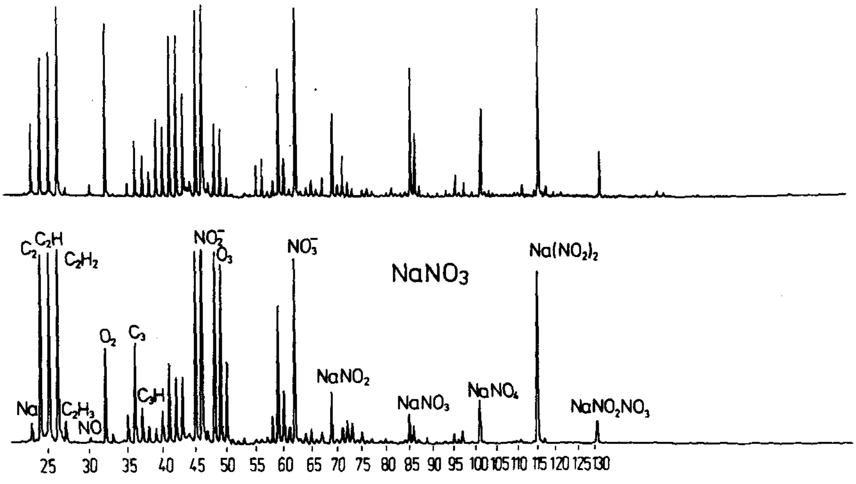

FIGURE 9 Negative mass spectrum of a typical particle from Chapiquina (top) and negative fingerprint mass spectrum of $NaNO_3$ particle.

Cape Grim

Mass spectra of individual particles are representative for 2 distinct types: sea-derived particles of NaCl and exceptionally crust-derived particles. The cubic NaCl-crystals are highly variable in composition as can be seen in typical examples, Figure 10. Morphologically, these particles can be easily distinguished from their appearance under microscopical observation for a number of them. However, sometimes irregularly shaped objects have a similar spectrum to the ones shown in Figure 10. The crustal component is less rich in calcium compared to the ones discussed earlier and elemental ions from Zn, Cu, Sn, Sb, La, Ce and Pb occur in the spectra (Figure 11). With the absence of any other continental land masses, they probably originate in the Australian continent at a distance of more than 500 km. It is not clear without further study whether they are affected by anthropogenic influences.

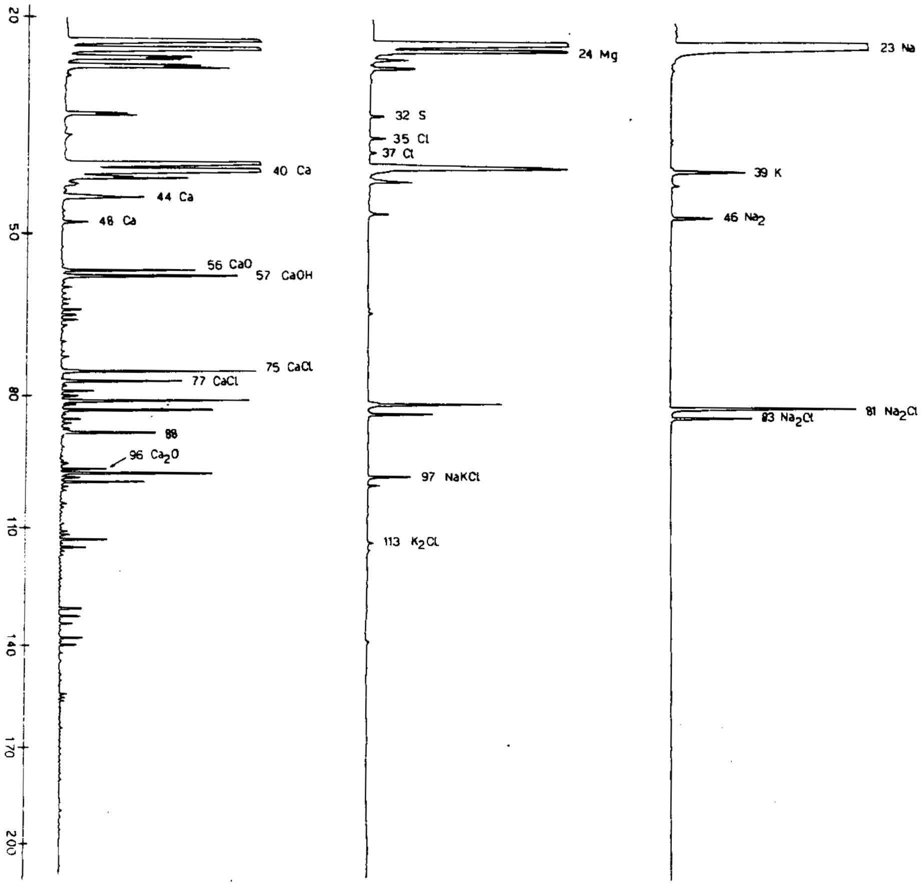

FIGURE 10 Positive mass spectra of sea spray produced particles from Cape Grim.

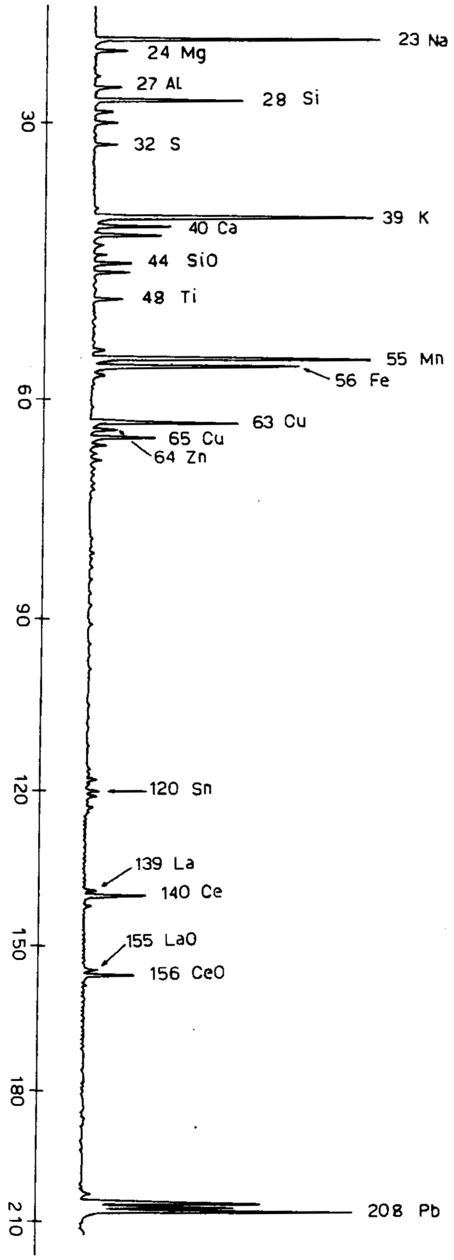

FIGURE 11 Positive mass spectrum of a continentally derived particle at Cape Grim.

Samples collected in a central location of the same island (Pencil Pine River) contain the same sea-derived particles, several hitherto unidentified components and also one needle-like particle, whose mass spectrum corresponds with asbestos, could be detected.

Analysis and characterization of asbestos fibres

On the list of potentially harmful pollutant species published by the Environmental Protection Agency, U.S.A.,[19] the only material without a recommended method of analysis is asbestos. Asbestos fibres are present in the respirable fraction of urban aerosols in concentrations above the ngm^{-3} level. They exist in much higher concentrations in or near factories which manufacture asbestos products, or near mining sites. The analysis is extremely difficult since the concentration is very low and the fibres are small. The only more or less successful approach is single particle quantitative X-ray analysis with the electron microscope in combination with morphological characterization and selected area electron diffraction.

Spurny *et al*[20] obtained LAMMA spectra and point to the possibility to differentiate between the serpentines and amphibole variety and between amosite and crocidolite. In what follows we report additional experiments which were intended to ascertain to what extent LAMMA is a useful substitute for electron microscopy to recognize asbestos fibres in environmental samples.

Recognizing and characterizing asbestos fibres must necessarily rely on the morphological information as obtained with the optical microscope assisted with the chemical information derived from the mass spectra. The average relative concentration of 5 UICC (International Union against Cancer) asbestos standards is shown in Figure 12. The reproducibility of the analysis of individual fibres is also presented in these graphs. They reflect the intrinsic variability of the LAMMA-method and the inhomogeneity of the samples. Indeed, neither of these standards can be considered homogeneous on the single fiber level and of the order of 10 mg is necessary as a representative sample. One standard, the Canadian Chrysotile, is a pooled mixture of material from 8 different mines roughly in proportion to their annual production.[21]

Taking into account that the UICC standards covers about 98% of the commercially used asbestos,[22] it is tempting to conclude from Figure 12 that LAMMA is a suitable alternative to the electron microscope for microchemical characterization of asbestos fibers even distinguishing between the different varieties. The following comments can be made however:

1) The resolution of the optical microscope is marginally adequate

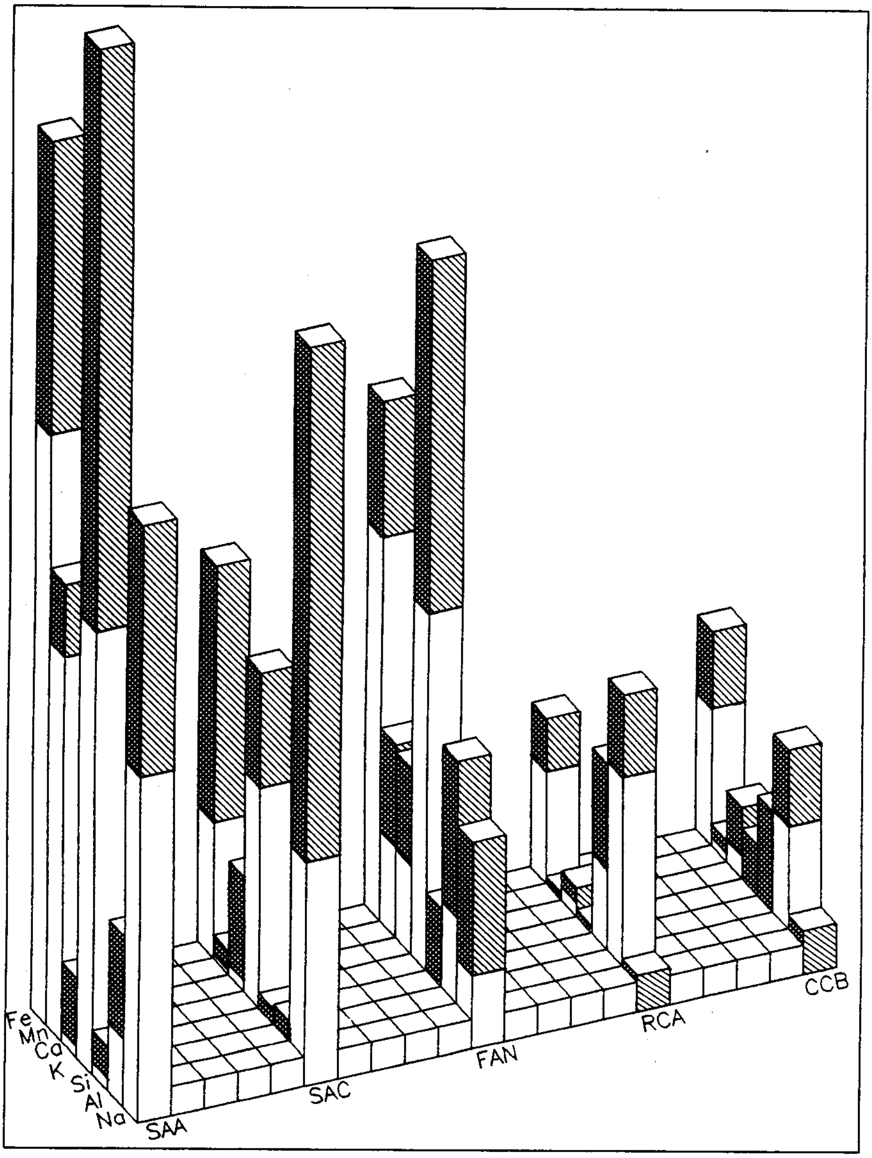

FIGURE 12 Relative intensity to ^{24}Mg of a number of constituents in UICC asbestos. SAA and SAC: South African amosite and crocidolite; RCA and CCB: Rhodesian and Canadian chrysotile; FAN: Finnish anthrophyllite. One standard deviation is indicated for repeated analysis of different fibers.

except for the largest fibers. Only scanning transmission electron microscopy can recognize the smaller fibers.

2) Asbestos is used in over 3,000 fields of applications (about 70% in asbestos cement).[23] It is often transferred to products whose composition may drastically differ from that of the raw fibres.

3) Fibers from a given mineralogy can provide significantly different fingerprint mass spectra, as occurs e.g. for the two UICC chrysotile standard in Figure 12. An other example is shown in Figure 13 which

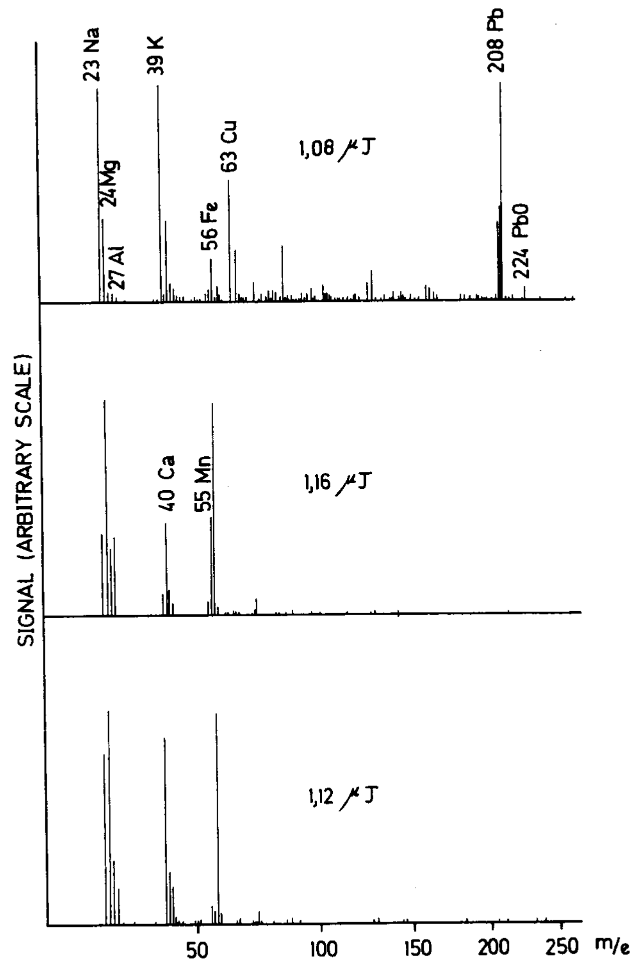

FIGURE 13 Three positive mass spectra of chrysotile asbestos from the Balangero mine in Italy.

shows spectra obtained from chrysotile asbestos fibers from the Balangero mine in Italy, which is the 10th largest asbestos mine, with a production of 165,000 tons year^{-1}.[23] Finally Figure 14 shows three positive spectra obtained from a fibrous Turkish zeolite (erionite). Though taken in rigorously the same instrumental conditions, especially a closely similar laser irradiance, the mass spectra differ considerably.

Despite all this there is a fair possibility that the method can be of advantage in asbestos pollution research. As an example, the needle-like particle present in the Pencil Pine River aerosol can be classified as a crocidolite fiber.

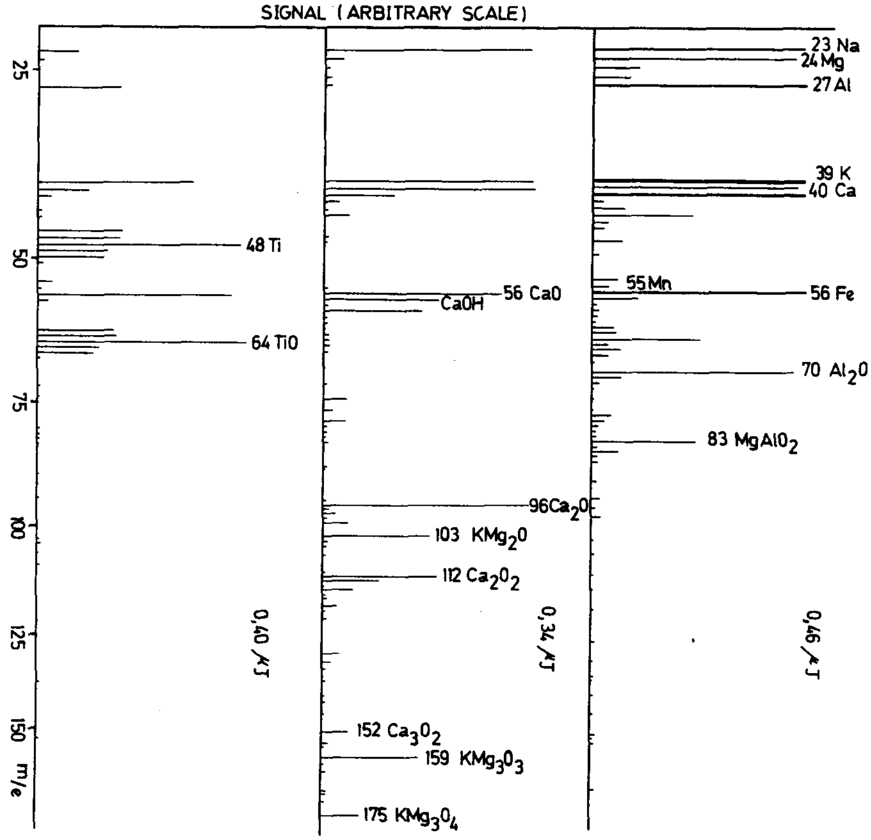

FIGURE 14 Three positive spectra of a fibrous zeolite (erionite) from Karain, Turkey.

DISCUSSION

Laser microprobe mass analysis allows a very quick analysis of air particulate matter. The method shows promise for source tracing purposes.[24] Specific components emitted in industrial processes can be easily recognized from the elemental composition as reflected in the positive and to a smaller extent the negative mass spectra obtained. The sensitivity for elemental analysis is such that a number of impurities can be detected with superior detection limits, to those obtainable with the scanning electron microscope.

As is apparent from the examples in this paper, however, other advantages of the method reside in its ability to obtain molecular inorganic information. The information derived from the mass spectra provides clues to the sources of anomalous enrichment in the unpolluted atmosphere. The information derived from the fingerprint mass spectra can also be used to detect asbestos in air particulates and to further characterize the fibers.

The method when exploited at low irradiance provides laser desorption spectra of organic material adsorbed on the surface of microscopical samples such as fly-ash particles[8] and asbestos fibers.[9] A significant example is the ability to detect organic components present at the surface of single microscopical fibers of the UICC-standards. These organic components have been detected previously using extractions from gram amounts of material and subsequently applying gaschromatographic and mass spectrometric analysis.[25] The significance of LAMMA for organic analysis of air particulates and asbestos will be published in due course elsewhere.

Acknowledgement

This work was supported by the "Instituut voor de Aanmoediging van het Wetenschappelijk Onderzoek in Nijverheid en Landbouw" (IWONL), Belgium by the Interministerial Commission for Science Policy, Belgium (project 80-85-10) and Nato Research Grants ES-007 and MS-020.

References

1. P. Wieser, R. Wurster and H. Seiler, *Atmos. Environ.* **14**, 485 (1980).
2. P. Wieser, R. Wurster and U. Haas, *F.Z. Anal. Chemie* **308**, 195 (1981).
3. R. Kaufmann and P. Wieser, *Modern Methods in Fine Particle Characterisation III*, in press.
4. E. Denoyer, D. F. S. Natusch, F. Adams and R. Van Grieken, *Anal. Chem.* **54**, 26A (1982).

5. R. Wechsung, F. Hillenkamp, R. Kaufmann, R. Nitsche and H. Vogt, *Microsc. Acta, Suppl.* **2**, 611 (1978).
6. R. Kaufmann, F. Hillenkamp, R. Wechsung, H. J. Heinen and M. Schürman, *Scanning Electron Microsc.* **II**, 279 (1979).
7. P. Bloch, P. Geladi, F. Adams and J. Van Landuyt, *J. Trace Microprobe Techniques*, in press.
8. E. Denoyer, T. Mauney, D. F. S. Natusch and F. Adams, *Proc. 16th Ann. Meeting Microbeam Analysis Society*, Washington D.C., U.S.A., Aug. 9–13 (1982), in press.
9. J. De Waele, P. Van Espen, E. Vansant and F. Adams, *Proc. 16th Ann. Meeting Microbeam Analysis Society*, Washington D.C., U.S.A., Aug. 9–13 (1982), in press.
10. K. A. Rahn, *Techn. Report of the Graduate School of Oceanography*, Univ. Rhode Island, Kingston R.I., U.S.A.
11. R. J. Lantzy, F. T. Meckenzie, *Geochim. Cosmochim. Acta* **43**, 511 (1979).
12. F. Adams, R. Dams, L. Guzman and J. W. Winchester, *Atmos. Environ.* **11**, 629 (1977).
13. F. Adams, M. Van Craen, P. Van Espen and D. Andreuzzi, *Atmos. Environ.* **14**, 879 (1980).
14. B. Mason, *Principles of Geochemistry*, Wiley, New York.
15. P. Van Espen, F. Adams and W. Maenhaut, *Atmos. Environ.*, to be published.
16. D. R. Lawson and J. W. Winchester, *Geophys. Research Letters*, **5**, 195 (1978).
17. A. J. Annegarn, R. Van Grieken, D. M. Bibby and F. Von Blottnitz, *Atmos. Environ.*, in press.
18. H. J. Heinen, *Int. J. Mass Spectr. Ion Phys.*, **38**, 309 (1981).
19. L. M. Keith and W. A. Telliard, *Environ. Sci. Techn.* **13**, 417 (1979).
20. K. R. Spurny, J. Schörmann and R. Kaufmann, *F.Z. Anal. Chemie* **308**, 274 (1981).
21. V. Timbrell and R. E. G. Rendall, *Powder Technology*, **5**, 279 (1972).
22. V. Timbrell, J. C. Gilson and I. Webster, *Int. J. of Cancer* **3**, 406 (1968).
23. P. Ney, *Naturwissenschaften* **68**, 597 (1981).
24. F. Adams, P. Bloch, D. F. S. Natusch and P. Surkyn, *Proc. Int. Conf. for Source Ident. in Air Chem. and Air Pollution*, Thessaloniki, Greece, Sept. 20–24, 1981.
25. B. T. Commins and G. W. Gibbs, *Brit. J. Cancer* **23**, 358 (1969).