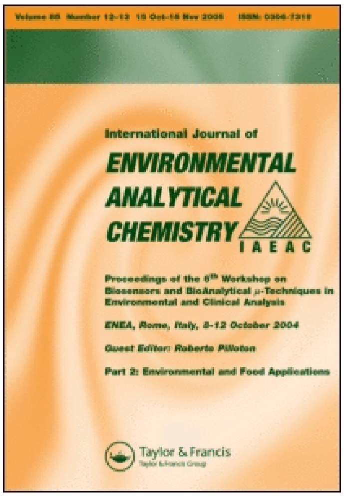

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Characterization of Individual Particle Types in Coastal Air by Laser Microprobe Mass Analysis

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Characterization of Individual Particle Types in Coastal Air by Laser Microprobe Mass Analysis

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Laser Microprobe Mass Analysis (LAMMA) was used in a preliminary study to characterize aerosol particles from a beach and inland sites and from a heavily industrialized area. As many as six types of both positive and negative mass spectra with different inorganic and organic signals could be distinguished in the different particle size ranges. Information about the elemental composition and the speciation of *S* and *N* was obtained. With increasing distance from sea, progressive uptake of nitrate in seasalt particles was found. Complex particles, containing soot and organic ammonium sulfate, were also detected.

KEY WORDS: Single particle analysis, LAMMA, atmospheric chemistry, aerosols, pollution, marine air.

INTRODUCTION

The use of Laser Microprobe Mass Analysis (LAMMA) is not well established in the field of aerosol research. However, it is a fast and sensitive analytical technique that yields the organic and inorganic

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composition of individual particles with sizes in the micrometer range.[1] By studying the relative mass peak intensities, and the elemental composition of the cluster ions and by comparison with reference fingerprint spectra of pure compounds, LAMMA can provide the semi-quantitive determination of the elements present down to ppm-levels[2], indicate the speciation of certain elements[3] and even provide fingerprint information about the organic compounds.[4]

In the present paper, the LAMMA technique has been applied to a set of samples collected with a cascade impactor on a transect from a beach site under the constant influence of steady clean onshore trade winds, towards and through a very heavily polluted industrialized area. The aim was to evaluate the general potential of this single particle analysis technique to remote and polluted marine aerosol studies, to find out to what extent information about the chemical diversity of individual particles is obtained, and to contribute to answers concerning sources, transport processes and physico-chemical changes of airborne particulate matter.

EXPERIMENTAL

Sampling sites

The samples were taken near the Brazilian coast, in the state of Bahia, north of the city of Salvador, under stable landinward wind from the East. The sample inlet of the cascade impactor was held at 2 m above the ground. The sites were:

1) a beach location, about 20 m from the waterline of the Atlantic Ocean, 20 km northeast of Salvador;
2) a hill with low vegetation, 10 km from the coast and 15 km north of the beach location;
3) a residential area, 30 km from the ocean, 20 km downwind from site No. 2, and downwind from a zone with tropical vegetation but also downwind from cement and metallurgy plants;
4) a strongly polluted site 10 km more to the North, 20 km from the coast, in the centre of a large industrial complex including petrochemical, fertilizer and metallurgical plants.

Sample collection and preparation

Atmospheric aerosol particles were sampled by means of a five-stage single-orifice Battelle-type cascade impactor, operated at a flow rate of $1\,l\,\mathrm{min}^{-1}$. The aerodynamic diameter ranges for the particles collected at the different stages are: $>4\,\mu$m, 4–2 μm, 2–1 μm, 1–0.5 μm, 0.5–0.25 μm for stages 1 to 5, respectively.

The particles were deposited on a 100 nm thick foil of Formvar supported by 300 mesh electron microscope (EM) grids, which were mounted on Mylar backings. The sampling time was restricted to ten minutes; experience has shown that, with the experimental system used, much longer collection times in marine environments lead to overloading and to the resulting particle–particle interactions.

In the laboratory the Mylar backing was removed from the EM-grids to yield suitable targets for LAMMA-analysis. The loaded EM-grids were mounted in the LAMMA sample chamber and for each stage 50–100 particles were randomly selected for LAMMA-analysis.

LAMMA-technique

A detailed description of the LAMMA-system can be found in the literature.[5] In de LAMMA®-500 instrument (Leybold–Heraeus, Köln, FRG), the pulsed laser light ($\lambda = 265$ nm, $\tau = 15$ ns) of a frequency quadrupled neodymium-YAG laser (maximum power density of $10^{11}\,\mathrm{W\,cm^{-2}}$) is focussed onto the sample through an optical microscope with the aid of the red spot of a continuous He–Ne laser beam that follows the same optical path as the high power laser. The laser beam power density can be attenuated to 1% by a 25-step optical filter system. An adaptable ionization source is thus available to either excite the total particle with the full laser energy (10–100 μJ), or perform a selective excitation of the surface material in the "laser desorption mode" (low laser energy of 0.1–1 μJ). Indeed irradiances a factor 3–10 above this threshold will lead to evaporation of the whole particle volume and yield information on the bulk composition, while the high-power ionisation causes extensive fragmentation (laser pyrolysis) and molecular rearrangement. Irradiances close to the threshold of ion formation, however, will preferentially desorb ions from the particle surface facing the spectrometer (surface characterization) and promote parent ion formation. The laser generated ions are analysed in a time-of-flight mass spectrometer in either the positive or negative ion mode. The ions are detected by an open Cu–Be secondary electron multiplier and recorded by a 100 MHz transient recorder. An on-line Digital Minc-11 computer is used for mass calibration and for integration of the mass spectra, that are stored on floppy disk.

RESULTS

In order to characterize the different types of aerosol particles, the LAMMA-spectra were classified according to the major elemental and cluster ion mass peaks, that are characteristic for a given sampling site and associated with specific particle size ranges. The positive and negative LAMMA-spectra of nearly all particles could each be classified as belonging to one of six specific particle types.

In Table I the distribution of the mass spectral types over the different impactor stages is shown for the four sampling sites. A representative spectrum of each type is shown in Figures 1 and 2.

Impactor stage 4 from site No. 2 was not suitable for LAMMA analysis because the organic background spectrum of the foil was too high, but electron probe X-ray micro-analysis on this sample revealed the presence of sulfur rich particles.

DISCUSSION

The sea salt particles, formed by direct particle production by the oceans, through the mechanism of bubble bursting,[6] are, as expected for a coastal region, abundantly present in the giant particles ($>1\,\mu$m). The major mass peaks in their positive mode LAMMA spectra (Fig. 1a) are identified as Na- and K-chlorides ($M_nCl^+_{n-1}$ with $M=Na$ and/or K). The intensity of the cluster ions at m/z = 149 ($Na_3SO_3^+$) and m/z = 165 ($Na_3SO_4^+$) is typical for alkali sulfates.[3] The negative LAMMA spectra are dominated by $M_{n-1}Cl_n^-$ (M = Na, K), $MgCl_3^-$, $(MgCl_2)OH^-$ and $CaCl_3^-$ (Fig. 2a).

When applying the laser desorption mode to the seasalt particles, it becomes clear that a significant fraction of these particles are coated with a layer of $NaNO_3$ devoid of chloride. Spectra proving that LAMMA can give direct evidence for such coatings on sampled aerosols have been presented and discussed earlier.[7] The negative mode spectra are most indicative (Figure 2b), although the positive mode spectra can also give important clues. These observations might not provide direct evidence that the surface layer of $NaNO_3$ is actually present when these seasalt particles are airborne. Indeed, it can be a result of differential crystallisation of liquid seawater droplets containing nitrate as a result of a heterogeneous reaction between HNO_3 vapour and the particles. Also the seasalt particles may have reacted heterogeneously after solidification in the impactor with HNO_3 in the passing air stream, resulting in a $NaNO_3$ coating. Several authors have already shown that the homogeneous gas phase condensation of HNO_3 is rather improbable under normal atmospheric conditions and that particulate nitrate is formed by a heterogeneous reaction between HNO_3 vapour and the atmospheric particulate matter resulting in the release of HCl from seasalt.[8-14] Only a minor fraction of the 1–2 μmad seasalt particles are found to be rich in $NaNO_3$ in the samples taken at the beach location; inland the NaCl-$NaNO_3$ particles become predominant in the 1–4 μmad size range and, in the industrial area, pure seasalt particles are not observed in this size range at all. The drastic abundance difference of $NaNO_3$-rich particles between the beach site and the industrial area samples gives direct indication for a very fast gas-to-particle conversion of a fraction of the seasalt towards sodium nitrate in polluted air.

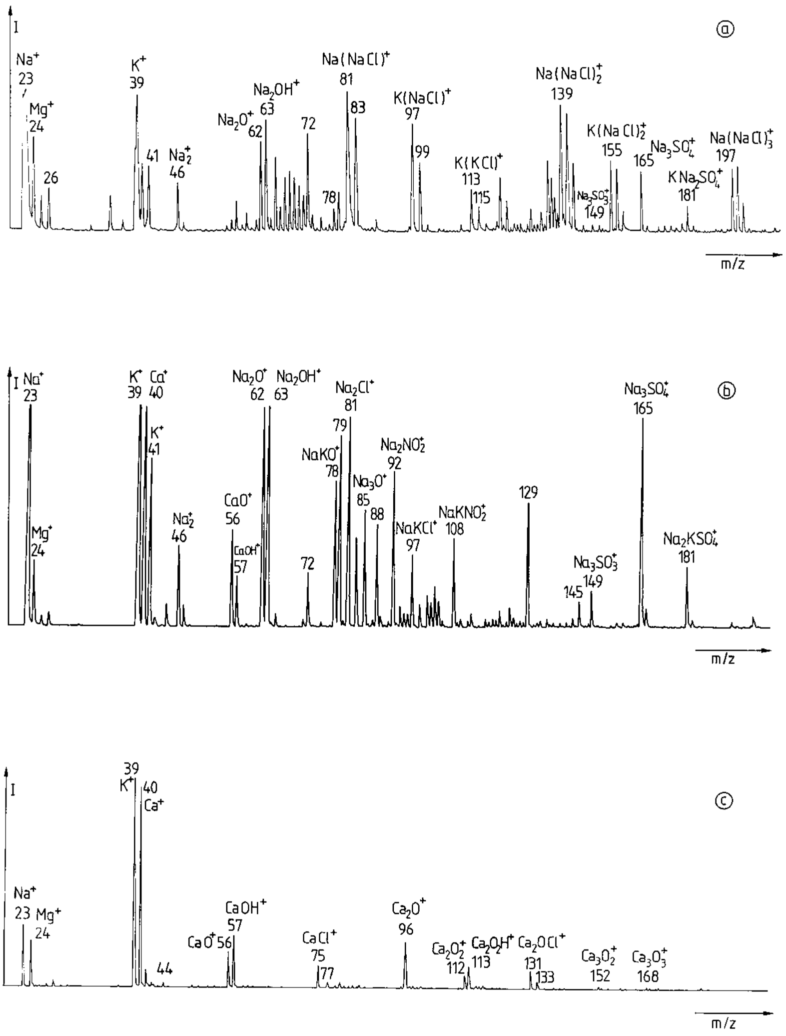
The positive spectra of the Ca-rich particles as shown in Figure 1c can result from various Ca-compounds as e.g. $CaSO_4$, $CaCO_3$ and CaO; indeed these all yield predominantly $Ca(CaO)_n^+$, $(CaO)_n^+$ and $(CaO)_nH^+$ mass peaks.[15] In some cases the negative mode spectra reveal the presence of the sulfate ion by the SO_n^--distribution ($n=0$ to 3) (Figure 2c) and identify the particles as $CaSO_4$. Besides the $CaSO_4$-particles, EPXMA shows the presence of $CaCO_3$ by an intense Ca-signal in the X-ray spectrum and the absence of other elements with $Z>11$. Microanalyses on aerosols, sampled under clean as well as polluted conditions, also confirm the presense of $CaSO_4$-particles. They are supposed to result from e.g. differential crystallisation of seaspray droplets and subsequent breakup of particles, or from the reaction of acid gases with $CaCO_3$.

TABLE I

Composition, as inferred from LAMMA-analyses, and size distribution of the different particle types at the four locations (+ =present).

Sample site	1: Beach					2: Inland				3: Inland					4: Industrial area				
Size range (μm) Particle type	>4	4–2	2–1	1–0.5	0.5–0.25	>4	4–2	2–1	0.5–0.25	>4	4–2	2–1	1–0.5	0.5–0.25	>4	4–2	2–1	1–0.5	0.5–0.25
P1. Sea salt particles	+	+	+			+	+	+		+	+	+			+				
P2. Sea salt particles rich in $NaNO_3$			+				+	+			+	+				+	+		
P3. Ca-rich particles	+	+		+	+						+		+						
P4. Na, Mg, Al, Si, K, Ca, Ti, Fe-rich particles				+	+													+	
P5. Particles containing some elements such as Al, Si, Ti, V, Mn, Fe, Co, Sr, Ba																		+	

P6. Particles also yielding positive mass peaks at m/e= 18, 30, 42, 44, 56, 86, 88, 100									+				+	+				+	+
N1. Sea salt particles	+	+	+			+	+	+		+	+	+			+				
N2. Sea salt particles rich in $NaNO_3$			+				+	+			+	+				+	+		
N3. SO_n^--rich particles	+	+									+								
N4. HSO_4^--rich particles containing organic materials				+	+				+				+	+				+	
N5. Particles containing PO_n^- and NO_n^--anions																		+	
N6. Particles containing HSO_4^-, NO_n^--anions and organic material																			+


ⓐ
I
Na+ 23
Mg+ 24
26
K+ 39
41
Na2+ 46
Na2O+ 62
Na2OH+ 63
72
78
Na(NaCl)+ 81
83
K(NaCl)+ 97
99
K(KCl)+ 113
115
Na(NaCl)2+ 139
Na3SO3+ 149
K(NaCl)2+ 155
Na3SO4+ 165
KNa2SO4+ 181
Na(NaCl)3+ 197
m/z
ⓑ
I
Na+ 23
Mg+ 24
K+ 39
Ca+ 40
K+ 41
Na2+ 46
CaO+ 56
CaOH+ 57
Na2O+ 62
Na2OH+ 63
72
NaKO+ 78
79
Na2Cl+ 81
Na3O+ 85
88
Na2NO2+ 92
NaKCl+ 97
NaKNO2+ 108
129
145
Na3SO3+ 149
Na3SO4+ 165
Na2KSO4+ 181
m/z
ⓒ
I
Na+ 23
Mg+ 24
39 K+
40 Ca+
44
CaO+ 56
CaOH+ 57
CaCl+ 75
77
Ca2O+ 96
Ca2O2+ 112
Ca2O2H+ 113
Ca2OCl+ 131
133
Ca3O2+ 152
Ca3O3+ 168
m/z

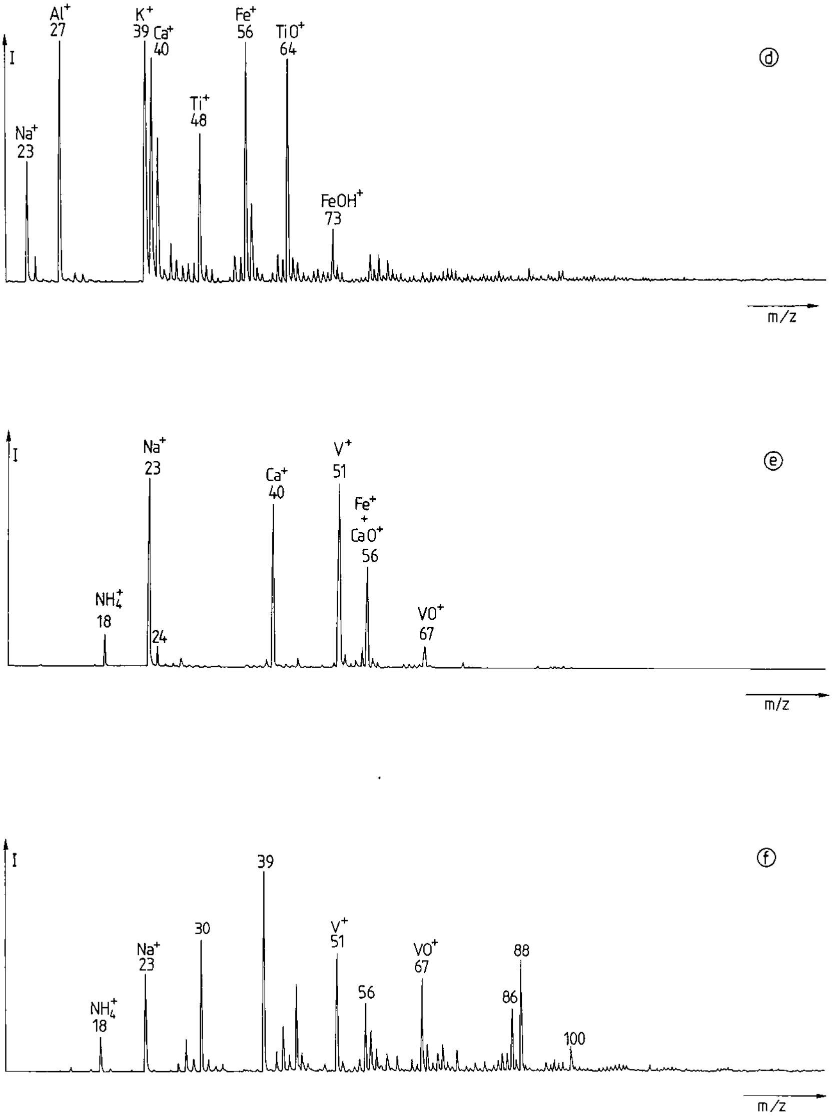
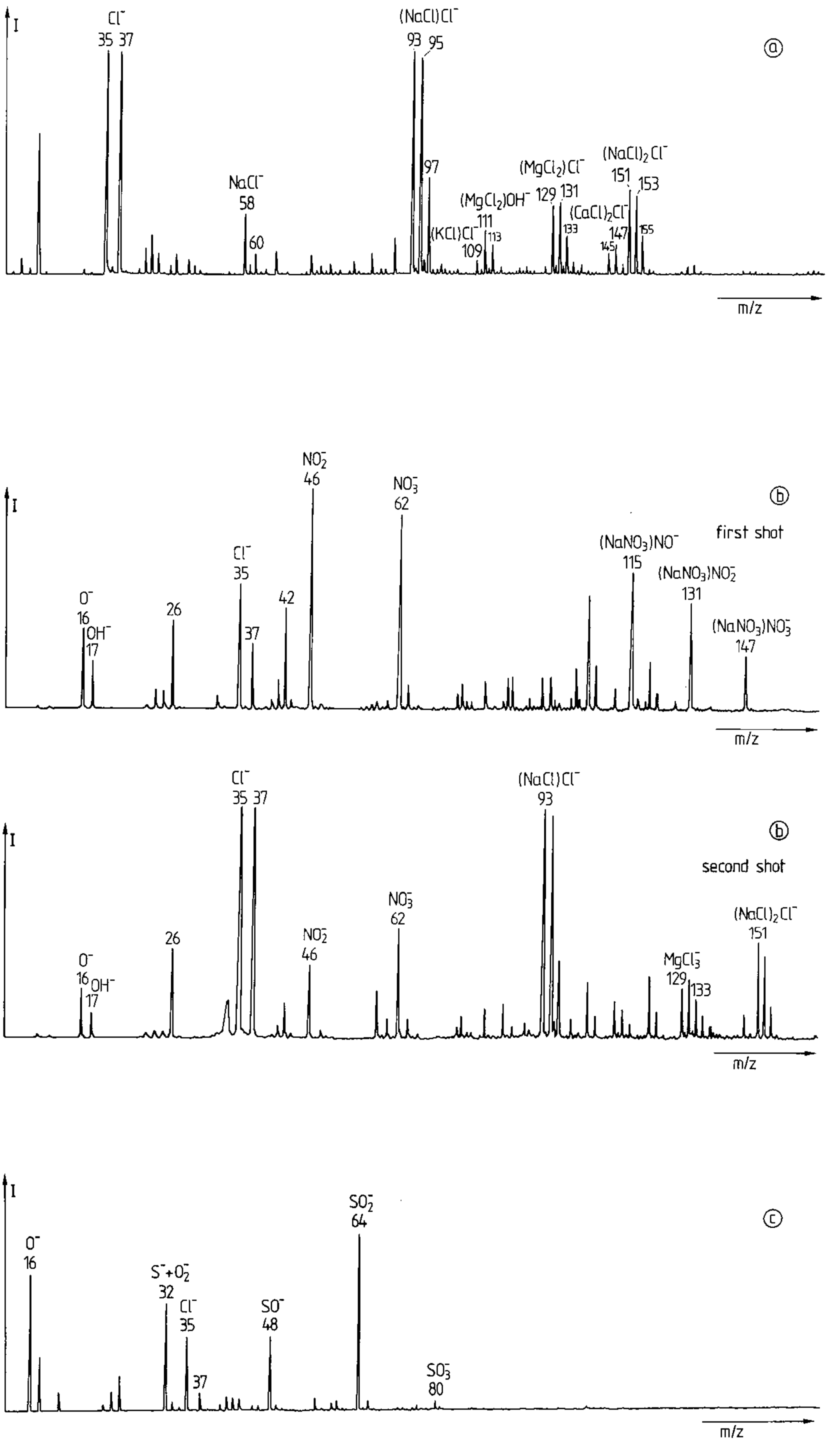


FIGURE 1 (a) to (f) Positive LAMMA-spectra of the type P1 to P6, respectively. The corresponding particle types are indicated in Table I.


I
Cl⁻
35 37
(NaCl)Cl⁻
93 95
97
NaCl⁻
58
60
(KCl)Cl⁻
109
(MgCl₂)OH⁻
111
113
(MgCl₂)Cl⁻
129 131
133
(CaCl)₂Cl⁻
145
147
(NaCl)₂Cl⁻
151
153
155
ⓐ
m/z
I
O⁻
16
OH⁻
17
26
Cl⁻
35
37
42
NO₂⁻
46
NO₃⁻
62
(NaNO₃)NO⁻
115
(NaNO₃)NO₂⁻
131
(NaNO₃)NO₃⁻
147
ⓑ
first shot
m/z
I
O⁻
16
OH⁻
17
26
Cl⁻
35 37
NO₂⁻
46
NO₃⁻
62
(NaCl)Cl⁻
93
MgCl₃⁻
129
133
(NaCl)₂Cl⁻
151
ⓑ
second shot
m/z
I
O⁻
16
S⁻+O₂⁻
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Cl⁻
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SO⁻
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SO₂⁻
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SO₃⁻
80
ⓒ
m/z

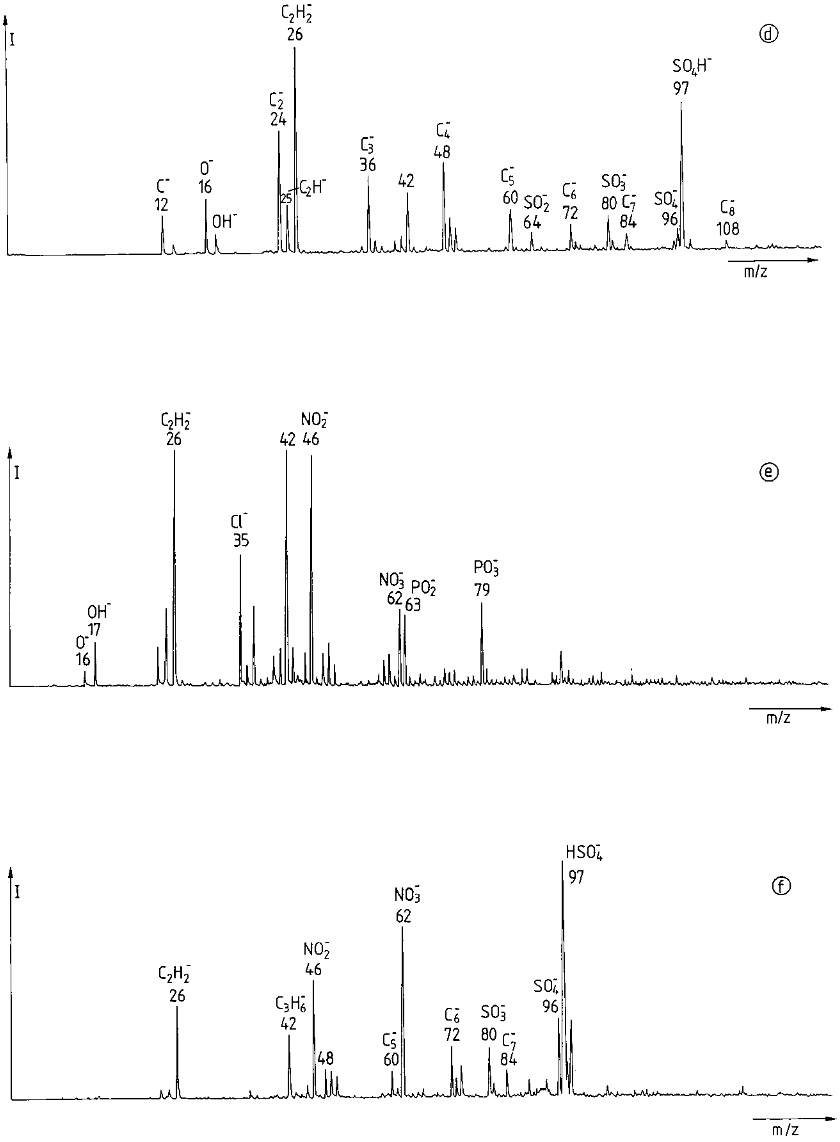

FIGURE 2 (a) to (f) Negative LAMMA-spectra of the type N1 to N6, respectively. The corresponding particle types are indicated in Table I.

Type No. P4 spectra (Figure 1d) are derived from particles which contain typical crustal elements but whose size distribution does not plead for local soil dispersion as their source. EPXMA measurements on the 0.5-0.25 μm stage of sample No. 1 showed particles rich in Al, Si, Fe and Si, all with a non-crystalline aspect, and predominantly particles rich in Al and Si and less S and Fe in the 1–0.5 μm size range (in addition to the Ca-compound particles). In view of the presence of S and the fact that the only negative spectrum type seen for $<1\,\mu$m particles at the beach is No. N4, it is likely then that the spectra of type No. P4 and No. N4 are derived at least partially from the same particles. In mass spectra No. N4 (Figure 2d) which are frequently seen and are related to different particle types, the peaks at $m/z=64$, 80, 96 and 97 are abundant, corresponding to SO_2^-, SO_3^-, SO_4^- and HSO_4^-, respectively. This cluster ion pattern is typical for sulfur compounds such as $(NH_4)_2SO_4$ or NH_4HSO_4. The abundance of C_n^- cluster ions is typical for carbonaceous material in these particles. They are therefore identified as fly ash particles associated with carbonaceous material and sulfate, either derived from the common charcoal fires on the beach or related to the diurnal wind directions in the coastal region.

The heterogeneous group No. P5 (Figure 1e) gathers diverse spectra which exhibit mass peaks from a combination of the following elements: Al, Si, Ca, Ti, V, Mn, Fe, Co, Sr, Ba and NH_4^+. Because of the high variability in composition and the unusual metal enrichments, the corresponding particles are classified as pollution particles from the industrial complex and the local metallurgy. The negative mode type No. N6 (Figure 2e) and No. N4 LAMMA-spectra might be derived from the particles yielding No. P5 positive spectra. Indeed spectra No. P5 and No. N5 are both only seen for 1–0.5 μm particles in the industrial zone.

The mass peaks in No. N5 do not point to soot or sulfur compounds but to phosphorus and nitrogen oxy-salts. Since No. N5 spectra are seen much less frequently than No. P5 spectra, since EPXMA showed transition elements such as Ti, V, Mn, Fe and Co to occur together with S and since all No. P5 spectra contained a strong NH_4^+ signal, confirming the presence of $(NH_4)_2SO_4$ or NH_4HSO_4 also demonstrated by No. N4 spectra, it can be assumed that spectra No. P5 and some of the No. N4 spectra result from the same particles formed by combustion processes or that have reacted with sulfur compunds in the atmosphere.

Group No. P6 refers to particles, which in addition to crustal elements or V, yield positive mass peaks at m/z= 18, 30, 42, 44, 56, 86, 88 and 100 (Figure 1f). These particles are found in the smallest size-range and their relative abundance increases inland and in the industrial area. Most of the observed peaks could be interpreted as originating from organic N-compounds such as amines. Indeed the electron impact mass fragments of amines include: $CH_2=NH_2^+$ (m/z=30), $C_3H_6^+$ (m/z=42), $C_2H_6N^+$ (m/z=44), $C_4H_8^+$ (m/z=56), $C_5H_{12}N^+$ (m/z=86), $C_6H_{14}N^+$ (m/z=100). Amines can be released into the atmosphere by decomposition of proteins of biogenic origin or by the combustion of polyamides or they could be emitted by the amine-producing industry near site No. 4. The occurrence of type No. P6 spectra as a function of particle size and sampling location suggests that they are related to some of the negative spectra No. N4, may be to No. N5 but also to No. N6 (Figure 2f). The latter spectra are only seen for the smallest size range and show HSO_4^-, carbonaceous clusters and NO_n^- anions simultaneously.

CONCLUSION

This preliminary study shows that LAMMA can be used for the characterization of the atmospheric aerosol on a single particle basis allowing the retrieval of different types of composition and the evaluation of the influence of the different sources while providing evidence of transformations during the transport.

LAMMA has shown that the formation of particulate nitrate is actually occurring in coastal areas with their high atmospheric sea salt load, and that polluted air enhances this production mechanism. In the accumulation mode particles, sulfur is present in compounds such as NH_4HSO_4 or $(NH_4)_2SO_4$, containing significant quantities of carbonaceous material. Besides inorganic nitrogen as NH_4^+ and NO_n^-, organic N–compounds (probably amines) were also detected in the industrial area.

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