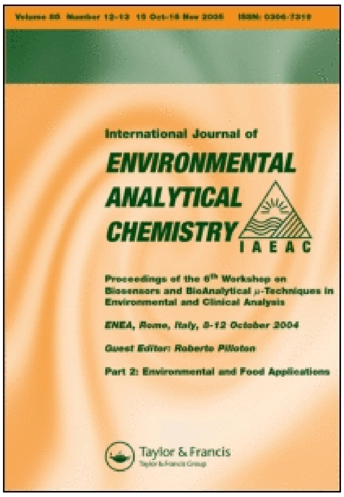

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Speciation of Elements in the Environment by Laser Microprobe Mass Analysis (LAMMA)†

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The laser microprobe mass analyser (LAMMA) is being used in our laboratory for the mass spectral identification of inorganic substances. Examples are given showing the characteristic ion species obtained for some of the authentic salts studied namely those of sodium nitrate, potassium chloride and sodium sulphate. The ions observed seem to be formed by decomposition of the parent molecules followed by ion-molecule interactions. The knowledge acquired from this study has been applied to the elucidation of the mass spectra of environmental samples. The examples given show that the speciation of elements in the environment by LAMMA is possible. However, at the present state of the art due to the irreproducibility of the laser energy and the inhomogeneity of the samples a quantitative approach is impossible.

KEY WORDS: Mass spectrometry, laser desorption, air particulate matter, speciation.

1. INTRODUCTION

In the context of ecotoxicology the chemical speciation of elements in our environment is becoming increasingly important. Information

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is now required not only about the toxic elements present in the environment but also on their specific chemical forms as indeed these govern their toxicity and transportation properties.

Laser microprobe mass analysis (LAMMA) is a technique that is very useful for studying environmental particles due to its high lateral resolution and good detection sensitivity.[1,2] In the LAMMA, ions are produced by impact of a focused laser beam on a microvolume of the sample. The elemental and molecular ions formed are mass analysed in a time-of-flight (TOF) mass spectrometer. However, as data is scarce on the mass spectra of inorganic substances a study of the behaviour of the latter after laser induced ionisation is compulsory in order to attempt the interpretation of unknown spectra. We will therefore start by giving a few examples of spectra obtained for some inorganic compounds and then proceed to show how this knowledge allows one to elucidate the spectra of environmental samples.

2. EXPERIMENTAL

2.1 The laser microprobe mass analyser

The LAMMA-instrument has been described in detail elsewhere.[1,2] The LAMMA principle is represented schematically in Figure 1. The instrument consists of a combination of a laser microscope and a time-of-flight mass spectrometer. The specimen is viewed by means of a high power light microscope. The system is equipped with two lasers, a He-Ne pilot laser that can be focused to a spot (~0.5–10 μm) and a Q-switched (pulse-duration = 15 ns) neodynium-YAG laser whose output is quadrupled in frequency to give a laser beam with a wavelength of 265 nm. The two laser beams are made collinear by means of the optical system after which they are reflected through the light microscope and focused on the target area. Ions produced after excitation by the ionising laser beam are extracted in the TOF for mass analysis.

2.2 Materials and methods

All the authentic inorganic compounds studied were of the pro analysis type purchased from Merck.

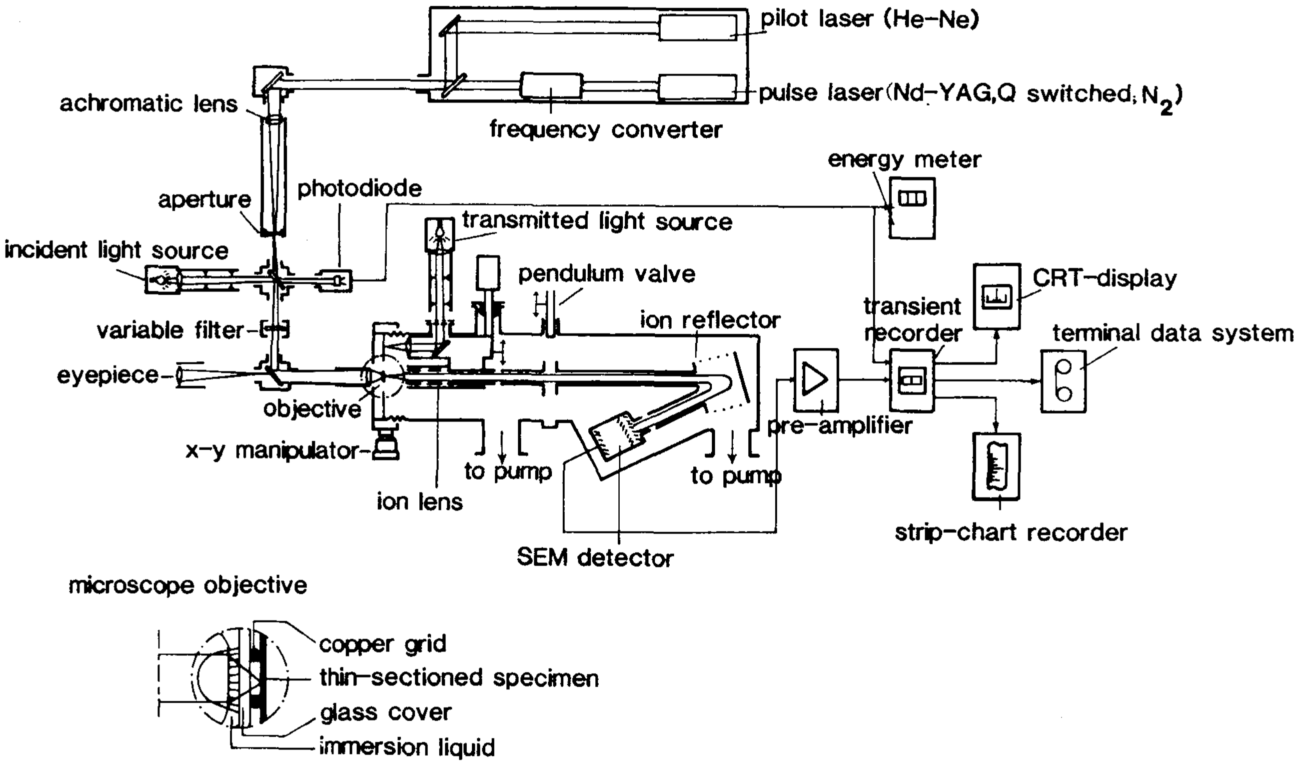

FIGURE 1 Schematic diagram of LAMMA principle.

Samples of fly-ash were collected from the rotary furnace type incinerator of the Republic and Canton of Geneva. As the ashes leave the furnace they fly past a boiler (heat exchanger) on their way to a two stage scrubber. Ashes which adhered to the boiler pipes were scraped off for analysis.

Sea water samples came from the Santa Pola region down the southeast coast of Spain. Some of the samples were collected from the salt marshes of the area and some from the open sea.

The sea water samples were dry-freezed before analysis. All samples were ground to a fine state before being placed between electron-microscopic grids. The grids were fixed on the sample holder which was then mounted on the mass spectrometer.

3. RESULTS AND DISCUSSION

We will start by reviewing the type of spectra that are obtainable for inorganic substances after laser induced ionisation. The examples that will now be given will prove of tremendous help in the interpretation of the spectra of unknown samples.

3.1 Mass spectrometry of inorganic salts

The LAMMA spectra of sodium nitrate are given in Figure 2. A striking feature of the spectra of inorganic compounds is the formation of ion clusters where ion species with m/z values greater than the molecular weight of the compound under study are observed.[3] The positive and negative spectra of Figure 2 indicate the presence of sodium nitrate (Na^+ m/z 23 in the positive spectrum and NO_2^- m/z 46, NO_3^- m/z 62 in the negative spectrum), however, the other peaks present can be misleading in the interpretation of an unknown unless a systematic study of the nitrates is undertaken. Our study on the nitrates of groups I and II of the periodic table has shown that all members of the same group behave in the same way. For example the characteristic ion species and their relative intensities are given in Table I for the nitrates of group I. In all cases the most intense ion is the $MN_2O_4^-$ species, where M is the cation of group I. The characteristic ion species seem to be formed by the following ion-molecule interactions.

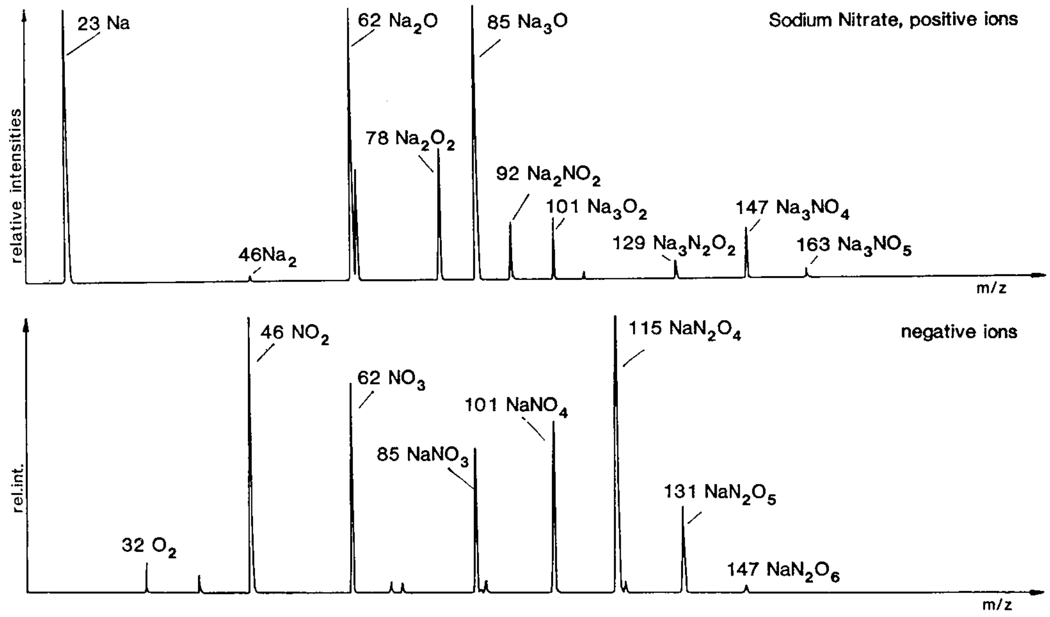

FIGURE 2 LAMMA positive and negative spectra of sodium nitrate.

TABLE I

Shows the relative intensities of the characteristics ions of the nitrates with $MN_2O_4^-$ being the most intense ion.

Negative Ions

	O	OH	O_2	NO_2	NO_3	M	MO	MNO_2	MNO_3	MNO_4	MN_2O_4	MN_2O_5	MN_2O_6
Lithium	+++	++	+	+++	+++				2,0	0.9	3.2	2,6	1.0
Sodium	+++	++	+	+++	++				1.7	2.0	9.1	1.0	0.1
Potassium	+++	+	+	+++	+++				0,6	0.7	4.0	1.0	0,2
Rubidium	+++	+	+	+++	++				0,3	0.4	2.1	1,0	0,2
Caesium	+++	+	+	+++	+++	1.7	0.4	0,1	0,3	1,0	60,0	1.0	

Positive Ions

	M	M_2	M_2O	M_2O_2	M_3O	M_3O_3	M_2NO_2	M_2NO_3	M_3NO_2	$M_3(NO)_2$	M_3NO_4	M_3NO_5	M_5NO_3
Lithium	3,2	~ 0	1,8		7,2	~ 0	0.4 or (Li_4O_2)	0,4	1 or (Li_5O_2)				0.1
Sodium	>>20	0.5	20	5.3	15	1	2,1	~ 0		0,5	0,6	~ 0	
Potassium	>>10	0,6	>>10	5.5	3,8	1	4.0	0.8		0.6			
Rubidium	20	0,6	9,7	3,7	1	0,2	1.4			~ 0			
Caesium	>>10	0,1	>5	0,9	1	0.1	0.7	0.1		0.4			

For the positive ions

$Na_2O + Na^+ \rightarrow Na_3O^+$

$NaNO_2 + Na^+ \rightarrow Na_2NO_2^+$

$Na_2O_2 + Na^+ \rightarrow Na_3O_2^+$

$NaNO_3 + Na_2O^+ \rightarrow Na_3NO_4^+$

$NaNO_3 + Na_2O_2^+ \rightarrow Na_3NO_5^+$

For the negative ions

$NaNO_2 + O_2^- \rightarrow NaNO_4^-$

$NaNO_2 + NO_2^- \rightarrow NaN_2O_4^-$

$NaNO_3 + NO_2^- \rightarrow NaN_2O_5^-$

$NaNO_3 + NO_3^- \rightarrow NaN_2O_6^-$

In Figure 3 the LAMMA spectra of potassium chloride are shown. Here again the characteristic ion species are formed by ion-molecule interactions as shown below.

For the positive ions

$KCl + K^+ \rightarrow K_2Cl^+$

$KCl + K_2Cl^+ \rightarrow K_3Cl_2^+$

$KCl + K_3Cl_2^+ \rightarrow K_4Cl_3^+$

For the negative ions

$KCl + Cl^- \rightarrow KCl_2^-$

$KCl + KCl_2^- \rightarrow K_2Cl_3^-$

The diagnostic ions for KCl is the presence of the ion species K_2Cl^+ in the positive spectrum confirmed by the ion species KCl_2^- in the negative spectrum.

In Figure 4 the positive and negative spectra of sodium sulphate are shown. The presence of a sulphate is characterised by the presence of the ions SO^-, SO_2^-, SO_3^- and SO_4^- in the negative spectrum at m/z values 48, 64, 80 and 96 respectively. Characteristic ion species are found at m/z 149 and 165 for $Na_3SO_3^+$ and $Na_3SO_4^+$ respectively in the positive spectrum and at m/z 103 and 119 for the ions $NaSO_3^-$ and $NaSO_4^-$ respectively in the negative spectrum.

The above examples show that given a good knowledge of the mechanism of ion formation in the context of inorganic mass spectrometry, the speciation of elements in the environment seems quite feasible.

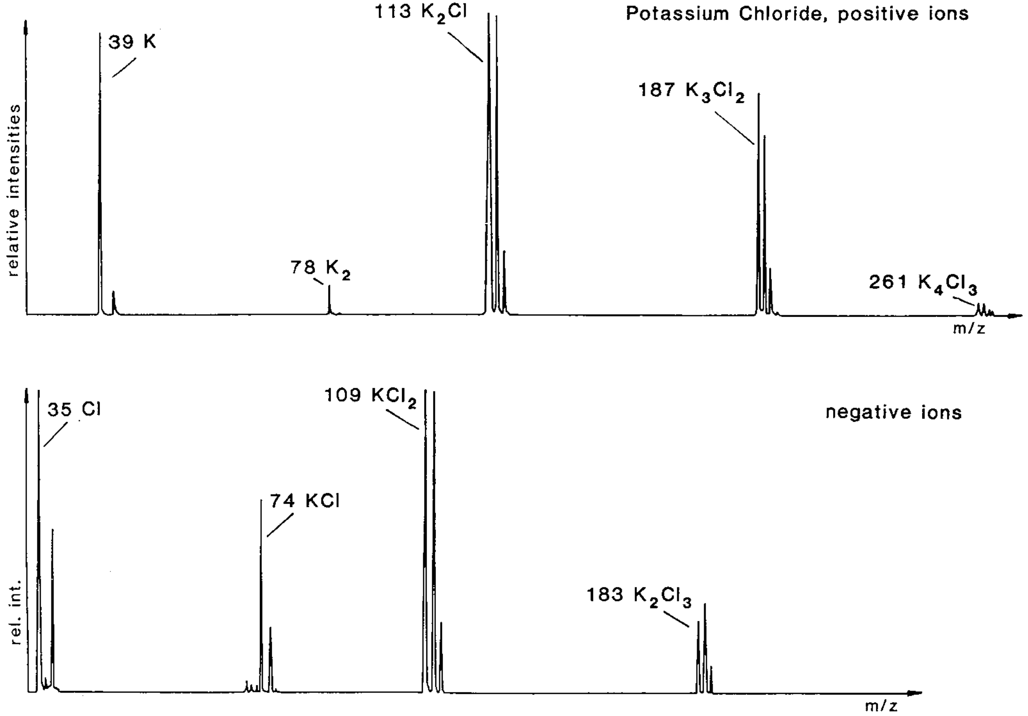

FIGURE 3 LAMMA positive and negative spectra of potassium chloride.

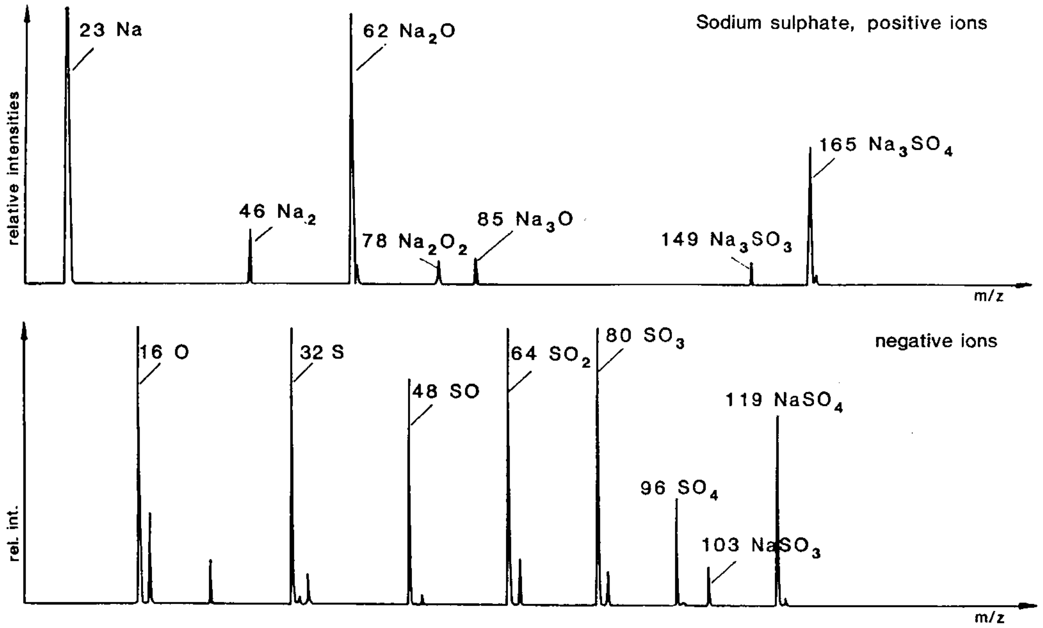

FIGURE 4 LAMMA positive and negative spectra of sodium sulphate.

3.2 LAMMA spectra of fly-ash particles sampled from the Incineration Station of the Republic and Canton of Geneva

Figure 5 shows typical spectra that can be obtained for ash particles in general. The identification of peaks other than simple cations and anions in these spectra can be cumbersome. Our present knowledge about ion formation, however, allows us to make unambiguous mass assignments of most of the other peaks that are present. In the positive spectrum for example all the peaks characteristic of sodium sulphate are identified. The ratio of the ion intensities of $Na_3SO_3^+$ to $Na_3SO_4^+$ and that of $NaSO_3^-$ to $NaSO_4^-$ confirm the presence of sodium as sodium sulphate. For a sulphite, the relative intensities of these characteristic ion species should be about equal for $Na_3SO_3^+/Na_3SO_4^+$ whereas the ratio $NaSO_3^-/NaSO_4^-$ is about 0.5 as indicated in Table II below.

There is no evidence in favour of magnesium, potassium and lead being present in any other form but elemental. Calcium is present as the oxide.

TABLE II

Relative intensities of the characteristic ion species of sodium sulphite and sodium sulphate.

Negative ions

	O	OH	S	SO	SO_2	SO_3	SO_4	M	MSO_3	MSO_4
Sulphite	1.5	1.4	2.2	0.6	4.0	4.3	0.3	0.1	1.0	1.9
Sulphate	8.0	2.3	7.1	5.9	7.5	7.2	2.8	1.1	1.0	5.0

Positive ions

	M	M_2	M_2O	M_2O_2	M_3O	M_3O_2	M_3SO_3	M_3SO_4
Sulphite	12	9.5	12	1.6	4.4	1.0	5.6	5.3
Sulphate	15.5	2.5	13.0	1.0	1.3	<0.1	1.0	6.5

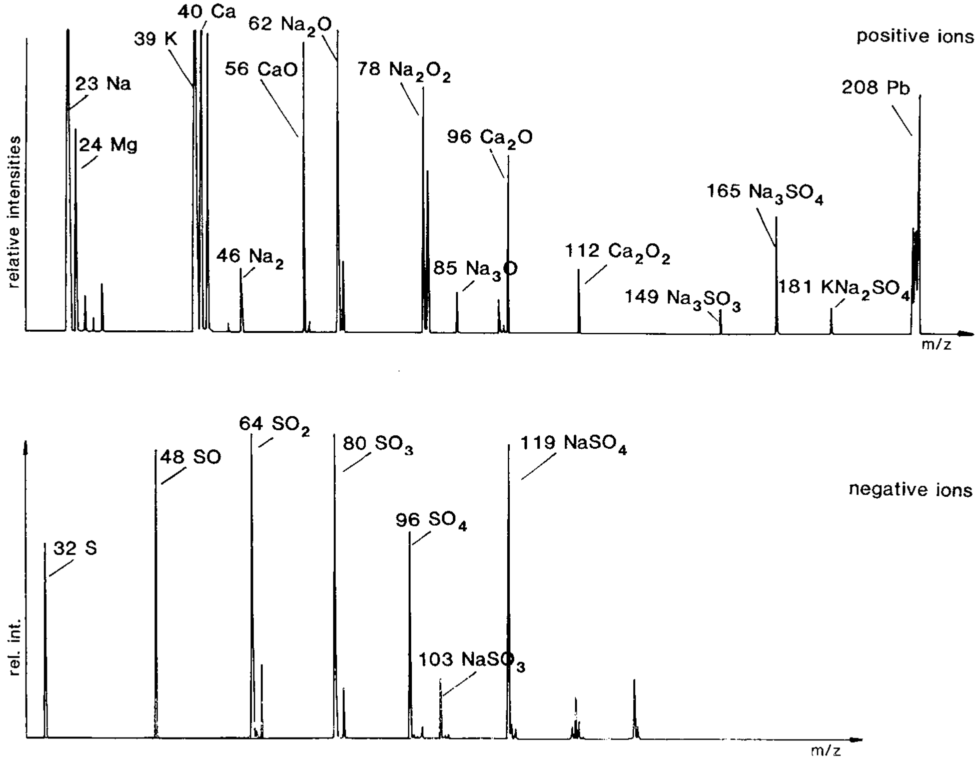

FIGURE 5 LAMMA positive and negative spectra of fly ashes from an incineration station.

3.3 LAMMA spectra of dry-freezed sea water sampled from salt marshes

As expected the positive and negative spectra of Figure 6 show the presence of sodium chloride only. Potassium is here present as an inclusion in the sodium chloride matrix. Indeed if potassium were present as KCl an intense peak corresponding to the ion species K_2Cl^+ would have been observed in the positive spectrum. The peak at m/z 97 is due to the interaction between potassium as a cation and sodium chloride as a neutral molecule.

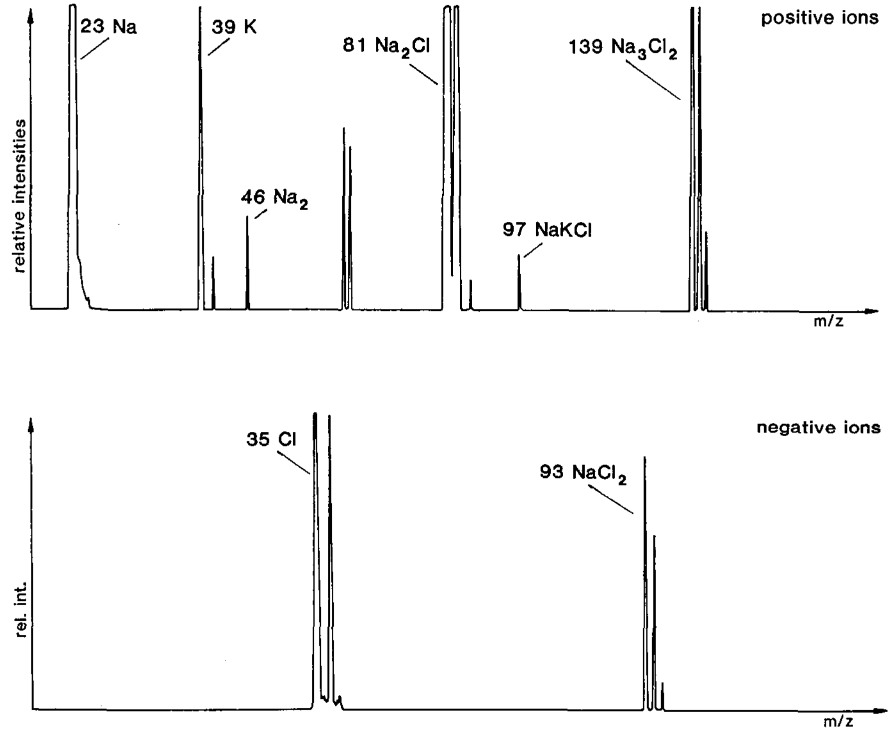

FIGURE 6 LAMMA positive and negative spectra of dry-freezed sea water sampled from salt-marshes.

3.4 Positive LAMMA spectrum of dry-freezed sea water sampled from the open sea

Figure 7 shows that sea water sampled at a location where no precipitation is expected, $[K^+] = 1.26 \times 10^{-2}$M, displays the presence of cations other than sodium. Magnesium, potassium and calcium are present in intensities comparable to that of sodium. Sulphur and strontium are also present in trace amounts. Calcium and calcium related oxides are also identified as expected.

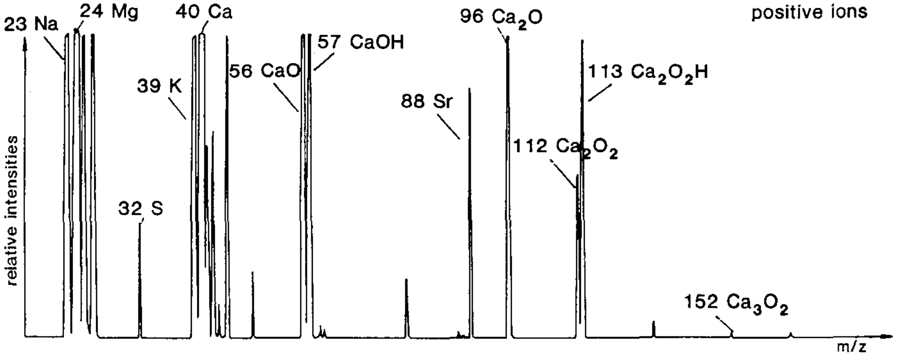

FIGURE 7 LAMMA positive spectrum of dry-freezed sea water sampled from the open sea.

4. CONCLUDING REMARK

The above examples show that it is possible to deduce the chemical species of the elements identified in the spectra given a good knowledge of the mechanism of ion formation of inorganic substances after laser induced ionisation. To date this technique has been extended to quite different fields, for example, criminalistic, fibre and particle analysis.

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