SPECIATION OF ELEMENTS IN THE ENVIRONMENT BY LASER MICROPROBE MASS ANALYSER (LAMMA)

BY

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ABSTRACT

The laser microprobe mass analyser is an instrument which permits the mass spectral analysis of non volatile organic compounds and of inorganic substances. We have used this technique to study the behaviour of inorganic compounds after laser impact.

Our preliminary studies on the fragmentation pattern of the nitrates of groups I and II of the periodic table indicate that ions are formed by decomposition of the parent molecules followed by ion-molecule interactions. This knowledge has been extrapolated to the interpretation of the spectra obtained from urban air particulate matter and from ash particles sampled from urban incinerators. Examples are given illustrating the potentialities of the technique for the speciation of elements in the environment.

RÉSUMÉ

La microsonde laser couplée à la spectrométrie de masse est un appareil qui permet d'obtenir les spectres de masse des composés organiques non volatils et des substances minérales. Nous avons étudié à l'aide de cette technique le comportement des substances minérales après impact au laser.

Notre étude préliminaire sur le mode de fragmentation des nitrates des groupes I et II du tableau périodique montre que des ions sont formés d'une part à la suite de la décomposition thermique des molécules mères et d'autre part, après interactions entre ions et molécules neutres. Ces informations nous ont permis d'interpréter les spectres de masse obtenus à partir d'échantillons de particules prélevées de l'atmosphère urbaine et des cendres prélevées des usines d'incinération. Des exemples sont donnés montrant ainsi le potentiel d'une telle technique en matière de spéciation des éléments dans l'environnement.

1. INTRODUCTION

Numerous articles have been published on the topic of the toxic elements present in our environment. Although we are heavily documented on the sources and concentrations of these elements in air, water and soil, not much is known,

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however, about their specific chemical forms. As our knowledge of the chemistry and toxicology is improving, it is becoming increasingly evident that from an ecotoxicological point of view it is more and more important to know the chemical form or forms in which the element is present and the concentrations of each species (speciation). Indeed different chemical forms mean different degrees of toxicity and different transport properties.

Furthermore, as speciation is of prime importance for the understanding of processes regulating uptake of chemical components, there is consequently a growing need for analytical methods to determine chemical species.

In the field of aerosol research we are at present experimenting with a fairly new instrument, the Laser microprobe mass analyser (LAMMA 500), that holds great promise in the context of mineral speciation. The LAMMA was originally designed for studying elemental distribution in thin sections of biomedical samples, the instrument having high lateral resolution and extreme detection sensitivity [1, 2]. in the LAMMA, ions are produced by excitation of a microvolume of the sample by a focused laser beam. These ions are subsequently analysed by mass spectrometry. All elements of the periodic table and their isotopes can be detected. Various applications have demonstrated that besides element detection the insrument can be used for the detection of organic and inorganic compounds.

However, as hardly anything is know about the fragmentation pattern of ınorganic substances, a prerequisite to the interpretation of the spectra obtained from aerosol particles is a systematic study of the behaviour of these inorganic compounds when subjected to laser induced ionisation.

In this paper therefore, a part will be devoted to describing the mechanism of fragmentation of inorganic salts. In our laboratory we have undertaken a systematic study of the fragmentation pattern of the nitrates, sulphates, carbonates, halides and a few other salts, but only the case or the nitrates of groups I and II of the periodic table will be discussed here by way of illustration.

Examples will then be given showing how a knowledge of the fragmentation pattern is necessary in the elucidation of the spectra obtained from different sources.

2. EXPERIMENTAL

2.1. THE LASER MICROPROBE MASS ANALYSER

The LAMMA-instrument has been described in detail elsewhere [3, 4, 5]. The LAMMA principle is shown in figure 1. Basically, the instrument consists of a laser microscope combined with a time-of-flight mass spectrometer (TOF).

The specimen is viewed by means of a high power light microscope. The ionising laser is generated by means of a Neodynium-Yttrium, Aluminium garnet laser which

is Q-switched to give a pulsed laser of 15 ns duration and a wavelength of 1065 nm. This pulsed laser beam then goes through a frequency quadrupler where it is converted to 265 nm. In order to focus this pulsed UV-laser on the target a second laser, He-Ne pilot laser, emitting continuously in the red is required. These two laser
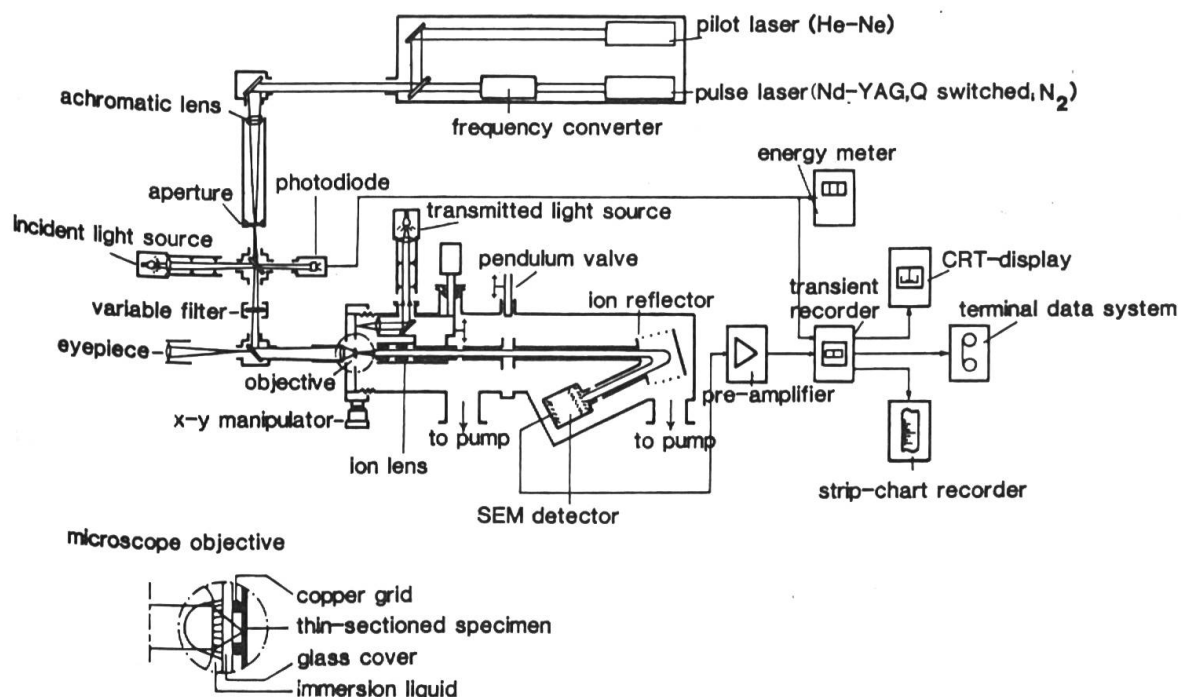
FIG. 1. — Schematic diagram of LAMMA principle.

beams are made collinear by means of an optical system after which they are reflected through the light microscope and focussed on the target area. Ions produced after excitation by the ionising laser beam are then accelerated in the TOF where both positive and negative spectra can be recorded.

2.2. MATERIALS AND METHODS

No special sampling technique was necessary in any of the cases studied. Fly ashes were sampled from the chimneys of urban incinerators dealing with domestic refuse as well as chemical and industrial wastes of the Republic and Canton of Geneva.

Sampling was done under isokinetic conditions with a pipe and Pitot tube of the BCURA apparatus.

Air particulate matter from the Sahara desert, blown over the mediterranean by a south west air current, was collected from the roof of motocars stationed in the private car parks of our institute.

A mineral, ellipsoidal in form (3 × 2 cm), collected in Brittany and suspected as being a meteorite was also analysed.

All the nitrates of groups I and II of the periodic table were of the pro analysis type, purchased from Merck and recrystallised when necessary in our laboratory.

No sample treatment was necessary before analysis by the LAMMA. Fine particles of the sample were placed between electron-microscopic grids and fixed on the sample holder which was then mounted on the mass spectrometer. In the case of the "meteorite" the specimen was broken apart and coarse particles sampled from the interior were ground to a fine powder before being sandwiched between copper grids.

3. RESULTS AND DISCUSSION

3.1. MASS SPECTROMETRY OF THE NITRATES OF GROUPS I AND II

Although we have been referring so far to the fragmentation pattern of inorganic compounds it will soon become evident as we look at the spectra of the nitrates of groups I and II that one should talk instead of ion formation during laser induced ionisation. The typical spectra obtained for sodium and potassium nitrate are shown in figures 2 and 3 respectively. In the positive spectrum of figure 2 one immediately gets information about the cation present in the compound, in this case sodium at m/z 23. A small peak at m/z 46 corresponding to Na_2^+ is also obtained. Cluster
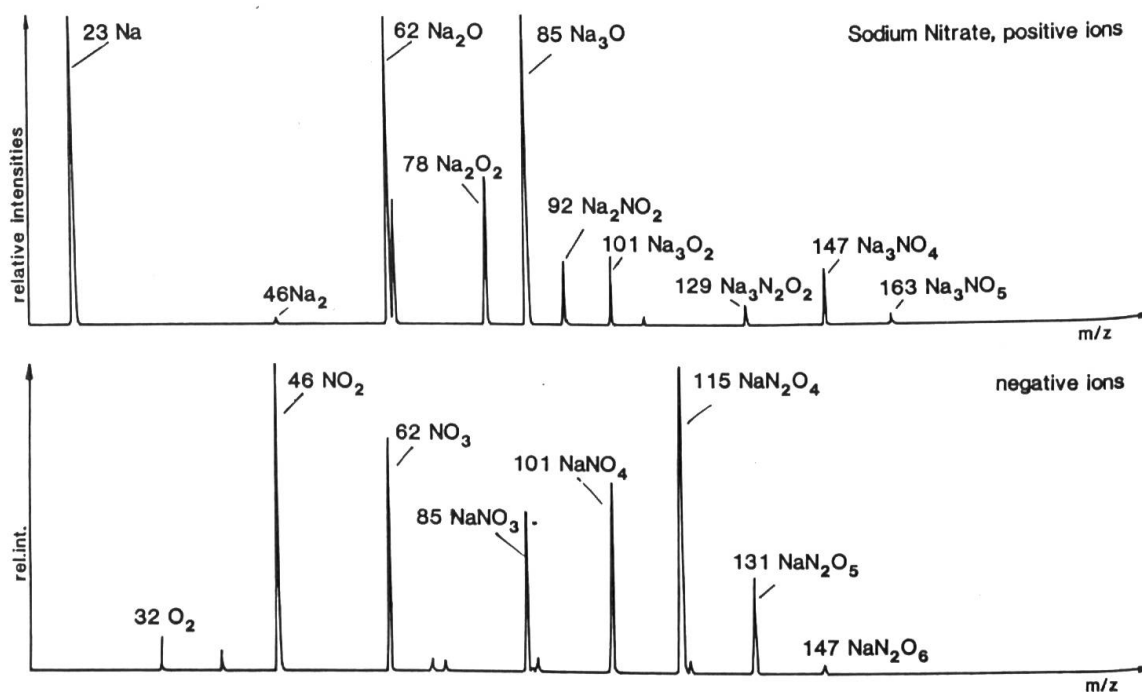
FIG. 2. — LAMMA spectra obtained for sodium nitrate.

formation is quite a common feature of inorganic mass spectrometry and ions such as Na_3^+, Na_4^+ up to Na_8^+ have been observed [6, 7]. The presence of the oxide Na_2O^+ (m/z 62) and the peroxide $Na_2O_2^+$ (m/z 78) in the positive spectrum and that
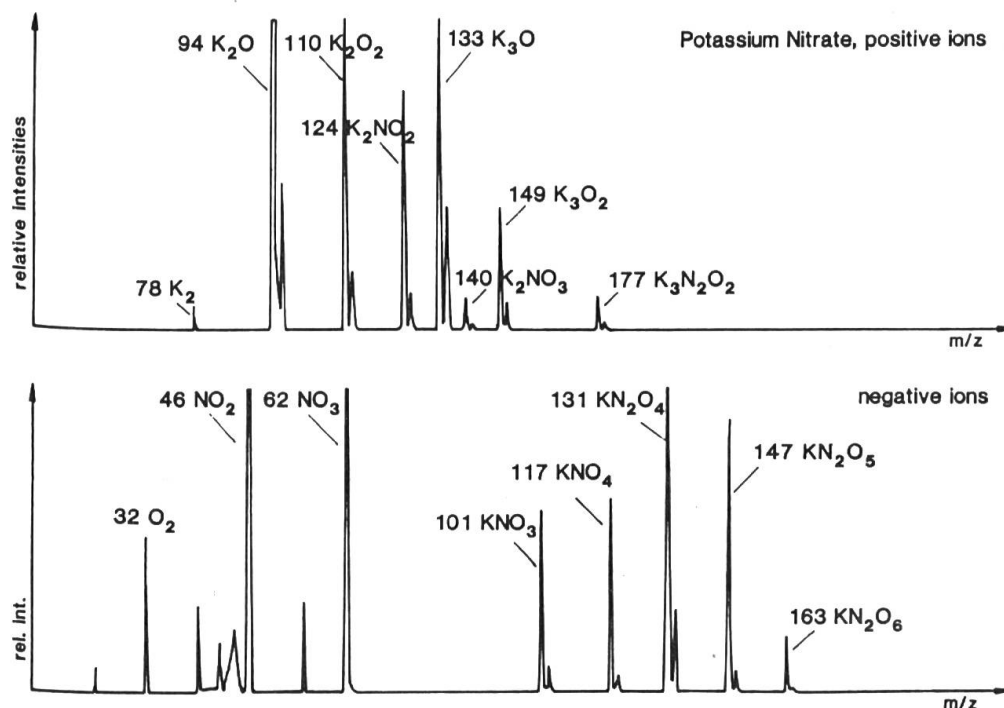
FIG. 3. — LAMMA spectra obtained for potassium nitrate.

of the oxides of nitrogen in the negative spectrum NO_2^-, m/z 46 and NO_3^-, m/z 62 indicate that those ions are formed by thermal decomposition of the parent molecule [8, 9]. The presence of all the remaining peaks are asssumed to be formed by ion-molecule interactions taking place in the gas phase region. The principle being that a cation or an anion adds on to a neutral to generate the observed ion-species.

For example in the positive spectrum of sodium nitrate the ion species Na_3O^+, $Na_2NO_2^+$, $Na_3O_2^+$, $Na_3NO_4^+$ and $Na_3NO_5^+$ are formed according to the following interactions:

$$Na_2O + Na^+ \rightarrow Na_3O^+$$
$$NaNO_2 + Na^+ \rightarrow Na_2NO_2^+$$
$$Na_2O_2 + Na^+ \rightarrow Na_3O_2^+$$
$$NaNO_3 + Na_2O^+ \rightarrow Na_3NO_4^+$$
$$NaNO_3 + Na_2O_2^+ \rightarrow Na_3NO_5^+$$
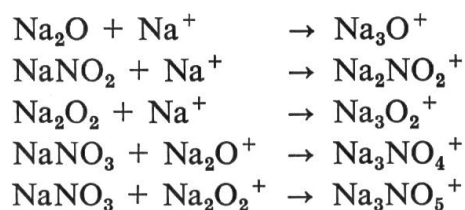
The ion species $Na_3N_2O_2$ is presumed to be formed by the interaction between sodium hyponitrite [10, 11] as a neutral and sodium cation:

$$Na_2N_2O_2 + Na^+ \rightarrow Na_3N_2O_2^+$$
sodium hyponitrite
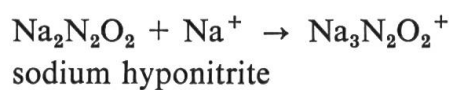
Unfortunately the peaks at m/z 92, 129, 147 and 163 although they carry the identity of a nitrate are too small in intensity to be of real diagnostic value. The negative spectrum, however, gives intense peaks showing that we are dealing with a nitrate m/z 46 and 62 for NO_2^- and NO_3^- respectively together with m/z 115 for $NaN_2O_4^-$. These ions are indicative of the presence of sodium nitrate in the sample. The molecular ion is always present in the negative spectrum m/z 85 for $NaNO_3^-$. Again each ion species can be explained in terms of a neutral plus an ion. For example the ions $NaNO_4^-$, $NaN_2O_4^-$, $NaN_2O_5^-$ and $NaN_2O_6^-$ are accounted for as follows:

$$NaNO_2 + O_2^- \rightarrow NaNO_4^-$$
$$NaNO_2 + NO_2^- \rightarrow NaN_2O_4^-$$
$$NaNO_3 + NO_2^- \rightarrow NaN_2O_5^-$$
$$NaNO_3 + NO_3 \rightarrow NaN_2O_6^-$$
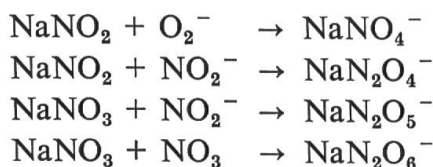
If we now compare these spectra with those of potassium nitrate, figure 3, we find that the same ion species are present. Again the diagnostic peaks are present in the negative spectrum. Indeed if we run through other members of the group we will find the same ion species appearing in each case with MN_2O_4 being the most characteristic in all cases.

Figure 4 shows the spectra obtained for a member of group II, calcium nitrate. Here again we observe that the mechanism of ion formation is the same although in group II the positive spectra have no diagnostic value, only the oxides are present.
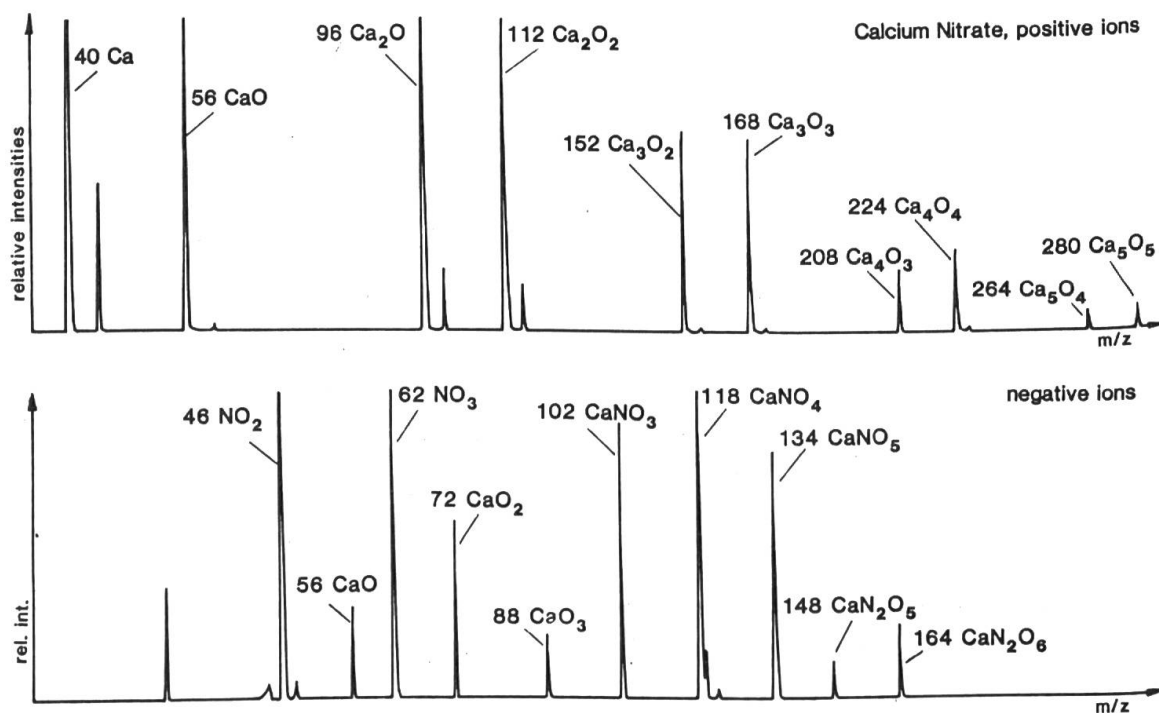
FIG. 4. — LAMMA spectra recorded for calcium nitrate.

A close examination of the positive spectrum of figure 4 shows that all these calcium related oxides can be explained on the basis of a neutral plus a cation for example:

$$CaO + Ca^+ \rightarrow Ca_2O^+$$
$$CaO + CaO^+ \rightarrow Ca_2O_2^+$$
$$CaO + Ca_2O^+ \rightarrow Ca_3O_2^+$$
$$CaO + Ca_2O_2^+ \rightarrow Ca_3O_3^+$$
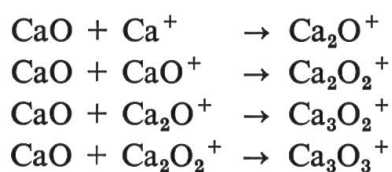
and so on until one reaches Ca_5O_5.

All the diagnostic peaks are present in the negative spectrum and ion species are again formed by ion-molecule interactions, although, as we go down the group, the formation of these specific ions becomes more difficult. This is exemplified, by the negative spectra of strontium and barium nitrates, in figure 5.

FIG. 5. — LAMMA spectra of strontium and barium nitrate recorded in the negative mode.

These studies are, as mentioned above, a prerequisite to the interpretation of the spectra that will now be discussed.

Table I and II summarize the ion species obtained for the alkali and alkaline earth nitrates.

NITRATES OF GROUP I

Positive ions :

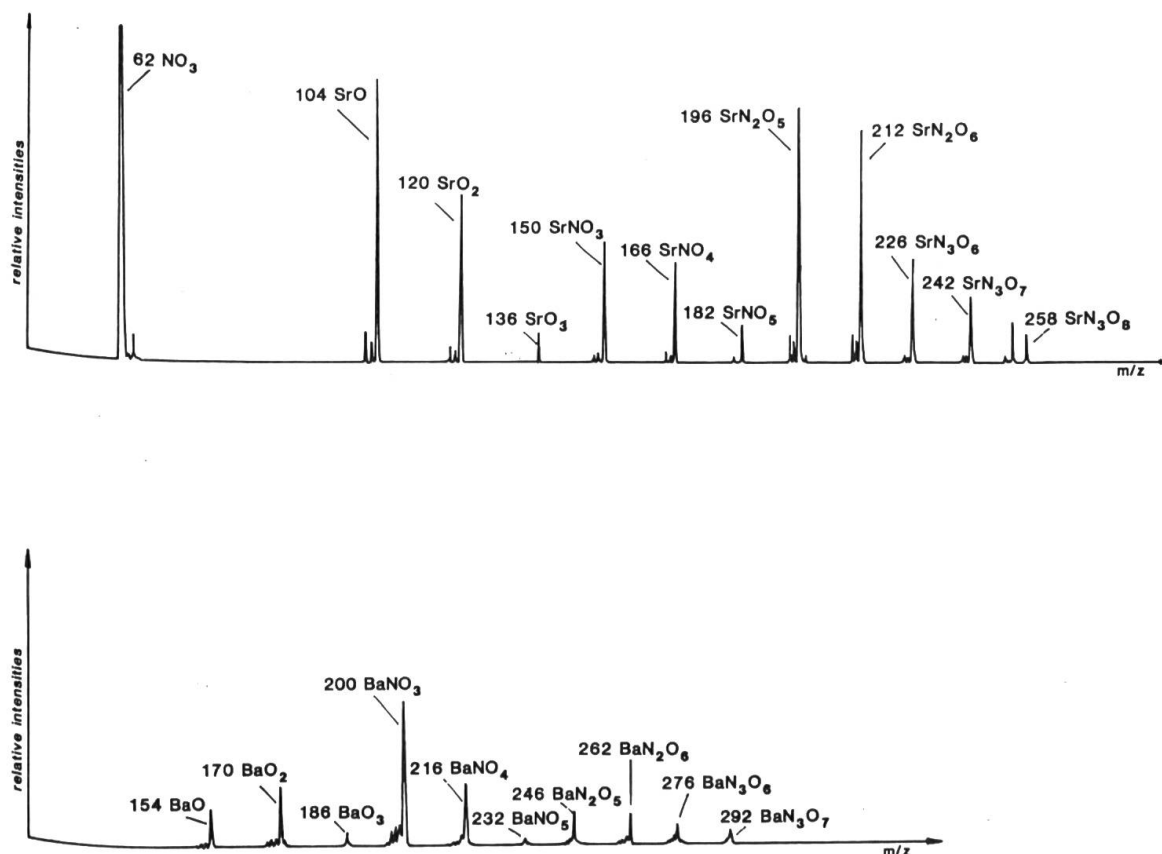|				
7 Li	23 Na	39 K	85 Rb	133 Cs
14 Li_2	46 Na_2	78 K_2	170 Rb_2	266 Cs_2
30 Li_2O	62 Na_2O	94 K_2O	186 Rb_2O	282 Cs_2O
46 Li_2O_2(vs)	78 Na_2O_2	110 K_2O_2	202 Rb_2O_2	298 Cs_2O_2
37 Li_3O (s)	85 Na_3O	133 K_3O	271 Rb_3O	415 Cs_3O
53 Li_3O_2 (s)	101 Na_3O_2	149 K_3O_2	287 Rb_3O_2	431 Cs_3O_2
60 Li_2NO_2	92 Na_2NO_2	124 K_2NO_2	216 Rb_2NO_2	312 Cs_2NO_2
67 Li_3NO_2				
(Li_5O_2)	129 $Na_3(NO)_2$	177 $K_3(NO)_2$	315 $Rb_3(NO)_2$	459 $Cs_3(NO)_2$
76 Li_2NO_3	108 Na_2NO_3	140 K_2NO_3		328 Cs_2NO_3
	147 Na_3NO_4			
	163 Na_3NO_5			
97 Li_5NO_3				

Negative ions :

16 O	16 O	16 O	16 O	16 O
32 O_2	32 O_2	32 O_2	32 O_2	32 O_2
46 NO_2	46 NO_2	46 NO_2	46 NO_2	46 NO_2
62 NO_3	62 NO_3	62 NO_3	62 NO_3	62 NO_3
69 $LiNO_3$	85 $NaNO_3$	101 KNO_3	147 $RbNO_3$	195 $CsNO_3$
85 $LiNO_4$	101 $NaNO_4$	117 KNO_4	163 $RbNO_4$	211 $CsNO_4$
99 LiN_2O_4	115 NaN_2O_4	131 KN_2O_4	177 RbN_2O_4	225 CsN_2O_4
115 LiN_2O_5	131 NaN_2O_5	147 KN_2O_5	193 RbN_2O_5	241 CsN_2O_5
131 LiN_2O_6	147 NaN_2O_6	163 KN_2O_6	209 RbN_2O_6	256 CsN_2O_6
				133 Cs
				149 CsO
				195 $CsNO_2$

TABLE I. — Characteristic ion species of the nitrates of group I.

The objective in mass spectrometry is to record a spectrum which is representative of the relative abundances of ions in the ion source. In the laser microprobe mass analysis technique for reason of better mass resolution only part of the mass scale is recorded at any one time. Although in many cases the mass range selected is sufficient to allow all the ions produced to be recorded, we have found with inorganic substances that it is not always possible to obtain information at the low

NITRATES OF GROUP II

Positive ions :

24 Mg	40 Ca	88 Sr	138 Ba
40 MgO	56 CaO	104 SrO	154 BaO
64 Mg_2O	96 Ca_2O	192 Sr_2O	292 Ba_2O
80 Mg_2O_2	112 Ca_2O_2	208 Sr_2O_2	308 Ba_2O_2
96 Mg_2O_3	128 Ca_2O_3 (s)	224 Sr_2O_3 (s)	324 Ba_2O_3 (s)
	152 Ca_3O_2	296 Sr_2O_2	446 Ba_2O_2
120 Mg_3O_3	168 Ca_3O_3	312 Sr_3O_3	452 Ba_3O_3
144 Mg_4O_3	208 Ca_4O_3	400 Sr_4O_3	
160 Mg_4O_4	224 Ca_4O_4	416 Sr_4O_4	
184 Mg_5O_4	264 Ca_5O_4	504 Sr_5O_4	
200 Mg_5O_5	280 Ca_5O_5	520 Sr_5O_5	

Negative ions :

16 O	16 O	16 O	16 O
32 O_2	32 O_2	32 O_2	32 O_2
46 NO_2	46 NO_2	46 NO_2	46 NO_2
62 NO_3	62 NO_3	62 NO_3	62 NO_3
		104 SrO	154 BaO
	72 CaO_2	120 SrO_2	170 BaO_2
	88 CaO_3	136 SrO_3	
86 $MgNO_3$	102 $CaNO_3$	150 $SrNO_3$	200 $BaNO_3$ s
102 $MgNO_4$	118 $CaNO_4$	166 $SrNO_4$	216 $BaNO_4$
118 $MgNO_5$	134 $CaNO_5$	182 $SrNO_5$	232 $BaNO_5$
	148 CaN_2O_5	196 SrN_2O_5	246 BaN_2O_5
148 MgN_2O_6	164 CaN_2O_6	212 SrN_2O_6	262 BaN_2O_6
164 MgN_2O_7			
		226 SrN_3O_6	276 BaN_3O_6
	194 CaN_3O_7	242 SrN_3O_7	292 BaN_3O_7
194 MgN_3O_8	210 CaN_3O8	258 SrN_3O_8	
	226 CaN_3O_9	274 SrN_3O_9	
	250 $Ca_2N_3O_8$		
	266 $Ca_2N_3O_9$		

TABLE II. — Characteristic ion species of the nitrates of group II.

mass end and the high mass end simultaneously. As a consequence more than one laser shot proves necessary in order to record all the ion species produced. This undoubtedly poses the problem of homogeneity of the sample. The relative intensities therefore cannot be defined in this context as precisely as is the case in the technique

NITRATES OF GROUP I — RELATIVE INTENSITIES

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		

TABLE III. — Relative intensities of the ion species recorded for the nitrates of group I of the periodic table.

+ = weak intensity
++ = medium intensity
+++ = strong intensity

of electron impact. Essential factors that have to be taken into account to ensure reproducibility are:

1º The mode of impact on the crystal.
2º Reproducibility of the laser energy.

We will not at this stage of our study discuss these problems. Nevertheless, with reference to table III which gives an appreciation of the relative intensities of the ions recorded for the nitrates of group I, the following observations can be made.

It can be seen from this table that in the negative mode, the ions NO_2^- and NO_3^- are formed in great abundance. O^- is also present in great intensity whereas OH^- is of much less intensity. The intensity of OH^- decreases as one goes down the group. This ion, however, is of no real value in speciation analysis as it is generally observed for all hydrated salts. In the case of the nitrates of group I the intensity of OH^- ion increases with the ease of hydration of the respective salts. It can also be observed, with respect to the characteristic ion species that less and less information

is obtained with increasing molecular weight. In all cases the most intense diagnostic peak is the species $MN_2O_4^-$.

In the positive mode the situation is more complex. M^+ is always very intense if not the most intense. The normal oxide ion M_2O^+ is always very characteristic. The ion $M_2O_2^+$ has never been observed in the case of lithium in agreement with the instability of lithium peroxide. For the other members of the group $M_2O_2^+$ is always present and is of medium intensity. The ion M_3O^+ is of great intensity but decreases rapidly as the molecular weight increases. In the positive mode, however, not much useful information can be obtained from a speciation point of view. The question of relative intensity is at the moment left open as more work is being done in that direction.

3.2. CHARACTERISATION OF THE MINERAL FOUND IN BRITTANY AND PRESUMED TO BE A METEORITE

The spectra obtained for this sample are shown in figure 6. Spectra A and B have been recorded in the positive mode, the mass range studied for spectrum A being different to that studied for spectrum B. Figure 6C shows the negative spectrum obtained. In the positive mode the elements ^{23}Na, ^{39}K, ^{40}Ca and iron with its characteristic isotopes ^{54}Fe, ^{56}Fe, ^{57}Fe, (the shoulder on peak 56) are identified. The negative spectrum, figure 6C, shows the presence of oxygen and of the hydroxyl group at m/z 16 and 17 respectively. The isotopic abundance of the peaks at m/z 35 and 37 allows us to ascertain the presence of chlorine. These is no evidence for the presence of other anions such as nitrates, sulphates, carbonates and others. The elements found in the positive spectra are therefore either present as oxides or chlorides.

Our preliminary work has shown that under laser induced ionisation all inorganic compounds, at least for the classes we have studied so far, will give rise to ion species characteristic of the compound under study. Furthermore it is known that oxides of metals and inorganic salts containing an oxygenated anion will all give, depending on their ease of "ionisation", the normal oxide of the metal and more complex oxide species as was exemplified by the positive spectrum of calcium nitrate. Of the four elements identified in the positive spectra only iron oxide and iron related oxides can account for the other m/z values obtained. Indeed, the number of iron atoms in each ion species can be determined from their abundance relationship calculated from the isotopic ratios. For two iron atoms, for example, the calculated abundance is 10.7% of the total for the 54-56 combination, 84.0% for the 56-56 combination and 4.0% for the 56-57 combination. That corresponds indeed to the abundance relationship found at m/z 128 and 144.

The correct abundance relationship is also found for ion species with three iron atoms, (m/z 200 and 216). The presence of the hydroxyl group in the negative spectrum is strong evidence for the mass assignment of m/z 73 as FeOH. The relative
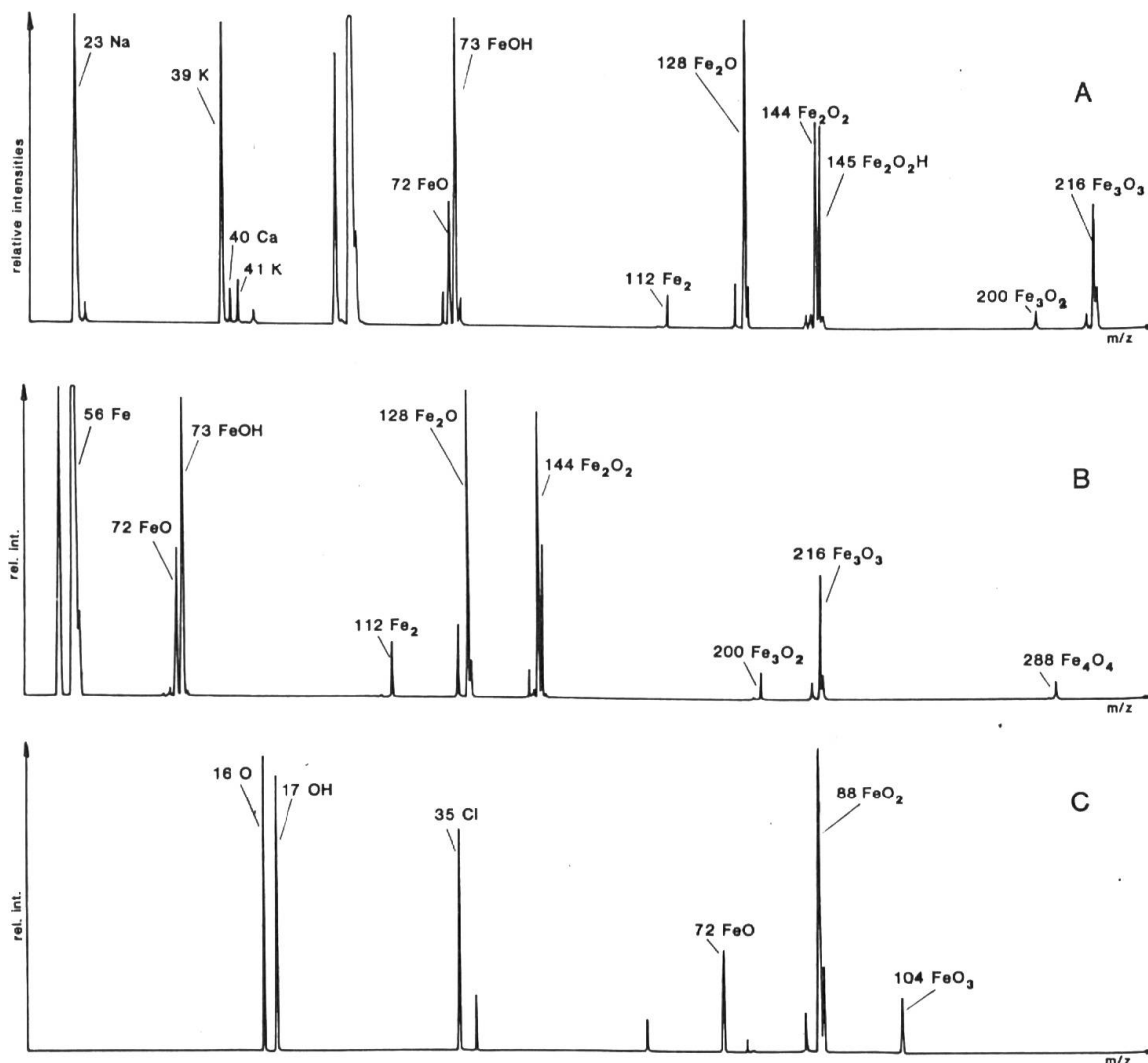
FIG. 6. — LAMMA spectra recorded for particles obtained from the "meteorite" collected in Brittany. A and B recorded in the positive mode, C in the negative mode.

intensities of peaks 72 and 73 as well as those of peaks 144 and 145 vary considerably. This variation depends on the concentrations of the components in the region directly above the sample after laser impact and also on the various interactions taking place in the gas phase region.

The interpretation of these spectra shows that we are here dealing with a sample made up of oxides of iron and a few impurities.

The sample is therefore most likely a specimen of haematite and not a meteorite.

Indeed the absence of elements such as Ni rules out the possibility for this specimen to be a meteorite. Furthermore, the components of meteorites would always show the elements in metallic forms only.

3.3. TENTATIVE INTERPRETATION OF SPECTRA RECORDED FROM FLY ASHES SAMPLED FROM THE GRATE FURNACE « MARTIN » OF AN INCINERATION STATION

This furnace is used exclusively for the incineration of domestic refuse. Fly ashes have been sampled at a height of 26 m above ground level by introducing the sampling pipe of a BCURA apparatus in the chimney through an aperture specially designed for that purpose. Sampling is done under isokinetic conditions.

Figure 7, A and B, shows characteristic spectra recorded for positive and negative
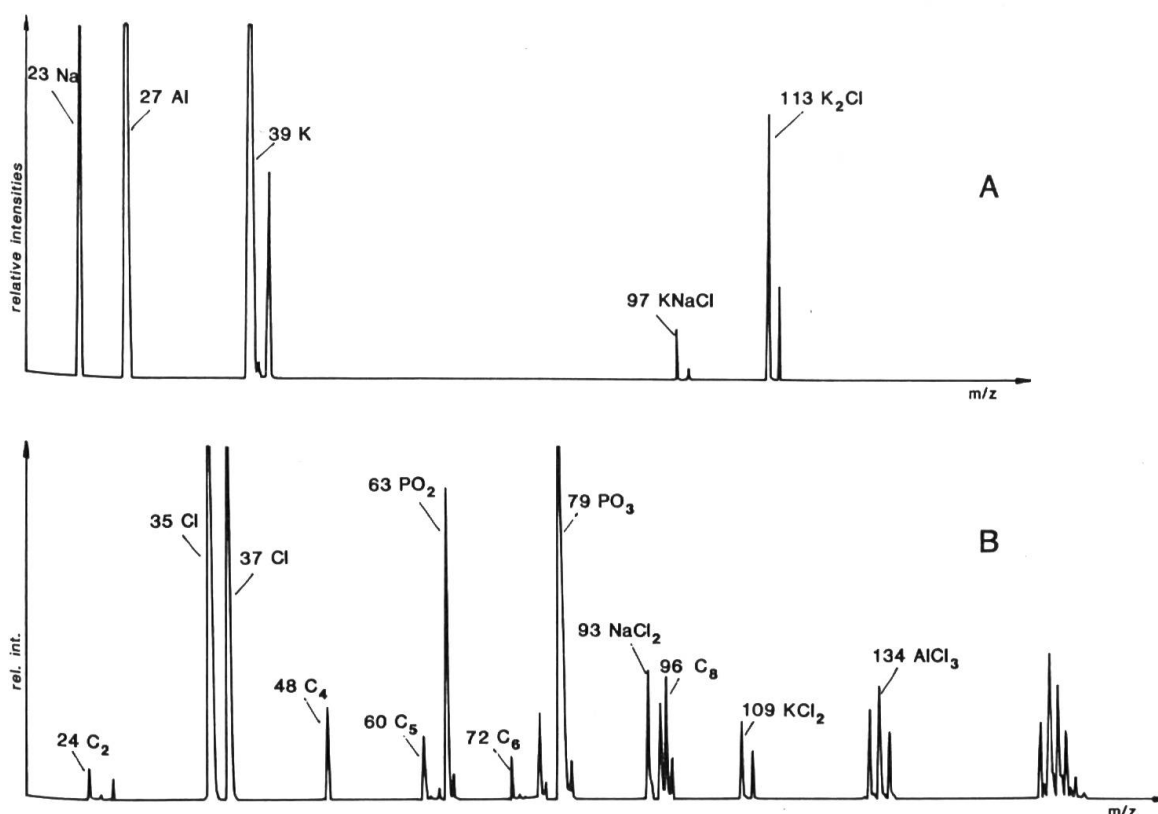

FIG. 7. — LAMMA spectra of ash particles from a grate furnace.
A positive spectrum; B negative spectrum.

ions respectively for ash particles. It should be pointed out that each spectrum is obtained from a particle which after irradiation is completely volatilised. In the positive spectrum the elements Na, Al and K are easily identified. Mass assignment of the other peaks present in this spectrum is greatly facilitated by an inspection of the negative spectrum. Only chorides and phosphates are indicated in the negative spectrum. The peaks at m/z 97 and m/z 113, in the positive spectrum, are therefore assigned as $KNaCl^+$ and K_2Cl^+ respectively. Potassium is therefore present as KCl since K_2Cl^+ is its specific ion. $KNaCl^+$ is formed as a result of the interaction

between molecular KCl and a sodium ion. It is impossible in that spectrum to deduce, at least for this particle, the chemical form of sodium; if present as NaCl a prominent peak at m/z 81 corresponding to the ion species Na_2Cl^+ would have been observed. In the negative spectrum the peak at m/z 109 corresponding to the ion species KCl^-_2 confirms the chemical species of potassium as potassium chloride. The group of peaks at m/z 93, 95 and 97 is due to the ion species $NaCl_2^-$ and confirms the presence of sodium as sodium chloride in this particle. The anionic species of aluminium chloride is also present, $AlCl_3^-$ at m/z 134. The quadruplet at m/z values 168-174 has not been identified yet. The phosphate ions at m/z 63 and m/z 79 corresponding to PO_2^- and PO_3^- respectively are most probably due to the presence of organic phosphate in the sample for example tributylphosphate which is used as a plasticizer.

The peak at m/z 96 which could be assigned to SO_4^- is not due to the presence of sulphate in this particle as can be deduced from our systematic study on the mechanism of ion formation of the sulphates of groups I and II. Indeed peaks at m/z 64 and 80 of almost equal intensity to the observed peak at m/z 96 would have been identified. Figure 8 shows the spectral pattern obtained for a particle on which organic matter has been adsorbed. The typical negative ion feature being the C_n^-, C_nH^- ions where the odd n ions show lower intensity.
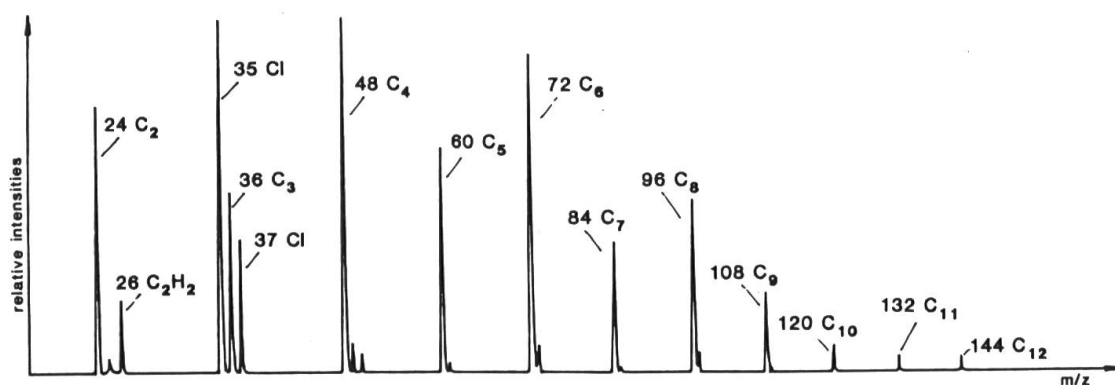

FIG. 8. — Typical negative LAMMA spectrum on which organic matter has been adsorbed.

3.4. LAMMA MASS SPECTRA OF ASH PARTICLES FROM A ROTARY FURNACE

This rotary furnace has been designed for the high temperature incineration of special products such as wastes from the chemical and printing industries, drained oils, worn out tyres and so forth. Ashes were sampled at the control orifice of the installation.

Characteristic spectra of these particles are shown in figure 9 A, B and C. Figure 9 (A & B) shows the spectra recorded in the positive mode for shots taken from two different particles. From what we know about ion formation in the context
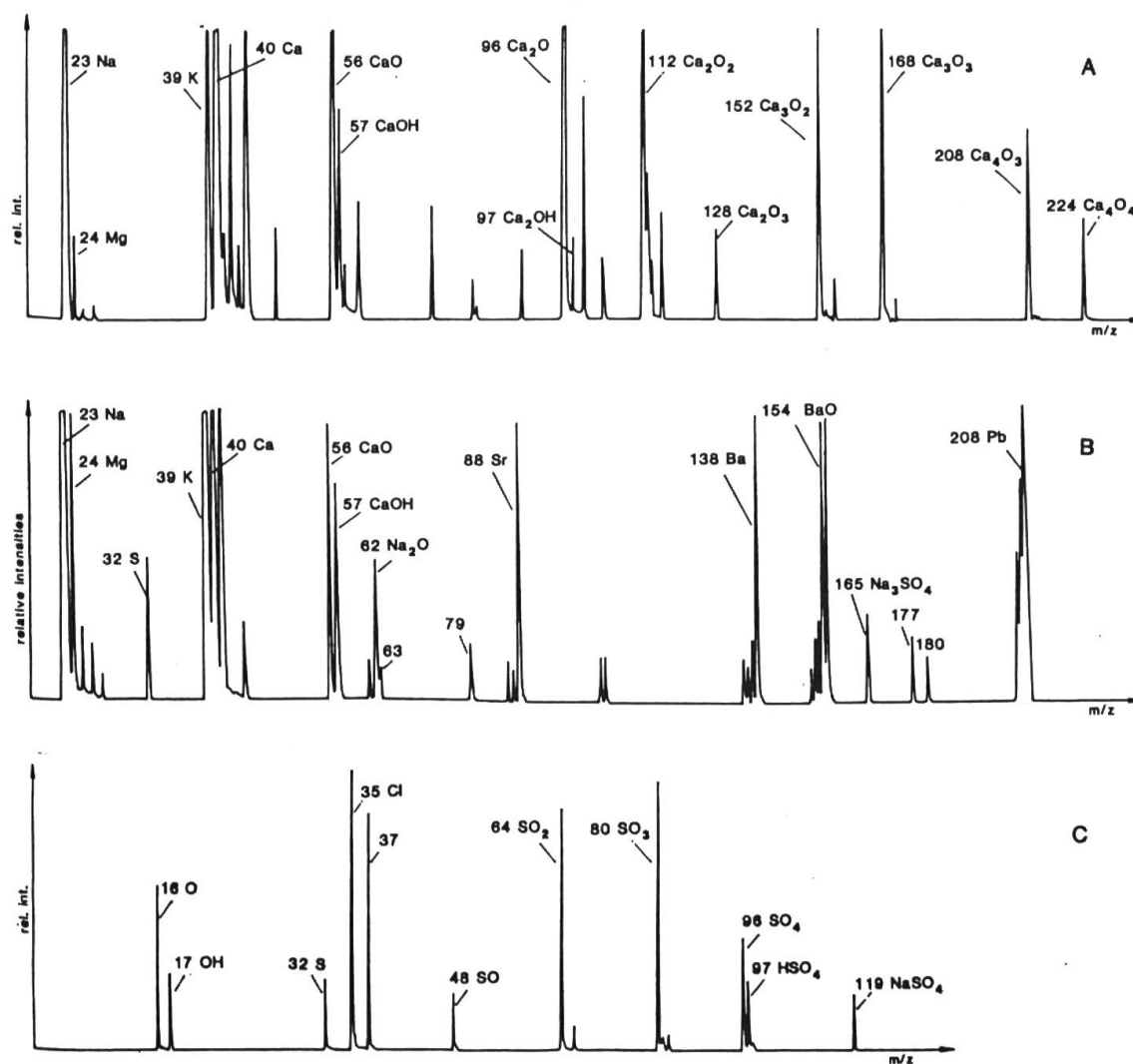
FIG. 9. — LAMMA spectra of particles sampled from the rotary furnace.
A and B are positive spectra, C is a negative spectrum.

of laser induced ionisation, one could attribute the oxide ions CaO^+, Na_2O^+ and BaO^+ to chemical compounds having an oxygenated anion. The only oxygenated anion present is a sulphate as exemplified by figure 9 C. In this negative spectrum, only sodium shows a specific ion species at m/z 119 corresponding to $NaSO_4^-$. Of these three oxides identified therefore, only sodium is present as sodium sulphate. This is confirmed by the peak at m/z 165 in spectrum B, where the characteristic positive ion species of sodium sulphate is identified as $Na_3SO_4^+$. These spectra can be compared with those obtained for sodium sulphate as shown in figure 10. In figure 9 A the whole series of Ca related oxides: CaO^+, Ca_2O^+, $Ca_2O_2^+$, $Ca_3O_2^+$, $Ca_3O_3^+$ and so on can be identified as was illustrated before in the discussion on calcium nitrate (figure 4).
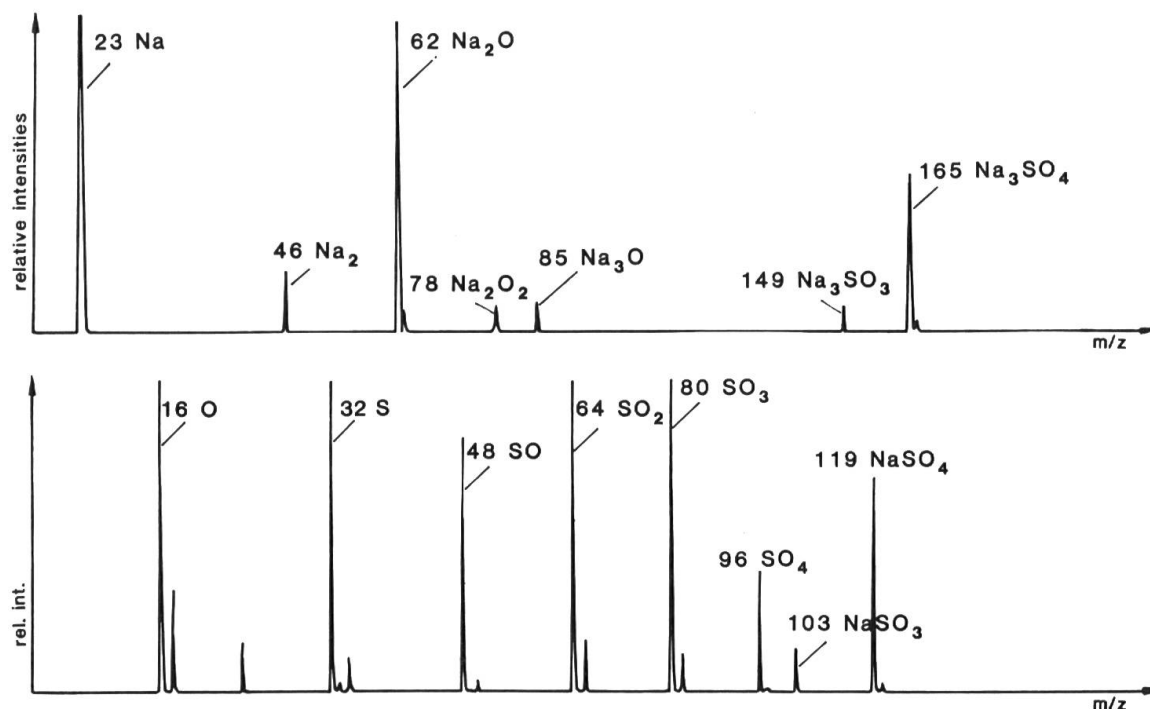
FIG. 10. — LAMMA spectra of sodium sulphate. Top spectrum recorded in the positive mode and bottom spectrum in the negative mode.

Although the presence of chloride is indicated in figure 9 C, an inspection of spectra A and B shows that there is no evidence for any of the elements identified to be present as a chloride. They are therefore present either in the elemental form or as an oxide. Strontium is commonly used as a stabiliser in the plastic industry while barium and lead are found in many formulations.

3.5. LAMMA MASS SPECTRA OF AIR PARTICLES BLOWN OVER FROM THE SAHARA DESERT

The particles analysed gave the spectra shown in figure 11 A, B and C. In the positive spectra A and B the elements sodium, magnesium, aluminium, silicon, potassium, calcium, titanium and iron are identified. Not enough particles were available, however, to allow us to discuss the problems of homogeneity. It is not therefore possible for us to ascertain whether we were dealing with two types of particles one rich in titanium and the other containing only traces. The negative spectrum C, however, gives convincing evidence that an aluminosilicate matrix is present. These particles unlike the urban ones we have studied show a very simple spectral pattern in the positive mode. In urban particles the presence of barium and lead is commonly observed in the positive spectra. On the other hand characteristic ion species providing evidence for a silicate is rare in the negative mode.
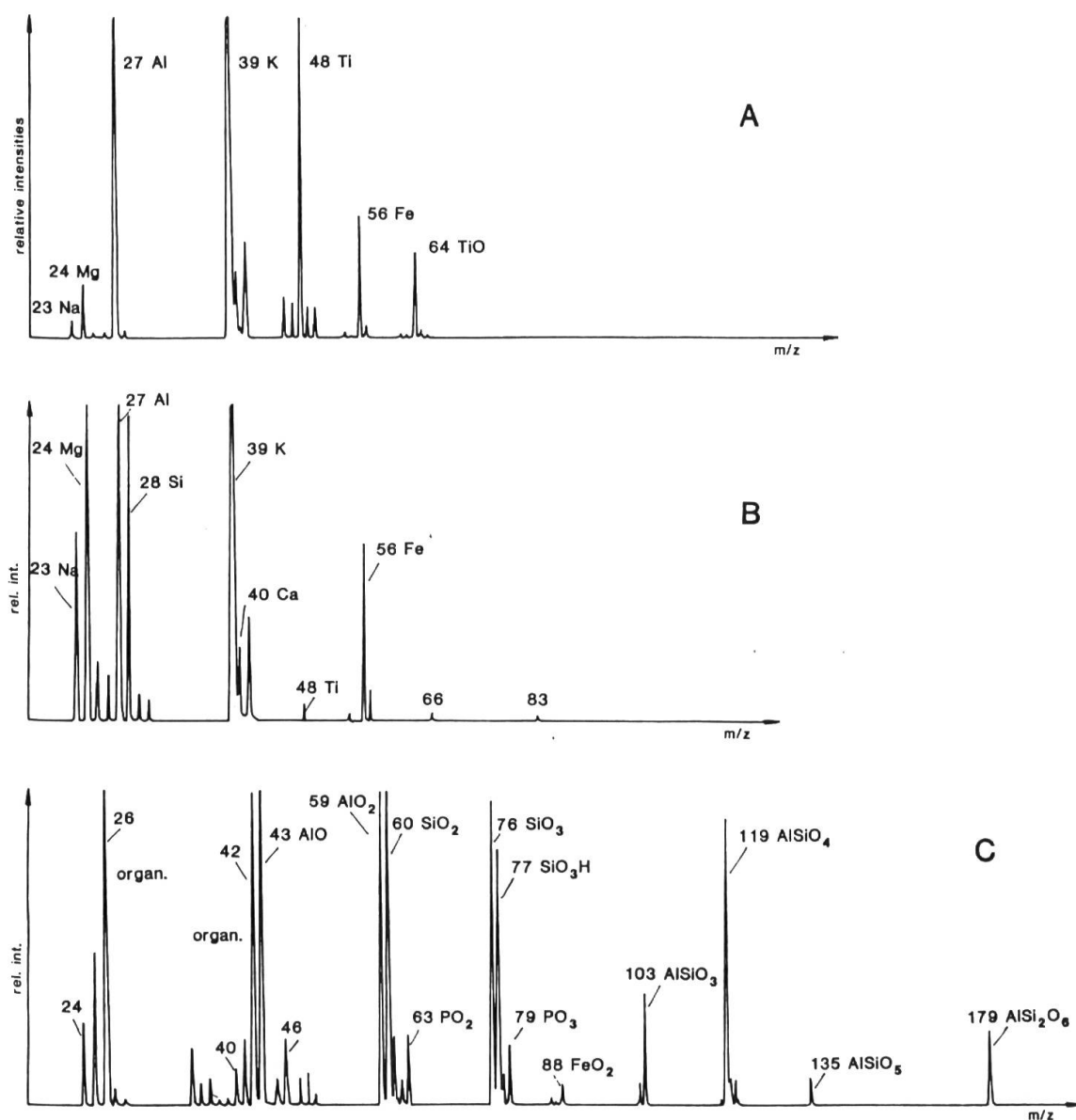
FIG. 11. — LAMMA spectra of air particles blown over from the Sahara desert.
A and B are positive spectra, C was recorded in the negative mode.

4. CONCLUSION

This study shows that only after an extensive knowledge of the mechanism of ion formation will one be able to rule out this instrument as a useful tool for speciation analysis. The examples presented in this paper, with due regard to the present state of knowledge, clearly demonstrates the potentialities of LAMMA in that context. We believe that the LAMMA holds great promise in the field of inorganic mass spectrometry.

The technique has many applications in trace analyses, however, since in many cases no preseparation is possible, information about organic as well as inorganic substances is obtained at the same time, making the interpretation more difficult. We are at present pursuing our study on the mechanism of ion formation with a view to elaborating the problems encountered in speciation analysis.

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