Laser Microprobe Mass Analysis (LAMMA) as a Method for the Identification of Inorganic Substances**

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LAMMA, the Laser Microprobe Mass Analysis, is a fast and sensitive technique that has found many applications in chemistry. The characterization of inorganic compounds by this technique, however, is limited by a lack of understanding regarding the formation of ions. Indeed, after laser-induced ionization one cannot talk of the fragmentation pattern of the molecules, instead cluster formation and recombination reactions prove to be the commonly observed feature. As a result most of the interpretation so far has been done by way of comparison or «fingerprint» matching. – In this account we report on the work carried on in our laboratory with a view to understanding the mechanism of ion formation. The interpretation of unknowns in the light of present knowledge is discussed with special reference to the nitrates, halides, and silicates. For example the three most common types of asbestos fibres (chrysotile, amosite, and crocidolite) are easily identified and differentiated from each other and the other asbestos fibres.

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1. Introduction

The LAMMA originally designed for studying elemental distribution in thin sections of biomedical samples[1] has now found applications in quite different fields[2,3]. The technique is used in our laboratory mainly for identifying inorganic substances. Samples under investigation have quite different origins namely environmental pollution, forensic science, oceanography, and general chemistry.

The most difficult problem with which we are faced is the interpretation of unknowns as not much is known about the mechanism of ion formation after laser-induced ionization. Contrary to classical organic mass spectrometry, where the samples all reach the ion source in a gaseous form to be ionized by an electron beam of constant energy, with the laser microprobe the energy deposited on the sample is not constant and the sample analyzed is rarely in an homogeneous state. It is therefore impossible to get reproducible spectra as is the case with organic mass spectrometry.

Our study shows, however, that this is not a drawback in what concerns the interpretation of unknowns. Indeed, spectra of positive and negative ions obtained at low and high irradiance are all useful for the interpretation. Samples from the nitrates, halides, and silicates illustrate very well that the ion species observed are formed by decomposition of the parent molecules followed by ion-molecule reactions taking place in the plasma phase after laser impact.

The identification of all samples studied have been done on the basis of this proposed mechanism.

2. Experimental Set-Up

2.1. The Laser Microprobe Mass Analyzer

The laser microprobe mass analyzer LAMMA-500 (Leybold-Heraeus) is represented schematically in Fig. 1. This instrument has been described in detail elsewhere[4–6]. The pulsed Nd-YAG laser (Q-switched, frequency quadrupled, wavelength 265 nm, pulse duration 15 ns) and the co-aligned He-Ne laser are focused on the sample by means of an optical microscope. The sample volume is about 1 µm^3 and the detection limit is in the ppm range. The ions formed are analyzed in a time-of-flight (TOF) mass spectrometer where both positive and negative spectra can be recorded.

2.2. Materials and Methods

All the nitrates and halides studied were of the pro analysis type, purchased from Merck. The silicates including the asbestos fibres were all obtained from the private collection of the Natural History Museum of Genève. Samples of rat lungs exposed to an atmosphere of asbestos were obtained from the Centre d'Etudes et Recherches des Charbonnages de France, CHERCHAR.

No sample treatment was necessary except for some silicates which were treated at 700°C to eliminate all the adsorbed organic material. The powdered samples or fibres were placed between electron microscopic grids and fixed on the sample holder which was then mounted on the mass spectrometer.

3. LAMMA Spectra of Nitrates and Halides of Alkali Metals

In a previous paper we discussed the spectra of the nitrates[7] and showed that the ion species obtained could all be explained on the basis of the decomposition products of the nitrate followed by ion-molecule reactions. Fig. 2 and Fig. 3 show the positive and negative LAMMA spectra obtained for sodium nitrate. Of interest are the extra ion species that are obtained at high laser irradiance. All these extra ion species are accounted for by dissociative ionization and recombination reactions.

In the positive mode (Fig. 2B) the ion species $Na_2NO_3^{\oplus}$, $Na_2NO_4^{\oplus}$, and $Na_2NO_5^{\oplus}$ are further evidence of the presence of sodium nitrate in the sample. Although it would appear confusing at first to obtain different spectra for the same sample, the spectra of Fig. 2 and 3 show that it is necessary to identify all ion species in order to confirm beyond doubt that one is dealing with one and the same sample.

The ion species $NaO^{\ominus}$, $NaO_2^{\ominus}$, and $NaO_3^{\ominus}$ in the negative spectrum (Fig. 3B), although of no real significance in the identification of a nitrate, are useful reminders that sodium in the sample is originally linked to oxygen. The corresponding ions in the spectra of the silicates (Section 4) will demonstrate how useful they are in characterizing these samples.

Fig. 4 shows the ion species obtained for potassium chloride. The spectra obtained are very much simpler than those of the nitrates, because it is obvious that the only decomposition products of the halides of group 1 are formed by dissociative ionization of the parent molecule to give the

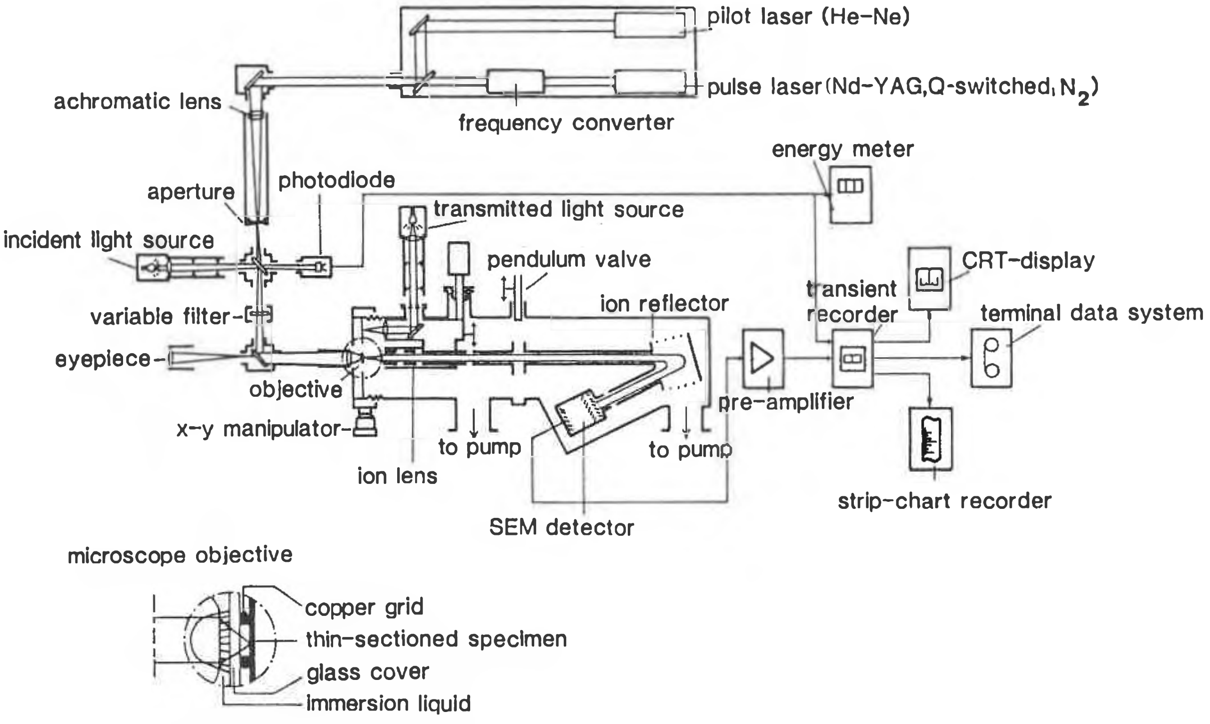

Fig. 1. Schematic diagram of LAMMA principle.

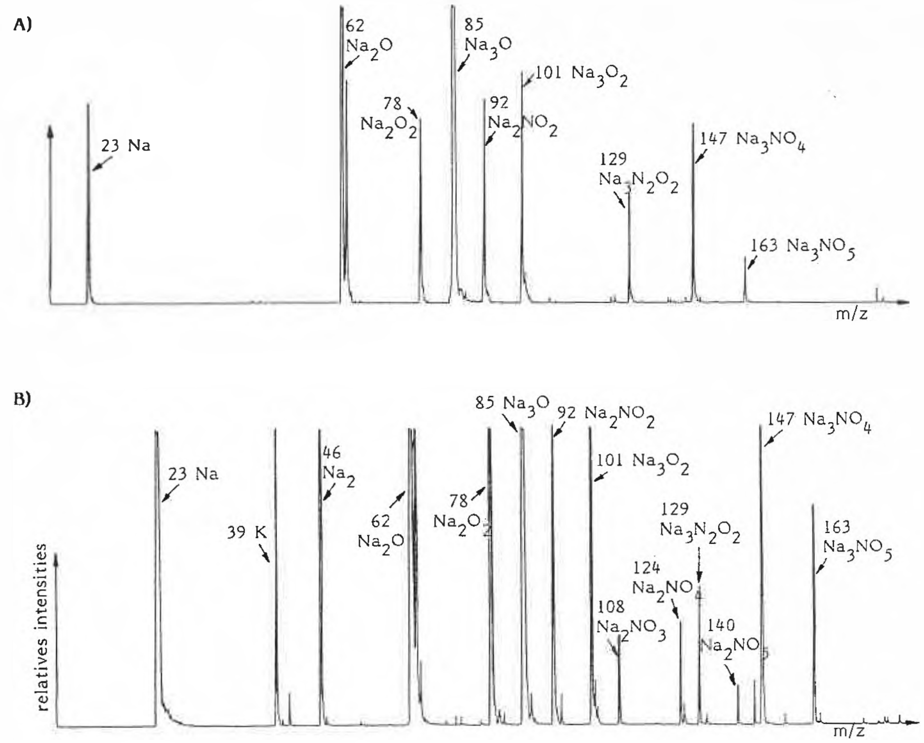

Fig. 2. Positive LAMMA spectra of sodium nitrate: A) low laser irradiance; b) high laser irradiance.

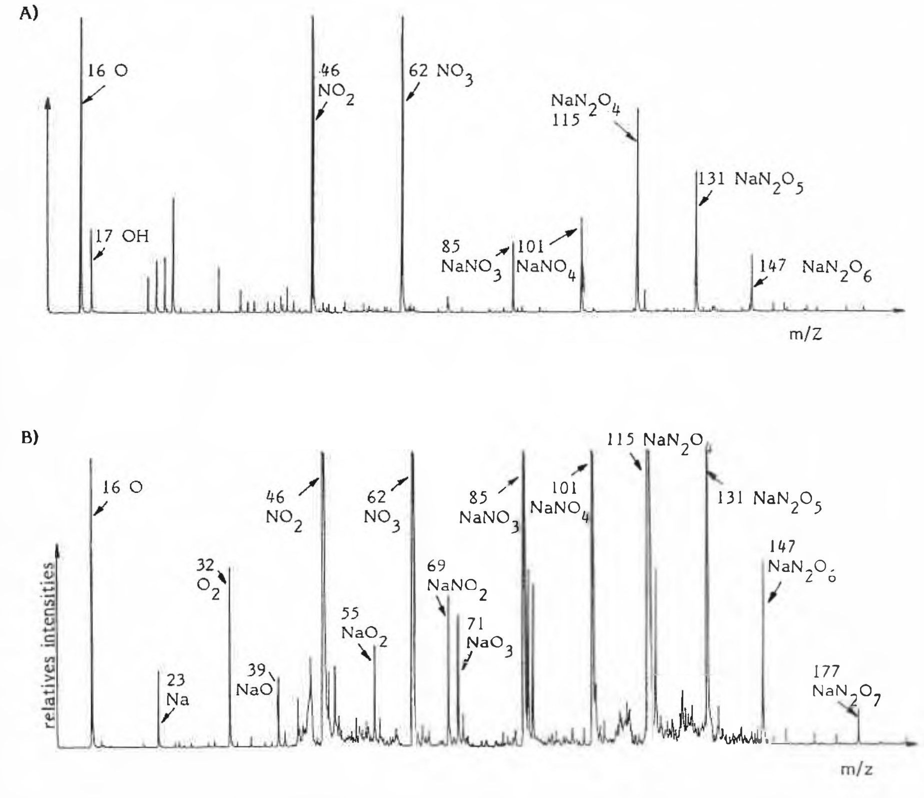

Fig. 3. Negative LAMMA spectra of sodium nitrate: a) low laser irradiance; b) high laser irradiance.

corresponding positive ion and negative ion, for example:

$KCl \rightarrow K^{\oplus} + Cl^{\ominus}$

These ions ($K^{\oplus}$ and $Cl^{\ominus}$) suggest therefore the presence of KCl in the sample. These are confirmed by the possible ion-molecule reactions that can take place between these primary ions and the neutral KCl molecule. For example in the positive mode, the ion species $K_2Cl^{\oplus}$ and $K_3Cl_2^{\oplus}$ are explained as follows:

$K^{\oplus} + KCl \rightarrow K_2Cl^{\oplus}$

$K_2Cl^{\oplus} + KCl \rightarrow K_3Cl_2^{\oplus}$

In the negative mode the ions $KCl_2^{\ominus}$ and $K_2Cl_3^{\ominus}$ are formed according to the following reactions:

$Cl^{\ominus} + KCl \rightarrow KCl_2^{\ominus}$

$KCl_2^{\ominus} + KCl \rightarrow K_2Cl_3^{\ominus}$

At higher energies, ions of higher *m/z* values of the type $M_nX_{n-1}^{\oplus}$ and $M_nX_{n+1}^{\ominus}$ are obtained in the positive and negative mode, respectively, M being the metal cation and X the anion.

4. LAMMA Spectra of Silicates

Positive and negative LAMMA spectra of kaolinite $Al_2Si_2O_5(OH)_4$ are shown in Fig. 5. The positive spectrum is very simple and shows the presence of aluminium and potassium. No indication is obtained in the positive spectrum of kaolinite suggesting that a silicate is present.

In the negative spectrum the presence of a silicate is indicated by the characteristic ion species $SiO_2^{\ominus}$ and $SiO_3^{\ominus}$ at *m/z* 60 and 76, respectively. The ions $AlO^{\ominus}$ and $AlO_2^{\ominus}$ strongly suggest that they are present due to the destructive ionization of an aluminosilicate. These ions are indeed important in the spectrum as they are the ones that tell us that we should look for the ion species characteristic of an aluminosilicate: In this particular case $AlSiO_3^{\ominus}$ and $AlSiO_4^{\ominus}$. These ions can be accounted for by the following ion-molecule reactions:

$AlO^{\ominus} + SiO_2 \rightarrow AlSiO_3^{\ominus}$

$AlO_2^{\ominus} + SiO_2 \rightarrow AlSiO_4^{\ominus}$

The other ion species $Si_2O_5^{\ominus}$ and $AlSi_2O_6^{\ominus}$ are explained as follows:

$SiO_3^{\ominus} + SiO_2 \rightarrow Si_2O_5^{\ominus}$

$AlSiO_4^{\ominus} + SiO_2 \rightarrow AlSi_2O_6^{\ominus}$

It can be seen from the negative spectrum of kaolinite that once we have identified the primary ions $AlO^{\ominus}$, $AlO_2^{\ominus}$, $SiO_2^{\ominus}$, and $SiO_3^{\ominus}$ we know immediately what other ion species to look for in order to positively confirm the presence of an aluminosilicate.

The spectra obtained for talc (Fig. 6), a form which contains iron, illustrate this very well. In the positive spectrum sodium,

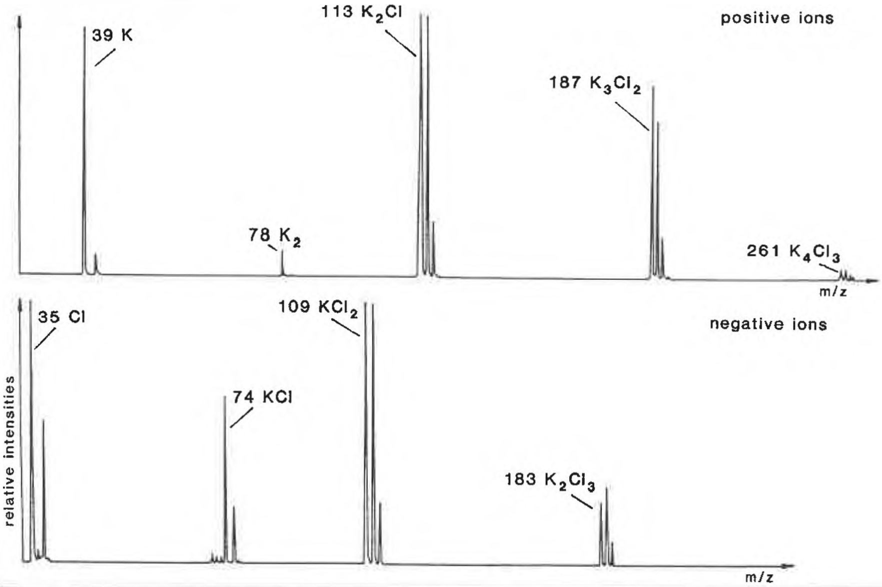

Fig. 4. Positive and negative LAMMA spectra of potassium chloride.

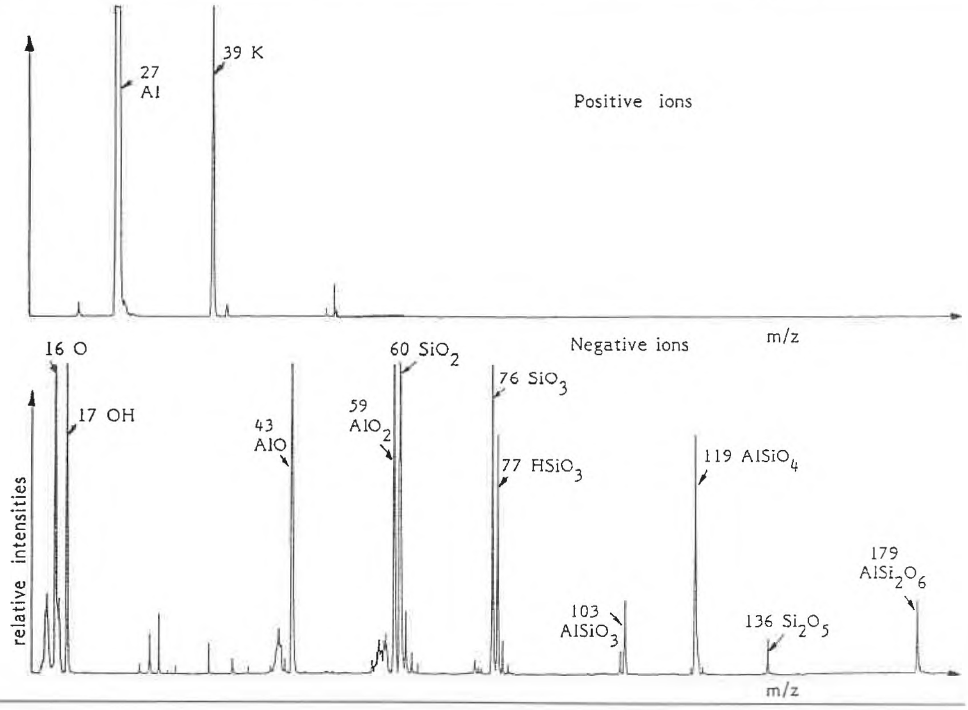

Fig. 5. Positive and negative LAMMA spectra of kaolinite.

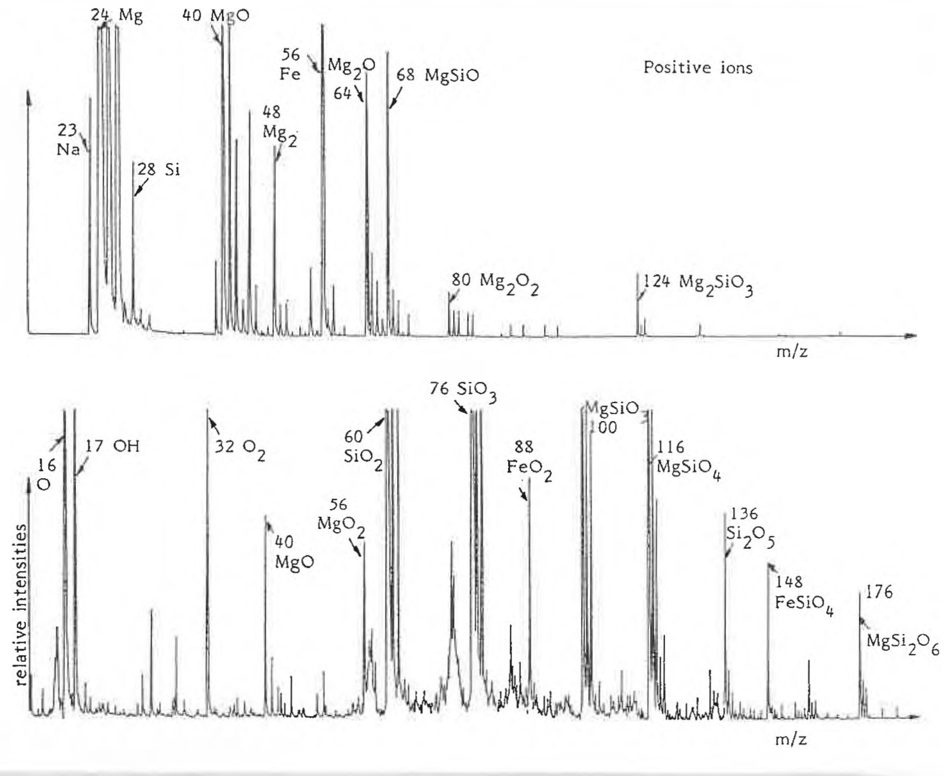

Fig. 6. Positive and negative LAMMA spectra of talc (iron talc).

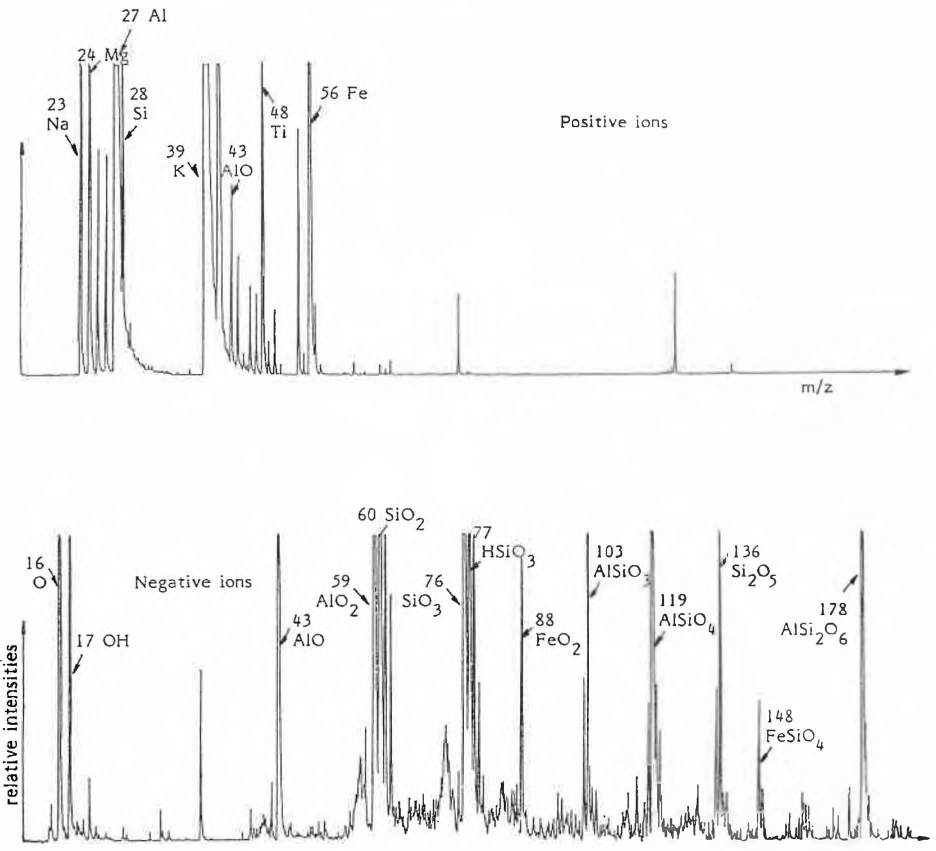

Fig. 7. Positive and negative LAMMA spectra of biotite.

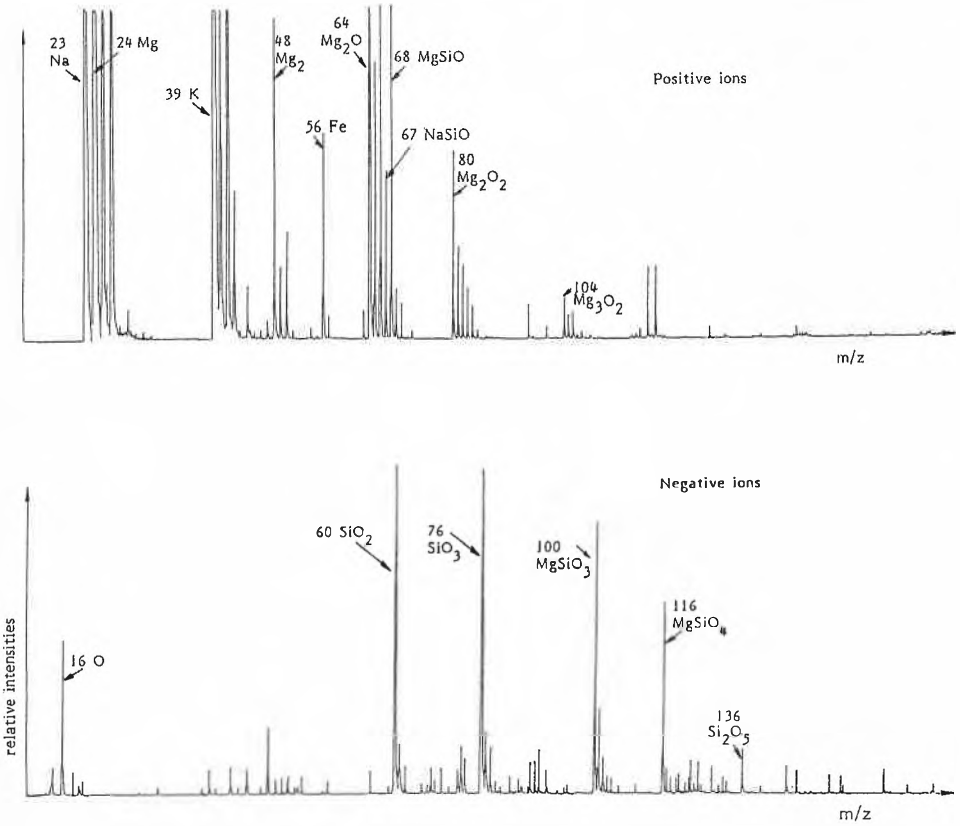

Fig. 8. Positive and negative LAMMA spectra of chrysotile.

magnesium, silicon, and iron are easily identified. The ions $MgO^{\oplus}$ and $Mg_2O^{\oplus}$ indicate that magnesium is linked to an oxygenated anion. The ions $MgSiO^{\oplus}$ and $Mg_2SiO_3^{\oplus}$ although they bear the identity of a silicate have no real diagnostic value. The confirmation that we are dealing with a magnesiosilicate comes from the ion species observed in the negative spectra. Indeed, the primary ion species $MgO^{\ominus}$, $MgO_2^{\ominus}$, $SiO_2^{\ominus}$, and $SiO_3^{\ominus}$ tell us that $MgSiO_3^{\ominus}$ and $MgSiO_4^{\ominus}$ should be present. The presence of $FeO^{\ominus}$ (*m/z* 72) and $FeO_2^{\ominus}$ (*m/z* 88) is also indicative of ferrosilicate in the sample. This is confirmed by the ions $FeSiO_3^{\ominus}$ and $FeSiO_4^{\ominus}$ at *m/z* 132 and 148, respectively. This sample therefore is an example of a specimen of talc where some of the magnesium has been replaced by iron.

Biotite is another example of a complex silicate where Al can be replaced by Fe or Mg. In Fig. 7, the negative spectrum of biotite shows that only aluminosilicate and ferrosilicate are present. There is no evidence of a magnesiosilicate. However, one will have to use more laser energy in the negative mode in order to ascertain that the primary ions $MgO^{\ominus}$ and $MgO_2^{\ominus}$ and the characteristic silicate ions $MgSiO_3^{\ominus}$ and $MgSiO_4^{\ominus}$ are absent before ruling out the possibility of the presence of magnesium silicate in this sample.

The above examples show that by a careful study of the positive and negative LAMMA spectra it is possible to make the correct mass assignment of all the peaks present. The following examples concerning asbestos fibres will further exemplify the approach to the interpretation of unknowns.

The positive and negative spectra of chrysotile, the only serpentine form of asbestos, are shown in Fig. 8. The elements identified in the positive spectrum are sodium (*m/z* 23), magnesium (*m/z* 24, 25, 26), potassium (*m/z* 39, 41), calcium (*m/z* 40, 44), and iron (*m/z* 54, 56). Of all these elements only magnesium has oxygenated ion species showing that it is linked in the sample to some oxygenated species. The characteristic ion species $SiO_2^{\ominus}$ (*m/z* 60) and $SiO_3^{\ominus}$ (*m/z* 76) indicate that the oxygenated species is most likely a silicate. Ion species at *m/z* 100 corresponding to $MgSiO_3^{\ominus}$ and *m/z* 116 corresponding to $MgSiO_4^{\ominus}$ confirm the presence of magnesium silicate in the sample.

In Fig. 9–13 are shown the spectra of the amphibole asbestos. It is evident from Fig. 9 that amosite is a mixed silicate consisting of iron and magnesium and cannot be confused with the spectra of chrysotile.

The third most commonly used type of asbestos, crocidolite, is another mixed silicate of iron and sodium. It is seen from the spectra of crocidolite (Fig. 10) that the characteristic ion species of sodium silicate appear in the positive mode at *m/z* 106, 122 and 145 corresponding to the species $Na_2SiO_2^{\oplus}$, $Na_2SiO_3^{\oplus}$ and $Na_3SiO_3^{\oplus}$, respectively. It is obvious when comparing Fig. 8, 9

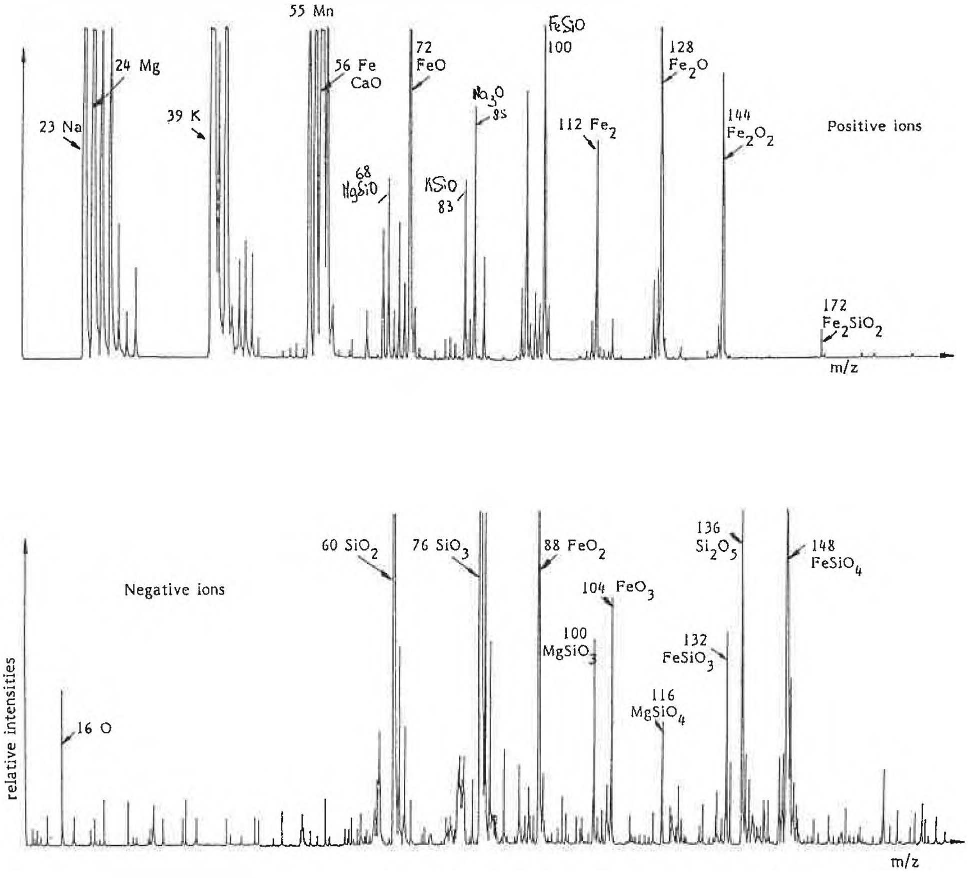

Fig. 9. Positive and negative LAMMA spectra of amosite.

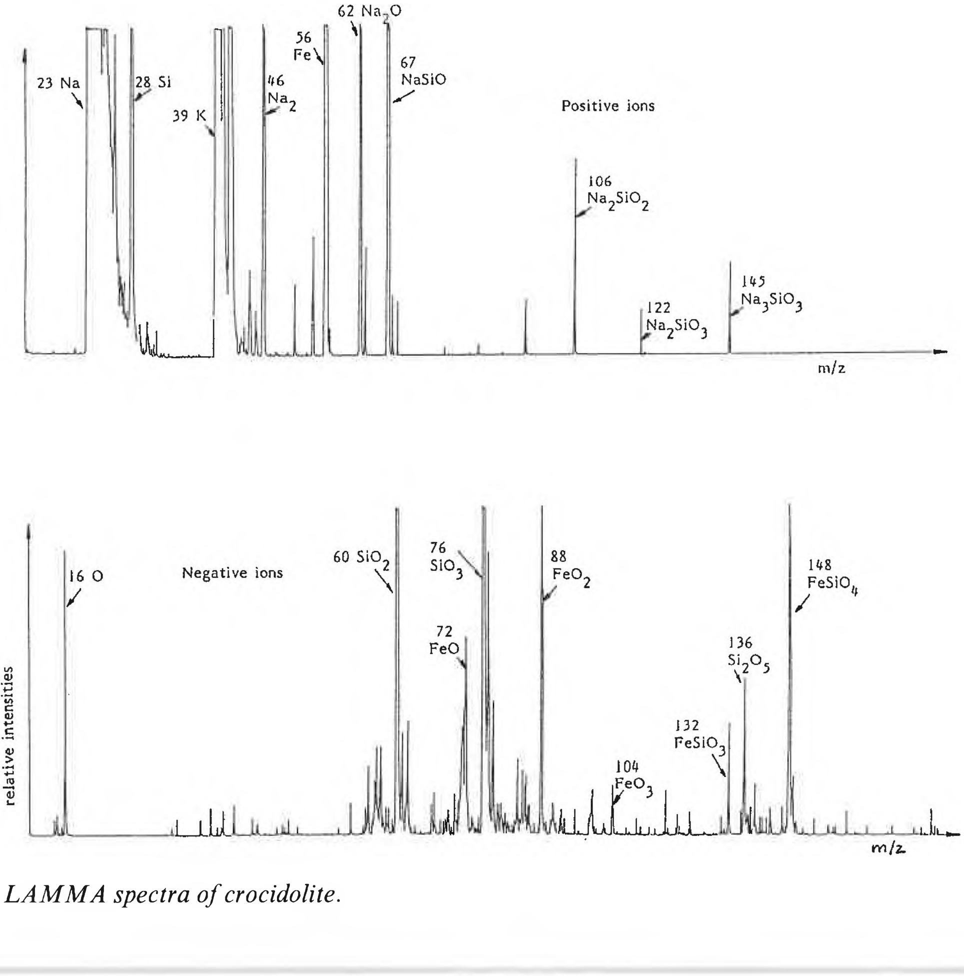

Fig. 10. Positive and negative LAMMA spectra of crocidolite.

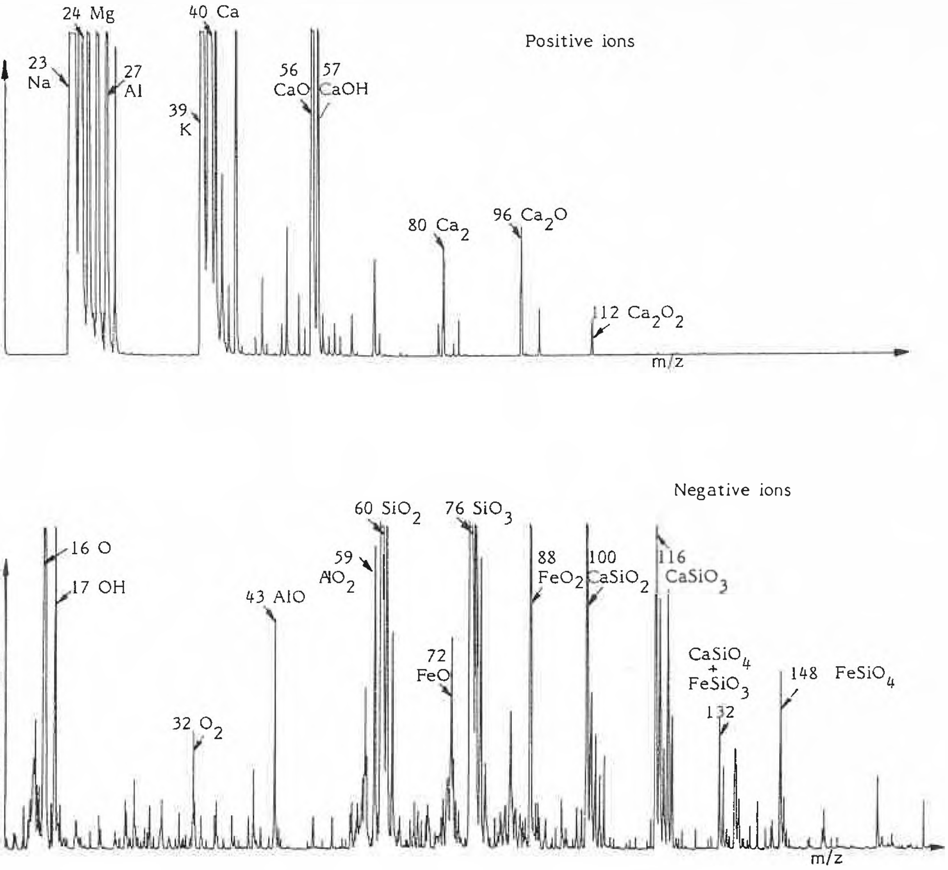

Fig. 11. Positive and negative LAMMA spectra of actinolite.

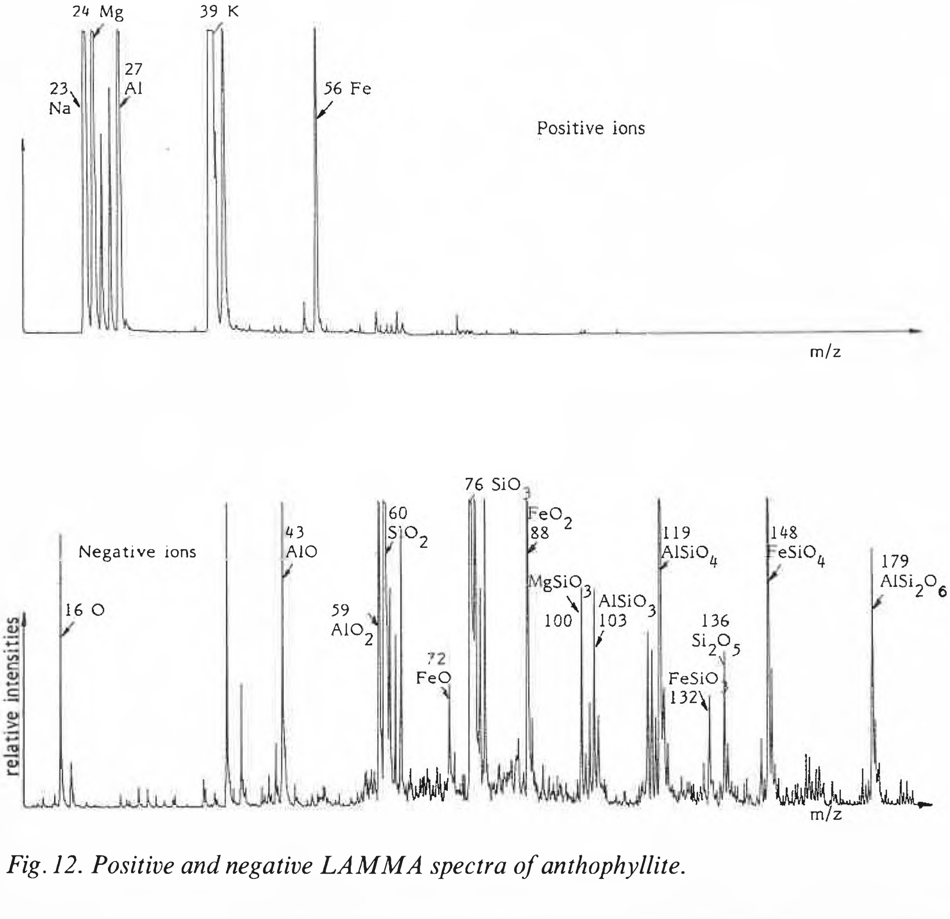

Fig. 12. Positive and negative LAMMA spectra of anthophyllite.

and 10 that those three most commonly used type of asbestos are easily differentiated from each other.

The positive and negative spectra of actinolite are shown in Fig. 11. The presence of calcium silicate is obvious. The occurrence of Al in the positive spectrum plus the ion species AlO$^\ominus$ (*m/z* 43) and AlO$_2^\ominus$ (*m/z* 59) indicate that an aluminosilicate should be present. Indeed, *m/z* 103 and 119 correspond to the ion species AlSiO$_3^\ominus$ and AlSiO$_4^\ominus$, respectively, confirming the presence of an aluminosilicate in this sample of actinolite.

Fig. 12 shows the spectra obtained for anthophyllite, another mixed iron and magnesium silicate similar to amosite. However, these two types can be easily differentiated by comparing the relative intensities of iron and magnesium in the positive spectrum. For amosite (Fig. 9), these two ions have approximately the same intensities whereas for anthophyllite the intensity of iron is always less than that of magnesium. Also in that particular sample of anthophyllite it is clear that an aluminosilicate is present. The presence of the peaks at *m/z* 63 and 79 could correspond to ion species SiOF$^\ominus$ and SiO$_2$F$^\ominus$ if fluorine could replace OH in the sample. However, the absence of F$^\ominus$ in the negative spectrum makes this assignment rather hazardous since many silicates contain phosphate ions which after laser-induced ionization produce the species PO$_2^\ominus$ and PO$_3^\ominus$ at *m/z* 63 and 79, respectively.

The presence of F$^\ominus$ in the negative spectrum of tremolite (Fig. 13) definitely confirms the peaks at *m/z* 63 and *79* as SiOF$^\ominus$ and SiO$_2$F$^\ominus$, respectively. Also the ion-molecule reaction between SiO$_2$ and SiO$_2$F$^\ominus$ accounts for the ion species Si$_2$O$_4$F$^\ominus$. All these examples show that the asbestos fibres can all be differentiated from each other by LAMMA.

Examples of the identification of unknowns are given in Fig. 14 and Fig. 15. The former exemplifies that chrysotile is easily identified from samples prepared from rat lungs, these animals having been exposed to a chrysotile fibres containing atmosphere over a period of two years.

In Fig. 15 the unknown is easily identified as emerald. Identification of the primary ions BeO$^\ominus$, BeO$_2^\ominus$, AlO$^\ominus$, AlO$_2^\ominus$, SiO$_2^\ominus$, and SiO$_3^\ominus$ allow all the other ion species to be assigned with subsequent confirmation of the presence of beryl.

5. Conclusion and Outlook

The analysis of some silicates has been performed with the laser microprobe mass analyzer (LAMMA 500). The technique shows that, although the laser energy is not reproducible from shot to shot and the sample is not presented for analysis in an homogeneous form, characterization of inorganic substances is possible. Identification of all the primary ions, often obtained after high laser irradiance, is necessary in order to account for all the ion species present in the spectra.

The technique holds much promise for future work in the inorganic domain for example for the investigation of complexes, a topic which is at present under study.

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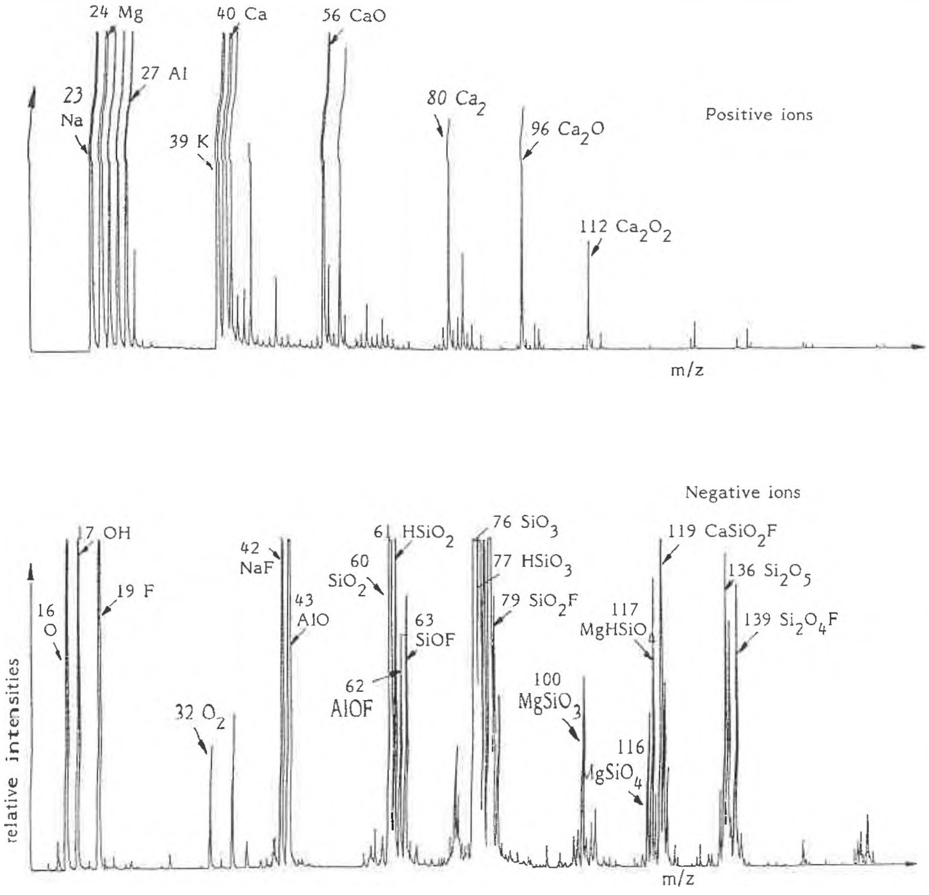

Fig. 13. Positive and negative LAMMA spectra of tremolite.

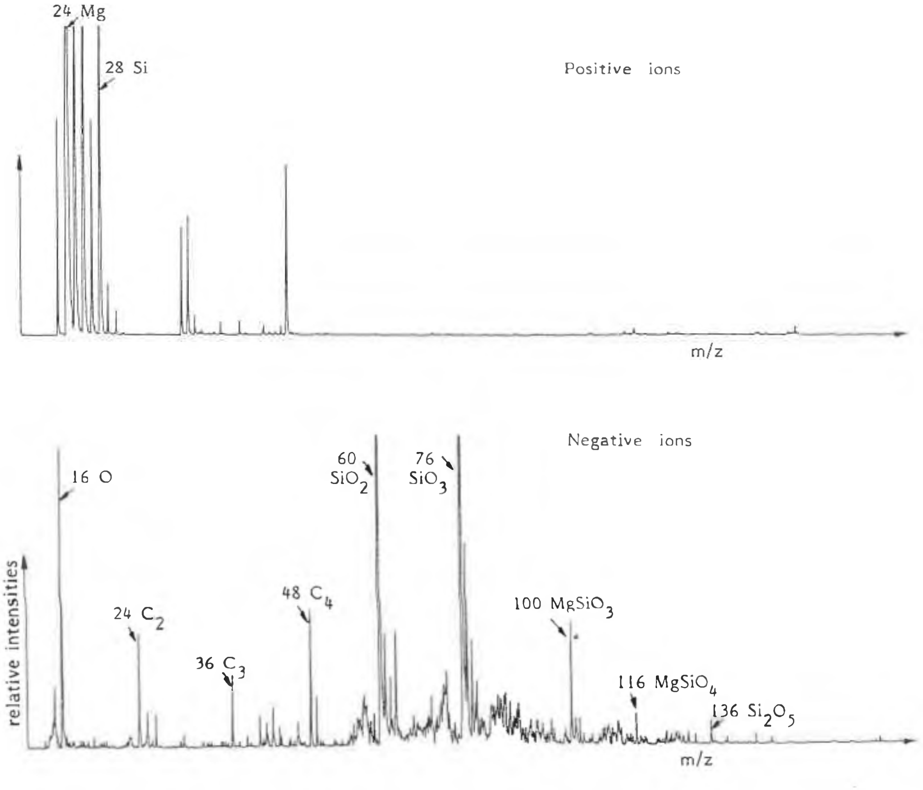

Fig. 14. Positive and negative LAMMA spectra of chrysotile identified in rat lung sample.

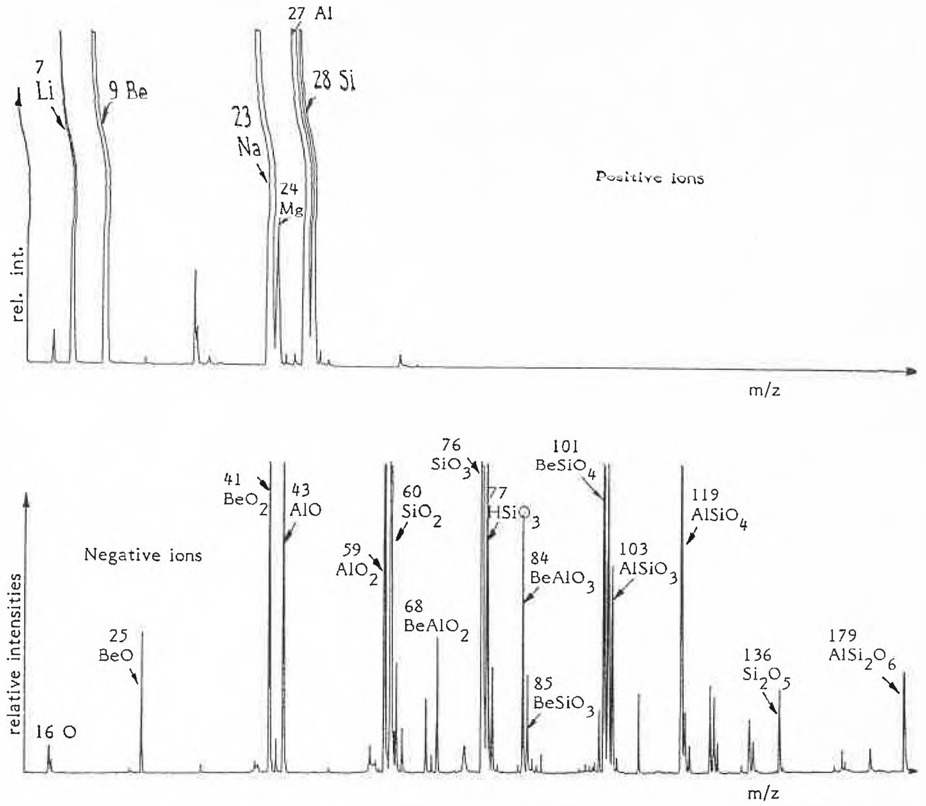

Fig. 15. Positive and negative LAMMA spectra of an unknown identified as emerald (beryl).