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APPLICATIONS OF LASER MICROPROBE MASS ANALYSIS FOR CHARACTERIZATION OF ASBESTOS

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Abstract

Laser microprobe mass analysis with the commercial LAMMA-500 (transmission type) instrument when utilized in laser desorption conditions provides information which allows the identification of particular asbestos varieties, in various types of samples, including lung tissue. Also it has detection capability of adsorbed organic material and it is a valuable tool for the study of the surface of chemically modified asbestos fibers manufactured by silanation or through phosgene treatment (chrysophosphate). Recent progress within our laboratory is discussed, and shortcomings of the methodology are indicated.

KEY WORDS : Laser microprobe mass analysis (LAMMA), surface characterization, asbestos, organic microprobe, molecular microprobe.

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Introduction

The laser microprobe mass analyser (LAMMA-500, Leybold Heraeus, F.R. Germany) was primarily developed for sensitive elemental analysis in the biomedical field[13,15]. Since its commercial introduction applications have expanded into many other areas such as particulate analysis (fibers and particles) e.g., in environmental applications, polymer analysis and material science. Moreover, it appeared recently that organic and inorganic molecular information can be obtained when the instrument is used in mild ionization conditions, usually defined as laser desorption (LD) excitation[14]. In this LD mode a rather small number of different ion species is formed which are closely related to the structure of the material studied. The LAMMA-methodology is presently intensively studied as an organic and inorganic molecular microprobe. The state of development was reviewed by Michiels et al. in 1984[20].

Asbestos and related fibrous materials can be easily studied with the transmission type LAMMA-instrumentation. The following sections report progress in our laboratory on recent advances of the methodology in the field of fibrous dust research : for the characterization of individual asbestos and asbestiform fibers, the detection of organic constituents at the asbestos surface and the characterization of the surface structure of industrially modified asbestos fibers. In all these applications results are of a quantitative nature. Indeed, present drawbacks of the methodology give rise to unpredictable fluctuations in both the absolute and relative spectral intensities which corrupt quantitative analyses.

Identification and Characterization of Asbestos and Other Fibers

The qualitative assessment of asbestos in environmental samples relies on analytical techniques which provide an unambiguous detection of fibers and hence allow a determination of their concentration by counting. The problem is compounded by the existence of different asbestos varieties with closely related (silicate) bulk

composition but with different toxicity. Also a range of other fiber-like microobjects (e.g., glass fibers and natural fiber-like objects) occur in nature. Moreover, asbestos fibers may vary considerably in their natural composition, they are frequently subjected to modifications before commercial use and their composition may be altered after emission into the environment.

Presently, the most trustworthy approach to environmental asbestos measurement relies on transmission or scanning transmission electron microscopy (TEM or STEM). Single particle X-ray analysis is required and for a safe identification selected area electron diffraction is often considered mandatory[11]. The procedure is extremely time consuming and costly and any cost effective alternative should be considered. Other methods rely on the unique refractive indices in optical microscopy as they are recognized by dispersion staining when resolved by the light microscope[19].

LAMMA-analysis of asbestos fibers relies on their light microscopical (visual) detection, and on the ability to distinguish asbestos from non-asbestos fibers and also to discriminate different asbestos varieties on the basis of the mass spectra obtained. Spurny et al[25] first pointed to the possibility to differentiate between the serpentines and the amphibole classes of fibers, also between amosite and crocidolite on the basis of the fingerprint laser mass spectra produced. In what follows we will give additional information which aims at showing that LAMMA has a distinct potential to complement other existing methods for this important task.

Positive and negative LAMMA spectra were obtained for the 5 UICC (International Union against Cancer, Johannesburg, Rep. South Africa) asbestos standards[27], and also for a number of other asbestos samples of known origin. When obtained at high laser energy (> 2 μJ) the fibers are locally vaporized and the positive spectra are characterized by a number of elemental mass peaks which correspond with the isotopes of the major elemental constituents of the material (sodium, magnesium, aluminium, silicon, potassium, calcium, manganese and iron, in some cases titanium and chromium). Cluster ions may be present at low intensity. Fig. 1 shows a three dimensional plot of relative intensities normalised to ^{24}Mg for the major components in the UICC standards with an indication of the relative standard deviation for repeated analyses of different fibers[26]. Taking into account that the UICC materials cover about 97% of the commercially used asbestos, it is tempting to conclude that LAMMA is a suitable method for microscopical identification even for distinguishing between the different varieties. Negative spectra contain considerably less information, as they are characterized by a number of molecular fragment ions with variable intensity.

The following comments can be formulated :

- the resolution of the optical microscope is marginally adequate. The undetected fraction (< 0.5 μm diameter) may range up to ca 50% of the total number of particles present.

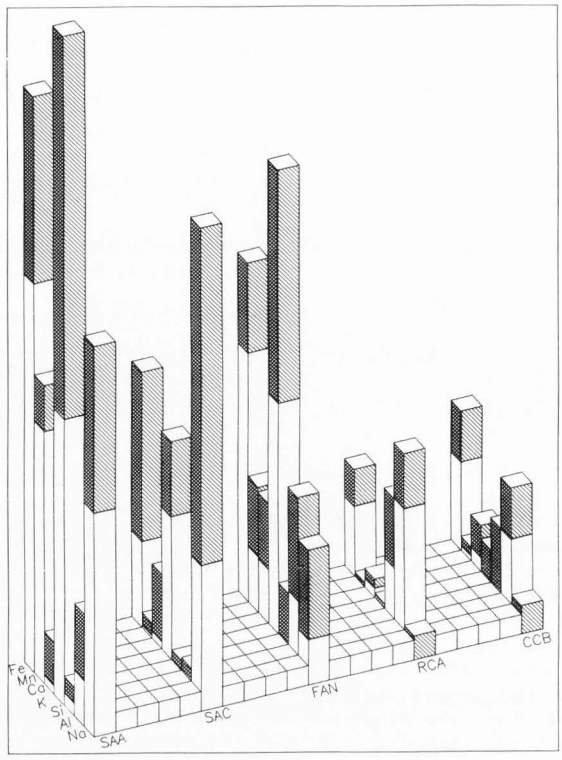

Fig. 1. Relative intensity to ^{24}Mg of a number of constituents in South African amosite (SAA) and crocidolite (SAC), Finnish anthophyllite (FAN), Zimbabwean and Canadian chrystotile (RCA and CCB). (shaded area is standard deviation).

- asbestos is used in over 3,000 fields of application and ca 70% of the use is through transferred products (e.g., asbestos cement) in which the composition is often drastically changed compared to the original product.

- day-to-day variability of the relative mass spectral intensities occur. They are due to, up to now, badly understood phenomena in laser-solid interaction, ion extraction/transmission and in the measurements. These factors may increase the variability of the results considerably.

When spectra are taken at low laser energy ($\leq$0.2 μJ), more or less intense molecular ion peaks appear in the positive spectra. These molecular fingerprint spectra are related to the chemical and crystallographical composition rather than to the elemental composition. Structural integrity of the material seems to be preserved and the spectra seem to reflect the outermost surface composition of the material rather than the bulk. Successive spectra from the same location of a fiber provide to a certain degree of structural information in depth. Fig.2 shows typical positive spectra of two chrysotiles originating from Zimbabwe and Canada measured at three different laser energies.

The LD-fingerprint spectra obtained at low laser energy cannot be fully explained as they

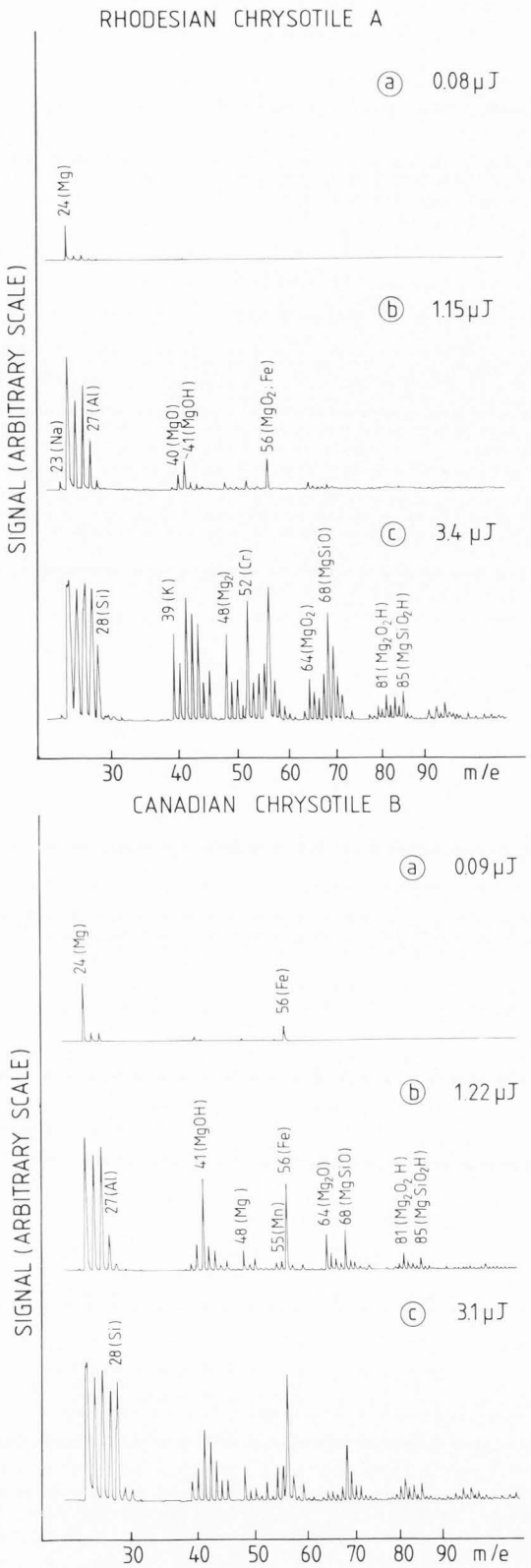

Fig. 2. Positive laser mass spectra of one chrysotile A and chrysotile B standard fiber, as a function of laser energy.

seem to depend on subtle structural differences. We have studied in detail a surprising difference in spectral appearance between chrysotile originating from Zimbabwe and the same material mined in Canada[4]. Although the iron content of both materials is nearly the same namely 4.1 and 3.0% respectively, the elemental iron peak at m/e = 56(Fe^+) is at least a factor 10 more intense in the Canadian material, as follows from Fig. 2. Part of the iron is known to be present as a magnetite impurity in both materials but the incorporation is different with intergrowth within the asbestos in the material from Zimbabwe and magnetite micro-crystallites as surface impurities in the Canadian asbestos[16]. The surface sensitivity of the method then explains the spectral difference. When the laser energy is increased to 3μJ spectra become nearly identical, since at high laser energy the spectra correspond more fully with the bulk composition (Fig. 2, bottom).

The utility of LAMMA for the characterization of fibers in lung tissue follows clearly from the following case study which tried to resolve the question whether elevated atmospheric fiber counts in the Austrian town Rechnitz[21] can be related to road surfacing (crushed stone) from a tremolite quarry or to brake lining emissions. LAMMA-analyses were performed on a reference quarry sample and on two samples of lung dust, collected after plasma incineration from two severely exposed persons. Fig. 3 shows positive and negative mass spectra of a reference tremolite quarry fiber, a fiber present in a dust sample extracted from the lung of a diseased man who suffered occupational exposure and of a diseased woman who only suffered environmental exposure. Taking into account the decrease in intensity of magnesium, calcium and aluminium, and enrichment of silicon, which could all be explained by surface modifications in the lung fluid, the three positive fingerprint spectra correspond closely, pointing to a similar origin. The interpretations of the negative spectra are compounded by the presence of sulphate and phosphate at the fiber surface. Nevertheless, the higher mass molecular species above m/e = 60 again correspond qualitatively. Electron microprobe analysis assisted with selected area electron diffraction provided the same conclusion.

Detection of Organic Surface Components

Respirable asbestos fibers have a considerable capacity to absorb other substances. They may selectively absorb the constituents of living cells and thereby upset the delicate balance of cell reproduction. They may also absorb pollutants from the atmosphere to be transported with the fibers to the lungs and lead to a localized deposition in the tissue. It is hence not surprising that the toxicity and the carcinogenic potential of asbestos fibers appear to be correlated with the adsorption power of pollutants[12].

It appeared in our work that LAMMA is able to detect the presence of organic adsorbents at the

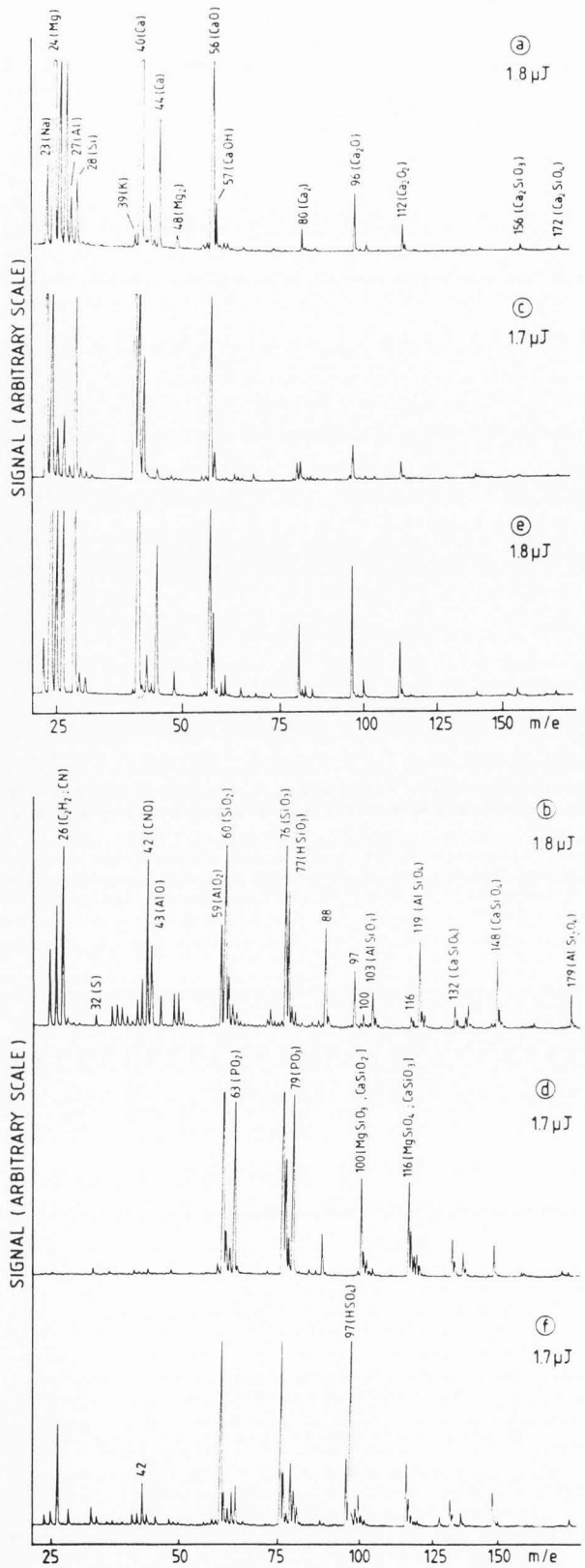

Fig. 3. Positive spectra (top) and negative spectra (bottom) of reference tremolite fiber (a and b), a fiber present in lung of diseased man (c and d), and diseased woman (e and f).

surface of individual asbestos fibers[3,6,9] and environmental particles.

Accidental asbestos contamination

The UICC asbestos standards are easily contaminated with organic additives of polyethylene packing material, as was reported already by Commins and Gibbs[1]. They detected the presence of 3,3',5,5' tetra-tertiary butyl dibenzoquinone (mol. mass = 408) on UICC crocidolite and chrysotile samples by bulk separations followed by high resolution mass spectrometry. Similar contaminations, though not with the same product were detected on individual fibers using LAMMA in LD conditions[9]. Fig. 4 shows one example. The spectrum results from a bulk contamination of 0.1 $mg.g^{-1}$ of organic products in crocidolite through storage of the material in a polyethylene bag which contained a mixture of several phtalate plasticizers, namely dimethyl phtalate (DMP), dibutyl phtalate (DBP), benzylbutyl phtalate (BBP) and dioctyl phtalate (DOP). All of these compounds were readily and systematically detected with detection limits which can be safely estimated at 10^{-15} to 10^{-16}g. Note that the most intense peaks correspond with cationized (Na) molecular species or cationized fragments.

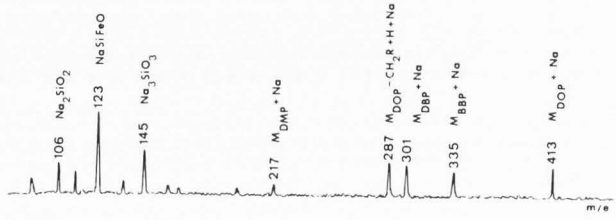

Fig. 4. Organic contaminants of crocidolite fiber as detected in positive spectra in laser desorption conditions.

Cationization is a feature which, at least in this phtalate contamination on crocidolite, is of considerable help for the detectability. Unfortunately this implies that detection limits are worse for other asbestos classes which do not contain sodium, or another alkali element, as a main constituent. Indeed, it appeared that detection limits are at least a factor of 10 worse for amosite fibers.

The extent of cationization and the general appearance of the mass spectra appeared to be different according to the process responsible for the contamination. Deliberately contaminated samples with the same phtalates from dilute benzene solution, did not give rise to spectra with cationized spectra components but gave significant peaks corresponding with the molecular ions. The identification of the components detected in the mass spectra, required the use of other analytical techniques as the mass resolution is inadequate for a safe differentiation between molecular ions of nominally the same mass.

Table 1 shows that the average reproducibility amounts to ca 20% rsd, that bulk contamination levels corresponding with 500 $\mu g.g^{-1}$ can be safely detected and finally that the method does not allow quantitative determinations. The reproducibility is considerably better than that obtained for organic surface contaminants on other particulate materials such as fly ash and soot[17], probably because the laser beam can be more easily and reproducibly focused onto an asbestos fiber than on other particles.

Table 1: Concentration of diethyl and dioctyl phtalates (DEP and DOP) on crocidolite after adsorption from benzene solution.

Concentration(M)	Concentration ($mg.g^{-1}$) DEP	DOP	Cationized molecular ion intensity (rel. units)
0.0100	5.2	4.9	39 ± 6
0.0050	4.2	1.0	24 ± 4
0.0010	0.46	0.52	17 ± 5
0.0005	0.42	0.41	0.6 ± 0.2

Contamination of asbestos with polyaromatic hydrocarbons, particularly benzo-pyrene could also be detected for concentration levels of the order of 500-600$\mu g.g^{-1}$, when the impurity was present at the fiber surface. Polyaromatic hydrocarbons present within the fiber interior could only be detected through the carbon fragmentation spectrum at high laser energy.

Adsorptivity and reactivity of asbestos surfaces

The UICC standards were treated with several organic products :

1. Aliphatic alkylammonium salts (R_4NCl with R = methyl to butyl) were adsorbed onto asbestos from aqueous solution[10]. The products could be detected in laser desorption conditions through the measurement of the molecular fragment R_4N^+. Table 2 shows results for the butyl compound (R_4N^+ corresponds with m/e = 242). There is a marked selectivity with at least a factor of 10 less adsorption for chrysotile asbestos fibers.

Table 2 : Relative intensities of elemental and molecular ion peaks for asbestos doped from a 0.02 M tetrabutylammonium chloride solution (24 hr exposure).

m/e	amosite	crocido-lite	antho-phyllite	chrysotile
23 (Na^+)	45±7	450±60	50±7	0.4±0.2
24 (Mg^+)	25±7	3.0±0.4	53±13	166±25
39 (K^+)	130±20	72±12	34±5	2.1±1.3
55 (Mn^+)	8±2	n.d.	3.1±0.8	1.4±0.6
56 (Fe^+)	47±11	2.9±0.6	25±7	33±17
242	14±2	25±4	22±4	n.d.

n.d. = not detected.

2. The oxidative properties of clay minerals (e.g., montmorillonite and kaolinite) were studied previously using organic products such as N,N'dimethyl aniline (DMA) which adsorbs and then reacts at the substrate yielding coloured oxidation products such as methyl violet[28]. It appeared in our work that when DMA and also ortho-phenylene diamine (OPDA) were adsorbed onto asbestos and sepiolite fibers, reaction products such as methyl violet and crystal violet for DMA and 2,3 diaminophenazine and higher molecular mass compounds for OPDA could easily be detected on individual fibers[7,8]. Fig. 5 shows a positive spectrum of a DMA treated amosite fiber and as a reference a spectrum of a fiber which was treated with crystal violet (mol. mass = 372). The peak at m/e = 358 corresponds with the molecular ion of methyl violet, those at m/e = 344, 330 and 316 are due to intermediate reaction products of DMA, which itself is barely detectable at m/e = 134.

In general, the adsorption of selected organic compounds provides information on the surface reactivity. This could allow the elaboration of simple procedures for the evaluation of the hazards of industrially produced fibrous materials e.g., transformed ashestos or substitution products such as those described in a later section.

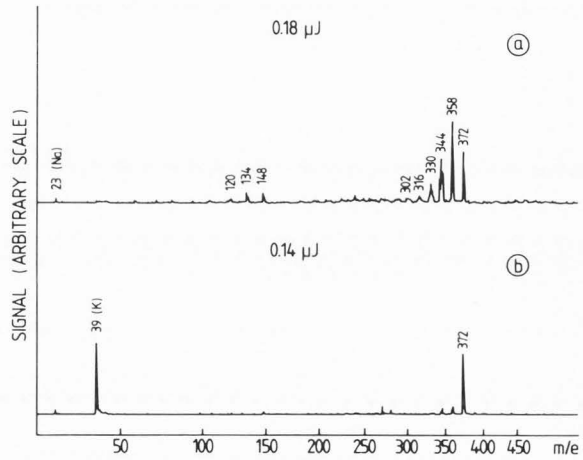

Fig. 5. Positive laser desorption mass spectra of amosite asbestos treated with dimethylanaline (top) and with Crystal violet (bottom).

When subsequent LD spectra are taken from one fiber location, the molecular peaks of the adsorbent gradually disappear until the spectrum becomes representative again for the inorganic substrate, when the organic material is removed. This is illustrated in Fig. 6 which represents the positive mass spectrum of an untreated amosite fiber and four sequential laser shots at similar but butylammonium chloride treated fibers. The spectrum of the fourth shot is nearly identical with that of original fiber. Fig. 7 shows a further example of the detection of surface adsorbents. A characteristic positive spectrum is shown of an amosite fiber which was briefly brought in contact with cigar smoke. It shows clearly the molecular ion of nicotine.

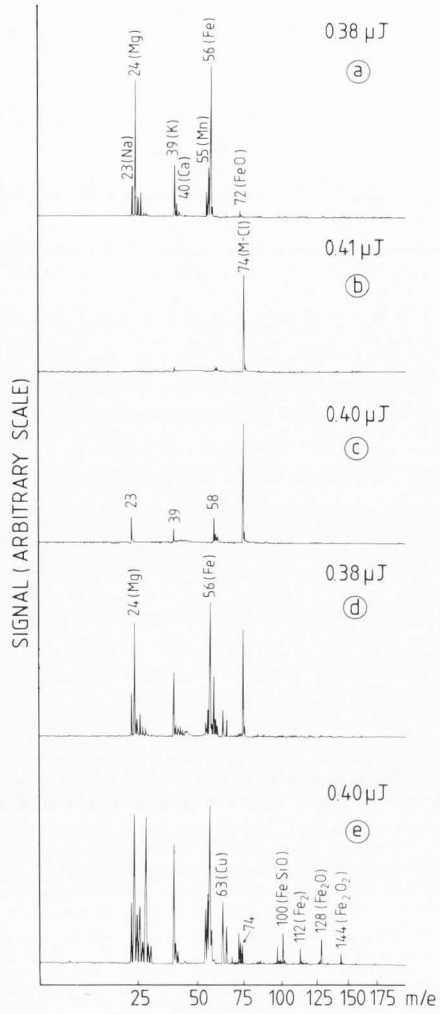

Fig. 6. Positive LAMMA spectra of amosite (a) and amosite treated with tetrabutylammoniumchloride (b to e).

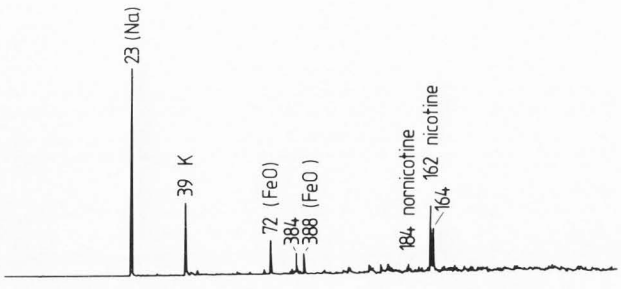

Fig. 7. Positive mass spectrum of amosite fiber with adsorbents originating from cigar smoke.

Characterization of Chemically Modified Fiber Surfaces

Concern over potential occupational and environmental hazards of asbestos and the realisation that the material's reactive surface is of importance for its toxicity has stimulated efforts to modify the fiber surface for a number of critical applications. Organosilane coated fibers and also modified fibers obtained by gaseous phosphorus oxychloride treatment of chrysotile (chrysophosphate) have been produced. In what follows we will show that LAMMA used in LD conditions provides information on the chemical composition of the modified fiber surface.

Organosilane coated fibers

Chrysotile asbestos may be rendered oleophilic and stabilized thermally and also chemically by coating of the mineral surface through reaction with organosilane compounds. Such coated fibers have found a number of industrial applications.

For organosilane coating of chrysotile the material is subjected to a mild mineral acid etch with H_2SO_4 or HCl in order to dissolve the outer magnesium hydroxide monolayer, thus performing free silanol groups on the surface of the fibers. These then react through condensation with an organosilane compound.

Fig. 8 shows positive mass spectra obtained in LD-conditions for a pure chrysotile fiber, an H_2SO_4 treated fiber and finally a triethyloxyoctylsilane coated fiber[5]. In the spectrum of the acid treated fiber, peaks at m/e = 40 (MgO^+), 41 ($MgOH^+$) and 56 (MgO_2^+) are decreased in relative intensity thus showing the removal of the outer brucite [$Mg(OH)_2$] layer. The Si^+ elemental ion peak is increased in intensity because of the presence of free silanol groups on the outer surface layer after the etch treatment. The organosilane peaks at m/e = 141 and 157 [$Si(C_8H_{17})^+$ and $OSi(C_8H_{17})^+$] are systematically measured in the spectra of the silanated fibers. When the laser energy is increased to ca. 0.2 μJ the spectra become complicated by the occurrence of molecular fragments of the chrysotile substrate material and also by fragmentation of the coating material. This proves that after the silanation treatment the structural integrity of the fibers is preserved.

Natural and organosilane grafted sepiolite fibers were also studied[2]. The mass spectra again show characteristic organosilane molecular and fragment ions, thus providing information on reactions of the free silanol groups at the sepiolite fiber surface. This confirms evidence which was independently obtained by infrared spectroscopy.[23]

Chrysophosphate fibers

Chrysophosphate could become a viable alternative for untreated chrysotile with possibly a significantly reduced adsorption capacity for organic compounds. Preliminary LAMMA-analyses of chrysophosphate and also of chrysophosphate-cement show interesting information especially in the negative spectra.

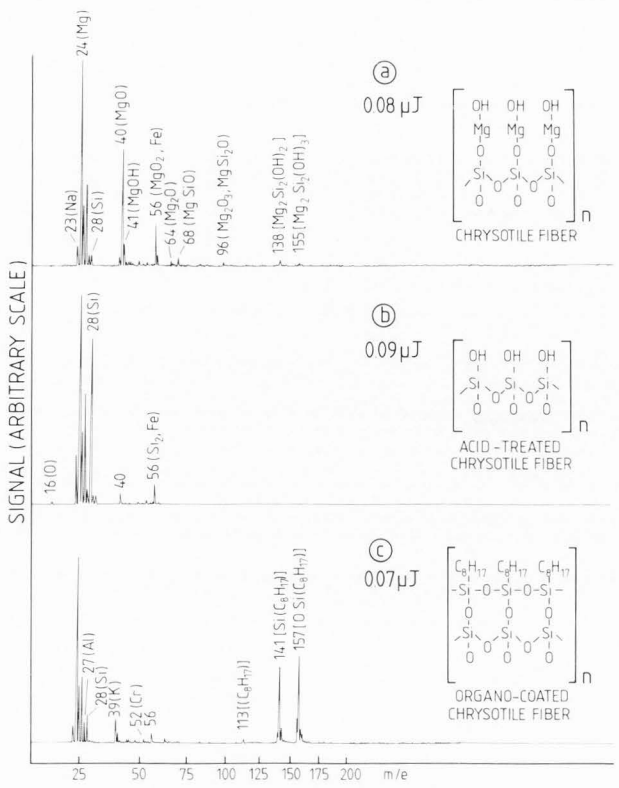

Fig. 8. LAMMA spectra of chrysotile (a) acid treated chrysotile (b) and triethyloxyoctylsilane coated fibers (c).

The spectra of the chrysophosphate show intense peaks at m/e = 35 (Cl) and m/e = 63 and m/e = 79 (PO_2^- and PO_3^-). This is illustrated in Fig. 9, which represents a cumulative negative mass spectrum of 20 individual analyses (top) and a representation of the standard deviation on channel intensity (bottom). Most of the significant features have a reproducibility of 20-30%. The positive spectra of chrysophosphate only show a small elemental ion peak at m/e = 31 (P^+) and a molecular fragmentation peak at m/e = 83 (probably Mg_2Cl^+ from $MgCl_2$ formed as a by-product in the $POCl_3$ treatment) as spectral differences compared with the original chrysotile. Fig. 10 shows a positive LD-spectrum of a chrysophosphate cement fiber. It is the summation of 20 individual mass spectra. The bottom spectrum again represents the standard deviation as a function of channel number. The cement coating becomes apparent through several Ca-containing fragments (CaO, CaOH, Ca_2O) besides the elemental calcium peak. Phosphor is present through a low intensity peak at m/e = 31 (P+) only.

Surface composition alterations

Magnesium and other elements are easily leached from the surface layers of asbestos fibers. For chrysotile the disappearance of magnesium has been related to changes in biological activity. Most attention has been paid to the acid attack of chrysotile of the fibers which leaves intact the fibrous morphology of the mineral and produces an ordered silica gel structure as indicated by NMR studies. Our experiments have shown that the depletion of magnesium from the chrysotile surface can be readily detected with LAMMA (see Fig. 8b) but that the results cannot be explained quantitatively as mass-spectrometrical results do not compare quantitatively with those obtained with either secondary ion mass spectrometry or complexometric titration of the magnesium in the attacking solution[29].

Discussion

The examples shown in the previous sections show qualitatively that laser mass spectrometry provides valuable information in the study of asbestos and other fibrous materials. The potential for qualitative measurements has, in general, not been actualized, however. For quantitative determinations the following design and performance features need to be taken into account :

- laser intensity at the sample : the quantity of energy deposited in the analytical volume, and also the irradiation profile in time and in space are the basic experimental parameters influencing the extent of sample vaporisation, fragmentation and ionization. Laser intensity may be changed by the operator but also varies randomly from shot to shot, whereas the focus of the laser varies within the range of the operator's visual discrimination, and the beam profile is not necessarily stable.

- sample position effects : atomic ions are predominantly formed in the intense central region of the laser beam whereas molecular ions may be simultaneously formed by laser desorption in the fringe of the beam[14]. In such circumstances the extraction of the two classes need not be the same as not only distribution in space but also velocity vectors and ionic temperatures differ. Hence, even for flat and uniform samples mass spectral intensity varies with position across the specimen and asymmetrical peak shapes may occur. For non-flat or irregularly shaped samples problems are compounded further.

- ion lens effects : the measured differences between kinetic energy distributions of different chemical species implies that the various ions will not experience identical transmission through the ion optical system due to chromatic aberration of the ion lenses[18], thus altering relative spectral intensities. Uncontrolled shifts in kinetic energy distributions, due to variation of laser or chemical conditions, can therefore produce unpredictable fluctuations in absolute/relative spectral intensities. Corrections for similar effects in secondary ion mass spectrometry have been estimated[22], but for LAMMA it is not possible to make such calculations rigorously until the efficiency of ion extraction is accurately known.

- spectrum recording : with currently available electronic technology the limitations of the performance of the detector and the

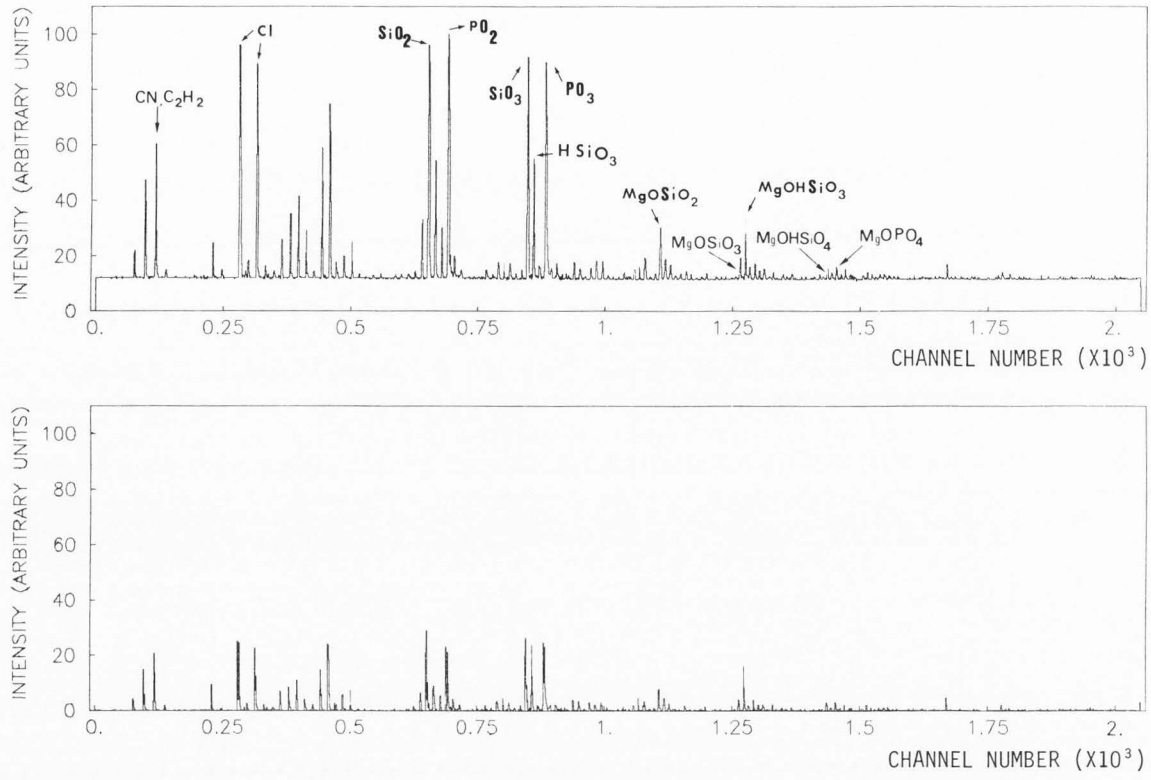

Fig. 9. Average negative mass spectrum (20 individual analyses) of chrysophosphate (top) and standard deviation as a function of channel number (bottom).

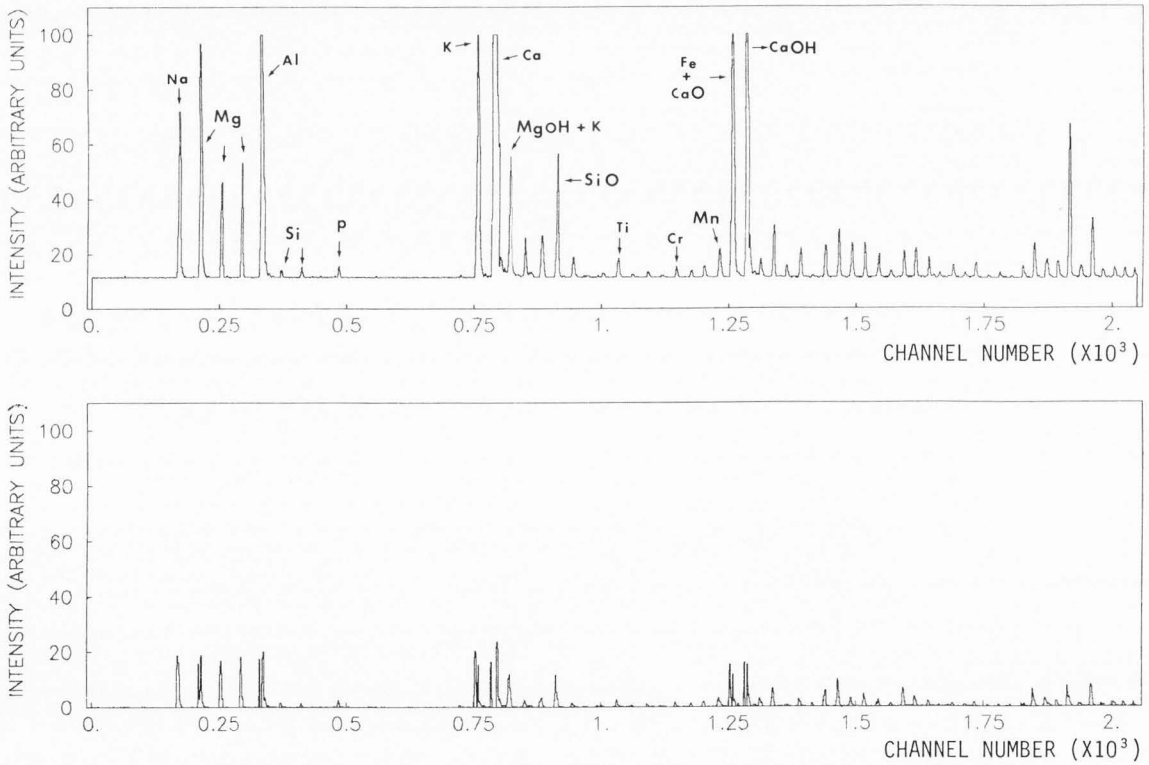

Fig. 10. Average positive mass spectrum of chrysophosphate cement (20 measurements) (top), and standard deviation as a function of channel number (bottom).

digital transient recorder are sufficiently great and these components of the spectrometer must be examined in any evaluation of the analytical characteristics of the system ; the recorder cannot be treated as an ideally performing signal transducer[24].

Results in all these areas are encouraging and lead to numerous questions, the answer to which should lead to improvements in the interpretability and reliability of practical LAMMA-analysis.

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Discussion with Reviewers

J.L. Abraham : One major problem is that many of the biologically important asbestos (and other) fibers cannot be analyzed by this technique which is dependent on light optical resolution. Since this depends on light optical visibility please compare and contrast the ability to identify types of asbestos by LAMMA vs dispersion staining.

D.S. Simons : Would the authors summarize the advantages and disadvantages of LAMMA analysis of asbestos fibers in comparison with STEM-EDS?

Authors : There are a number of microanalytical methods useful for the identification of asbestos. These include infrared absorption (IR), X-ray diffraction (XRD), differential thermal analysis (DTA), scanning electron microscopy (SEM) with energy-dispersive X-ray analysis (EDS), transmission electron microscopy (TEM) with selected area electron diffraction (SAED), and polarized light microscopy (PLM) with or without dispersion staining (DS). Each has its advantages and disadvantages. The LAMMA technique shares with optical microscopy the limitations in the detection of particles below ca. 0.5μm in diameter, albeit with a somewhat lesser resolving power, this as a result of design compromises made in fitting the optical microscope into a complex mass spectrometric instrumentation. If we disregard this small difference in optical resolution, the ability to recognise fibers within a complex particle aggregate for the optical microscope and the laser microprobe mass analyzer should be similar. As far as the identification of asbestos types is concerned LAMMA employs either the more or less characteristic elemental composition at high laser intensity, or the structural information present in the fingerprint spectra at low laser intensity. The information content of these positive and negative spectra is very high but the full exploitation is hampered at present by an insufficient understanding of the spectral characteristics resulting from the laser-solid interaction and the unpredictable fluctuations in both absolute and relative spectral intensities. This contrasts with the PLM and DS which is an effective method for rapid identification based on unique crystallographical properties (refractive indices, dispersion of refractive indices, birefringence, etc...). At present LAMMA cannot be considered as a competitor to PLM, but rather as an alternative method.

Energy dispersive X-ray analysis is much less safe as a means for identification of asbestos types, but TEM and STEM are not hampered by the limitations in particle dimensions. SAED which again is based on morphological rather than elemental analysis is required. Here, analysis is based on a complex instrumentation and lengthy analysis.

J.L. Abraham : How does residence in and method of isolation from biological tissue affect the results of LAMMA analysis of fibers ?

Authors : At low laser irradiance LAMMA spectra become dependent on surface composition and structure (see Fig. 2). Fibers that have resided within biological tissue often show spectral peaks which reflect these surface alterations, as shown in the example in Fig. 3. It is of importance to isolate the material for analysis so as to disturb the acquired surface composition as little as possible.

E. Steel : In the case study of the Austrian town, could LAMMA not be severely size-biased in comparing chrysotile with tremolite since the tremolite fibers are so much thicker therefore more visible ? Also can LAMMA distinguish tremolite from other minerals in the quarry such as diopside or other pyroxenes ?

Authors : Fig. 3. results from a short study in which we investigated a fiber sample from Rechnitz which was supplied to us by Prof. Neuberger (Technical University Vienna). Using STEM and SAED tremolite was identified in the sample and our work consisted in nothing more than verifying whether LAMMA could provide any supplementary information.

J.L. Abraham : What is the variation of signal intensity with fiber diameter ? How does the

surface crystallinity affect absorbed vs reflected or scattered laser light ?

Authors : Of the many experimental conditions affecting laser-induced ionization processes, the power density of the irradiating laser beam has been shown to be of primary importance (Consemius et al, 1984, Adams and Mauney, 1985). The area of the impacted spot has also been shown to affect ion production processes. Because both the area and the power density will be affected by placement of the specimen in the focal plane of the laser, attention must be given to the means used to focus the laser beam as well as to its inherent properties such as pulse energy and temporal and spatial characteristics.

All these factors being adequately taken care of, we may assume that up to a maximum diameter, spectral intensity is proportional to sample mass consumed as was shown on glass microspheres of variable size (Surkyn and Adams, 1982).

J.L. Abraham : How do the authors separate less adsorption from different ionization/sensitivity based on e.g., alkali availability in Table 2 ?

Authors : At present we cannot. Alkali availability is important when cationized species are detected in laser desorption conditions. At present, there is no way of obtaining quantitative measurements in such conditions. In Table 2, the situation is somewhat less complicated as molecular ions were measured but even then results have not more than a semi-quantitative meaning.

J.L. Abraham : A major problem with LAMMA analysis of mineral particulates has been the low sensitivity for silicon. For example, silicates containing aluminium and silicon may be misidentified as aluminium particles. How can such a variable, non-quantitative technique be of use to identify asbestos fibers when it could not always discriminate between aluminium silicate or magnesium silicate or aluminium oxide or magnesium oxides ?

Authors : Despite its lack of reproducibility, LAMMA usually provides sufficiently specific fingerprint spectra. To identify e.g., compounds as aluminium silicate and magnesium silicate, the following specific compound ions may be used in the negative spectra :

$MgSiO_3$: m/e = 60(SIO_2); 76(SiO_3); 77($HSiO_3$); 100($MgSiO_3$); 116($MgSiO_4$).

$Al_2(SiO_3)_2$: m/e = 43(AlO); 59 (AlO_2); 103($AlSiO_3$); 119($AlSiO_4$); 179($AlSi_2O_6$).

There are many examples in the recent literature that illustrate the identification of inorganic molecular species (Bruynseels and Van Grieken, 1984, Van Craen and Adams, 1984).

J.L. Abraham : Why did the accidentally contaminated asbestos samples show cationized phtalate peaks whereas those contaminated in the laboratory give rise to the presence of molecular ion peaks?

Authors : The adsorption process presumably from the gas phase for the accidental contaminations, and from solution in the laboratory experiments, is probably responsible for these different spectral data. These differences in spectral appearance again illustrate that the spectra obtained in laser desorption conditions depend critically on the surface morphology of the material studied. We refer to Fig. 2 for another example.

F. Hillenkamp : What, in your experience, are the chances for an improvement of the "day to day" reproducibility by a careful control of laser energy, power incident on the sample, the intensity distribution on the sample surface, and the focusing conditions ? Would you expect to obtain better reproducibility of results (at some expense of optical resolution) in a LAMMA 1000 arrangement, designed for bulk surface analysis ?

Authors : The quantity of energy deposited in the analytical volume is the most basic instrumental factor. With now available commercial equipment it is possible to achieve focusing of the laser beam to nearly the limit imposed by the law of optical diffraction. Power density variation from one laser shot to the next is dependent on the design features of the NdYAG lasers ; we do hope this feature is ameliorated in the near future but we do not know this equipment well enough to make any predictions. From the limited experience acquired from occasional use of the LAMMA-1000 instrument, we believe that reproducibility is ameliorated in this design, perhaps because reflection and transmission losses are controlled. However, a number of comments may be formulated :

1. In practice, absolute laser energies between 0.1 and 10 μJ may be available at the sample surface leaving a power density in the range of 10^9-10^{11} W/cm^2 for a spot of ca 1μm diameter. The latter figure is subject to considerable uncertainty and the pulse energies stated by different laboratories are not strictly comparable. We believe that this is a more disturbing situation than "day-to-day" variability in one laboratory as it violates one of the fundamentals of experimental science, namely that data should be reported in a way that they can be repeated and controlled by other investigators. Protocols for interlaboratory standardization should hence be developed.
2. In applied analysis, LAMMA instruments are able to produce spectra very rapidly and variability on a short term may be effectively reduced by employing spectrum averaging techniques. The summed spectra in Figures 10 and 11 thus give considerably more confidence than the unique spectra in the other figures in this paper.
3. While the laser intensity at the sample is certainly a major factor in governing spectral variability, a number of instrumental parameters downstream in the ion beam are of importance. They pertain to the ion formation process, the energy and the energy distribution of the ion cloud produced, extraction efficiency and measurement artefacts.

F. Hillenkamp : Could signals in the low energy

spectra of Fig. 2 possibly represent molecular rather than atomic ions, originating from surface contaminations ?

Authors : The limited mass resolution available in the instrumentation always puts some doubt on the identification of specific spectral features with elemental ions, molecular (cluster) ions, or organic fragments. In the particular case mentioned Mg and Fe were identified because of the isotopic information available. The m/e = 56 peak in the Zimbabwe chrysotile is partly due to iron, partly to MgO_2^+.

A.M. Langer: General comments: This is a very interesting technique. The application of LAMMA on the understanding of surface chemistry of minerals is extraordinarily promising. The authors are exploring new and promising areas. My following reservations are with the perception of the problem rather than with the techniques.

Wouldn't the authors agree that the most trustworthy approach to environmental asbestos measurement relies on the analytical electron microscope? Certainly all of the chemical and structural information which is required for asbestos fiber identification may be obtained with this instrument.

The single most important shortcoming associated with the use of LAMMA is the requirement of detection on the basis of light microscopy. In terms of environmental fibers, this would preclude from analysis virtually all fiber. The limitations are significant. The undetected fraction of asbestos may range considerably and the amount of fiber visualized by light microscopy may be only one in ten thousand.

The LAMMA signal cannot be used as "fingerprint spectra". The UICC B specimen contains a fiber mix from 8 different Canadian mines. These fibers differ in chemistry, both magnesium and iron contents. The danger presented is that any one fiber may represent one of eight specimens, fibers vary within the same mines (especially in terms of mineral intergrowths, i.e., brucite and magnetite).

LAMMA cannot be used to characterize fibers in human lung tissue. Virtually every fiber contained within human lung is below the resolution of the light microscope (approximately 99% < 0.20 µm in diameter). In terms of elevated atmospheric fiber count, there is simply no way that this light microscopic method for location of fiber can be used. Also, the alterations in the chemical signals concerning fibers recovered from pulmonary tissues contain observations not made by anyone in any other laboratory. That is, the decrease in intensity of calcium and aluminum as related to leaching of these elements within the lung fluid. Magnesium, yes. Calcium and aluminum, no. There are other explanations possible.

Authors: Thank you very much for your remarks on our article. As analytical chemists we are mostly interested in the asbestos minerals as unique model compounds to test LAMMA as an identification tool and a method for surface characterization. We strongly believe in the latter potential, less in the first, so we agree to a large extent with your comments. Our practical experience with the minerals as such is limited and we appreciate your comments because they clarify our understanding. Unfortunately the remarks come too late to take them into account for the paper.

We measured the 8 different chrysotiles which were used for UICC B standard. The similarity is sufficient to recognise them all as chrysotile.

We agree with your viewpoint that LAMMA cannot be used to identify systematically fibers in human lung tissue as the optical microscope resolution is insufficient to detect anything except abnormally large fibers. For these, on the other hand, the fingerprints help in the identification of the asbestos type.

A.M. Langer: The only problem which may be encountered concerning the chemistry of the different asbestos fibers is the resolution of the sodium peak which enables the analyst to distinguish between crocidolite and amosite. The fact that sodium cannot be detected to distinguish crocidolite from amosite is a serious drawback.

Authors: Sodium can be used to distinguish between crocidolite and amosite but the detection of adsorbed organic material is easier with crocidolite as the material supplies Na for the cationization with the organic matter.

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