Research Article

Identification of Asbestos Using Laser-Induced Breakdown Spectroscopy: A Viable Alternative to the Conventional Approach?

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Laser-induced breakdown spectroscopy has been performed on isolated samples of six types of asbestos—Chrysotile, Crocidolite, Amosite, Anthophyllite, Actinolite, and Tremolite—with analysis of optical emission in the visible region of the spectrum. The principal elements of Mg, Fe, Si, Na, and Ca have all been identified. By examining peak intensity ratios of these elements it is possible to identify the type of asbestos under examination solely from internal examination of the sample spectra. LIBS offers some significant advantages of speed of analysis and removal of subjectivity with potential for on-site rapid analysis.

1. Introduction

Asbestos has been widely used, particularly in the construction industry, because of its strength, flexibility, and resistance to chemical and thermal breakdown. It is now known that inhalation of high levels of asbestos can lead to increased risk of asbestosis, lung cancer, and mesothelioma [1]. Asbestos is considered a hazard to health and its use is positively discouraged. Nevertheless some 15,000 tons were used in the USA in 1999, and it is still in widespread use around the world.

Several well-established methods are currently available for identifying asbestos; these are transmission electron microscopy (TEM), scanning electron microscopy (SEM), and polarised light microscopy (PLM). Of these techniques PLM is the most widely used for reasons of cost and speed.

The current method of assessing asbestos involves surveying a building for potential materials containing asbestos, taking several small samples and then sending them to a laboratory for analysis. Suspect fibres are manually extracted from the sample and examined using PLM. An assessment of the nature of the fibre is made according to fibre morphology, refractive index, and birefringence.

This technique is usually sufficient to determine that the fibre is asbestos and identify its type. However, the process can be time consuming, labour intensive and relies on a potentially subjective assessment of what type of asbestos the fibre is likely to be (influencing the choice of refractive index matching fluid). Certain other fibres such as polyethylene, spider's web, and several other organic materials can sometimes be mistaken for asbestos using this process unless great care and experience are used in the assessment.

If, after completing the above process, the assessment is still not clear SEM can be used and the fibre's elemental composition can be determined. The ratio of the elements calcium, sodium, iron, and magnesium is a confirmation of the specific type of asbestos. This additional identification step increases the cost of the assessment and is unsuitable for large-scale applications due to low throughput.

Other techniques have been proposed such as light scattering measurements [2, 3] (for airborne asbestos particles) and Raman spectroscopy [4] for fibres on a surface. This technique has shown the potential to identify the specific type of asbestos, as has thermal analysis [5].

Laser-induced breakdown spectroscopy (LIBS) is an elemental analysis technique that has received a significant amount of attention due to its ability to provide a noncontact, rapid assessment of the elemental composition of a material and for which there are numerous overview review articles [6–10] and most recently [11]. The output from a pulsed laser,

TABLE 1: Asbestos type and composition.

Type	Chemical formula	Element count						
		Mg	Fe	Si	O	H	Na	Ca
Chrysotile (white asbestos)	$[Mg_3(Si_2O_5)(OH)_4]$	3	0	2	9	4	0	0
Amosite (brown asbestos)	$[(Fe,Mg)_7Si_8O_{22}(OH)_2]$	0	5	8	24	2	2	0
Crocidolite (blue asbestos)	$[Na_2Fe_2(FeMg)_3Si_8O_{22}(OH)_2]$	0	7	8	24	2	0	0
Anthophyllite	$[(Mg)_7Si_8O_{22}(OH)_2]$	1–7	6–0	8	24	2	0	0
Tremolite	$[Ca_2Mg_5Si_8O_{22}(OH)_2]$	5	0	8	24	2	0	2
Actinolite	$[Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2]$	0–4	5–1	8	24	2	0	2

most often a Q-switched Nd:YAG laser, focusses onto a sample where the energy density is so great that ablation of the surface material takes place. A luminous microplasma is formed just above the surface where temperatures can briefly reach 10,000 K. As the plasma cools, the optical emission from the plasma consists of the specific emission spectra of ions and atoms once present within the surface. This emission is collected by an optical system and directed, usually via an optical fibre, to a spectrometer where a computer is used to collect and interpret the spectrum. The flexible nature of LIBS analysis has seen applications in hazardous environments such as nuclear reactors and steel refineries [12, 13], where it would be difficult or expensive to manually collect or examine samples. The lack of need of sample preparation coupled with rapid, in some cases, single shot analysis has seen attempts at the identification of plastics [14] and alloys such as steels. Other applications include dating and restoration of arts and ceramics [15, 16], trace element analysis, and bacterial identification [17]. Portable systems have been demonstrated [18] and are commercially available. The elemental composition analysis made possible by LIBS has previously been applied to a selection of asbestos types by Caneve et al. [19] in the observing emission wavelengths in the ultraviolet at wavelengths around 290 nm. In this work all asbestos types were examined, and a different spectral region suitable for observing all the relevant elements was used. The work and data presented here are contemporary with that of [19].

2. Application to Asbestos Identification

Asbestos comes in six types, with white, brown, and blue the most commonly encountered. Identification of the particular type of asbestos is relevant to the potential hazard that the asbestos poses. The different types of asbestos have different chemical compositions, given in Table 1.

The LIBS spectrum of asbestos will reveal the presence of the elements Fe, Mg, and Si as principal components which when considered with the secondary, elements Ca and Na allow asbestos type to be identified in principle. This is before employing the extra information that can be obtained from relative quantities of the principal, secondary and matrix materials (O, H). On this basis asbestos is well suited to identification using LIBS where all the elements mentioned have easily identifiable spectra. However, there is some discrepancy in the openly and widely available elemental constitution of the various types of asbestos. This is further complicated by the observation that the elemental constitution is not
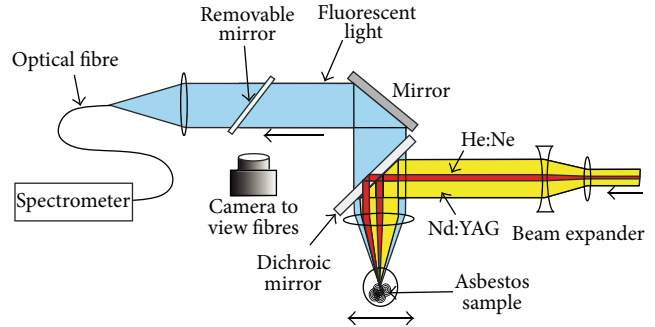

FIGURE 1: Experimental setup measuring the LIBS spectra of asbestos inside a glass container.

fixed. In several cases the precise composition is not known, only the total number of Fe and Mg atoms in the molecule. For this reason reliable identification of the asbestos type might not be possible and can only be made more difficult by the presence of background and matrix materials with a similar composition. The major use for asbestos has been in building materials where cords and fibres of asbestos have been mixed with the host material at levels generally below 10%. One of the major difficulties for a working identification system will be successfully differentiating fibres of asbestos (a silicate mineral) from the host material encompassing it, generally also a silicate.

3. The Experiment and Results

A schematic diagram representing the experimental arrangement is shown in Figure 1. The fundamental wavelength beam of an Nd:YAG laser (Spectron lasers) was used as the ablative source. This was chosen for its good beam quality and modest pulse energy of 20 mJ. Individual asbestos fibres are fine and therefore require a well-focussed beam to ensure efficient use of the laser pulse energy. The beam was directed towards a dielectric mirror at an angle of 45° and then focussed onto the sample using a 5 cm focal length lens. The asbestos sample was contained in a sealed glass container to prevent asbestos fibres escaping. In order to prevent plasma formation on the outer surface of the container, the combination of an expanded beam (3x using a Galilean telescope) and a short focal length lens was used. An He:Ne alignment laser served to show where the Nd:YAG laser was aiming but also revealed the focus of the system. The He:Ne underwent partial reflection from the front and rear surfaces of a dielectric mirror
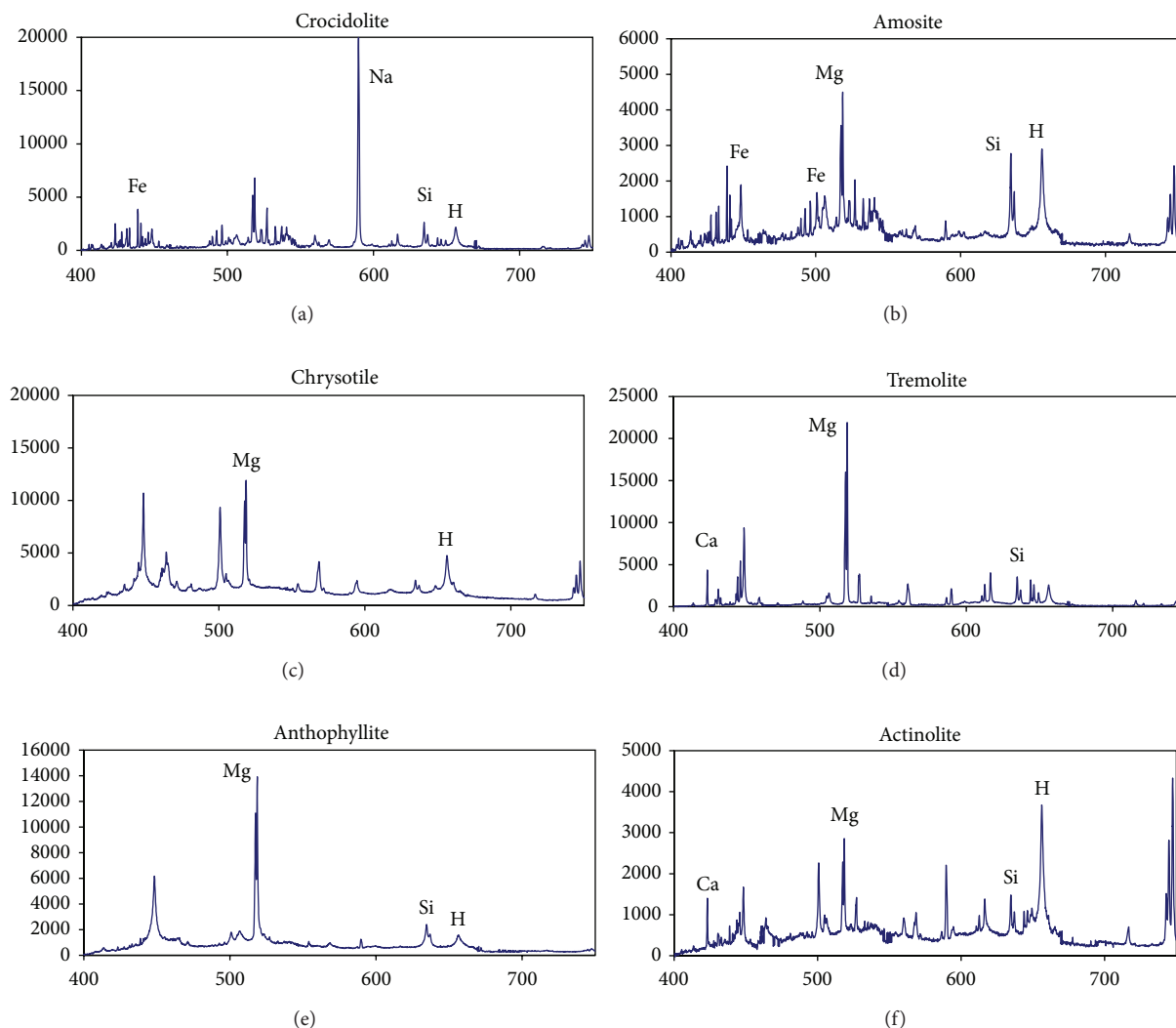
FIGURE 2: LIBS spectra for all six types of asbestos. The wavelength range on the horizontal axis ranges from 400 nm to 760 nm. The spectrometer acquisition was delayed by 400 ns and all spectra are the accumulation of 10 pulses.

producing two parallel beams. Two distinct spots were then visible on the sample if it was not at the correct focal plane of the lens. By adjustment of the sample height the two spots would merge into a single spot at the correct focus. A camera was used to view the sample through the dielectric mirror and via a removable mirror. In this way, translating the sample and adjusting the focus could target individual fibres. After focussing, the mirror directing light into the camera was removed and light from the plasma was directed into an echelle spectrometer (Mechelle 900, Multichannel Instruments) via collection optics matched to the numerical aperture of the input optical fibre.

The spectrometer requires 1.6 μs of pretrigger, and a DG535 timing unit (Stanford Research Instruments) was used to control the relative timing of the spectrometer and laser. Initial attempts at capturing LIBS spectra showed that the quality of the spectra was highly dependent upon the delay used for gating the spectrometer. The broadband plasma emission phase lasts for only a few hundred ns, and the

spectrum is of best quality when contributions from this are gated out. It was found that a pregate delay of 400 ns is optimum to remove the broadband emission whilst ensuring that, for example, the Fe in Amosite was easily observable.

The optimum delay will be dependent upon the pulse energy used with longer delays being required when higher pulse energies are used. Spectra for all six types of asbestos are shown in Figure 2. The captured spectra cover the visible region from 400 nm to 1000 nm, but the spectra shown in Figure 2 have been cut off at around 760 nm where oxygen lines appear. The region 400 nm–760 nm contains easily identifiable spectral lines for all the elements of interest. The spectra shown are the accumulation of emission spectra resulting from 10 laser pulses. In some cases the fibres were very fine and could only withstand a small number of pulses. The spectral contributions from significant elements are labelled

Table 2 shows the spectral peak intensities for a selection of identifiable spectral lines, along with the element, the wavelength of the line, and the type of asbestos analysed. This

TABLE 2: Spectral peak intensities for various elements and spectral lines measured in six forms of asbestos.

| Element	Wavelength	Actinolite	Amosite	Anthophyllite	Chrysotile	Crocidolite	Tremolite
Ca	397.01 nm	829	174	0	357	239	2275
Ca	423.17 nm	1829	864	0	498	844	4351
Fe	438.67 nm	1035	3720	372	0	1768	586
Fe	440.73 nm	697	2487	237	0	1128	0
Mg	517.51 nm	3704	7007	6097	6205	2171	16009
Mg	518.64 nm	5217	9106	8440	8979	2916	21897
Na	589.73 nm	2405	825	712	440	9944	2145
Si	634.71 nm	963	431	578	937	346	3564
Si	636.91 nm	594	270	332	567	0	1983
H	656.21 nm	1025	391	844	4021	0	2581
Na	744.74 nm	445	1058	0	1424	0	1036
K	766.83 nm	317	515	383	0	405	388
O	777.44 nm	3780	1337	1840	10990	890	9562
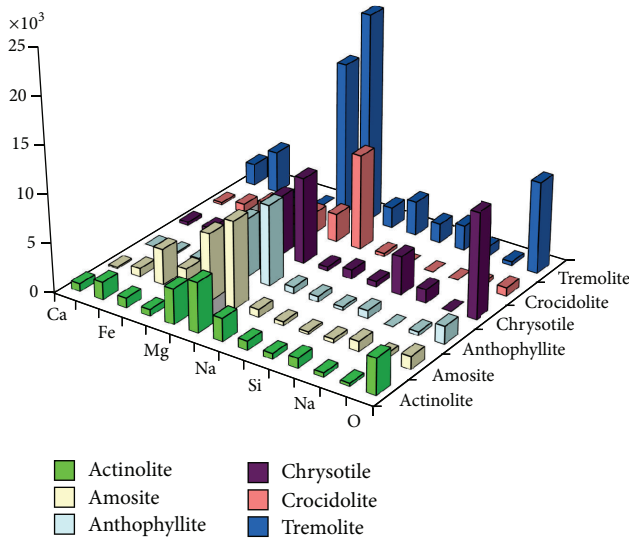
FIGURE 3: Spectral peak intensities (vertical axis) shown by element for each asbestos type.

data is plotted graphically in Figure 3 where features such as the dominance of the Mg lines (517, 518 nm), the visibility of sodium (586 nm), and calcium (436 nm) can be seen.

As previously mentioned a potential difficulty in identifying asbestos types is that the elemental composition for certain types can vary. Tremolite and Actinolite (belonging to the class of amphiboles) are examples of this variability, where the total number of Fe + Mg atoms forming the molecule is constant, but the ratio of Fe to Mg can vary (see Table 1). Tremolite represents the extreme end of the distribution with no Fe present (Ferro-actinolite represents the opposite end with no Mg but this has not been included for clarity). Whilst the samples examined were "pure", that is to say, their type was known and they were isolated from any background material; the exact chemical constitution was not known. Hence it would not be appropriate to treat the spectra from Anthophyllite or Tremolite as suitable generic

templates. The samples used here were known to be of a single type but it was not possible to measure precisely the elemental constitution with a technique such as SEM. The spectra should however be sufficient to allow an assessment of the potential for identification of asbestos type.

In a practical LIBS analysis system that might be used for *in situ* analysis, it would be impractical to expect a fully calibrated elemental quantification system to be implemented, due to uncertainties in the background materials present, the large difference in the transition strengths, and the uncontrollable nature of the sample size. Rather it is better to make an assessment based on what elements are present (or absent) and their relative strengths in the acquired spectra. Ratios were taken of the peak intensities for the most reliable transitions of the relevant elements. These ratios are provided in Table 3 and plotted in Figure 4. Data for the oxygen emission lines was taken and is shown in Table 2 but is not needed in the identification process, interactions between atmospheric oxygen and matrix effects reduce the reliability of this component. From the data it is easy to observe that both Chrysotile and Tremolite have no iron present and cannot therefore be mistaken for other types. Notice that the molecular form of Chrysotile contains fewer atoms of magnesium than Tremolite but shows a higher ratio of Mg:Si. This ratio Mg:Si shows the best variation between asbestos types and would be the most reliable principle component of an identification scheme. This is indeed the ratio chosen in [19]. The asbestos types with the most similar Mg:Si ratios are Crocidolite and Chrysotile, but in this case discrimination is straightforward due to the presence of Na in the Crocidolite which has a strong and easily identifiable spectral component at 589 nm. This is made possible in this case by use of wide spectral bandwidth across the visible spectrum. It also allows for calcium to be identified and used to help the identification process, something not done in the previous work [19]. The greatest similarity is then seen between Tremolite and Actinolite; however, it should be pointed out that Tremolite is in fact the extreme version of Actinolite with all iron replaced

Table 3: Peak intensity ratios for different types of asbestos.

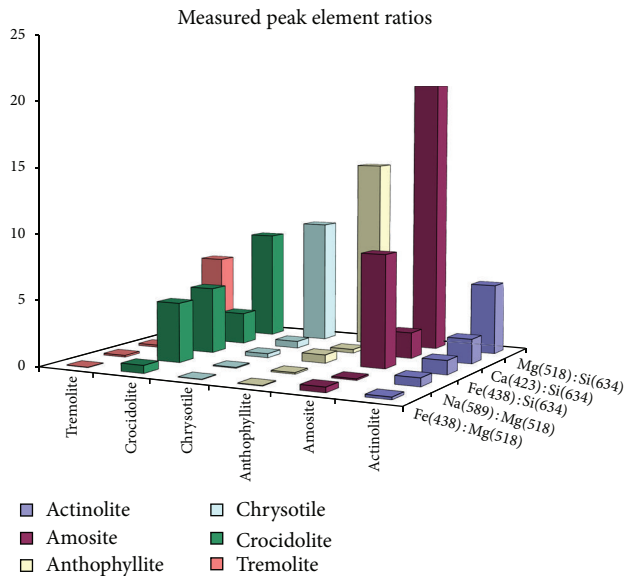| Element ratio	Actinolite	Amosite	Anthophyllite	Chrysotile	Crocidolite	Tremolite
Fe (438) : Mg (518)	0.198 (6)	0.408 (7)	0.044 (2)	0.033 (1)	0.606 (18)	0.027 (1)
Na (589) : Mg (518)	0.64 (1)	0.117 (3)	0.116 (3)	0.070903	4.58 (7)	0.133 (2)
Fe (438) : Si (634)	0.72 (4)	8.6 (4)	0.64 (4)	0.31 (2)	5.15 (30)	0.164 (7)
Mg (518) : Si (634)	5.41 (18)	21.1 (1.0)	14.6 (6)	9.5 (3)	8.4 (4)	6.14 (11)
Ca (423) : Si (634)	1.89 (8)	2.0 (1)	0.28 (2)	0.53 (3)	2.43 (15)	1.22 (2)

Figure 4: Element peak intensity ratios (vertical axis) for asbestos, showing the unique characteristics for each type.

by magnesium. It is therefore more difficult to get a pure sample of any variety of Actinolite.

4. Discussion

Having now established that LIBS in the visible region has the capability of discriminating asbestos types, is this a practical approach? This work has not compared LIBS to other proven and reliable techniques such as SEM as was done in 19, which in itself showed performance comparable to SEM. The objective here is to see if LIBS is capable of identifying asbestos type in a stand-alone fashion. In general PLM is the predominant method of identification for reasons of time and cost which makes SEM a much less commercially attractive approach. Although LIBS may suffer from difficulties due to asbestos generally being embedded in a building material (silicate) matrix, much of this difficulty can be removed due to the sample prefiltering that is performed. That is, materials that are fibrous in nature and located in environments or situations where asbestos is likely to be found are selected by a trained assessor. Matrix effects are a significant issue in obtaining reliable LIBS data, and this would add to the difficulty of using LIBS *in situ* for asbestos identification.

This application-specific use of LIBS—making use of the sample collection process—significantly helps to overcome issues of quantitation and calibration by restricting the likely

samples to those of a fibrous nature and then using the internal chemical distribution to both positively assert that the sample is asbestos and to identify its type, thus improving hazard assessments. As stated in [11] "..acceptance of LIBS to the larger user community will be aided by the publication of successful applications within the field of use." The fine fibrous nature of asbestos requires single shot analysis where possible and is thus well suited to analysis with a micro-LIBS system where focal spot sizes and pulse energies are smaller, less destructive, and well targeted [20, 21]. When used in this scenario LIBS is capable of offering advantage to the whole process by speeding up the analysis stage in the remote laboratory—thus allowing greater throughput of samples— By reducing the burden of mundane analysis upon skilled staff and by removing subjective elements to the assessment process, thus improving the quality of assessment. Further to this the use of portable LIBS equipment would make possible *in situ* analysis of suspect materials, drastically reducing the time for suspicious material to be confirmed from potentially days to just seconds. It should be noted however that the use of LIBS also offers some additional problems to the process. The somewhat violent action of plasma formation has a disruptive effect on the sample and could potentially release asbestos particulates into the air, where they become a health hazard. This is less of an issue in laboratory-based analysis where air extraction and filtering can be established but is a significant issue to an *in situ* approach, where suitable mitigation would have to be in place. On balance, therefore, the author feels that, when fused with inspection by an experienced assessor, LIBS has the potential to significantly improve the commercial process of asbestos assessment.

5. Conclusion

Laser induced breakdown spectroscopy has been performed on isolated samples of six types of asbestos—Chrysotile, Crocidolite, Amosite, Anthophyllite, Actinolite, and Tremolite. After a suitable delay emission spectra in the visible region were captured and analysed. Within these spectra the principle chemical elements present in the asbestos types were identified. By comparing the intensity ratios of elements from within the spectrum, in particular Mg:Si, Fe:Si, and Na:Mg, a signature for the specific type of asbestos could be established. This process is sufficient to identify the type, not to quantify the precise elemental composition of the sample, purely from the LIBS spectra and a knowledge of the elemental composition of asbestos types. LIBS has the potential to be of great benefit to the existing process of asbestos analysis and detection by significantly speeding up the analysis and removing

subjective stages of choice of index matching fluid from the process. LIBS is capable of being automated thus releasing well-trained staff from a tedious repetitive process of observation where they can be used in a more expert manner. LIBS equipment is also commercially easier to acquire than SEM equipment which would perform the same reliable identification. With careful consideration to the dramatic shock effects upon the sample that may release particulates into the air, LIBS has the potential to radically change the commercial landscape for asbestos detection.

Conflict of Interests

This work was carried when the author worked for QinetiQ, St. Andrews Road, Malvern, Worcestershire, UK. The author asserts no conflict of interests with any parties named in this work.

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