In situ spectroscopic identification of the six types of asbestos

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Abstract

Exposure to asbestos fibres is related to a number of severe lung diseases, and therefore, rapid, accurate and reliable in situ or on-site asbestos detection in real-life samples is of considerable importance. This work presents a comprehensive investigation of all six types of asbestos by mid-infrared ATR-FTIR, NIR spectroscopy and Raman microspectroscopy. Our studies demonstrate that for practical applications, NIR spectroscopy is potentially the most powerful method for asbestos identification in materials utilised by the construction industry. By focusing on the narrow spectral region, 7300-7000 cm^{-1} (~1370-1430 nm, overtones of O-H vibrations), which is highly specific to these materials, and optimising the sensitivity and resolution of the instrumentation, we have been able to discriminate and identify each of the six types of asbestos with the level of detection significantly better than 1 wt%. Furthermore, straightforward computational analysis has allowed for automated objective evaluation of the spectroscopic data.

Keywords: asbestos containing materials; mid-IR spectroscopy; Raman spectroscopy; NIR spectroscopy

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Introduction

Asbestos is a generic term for a group of six silicate minerals (chrysotile, amosite, crocidolite, actinolite, tremolite and anthophyllite), from the serpentine and amphibole groups, which possess an ósasbestiformô fibrous morphology. The amphibole type asbestos materials (all except chrysotile) have a chemical composition $M_7Si_8O_{22}(OH)_2$, where M stands for metal cations, such as calcium, iron, magnesium or sodium. Chrysotile, a serpentine mineral, has a distinctive $Mg_3Si_2O_5(OH)_4$ composition [1,2]. Asbestos has been widely utilised in industry owing to its valuable properties, including high tensile strength, heat and fire resistance, electrical resistance and chemical inertness. Chrysotile accounts for around 95% of naturally occurring asbestos, and hence has been most commonly employed on the industrial scale. Crocidolite and amosite were also widely used. Applications of these materials include brake shoes and gaskets, insulation board, cement, fire blankets, corrugated roofing tiles, membranes for chlorine production and many others [3,4,5,6,7,8]. In many countries, the use of asbestos is now restricted or banned due to the severe health risks it poses. The structural and chemical properties of the fibres inhaled into the lungs lead to severe tissue damage causing asbestosis, mesothelioma and other pleural diseases [9,10]. Considering the high potential risks resulting from the contact with asbestos containing materials (ACM), it is important to be able to efficiently and reliably detect them.

The current standard methods for asbestos identification are polarised light microscopy (PLM) for bulk samples, and phase contrast microscopy (PCM) for airborne fibres. In PLM, the optical properties of a solid sample, including pleochroism, refractive index and birefringence, are observed under plane polarised and cross polarised light. In PCM, a volume of air is passed through a filter and then the concentration of fibres is determined. PCM is less specific than PLM as very limited characterisation is carried out [5,11,12]. Limitations of PLM include the subjective nature of analysis, and its inability to provide quantitative information on the structure or chemical composition of the examined fibres. Other analytical techniques which could overcome some of these limitations include x-ray diffraction, electron microscopy and vibrational spectroscopy [12,13].

Studies of asbestos using vibrational spectroscopy began in the 1970s, and have been discussed in the literature since. The research documented has largely focused on collecting infrared and Raman spectra of asbestos minerals in order to determine the relationship between spectral bands and structural features [14,15,16,17,18,19]. The aim of this work is to explore the effectiveness of mid-IR, NIR and Raman spectroscopy for the ñeverydayò detection of asbestos in suspected ACM, particularly materials utilised in the construction industry. The challenge is to apply these techniques to the detection of asbestos in a wide range of possible organic and inorganic matrices which can interfere with the analysis, from bitumen and structural paints to

cement and plasterboards. The examined ACM may be presented as powdered, fibrous or compacted solid materials, which should be tested with minimal sample preparation. Furthermore, environmental, and health and safety agencies generally require to identify each of the six types of asbestos even when its concentration is below 1 wt%. The emphasis of our investigation is on the practical application of spectroscopic techniques for the reliable analysis of real-world materials, possibly on-site or in situ, that is to achieve identification of every type of asbestos present in a sample as a major constituent or in trace quantities. Spectra of reference asbestos samples, potential replacement fibres and matrix materials, and real-life ACM have been collected with virtually no sample preparation. The data have been analysed using a number of computational approaches, and the advantages and limitations of each spectroscopic technique are discussed. (The Supplementary Information files provide a comprehensive description of the experimental procedures.) The results of these investigations, which have been correlated with the PLM data, demonstrate that NIR spectroscopy is conceivably the most powerful technique for routine practical detection and identification of asbestos. Our work shows that NIR is a more viable option than Raman microscopy and ATR-FTIR for in situ screening of ACM samples, which is largely due to its greater penetration depth. Therefore, a dedicated computational analysis protocol is developed specifically for the evaluation of NIR data.

Experimental

To ensure safe working practices, all experiments were carried out using a negative-pressure ventilated safety box with an extraction system equipped with a H-type filter.

Materials. The reference samples characterised using FTIR and Raman spectroscopy are shown in Table S1. The samples were divided into two groups, geological asbestos reference samples (provided by the Health and Safety Laboratories, UK, and Geology department at Keele University) and non-asbestos matrix materials (sourced locally). ACM samples with unknown asbestos content were supplied by Greenwall Environmental and accompanied with the PLM analysis data. The original samples, including fibrous (reference asbestos and asbestos rope), powdered (cement and dry textured coating) and compacted solid (tiles and blocks) materials were analysed as received without any pretreatment, enrichment or fibre extraction. Typically, a sample, with the size of 10x10x5 mm, was fixed onto a sample holder of the relevant spectrometer and characterised using one of the vibrational spectroscopy techniques.

Vibrational Spectroscopy. FTIR spectra were collected using Thermo Nicolet Avatar 320 and iS10 FTIR spectrometers equipped with DTGS detectors and attenuated total reflectance (ATR) attachments. Two ATR attachments, with a diamond coated zinc selenide crystal and a diamond crystal, were used in order to ensure minimal sample preparation. The spectra were collected using 4 cm^{-1} resolution, 64-128 scans (~130 to 260 seconds data collection time;

sampling spot size ~2 by 2 mm), 4000-550 cm^{-1} range for the diamond coated zinc selenide ATR and 4000-400 cm^{-1} range for the diamond ATR. The Raman spectra were obtained using a Thermo Scientific DXR microscope, which is a dispersive instrument with interchangeable lasers and optical elements working with 780 nm and 532 nm excitation wavelengths. The typical parameters for the data collection were: 4 cm^{-1} resolution, 0.1-0.5 second exposure time, 200-2000 scans (~20 to 1000 seconds data collection time; sampling spot size ~10 to 50 μm), 10-24 mW laser power and a spectral range of 3300-40 cm^{-1}. NIR spectra were collected using a Thermo Antaris II spectrometer equipped with an InGaAs detector and a diffuse reflectance attachment. The spectra collection parameters were: 2-32 cm^{-1} resolution, 16-128 scans (~5 to 100 seconds data collection time) and 10000-4000 cm^{-1} spectral range.

Data Analysis. The analysis of vibrational spectra, including band search, intensity measurements and a multi-component search, was carried out using Omnic and Specta software (Thermo Scientific). For the spectra shown, no smoothing was applied; however, some spectra are offset along the y-axis for the clarity of presentation.

NIR spectra were analysed using our own basic computational tool Asbestos-Tester-4-v-0.1.0. The programôs source code was written in the Rust programming language and compiled with the 1.33.0-nightly tool-chain. The computational algorithm was designed for the analysis of NIR spectra obtained at a resolution of 4 cm^{-1}, in the region of 7300-7000 cm^{-1}, saved as csv files. The data analysis relies on the comparison between the NIR spectra of unknown samples and the reference spectra of asbestos, taking into account the band positions and intensities. The program was evaluated using 50 samples, including reference materials, and 9 data sets for each sample. The 9 data sets were obtained by collecting NIR spectra in 3 different locations for every sample, 3 times in each location. The results, computed for every data set, indicated the presence or absence of different types of asbestos. The program examined each spectrum for the presence of each type of asbestos. The current version of Asbestos-Tester-4 was compiled to test for the presence of four more common types of asbestos: chrysotile, actinolite, amosite and crocidolite. The number of reference asbestos types and the data analysis parameters can be easily changed by a competent user. This program is made freely available for not-for-profit use as part of this publication. The source code can be found at https://github.com/aleshaleksey/asbestos-test/.

Results and Discussion

ATR-FTIR characterisation. All six types of asbestos reference samples have been studied (Table S1), and Figures 1 and S1 show characteristic spectra of these materials exemplifying the key bands observed; their positions and assignment are summarised in Table S2. Two regions in the spectra are of particular interest: the 3700-3500 cm^{-1} region can be attributed to O-H stretching vibrations, whereas the bands observed in the 1200-500 cm^{-1} region can be ascribed to various lattice vibrations [15, 20, 21]. The mid-IR spectra demonstrate significant reproducible differences between all types of asbestos, and therefore, FTIR data could be used to distinguish asbestos samples by applying statistical techniques and computerised search of reference libraries. Within the scope of this study, a number of reference materials have been chosen that are likely to be present alongside asbestos, including matrix materials and asbestos replacement fibres, e.g. polyamide or glass fibres. FTIR spectra of such fibres are shown in Figure S2. Since the majority of the distinctive bands in the asbestos spectra are in the same region (1200-900 cm^{-1}) as the intense bands in the spectra of silica-based inorganic fibres, their presence in a material could impede the detection of asbestos. In contrast, the bands observed in the spectra of organic fibres are found predominantly in different regions, hence, the presence of most organic fibres is unlikely to affect asbestos detection. Figure S3 shows FTIR spectra of three common matrix materials: bitumen, cement and plasterboard, all of which contain bands, for instance in the 1300-500 cm^{-1} region, that may overlap with the asbestos bands in unknown ACM materials.

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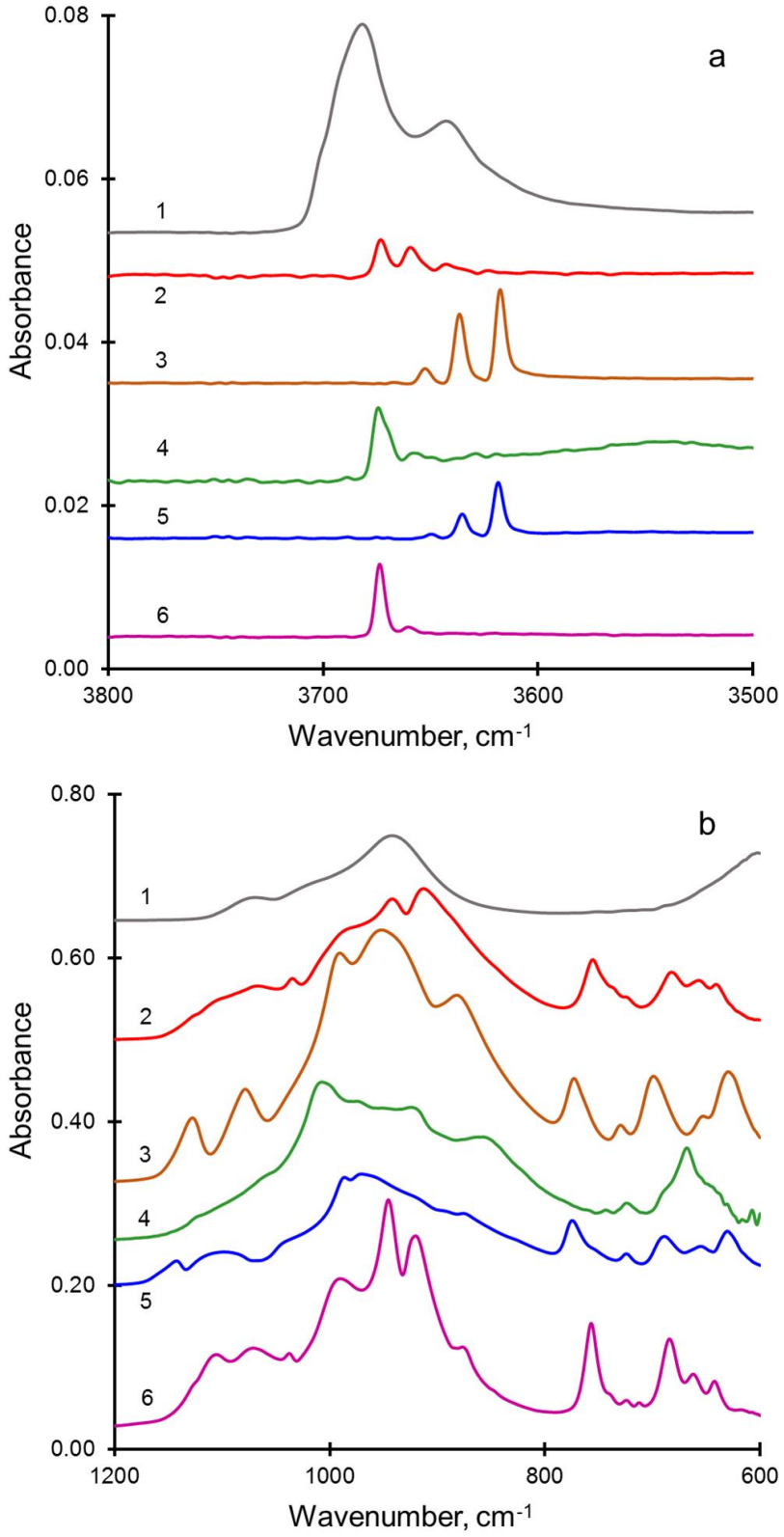

Figure 1. FTIR spectra of reference asbestos samples: (a) region of O-H stretching vibrations and (b) region of structural vibrations. Note ~10-fold difference in the absorbance scale. (1) ï chrysotile, (2) ï actinolite, (3) ï amosite, (4) ï anthophyllite, (5) ï crocidolite, (6) ï tremolite (resolution = 4 cm^{-1}).

A range of suspected ACM have been characterised by PLM and FTIR aiming to determine which type of asbestos may be present in each sample. The FTIR spectra of 43 samples have been initially analysed by comparing the band positions with those observed for the reference materials (Figure S4). In addition, specialised software Specta has been tested for the identification of individual components in ACM to match the unknown spectrum, utilising a multi-component search and producing a composite spectrum from the relevant library spectra. The simulated spectrum is rated in comparison to the spectrum of the examined sample using the proprietary match and composite values, which quantify how well the two spectra match and the percentage contribution of each reference spectrum to the composite spectrum (see Figures S5 and S6, and related discussion). The results obtained are in good agreement with those subsequently provided by PLM for 34 out of 43 ACM samples (Table S3), however, omissions in the spectral libraries can lead to very low match values for some samples. Indeed, for some ACM the data are inconclusive, particularly, when the asbestos percentage contribution to the composite spectrum is below 5%. Overall, ATR-FTIR spectroscopy can be successfully utilised for the analysis of ACM with a high asbestos concentration (estimated as above 20 wt%). Nonetheless, the low sampling depth typical of mid-infrared spectroscopy (a few microns), and the presence of interfering IR bands, owing to the vast range of matrix materials, can severely compromise the analytical power of this technique for the real-life asbestos identification. Moreover, the use of ATR requires direct contact with the sample, which in turn necessitates additional safety measures to prevent potential asbestos exposure.

Raman Spectroscopy. In general, Raman spectroscopy is a highly sensitive analytical tool widely used for structural characterisation and identification of pharmaceuticals, polymers and other materials. Spectra of the reference asbestos samples and a selection of ACM have been collected to determine the utility of this technique for asbestos identification (Figures 2, S7 and S8, and Table S4). Although this is probably the first reported study of all six types of asbestos using two different excitation wavelengths in the visible and NIR regions, which can therefore serve as a reference source, the effectiveness of Raman spectroscopy for the analysis of real-life ACM has not been satisfactory. A number of ACM samples and a range of sampling conditions have been tested, but in all cases the signal to noise ratio is low, the background from any non-asbestos constituent is significant and the spectral contribution from the matrix materials is rather high. While the spectra collected using different excitation wavelengths have yielded a better signal to noise ratio and decreased background for some samples, the identification of asbestos in real-life ACM using Raman spectroscopy has been unsatisfactory [16,17]. Furthermore, according to [20,22,23,24], Raman spectra of asbestos minerals and their non-fibrous analogues (chrysotile and lizardite, amosite and grunerite, crocidolite and riebeckite) are quite similar, making their identification even more challenging.

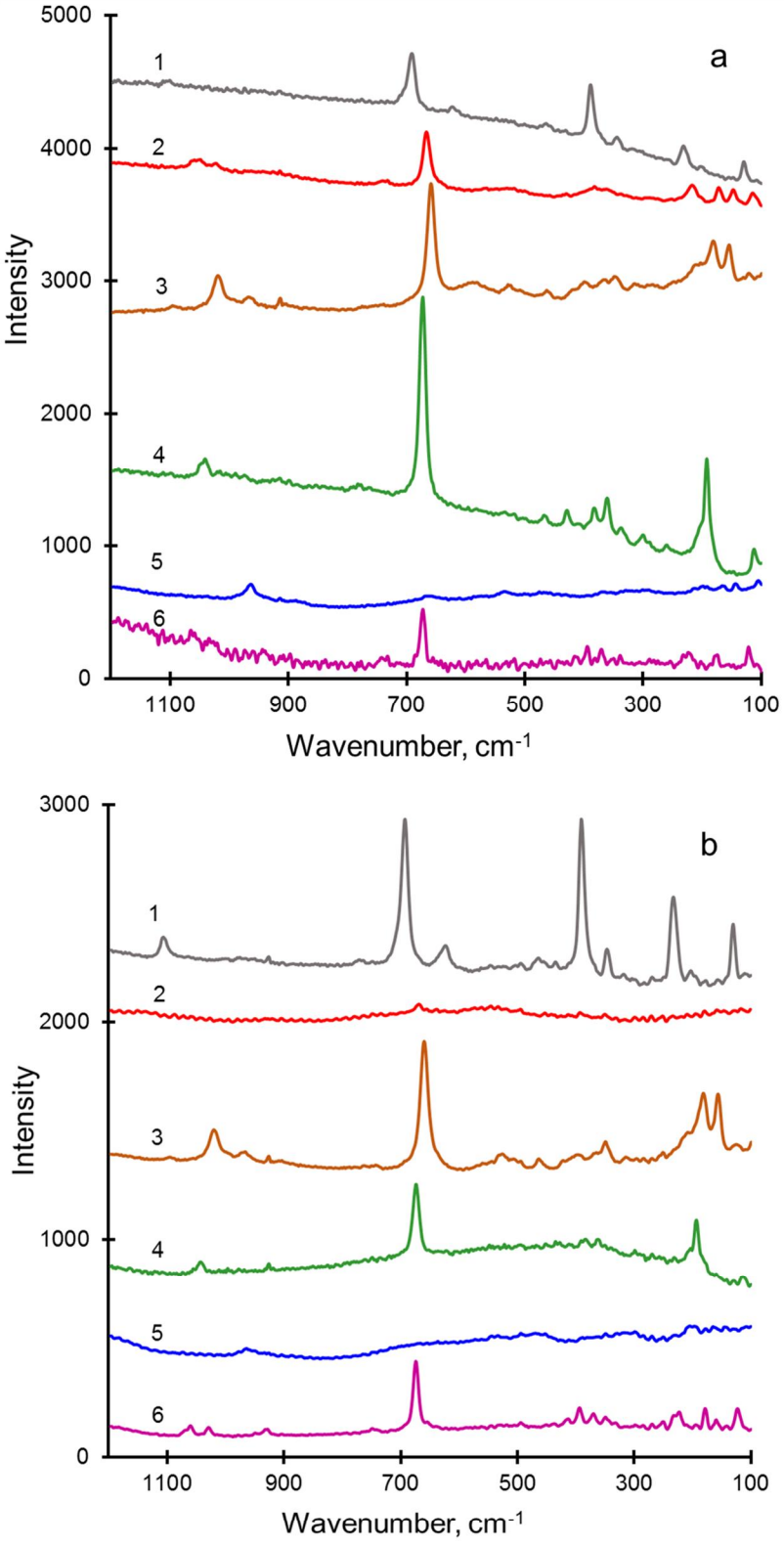

Figure 2. Raman spectra of asbestos reference samples collected using (a) 532 nm and (b) 780 nm excitation wavelength: (1) ï chrysotile, (2) ï actinolite, (3) ï amosite, (4) ï anthophyllite, (5) ï crocidolite, (6) ï tremolite (resolution = 4 cm^{-1}).

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Near-infrared spectroscopy. NIR has a wide range of applications in polymer, pharmaceutical and food industries. It is particularly useful for the identification and quantification of a known compound within a well understood mixture or matrix [25]. As stated previously, it is essential to achieve successful detection of asbestos in a wide range of unknown matrices and to identify each of the six types of asbestos even when its concentration is below 1 wt%. NIR spectra of six types of asbestos and those for a selection of matrix materials, collected at a relatively high resolution (2 cm^{-1}) in the region 7300-7000 cm^{-1}, are presented in Figures 3, S9 and S10. The observed bands, corresponding to the first overtone of the O-H stretching vibrations, show a distinctive pattern for each type of asbestos as compared to any organic or inorganic material examined in this work, including minerals of similar composition (e.g. non-fibrous tremolite, brucite and mica). For potential practical applications, it is important to note that the same high quality spectra have been obtained for asbestos samples analysed through a plastic bag or coated with paint, wet samples and those subjected to heat treatment, and also when a 1.5-metre NIR fibre-optic probe has been used.

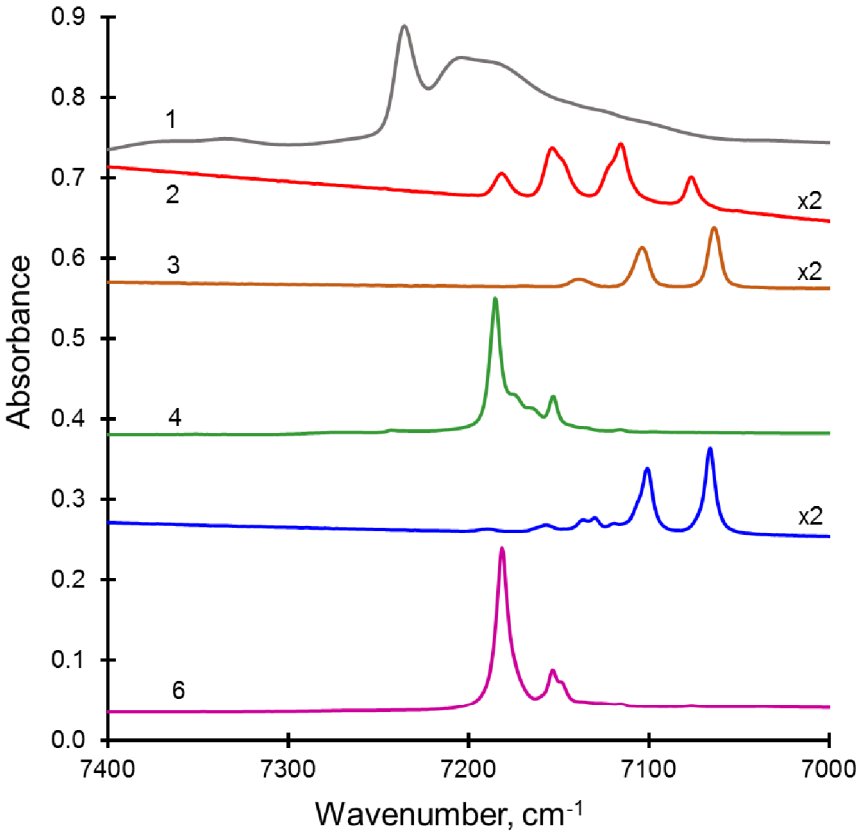

Figure 3. NIR spectra of asbestos samples: (1) ï chrysotile, (2) ï actinolite, (3) ï amosite, (4) ï anthophyllite, (5) ï crocidolite, (6) ï tremolite (resolution = 2 cm^{-1}).

Figures 4 and S11 present NIR spectra of amosite, crocidolite and chrysotile imbedded into different matrices at a range of concentration. The data show a high signal to noise ratio even for the samples with asbestos concentration of 0.1 wt%, making it evident that NIR spectra can be used for the detection of trace quantities of asbestos. In agreement with [19], the very high sensitivity of NIR spectroscopy in the overtone region of O-H vibrations can be explained by the very significant sampling depth (estimated as ~1 mm for NIR, as compared to ~10 μ for the mid-IR region) and the high values of the anharmonicity constants for these vibrations, which are summarised in Table 1 along with the OH band positions observed in the mid- and near-IR spectra.

Table 1. The positions of OH band, $з(O\text{-}H)_{0\to1}$ and $з(O\text{-}H)_{0\to2}$, and the values of the anharmonicity (χ_e) constant calculated for various O-H vibrations.

	$з(O\text{-}H)_{0\to1}$, cm^{-1}	$з(O\text{-}H)_{0\to2}$, cm^{-1}	ϖ_e, cm^{-1}	χ_e
Chrysotile	3700 (shoulder)	7236	3864	0.0212
	3683	7204	3842	0.0211
	3643			
Actinolite	3673	7182	3837	0.0214
	3659	7154	3823	0.0215
	3643	7116	3813	0.0223
		7076		
Amosite	3653	7136	3823	0.0222
	3637	7104	3807	0.0223
	3618	7064	3790	0.0227
Anthophyllite	3674	7185	3837	0.0212
	3658	7153	3821	0.0213
Crocidolite		7157		
	3650	7130	3820	0.0223
	3635	7101	3804	0.0222
	3619	7066	3791	0.0227
Tremolite	3674	7181	3841	0.0217
	3660	7153	3827	0.0218

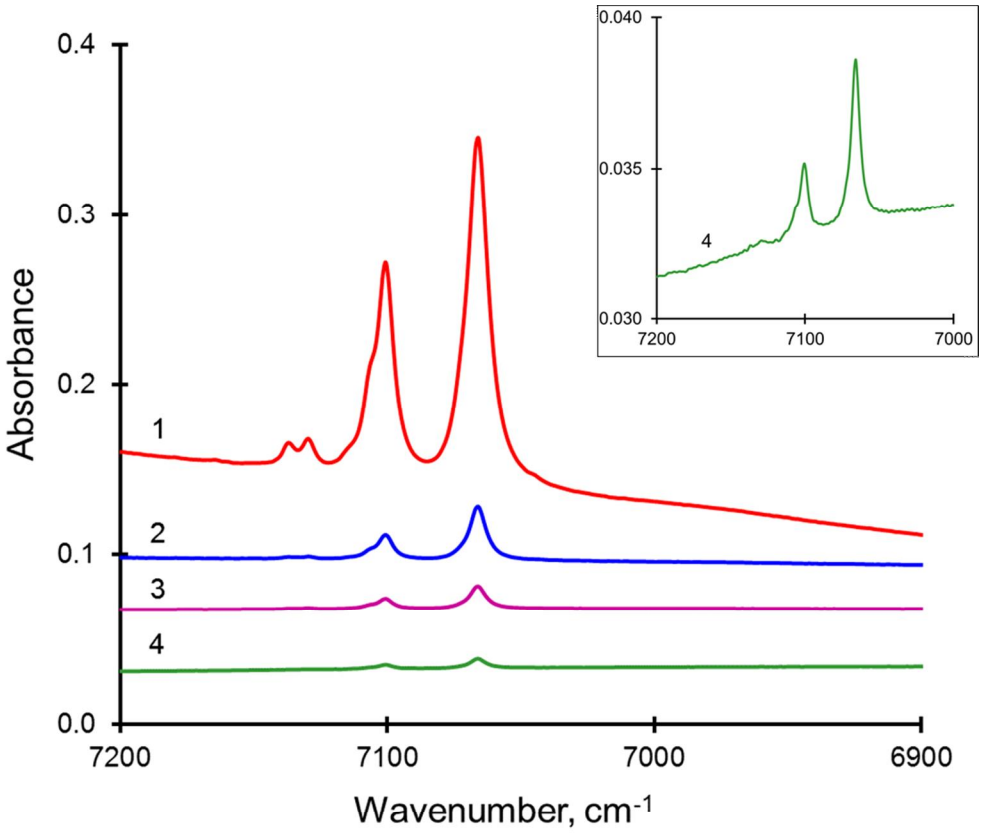

Figure 4. NIR spectra of crocidolite in $CaCO_3$: (1) ï 100%, (2) ï 10%, (3) ï 1%, (4) ï 0.1% (resolution = 2 cm^{-1}). Insert demonstrates the high signal to noise ratio in the NIR spectrum of the 0.1 wt% sample.

Figure S12 shows NIR spectra of most commonly found types of asbestos: chrysotile, amosite and crocidolite, as 1 wt% mixtures in calcium carbonate. For a combination of chrysotile with any amphibole, the identification of each component is straightforward, whereas the discrimination of amosite and crocidolite in their mixture is the most challenging task in spectroscopic analysis of asbestos. This can be successfully achieved if the data are collected at a high resolution, 2 or 4 cm^{-1}, in the region of 7300-7000 cm^{-1} (Figure S12b). Moreover, careful deconvolution of the spectra would yield the fraction of each type of asbestos present. The value of high resolution data is highlighted by Figure S13, which presents NIR spectra of actinolite, amosite, crocidolite and chrysotile recorded at different spectral resolution. As it changes from 2 to 32 cm^{-1} (this corresponds to ~0.39 and ~6.2 nm), a significant amount of information is lost. For instance, the NIR spectra of amosite and crocidolite, which can be readily distinguished at 2 cm^{-1}, become almost identical at the 32 cm^{-1} resolution (Figure S13e). It should be noted that most wide-range NIR spectrometers, particularly portable and hyperspectral models that could be used for on-site and remote analysis, operate at a rather low resolution, 10 to 50 nm [26,27]. Clearly, for a reliable real-world identification of asbestos, the NIR instrumentation should be capable of collecting the spectra at a high resolution in the 7300-7000 cm^{-1} range.

For practical asbestos detection, it is essential to develop analytical procedures which would be objective and could be readily automated. Therefore, we designed and tested a facile computational algorithm for the analysis of NIR spectra obtained at a high resolution, 2 or 4 cm^{-1}, in the region of 7300-7000 cm^{-1}. The program has been evaluated using 50 samples with 9 data sets for each sample (see Table S5). The results, computed for every data set utilising the position and intensity of the bands observed in each NIR spectrum, indicate the presence or absence of different types of asbestos. Table S6 presents a selection of the final outputs (a complete set is included in SI as a csv file), which demonstrate notable agreement with all available data for the composition of the questioned samples. Clearly, NIR spectra show high sensitivity between 7300 and 7000 cm^{-1}; focusing on this narrow region has the added advantage of eliminating most undesirable contributions from various matrix components and contaminants, while high resolution data facilitate excellent discrimination for all types of asbestos, making NIR an effective and objective tool for the analysis of ACM.

Conclusions

The following conclusions and recommendations result from this work:

1. FTIR spectroscopic studies using ATR sampling have demonstrated that asbestos can be detected in a wide range of materials. Chrysotile, crocidolite, amosite, tremolite, anthophyllite and actinolite show bands in the 3700-3500 cm^{-1} and 1200-500 cm^{-1} regions, which can be used to identify asbestos in mixtures with many other materials. Some of these materials, however, show bands in the same region as asbestos, and thus, can interfere with its detection. For instance, absorption bands in the OH-region and in the region of structural vibrations are observed in the infrared spectra of cement and inorganic fibres. Furthermore, in some ACM, asbestos fibres appear to be completely coated with paint or bitumen preventing their identification. Therefore, for samples with low asbestos concentration and for materials containing asbestos fibres fully encapsulated within a polymer matrix, the FTIR results have been inconclusive. For the samples with an unknown asbestos content, computational analysis provides a more confident identification, but only in ACM with over 20 wt% of asbestos. It should be noted that ATR-FTIR requires direct contact between the probe and the sample, whereas FTIR sampling in transmittance mode using KBr disks would require additional lab-based sample preparation.

2. Raman spectroscopy is potentially very well suited to the in situ or on-site analyses, as the spectra are not affected by the presence of water or container materials to any significant degree. However, despite the initial expectations, it has not been found useful for the identification of asbestos in ACM. The quality of the spectra has been poor, with low signal to noise ratio and considerable fluorescence background. Using two laser sources improved the results for reference samples providing more spectral information, however, asbestos identification has not

been possible in any of the studied building materials. It can also be expected that any impurity, which is characterised by either strong Raman scattering or intense fluorescence, would nullify any improvements achieved with this analytical technique.

3. NIR studies demonstrate that in the 7300-7000 cm^{-1} region, each type of asbestos has a distinct pattern of absorption bands corresponding to the first overtone of the O-H stretching vibrations. The remarkable sensitivity of this technique can be linked to the high anharmonicity of the O-H vibrations and a substantial sampling depth. Furthermore, NIR does not require direct contact between the probe and the sample, which can be therefore contained, avoiding asbestos exposure. By focusing on the narrow spectral range and optimising the resolution level, each of the six types of asbestos can be differentiated with the limit of detection as low as 0.1 wt%. Furthermore, straightforward computational analysis has been used for an automated objective processing of the spectroscopic data. The results of this work demonstrate that NIR spectroscopy is potentially the most powerful technique for rapid, accurate and reliable detection and identification of asbestos in real-life materials utilised by the construction industry.

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CRediT authorship contribution statement

VZ: supervision, methodology, data collection, data analysis, validation, writing - original draft, review and editing. FR: supervision, methodology, writing - review and editing. AZ: software, data analysis, validation, writing - review and editing. AH: data collection, data analysis, writing - original draft, review and editing.

Supplementary Information

Supplementary data for this article can be found on-line at:

Conflict of interest

The authors declare no competing financial or any other interest.

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