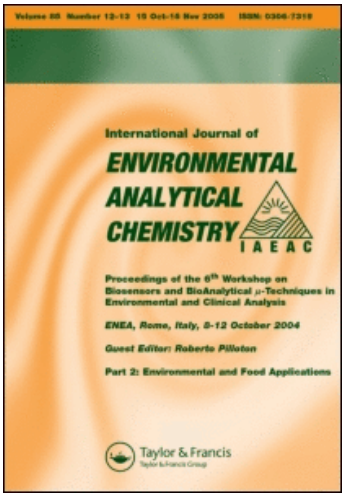

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Balducci, D. and Valerio, F.(1986) 'Qualitative and Quantitative Evaluation of Chrysotile and Crocidolite Fibers with IR-Spectroscopy: Application to Asbestos-Cement Products', International Journal of Environmental Analytical Chemistry, 27: 4, 315 — 323
To link to this Article: DOI: 10.1080/03067318608079824
URL: http://dx.doi.org/10.1080/03067318608079824

Intern. J. Environ. Anal. Chem., 1986, Vol. 27, pp. 315–323
0306-7319/86/2704-0315 $18.50/0

Printed in Great Britain

Qualitative and Quantitative Evaluation of Chrysotile and Crocidolite Fibers with IR-Spectroscopy: Application to Asbestos-Cement Products†

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Infrared (IR) spectrophotometry allows simple and quick qualitative and quantitative evaluations of different kinds of asbestos, as well as of other inorganic particles. In particular, chrysotile and crocidolite have characteristic IR spectra and optical density measures of 2,710 nm band for chrysotile, of 12,820 nm band for crocidolite permit quantitative evaluation of each fiber alone or in mixture.

IR spectra also give informations about changes of fiber structure and of chemical composition due, for example, to thermal treatment or acid leaching.

The analytical method we developed can detect levels as low as 0.1 mg of fiber in a 300 mg disk of KBr using a low cost IR spectrophotometer.

The use of a Fourier Transform IR spectrophotometer (FTIR) improves dramatically the sensitivity and selectivity. Computer assisted analysis of spectra offers the possibility to reduce matrix interferences and to compare different spectra. Examples of IR technique applied to asbestos-cement products and insulating materials are presented.

KEY WORDS: Asbestos, IR spectroscopy, fiber identification, matrix effects.

†Presented at the 16th Symposium on the Analytical Chemistry of Pollutants, Lausanne, Switzerland, March 17–19, 1986.

INTRODUCTION

Asbestos is a generic term that defines a class of fibrous silicates which differ greatly for their physical and chemical properties.[1] Their mineralogical classification is represented in Figure 1. Chrysotile and crocidolite fibers are the most commonly used.

In the United States, in 1974, 721,000 tons of chrysotile and 34,000 of crocidolite were used.

It has long been recognized that asbestos inhalation can induce lung fibrosy, as well as lung cancer and mesothelioma. As a consequence many countries have adopted stringent procedures for hygiene control during manipulation, use, and disposal of these mineral fibers.

Therefore, also for these reasons, the development of analytical techniques, able to identify asbestos type, and to give rapidly quantitative information are required. Obviously similar characteristics are well accepted for quality control in industry, were manufactures containing asbestos are produced.

However the most diffused analytical techniques developed for these purposes require expert and well trained personnel (polarized light microscopy),[2] or expensive equipment, with long and tedious analysis times (electron microscope, X-ray microanalysis)[3,4,12] and, in general, these techniques require very careful standardizations.[5]

Some authors have reported the use of IR spectrophotometry.[6-9,12,14] This method, also according to our experience, deserves more attention.

In fact, though affected by some limitations, due mainly to possible matrix interferences, it is capable of quickly furnishing qualitative and quantitative information on the type of asbestos contained in the sample material.

In our laboratory we have set up a simple IR spectrophotometric method, using a low cost instrument. This method allows the

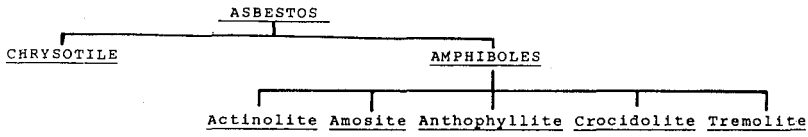

FIGURE 1 Mineralogical classification of asbestos.

quantitation of chrysotile and crocidolite fibers present in a sample mixture in about 90 min.

Using a FTIR spectrophotometer and a computer assisted program to analyse spectra, we have also tried to apply the IR techniques to asbestos cement samples. In this case matrix effect was easily overcome and sensitivity was improved.

MATERIALS AND METHODS

Crocidolite and Rhodesian chrysotile and amosite were furnished by the UICC.

Samples of asbestos cement manufactures, and components for their preparation (asbestos fibers and cement) were kindly supplied by ETERNIT.

KBr for IR spectrophotometry was obtained from Merck, as well as analytical grade ethanol.

A Perkin Elmer 710-B, double ray, and Perkin Elmer 1700 FTIR spectrophotometer were used.

Spectra were elaborated using a program produced by PE (PE 983) and a 3600 PE data station.

All the fiber samples were analysed using the KBr disk method. KBr was ground and dried in a oven at 110°C for 12 hours.

A suitable amount of each sample (asbestos, cement and their mixtures) was weighed and ground in an agata mill for 3 min with two drops of ethanol. As soon as most of the ethanol had evaporated, 300 mg of KBr were added. The sample was mixed until homogeneous and then heated to 110°C for one hour. The mixture was then placed in a press and a pressure of 12 tons was applied, under vacuum, for 10 min and the KBr disk was submitted to IR analysis.

IR spectrophotometric analysis was carried out by scanning in the range 2,500 to 16,000 nm. Absorbance at the selected analytical bands was calculated and adjusted according to the width of the disk. This procedure was used both with disks containing a single type of fiber and with disks containing a mixture of the two types of fibers.

Disks contained from 0.3 to 1 mg of single type of fiber, while the total amount of fiber in the disks containing a mixture, ranged from

1.1 to 2 mg. Each measurement was done in duplicate. Similar procedure was used to analyse insulating materials.

RESULTS AND DISCUSSION

Results obtained with asbestos standards have shown that in our experimental conditions 0.3 mg is the minimum measurable amount, using a PE 710 B IR spectrophotometer.

In Table I the main IR absorption peaks for chrysotile, crocidolite, amosite and corresponding vibrations are reported.[10] Quantitative evaluations were possible using the adsorbance of some characteristic bands for each type of fiber. For chrysotile the band at 2,710 nm, corresponding to the OH stretching vibration, was chosen. For crocidolite the band at 12,820 nm was taken into account.

Adsorbance was linearly correlated to the amount of each fiber in the KBr disk (Table II). This result was practically unmodified when a fixed amount of a fiber was mixed with a variable amount of the

TABLE I

Principal IR absorption peaks for asbestos minerals. (wave number cm^{-1})

	Chrysotile	Crocidolite	Amosite
O-H stretching vibration	3686 3640	3636 3619	3653 3637 3618
Si-O stretching vibration	1078 1020 960	1143 1110 989 897	1128 1082 996 981
Silica chain and ring vibration		778 725 694 668 636	775 703 638
Cation-oxygen stretching vibration	615	541 504	528 498 481 426

TABLE II

Equations of calibration graphs of pure and mixed asbestos fibers.

		Correlation coefficient
Chrysotile[a]	$= \frac{\text{Ads}^b + 0.0136}{0.491}$	0.960
Crocidolite[a]	$= \frac{\text{Ads}^b + 0.0097}{0.192}$	0.997
Chrysotile[a] and crocidolite[c]	$= \frac{\text{Ads}^b - 0.0006}{0.505}$	0.969
Crocidolite[a] and chrysotile[d]	$= \frac{\text{Ads}^b - 0.0051}{0.196}$	0.995

[a]Concentration was expressed as mg of fiber in 300 mg of KBr disk.
[b]Adsorbance was measured at 2710 nm for chrysotile and at 12820 nm for crocidolite.
[c]Variable amounts of chrysotile with 0.8 mg of crocidolite.
[d]Variable amounts of crocidolite with 1 mg of chrysotile.

other. Results were sufficiently reproducible. The standard deviation of absorbance values from the disks with the lowest amount of fiber was 11% of the mean value.

Possible interferences during IR analysis of chrysotile

Caoline and antigorite (non fibrous serpentines), absorbing at 3,770 and 3,650 cm^{-1}, can interfere with chrysotile.

In this case useful indications are given by the spectra between 400 and 300 cm^{-1} where chrysotile presents a characteristic band at 300 cm^{-1}. The presence of an absorption peak at 1,040 cm^{-1} may confirm the absence of antagorite in the sample.[14]

Possible interference with crocidolite

Some difficulties may arise in interpreting IR spectra when two amphiboles are contemporary present in the sample (for example crocidolite and amosite). Their spectra between 4,000 and 600 cm^{-1} are quite similar. Examination of the spectra between 600 and 300 cm^{-1} may give useful information to overcome this problem. In

fact crocidolite presents typical band at 315 cm^{-1} that is not present in amosite.

To avoid this problem some authors have suggested to submit mixtures to different physical and chemical treatments.[9,11]

For example, thermal treatment affects stretching of vibration of OH groups in chrysotile fibers which disappeares when temperatures are higher than 650°C.

Chrysotile is also very sensitive to acid treatment; on the contrary amosite and crocidolite are less affected.

Therefore when doubts exist about the real composition of the sample, thermal pretreatment or acid leaching may give useful supplementary information.

Fiber identification in insulating material and asbestos cement manufactures

The described analytical method was applied to identify insulating inorganic materials of unknown composition. The IR spectra obtained from a sample of insulating rope used during aluminium casting, and insulating materials sprayed on frames of a public building are shown in Figure 2 and Figure 3. The spectra of the first

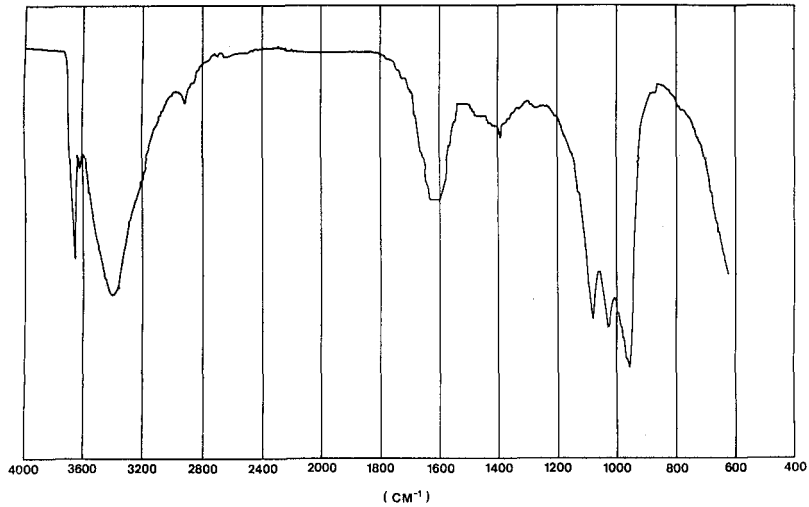

FIGURE 2 IR spectra (PE 710B) of insulating rope. The sample was identified as chrysotile.

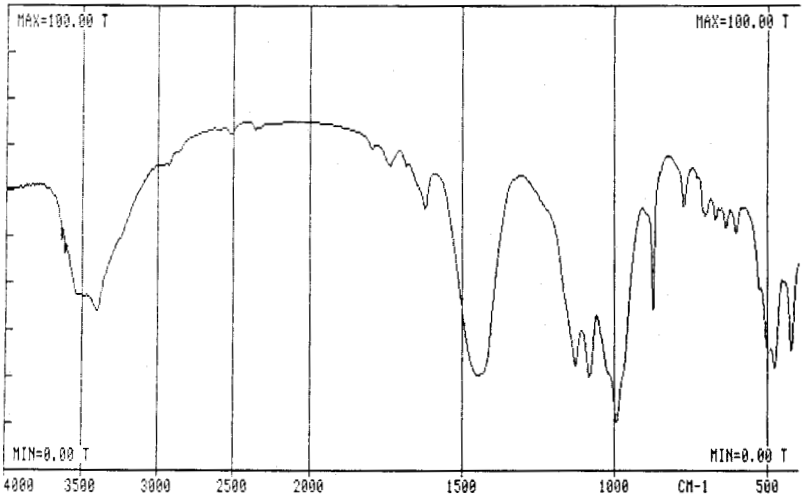

FIGURE 3 IR spectra (PE 1700 FTIR) of insulating material. Fiber identified as amosite.

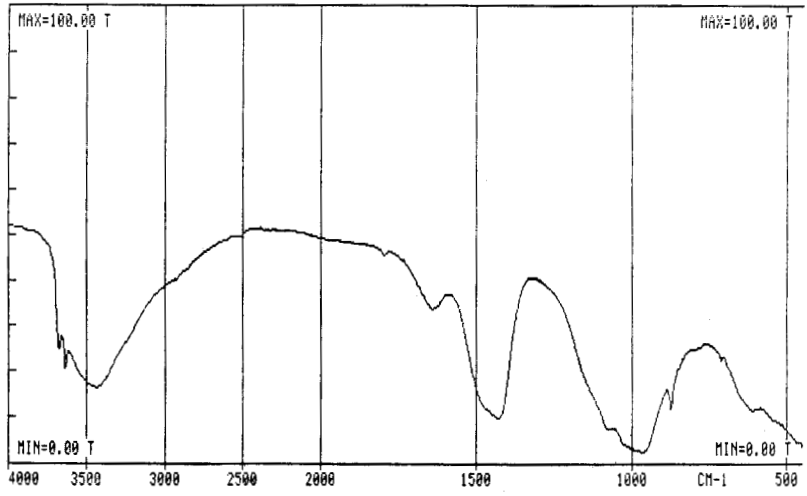

FIGURE 4 IR spectra of a sample from an asbestos-cement tile.

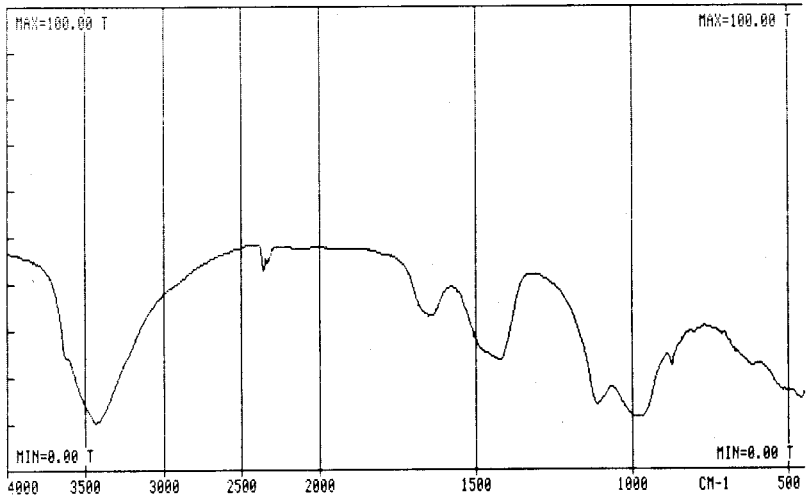

FIGURE 5 IR spectra of cement used to prepare asbestos cement tiles.

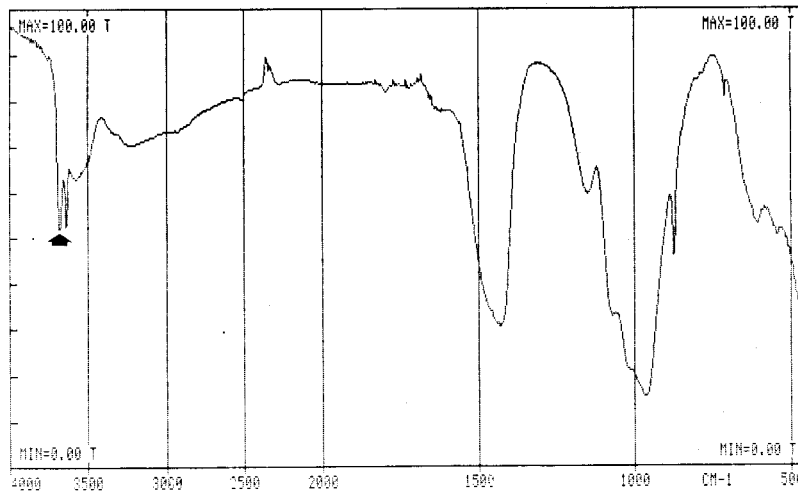

FIGURE 6 Spectra resulting as difference between samples showed in Figures 4 and 5. The program PE 983 for IR analyses was used, with a PE 3600 data station. Characteristic bands of chrysotile were evidentiated.

sample matched very well with that of chrysotile and the absence of interferences permitted to evaluate the percentage of asbestos fiber in the sample (25%).

In the second sample, a preliminary examination by constrast phase light microscopy, excluded the presence of crocidolite and the IR spectra showed a good correlation with that of amosite.

In more complex situations, as it occurs analysing asbestos cement manufactures, the use of a computer assisted program allowed to subtract spectra of pure cement (Figure 4) from the spectra of a sample of asbestos-cement tile (Figure 5). The obtained spectra (Figure 6) showed a pattern very similar to that of chrysotile.

Acknowledgements

The authors are grateful to ETERNIT who provided asbestos cement products, and to Italian Perkin Elmer, for their useful collaboration.

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