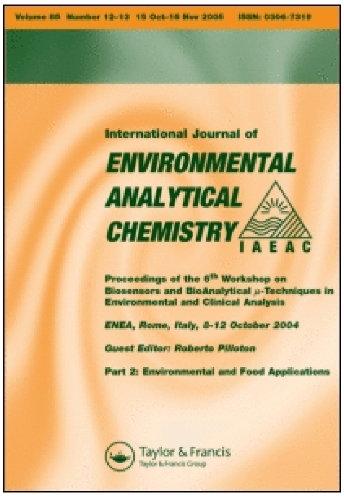

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# Quantitative X-RAy Diffraction Analysis of Four Types of Amphibolic Asbestos by the Silver Membrane Filter Method

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# QUANTITATIVE X-RAY DIFFRACTION ANALYSIS OF FOUR TYPES OF AMPHIBOLIC ASBESTOS BY THE SILVER MEMBRANE FILTER METHOD

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In this paper, the method that utilizes the X-ray diffraction technique combined with a procedure for X-ray absorption correction, already applied to chrysotile, was extended to the quantitative determination of microgram quantities of four types of amphibolic asbestos. These are: crocidolite, amosite, tremolite and anthophyllite. The effectiveness of the absorption correction procedure, based on the use of a silver membrane filter, was tested for crocidolite by preparing standards of this substance in three different matrices and comparing their diffractometric responses with those of pure analyte standards. These experimental data were also used to calculate the mass absorption coefficients of the matrices, which were compared with both the theoretical values and the values obtained in previous experiments where chrysotile was used as the analyte. The limits of detection of the four pure amphiboles, and crocidolite in matrix were established, and a detailed study of the most common interferences that disturb the analytical peaks of the four amphiboles, was performed.

KEY WORDS: Amphibolic asbestos, X-ray diffraction, X-ray absorption corrections, aqueous suspensions, sample handling.

## INTRODUCTION

The most recent national and international regulations require the quantitative determination of the various forms of asbestos both in bulk materials[1–4] and the emissions of asbestos-processing plants.[5]

This requirement has necessitated the development of less complex and costly analytical methods than those based on optical or analytical electron microscopy.

Presently, X-ray diffraction (XRD), traditionally applied to the analysis of crystalline substances, appears as one of the most adequate techniques for the fulfilment of this task.

Clearly, XRD is not capable of providing direct data about the numerical content of asbestos fibres, which is the parameter considered essential for the evaluation of the health hazards linked to the exposure to this substance. Nevertheless, the numerous applications of this technique carried out in the last decades according to different procedures have demonstrated its usefulness for the differentiated gravimetric determination of the various forms of asbestos.[6–25]

Moreover, it is possible to compare XRD gravimetric data with data obtained by means of numerical methods as those based on phase contrast optical microscopy, and thus calculate a count-to-mass conversion factor for asbestos fibres. A conversion factor can be very useful when routine controls are required as in the case of gaseous emissions from industrial plants.[26]

In a previous work,[25] dedicated to chrysotile, the XRD method developed by Lange and Haartz[19] that makes use of a crystalline silver membrane filter and allows the correction for X-ray absorption by the sample (Williams[27] and Leroux[28] correction procedure), was revised and improved in some aspects. The applicability conditions of the method to two different analytical cases, i.e., bulk samples and airborne powder samples collected on normal cellulose filters were also discussed in detail.

In the present work, the revised method was extended to the quantitative determination of four types of amphibole asbestos, i.e., crocidolite, amosite, tremolite and anthophyllite.

Although no longer employed in industrial processes, crocidolite is still present in many old products currently in use (asbestos-cement pipes, thermal insulation systems of various kinds, etc.). Amosite is still utilized in the production of asbestos-cement tubes whereas tremolite and anthophyllite, even if of no commercial interest, are present as contaminants either of chrysotile[29] and commonly used powders[30-33] or in the atmosphere in regions whose geological composition contains them.[34]

This work is organized as follows:

a) Calibration curves were constructed in the 10–100 microgram ($\mu$g) range for the four forms of amphibole asbestos.

b) The applicability of the Williams and Leroux correction procedure for X-ray absorption was studied in 500 $\mu$g samples containing crocidolite in the 10–100 $\mu$g range, dispersed in three different matrices.

c) The mass absorption coefficients of the matrices were calculated from the experimental data and compared with both the theoretical values and the values obtained from previous experiments where chrysotile was used as the analyte.

d) The lower limits of detection (LLD) for the four pure amphiboles, and crocidolite in different matrices were calculated.

e) The interferences—both reciprocal and due to other mineral phases—that disturb the analytical peaks of the four amphiboles were studied in detail.

## EXPERIMENTAL

### *a) Apparatus*

A conventional Philips DY 998 powder diffractometer was used with a scintillation counter and a pulse-height selector. The analytical conditions and the measurement parameters appear in Table 1.

As is usually done, integrated intensities were measured by counting the quanta diffracted by scanning over a peak and subtracting the background count. This latter value was obtained by counting for half the total scanning time on either

**Table 1** Analytical conditions and measurement parameters

*Analytical conditions*

Voltage: 40 KV
Current: 45 mA
Target: Copper
Divergence slit: 1°; Receiving slit: 0.2 mm; Scatter slit: 1°
$2\theta$ compensating divergence slit
Scan speed: 1/4°/min
Spinning rate of the sample holder: 100 rotations/min
Integration time: 400 sec.

*Measurement parameters*

| *Component* | *Analytical peak*[a] *($2\theta$)* | *Scan range ($2\theta$)* |
|---|---|---|
| Crocidolite | 10.49 | 9.65–11.32 |
| Amosite | 10.28 | 9.44–11.11 |
| Tremolite | 10.83 | 10.00–11.67 |
| Anthophyllite | 9.50 | 8.66–10.33 |
| Silver | 38.05 | 37.22–38.89 |

[a] Cu $K_\alpha$ radiation (1.54178 Å).

side of the peak and adding the two counts. The results, divided by the total scanning time, were expressed as counting rates (cps).

### *b) Reagents*

The surface-active agent Aerosol OT used for dispersing powder samples was purchased from Fisher and the silver membrane filters (pore size: 0.45 micron ($\mu$m)) from Millipore. The water used in all the experiments was previously filtered through Millipore cellulose filters (pore size: 0.22 $\mu$m). Crocidolite, amosite and anthophyllite were UICC Standard Reference Asbestos Samples with the following fibre lengths: crocidolite: $<5\,\mu$m (97.0%); amosite: $<5\,\mu$m (94.2%); anthophyllite $<5\,\mu$m (95.2%).[35] The tremolite used was a certified standard from the US Bureau of Mines, with fibre length $<5\,\mu$m (78.0%) and $<10\,\mu$m (92.0%).[36] This tremolite is the kind normally found as a contaminant of chrysotile and industrial talcs. The following certified standards were used for the preparation of the artificial matrices: Talc (TA99 NIOSH) with a mass median aerodynamic diameter of 5.5 $\mu$m;[37] Quartz (DQ12 $<5\,\mu$m, Fed. Rep. of Germany) with a geometric diameter $<5\,\mu$m;[38] Portland cement (Bureau of Analyzed Samples Ltd., UK) screened through a 124 $\mu$m (120 mesh) sieve.[39]

### *c) Preparation of Suspensions and Deposition of Thin Layers of Samples on Silver Filters*

In the case of suspensions containing only one form of asbestos, 20 mg of this substance, 200 mg of NaCl and 4 mL of a 50 mg/mL solution of Aerosol OT were

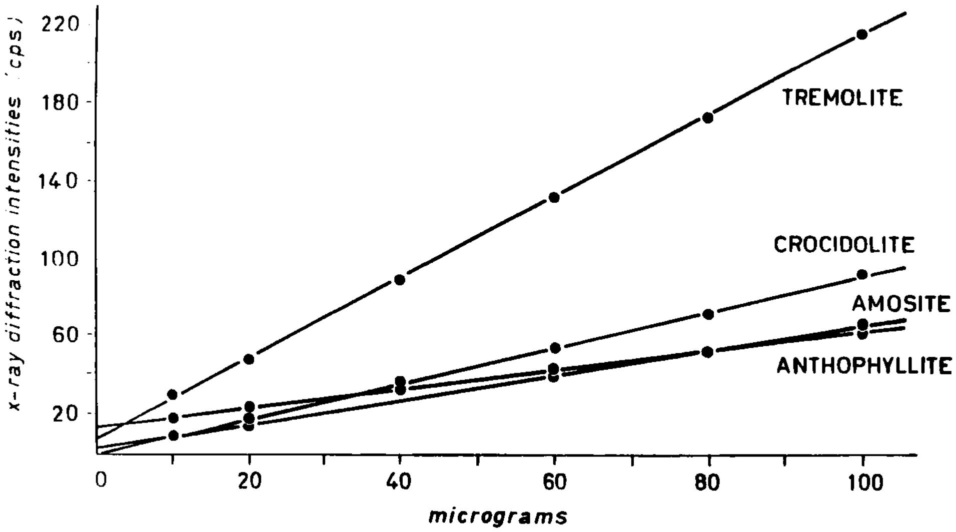

**Figure 1** Calibration curves for the four types of amphibole asbestos.

placed into a 200 mL volumetric flask with filtered water. After homogenization by magnetic stirring (400 rotations/min.) for three hours, aliquots ranging from 0.1 to 1.0 mL were withdrawn from the suspension and deposited on the filters.

In the case of suspensions containing both crocidolite and matrix, the following procedure was performed. First, two separate 500 μg/mL suspensions of each component were prepared, quadruplicating the concentrations of the dispersing agents with respect to the previous case. Then, the two separate suspensions were magnetically stirred for three hours. Later, aliquots ranging from 0.5 to 5.0 mL were transferred from the crocidolite suspension into 25 mL volumetric flasks, diluted to the final volume by means of the matrix suspension and magnetically stirred for two hours. At this point, 1 mL aliquots of the combined suspensions were deposited on silver filters. Standards of a constant weight of 500 μg, containing crocidolite in the 10–100 μg range, were prepared in this way.

Thin layers of samples were deposited on silver filters by means of a filtration apparatus containing a 2 cm diameter and a 1.5 cm height reservoir, with an effective deposition area of 1.02 $cm^2$.[25]

## RESULTS

### *a) Calibration Curves for the Four Amphiboles*

Standards ranging from 10 to 100 μg were prepared in quadruple for each form of amphibolic asbestos, their diffractometric responses measured, and intensity vs. mass calibrations curves constructed (Figure 1). No correction of the measured values was made, as the absorption effects were negligible within the considered mass interval.

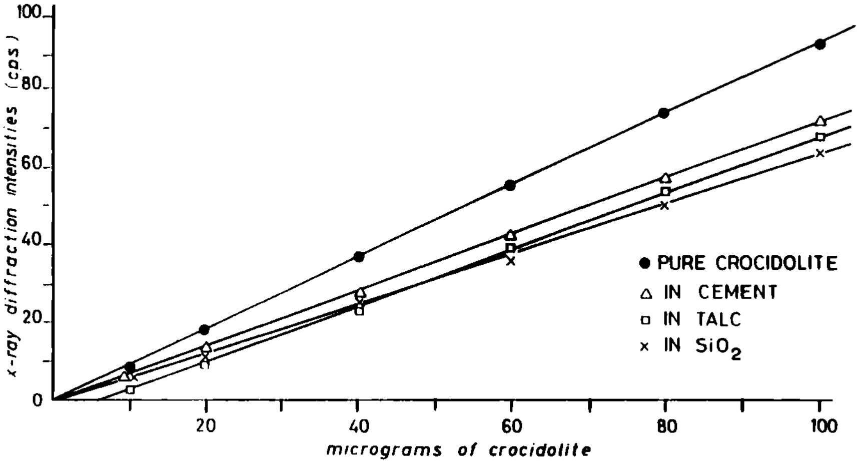

**Figure 2** Calibration curves for crocidolite in different matrices before X-ray absorption corrections.

As can be seen, tremolite is the amphibole with the highest 'sensibility' to XRD analysis: its diffractometric responses are about 3.5 times higher than those given by the same quantities of amosite and anthophyllite, and about 2.5 times higher than those given by the same quantities of crocidolite.

### *b) Evaluation of the Correction Method for X-ray Absorption*

When X-ray absorption by a sample is not negligible, it is necessary to introduce a correction in the diffractometric responses of an analyte. According to the Williams and Leroux's correction procedure, in order to obtain the true diffracted intensity, the measured intensity must be multiplied by a correction factor Γ defined as follows:

$$\Gamma = \frac{R \ln T_n}{1 - T_n^R} \tag{1}$$

where

$$R = \frac{\operatorname{sen} \theta_{Ag}}{\operatorname{sen} \theta_X}; \quad T_n = \frac{I_{Ag}}{I_{Ag}^0}$$

In their turn, $\theta_{Ag}$ and $\theta_X$ are the diffraction angles of silver and analyte, respectively; $I_{Ag}^0$ and $I_{Ag}$ are the intensities diffracted by silver before and after the sample deposition, respectively.

For the sake of simplicity, the applicability of this correction procedure was studied only in the case of crocidolite. The following matrices were used: talc, $SiO_2$, and Portland cement. Standards with a total weight of 500 μg containing crocidolite in the 10–100 μg range were prepared with these substances and their diffractometric responses measured.

Figure 2 compares the three calibration curves for crocidolite in the different

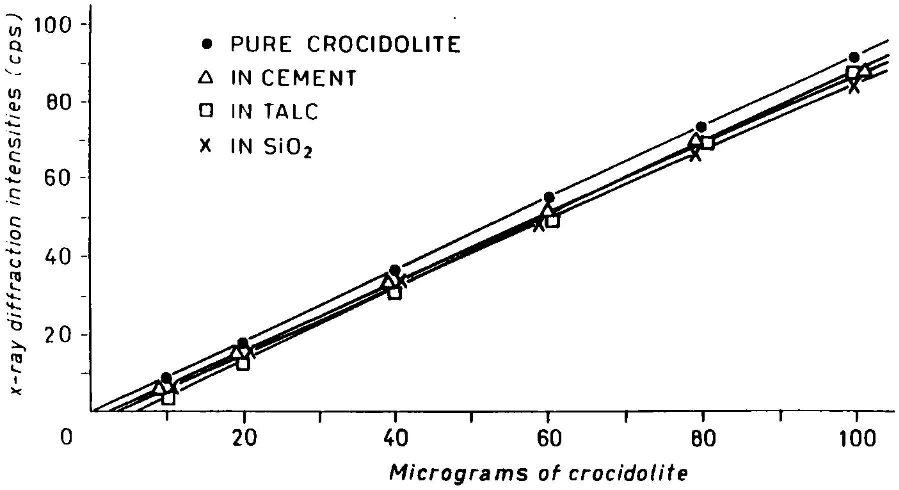

**Figure 3** Calibration curves for crocidolite in different matrices after X-ray absorption corrections.

**Table 2** Linear regression coefficients and linear correlation coefficients for the calibration curves of the four amphiboles (A) and crocidolite in the different matrices before and after absorption corrections (B).

| *Component* | *Linear regression coefficient (cps/μg)* | | *Linear correlation coefficient* | |
|---|---|---|---|---|
| (A) | | | | |
| Amosite | 0.69 | | 0.965 | |
| Tremolite | 2.08 | | 0.979 | |
| Anthophyllite | 0.47 | | 0.906 | |
| Crocidolite | 0.92 | | 0.984 | |
| | *Uncorrected* | *Corrected* | *Uncorrected* | *Corrected* |
| (B) | | | | |
| Crocidolite in: | | | | |
| Talc | 0.71 | 0.94 | 0.981 | 0.984 |
| Portland cement | 0.73 | 0.89 | 0.987 | 0.966 |
| $SiO_2$ | 0.63 | 0.88 | 0.974 | 0.964 |

matrices with the curve for pure analyte. The sample absorbing effects significantly lower the diffractometric responses of crocidolite. The decrease reaches 32% in the $SiO_2$ matrix.

Figure 3 shows the same curves after the absorption corrections. The latter remarkably reduce the differences between the responses of pure crocidolite and crocidolite-in-matrix: the highest differences are around 10% ($SiO_2$ matrix).

In Table 2 the linear regression coefficients (slopes) and the linear correlation coefficients for the curves of Figures 1, 2 and 3, are reported.

**Table 3** Mass absorption coefficients ($cm^2/g$) of the matrices

| *Matrix* | *Measured value (Crocidolite-containing samples)* | *Measured value (Chrysotile-containing samples)* | *Theoretical value* |
|---|---|---|---|
| Talc | 33.3 ± 8.7 | 34.2 ± 10.1 | 31.4 |
| Portland cement | 22.8 ± 10.9 | 28.2 ± 16.6 | - |
| $SiO_2$ | 42.4 ± 12.5 | 39.9 ± 8.2 | 34.6 |

### *c) Calculation of the Mass Absorption Coefficients of the Matrices*

The mass absorption coefficients of the three matrices were calculated by putting the experimental data, already used for the determination of the correction factors $\Gamma$, in the following equation:

$$\mu_M^* = \frac{-K \ln T_{Ag} - \mu_X^* \cdot f_X}{\rho_M} \tag{2}$$

where:

$$K = \frac{B \operatorname{sen} \theta_{Ag}}{2W_T}$$

In the formula, $\mu_M^*$ and $\mu_X^*$ indicate the mass absorption coefficients of the matrix and the analyte, respectively; $f_M$ and $f_X$ are their weight fractions; $W_T$ the weight of the sample; $\theta_{Ag}$ is the silver diffraction angle; $T_{Ag}$ is the sample transmittance at the silver diffraction angle; finally, $B$ is the deposition area of the sample.[25,40]

The values obtained were compared with the theoretical values and also with those calculated in a previous work where chrysotile was used as the analyte[25] (Table 3).

As can be seen, the agreement among the three sets of data appears acceptable, and therefore the total method—preparation of thin layers of sample on silver filters plus diffractometric measurements—can be considered sufficiently viable.

### *d) Calculation of the Lower Limits of Detection*

The lower limit of detection (LLD) is defined as the amount of a crystalline phase required to give a measured peak whose intensity is equal to three times the standard deviation of the background intensity.[41] The following expression[42] was used for the calculation of this factor:

$$\text{L.L.D.}(\mu g) = \frac{3}{m}\sqrt{\frac{R_b}{T_b}} \tag{3}$$

In the formula, $m$ is the slope of the regression curve $R_T$ versus weight of

**Table 4** Lower limits of detection (LLD) for the various pure forms of asbestos and crocidolite in matrix

| *Component* | *LLD* ($\mu g$) |
|---|---|
| Chrysotile | 7.4 |
| Amosite | 6.3 |
| Tremolite | 2.2 |
| Anthophyllite | 8.4 |
| Crocidolite | 4.2 |
| Crocidolite in talc | 5.3 |
| Crocidolite in Portland cement | 5.0 |
| Crocidolite in $SiO_2$ | 5.0 |

analyte. In its turn, $R_T$ (cps) is the counting rate of the overall integrated peak (analyte + background); $R_b$ and $T_b$ are the counting rate (cps) and the counting time (sec.) of the background, respectively.

The LLD's were calculated for the four pure amphiboles and crocidolite in the three matrices. The mean of the measured values of the background counting was used for the value of $R_b$. In the case of crocidolite in matrix, the uncorrected values of $R_T$ were used for the calculation of the slope $m$. The results appear in Table 4, where the datum relative to chrysotile is also reported, since it will be used in a subsequent comparative discussion.

## INTERFERENCES OF THE ANALYTICAL PEAKS OF AMPHIBOLIC ASBESTOS MINERALS

Various forms of asbestos can be simultaneously present in asbestos-containing materials and consequently in the atmosphere where the powders deriving from them happen to disperse. In addition, one or more asbestos forms can be associated with different types of minerals, especially silicates. For these reasons, any method of XRD analysis must take into account the possible interferences—either reciprocal or due to other types of minerals—that can disturb the analytical peaks of the various forms of asbestos.

In theory, the mineral phases that interfere with amphiboles are very numerous, but only those associated with them in the most common commercial products have a practical relevance from an analytical point of view.

Table 5 shows the main crystallographic characteristics of asbestos minerals and their more important interferents. In Figure 4 the relative positions of the primary and secondary peaks of these substances are reported.

It is evident that the XRD technique is unable to distinguish between amphiboles and their respective non-fibrous mineral phases (riebeckite, grunerite, non-fibrous tremolite, etc.). This discrimination can be accomplished only by means of other techniques such as optical or electronic microscopy that provide information about the morphological characteristics of an analyte.

As far as reciprocal interferences among the different asbestos forms are

**Table 5** Main interplanar spacings and relative reflection intensities for the various forms of asbestos and their most common interfering minerals

| *Mineral* | *Interplanar d(Å) spacings and relative intensities*[a] | *Mineral* | *Interplanar d(Å) spacings and relative intensities* |
|---|---|---|---|
| Chrysotile (antigorite, lizardite) | 7.37 (100) | Talc | 9.35 (100) |
| | 7.10 (100) | | 4.59 (45) |
| | 4.57 (50) | | 3.12 (40) |
| | 3.65 (70) | | 2.48 (30) |
| | 3.66 (80) | | |
| | 3.55 (50) | Kaolinite | 7.16 (100) |
| | 2.45 (65) | | 3.57 (80) |
| | 2.33 (80) | | |
| | | Alite (cement) | 3.02 (80) |
| | | | 2.96 (60) |
| Amosite (grunerite, cummingtonite) | 8.33 (100) | | 2.76 (100) |
| | 8.22 (100) | | 2.74 (90) |
| | 3.25 (70) | | 2.68 (90) |
| | 3.06 (80) | | 2.59 (90) |
| | 2.76 (70) | | 2.18 (90) |
| Crocidolite (riebeckite) | 8.35 (100) | Gypsum | 7.56 (100) |
| | 3.10 (55) | | 4.27 (50) |
| | 2.72 (35) | | 3.06 (55) |
| Tremolite (non-fibrous tremolite) | 8.43 (40) | Calcite | 3.04 (100) |
| | 8.38 (100) | | |
| | 3.14 (95) | Cellulose | 3.66 (100) |
| | 3.13 (100) | | |
| | 3.12 (100) | Chlorite | 4.1 (60) |
| | 2.71 (90) | | 7.1 (100) |
| | | | 4.7 (40) |
| Anthophyllite | 9.35 (55) | | 3.53 (80) |
| | 3.24 (60) | | 2.7 (40) |
| | 3.05 (100) | | 2.4 (60) |
| | 2.54 (40) | | |

[a] Referred to *Cu* $K_\alpha$ radiation (1.54178 Å). Data taken from reference minerals and ASTM (JCPDS) file.

concerned it can be said that such forms are very rarely found all together in commercial products.

A mixture of either chrysotile and amosite or chrysotile and crocidolite can be found in some types of asbestos-cement products such as old pipe-lines, water reservoirs, high pressure tubes, etc.

Tremolite and anthophyllite mixed together can be important contaminants of raw commercial chrysotile and of industrial or commercial talcs, where calcite and chlorites can also be present.[30,32]

Amosite and crocidolite have been used together and in mixture with various minerals such as calcium silicates of the alite type, gypsum, carbonates (calcite) or kaolinite, in many thermo-insulating and phono-absorbing products.

The XRD analytical discrimination between chrysotile and amphiboles is not difficult. On the contrary, to analyze a mixture of crocidolite and amosite can be a

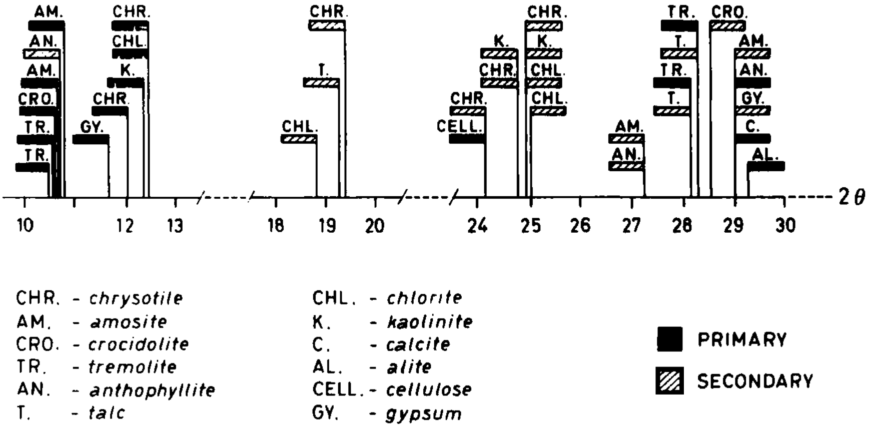

**Figure 4** Relative positions of the primary and secondary peaks of the different forms of asbestos and their most important interferents.

very problematic task that may be achieved using the step-scanning mode on the secondary peaks (placed between 27 and 29 2θ) of the two substances.

Tremolite and anthophyllite in mixture can be even more difficult to analyze since they are generally present in very small quantities in commercial products such as talcs.[30–32]

Some minerals that are more commonly found in association with amphiboles in insulating materials can be eliminated by means of an adequate chemical treatment. For instance, a weak acid such as 1 N acetic acid can decompose all carbonates and most of the calcium sulphate.

The quantitative determination of tremolite and anthophyllite in the presence of talc can be carried out on the 8.3 Å (10,27 2θ) peak which is practically the same for the two amphiboles.

Finally, it is important to observe that the interference problems are further aggravated by the intrinsic variability of the positions of the silicate diffraction peaks. Such variability makes it difficult to unequivocally identify an analyzed mineral by comparing its peaks with those of standard minerals. Moreover, the latter are not easily found and their characteristic reflections are not very accurate.

These drawbacks are especially relevant in the case of amphiboles, since they often show a wide range of chemical compositions, due to isomorphic substitutions, that generate alterations of the crystalline reticle and therefore of the diffractometric response.

## CONCLUSIONS

In synthesis, this work demonstrates that the XRD method, that makes use of a crystalline silver membrane filter, can be applied to the quantitative determination of the four forms of amphibolic asbestos with satisfactory results.

Regarding the lower limits of detection, the results show that these are different for each amphibole but never go beyond a few percent units when 500 $\mu$g samples are used as in our case. In particular, the LLD value of crocidolite was around 5 $\mu$g for the three matrices studied. We can easily suppose that the same is valid at least for tremolite, which is the asbestos form most sensible to diffractometric analysis.

Without repeating a long and tedious work for amosite and anthophyllite, we infer that they can be detected in a 500 $\mu$g sample when present in a percentage around 2–2.5%. This supposition is based on the ratio between their LLD and that of pure crocidolite.

If a lower LLD value, for instance a 1% value, is required for these substances, longer times for the integration of the peaks can be used. For example, the LLD for pure chrysotile, that was 7.4 $\mu$g for a 400 sec. integration time, dropped to 2.2 $\mu$g for a 1000 sec. integration time.[25]

Interferences, both reciprocal among the various amphiboles and due to other minerals, can seriously limit the applicability of the method. In some cases, this problem can be reduced or overcome by means of preliminary sample treatments—including the use of polarized light microscopy that allows the characterization of mineral fibrous particles[39,43]—or an adequate selection of the analytical peaks.

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