Solid analysis

Analysis of mineral fibres (i.e. asbestos) in water, soil and waste material using FTIR spectroscopy

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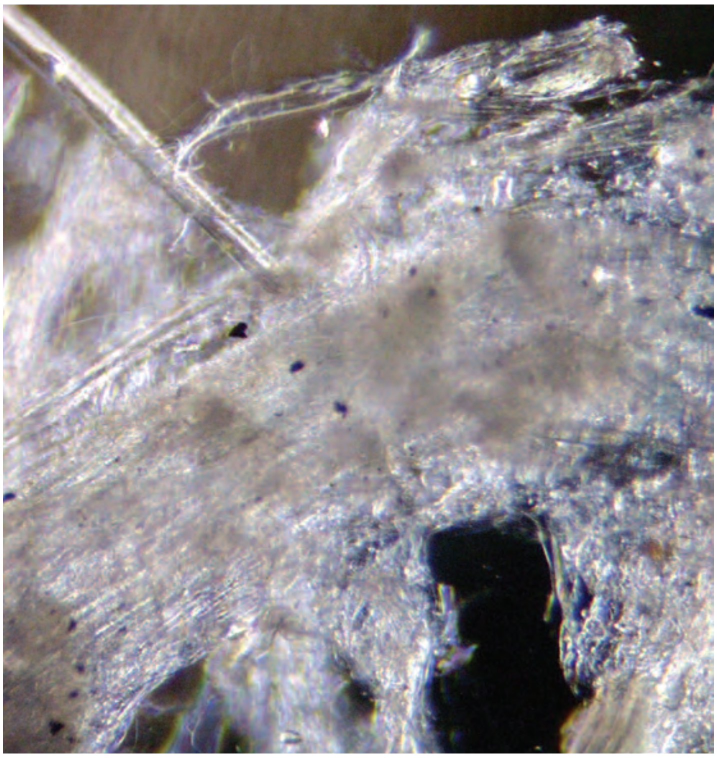

Figure 1: 100 x zoomed optical microscope image of Chrysotile

Figure 2a: Untreated sample

Figure 2b: Sample after solvent purification

Asbestos is a highly heat-resistant and non-flammable natural fibre. It has been used as a construction material and for many specific applications. However, since the 1970s, it has been proven to be a human carcinogen known to cause lung cancer. As a result, the use of asbestos was restricted before being banned in Austria (1990) and Germany (1993). Since 2005 the use of asbestos has been banned in the EU.

Asbestos occurs in natural rocks as well as technical materials such as raw materials used in the manufacture of cement. Fine fibre based asbestos particles can be found in the form of dusts and aerosols. Asbestos may also be found in natural water (spring water flowing through asbestos rocks) or in drinking water collected in asbestos cement ducts.

Former uses of asbestos were:
- building materials (in cement and concrete production)
- profile sheeting (Eternit)
- linoleum tile flooring
- heating pipe insulation coatings
- oven door rope seals and protective clothing for fire-fighters
- filtration purposes
- automotive brakes.

Controls must be established when natural asbestos is present. Part of this application is a procedure describing a successful sample treatment in combination with FTIR analysis.

Asbestos minerals and their chemical formulas

A wide range of naturally occurring asbestos minerals have been used for many technical and commercial applications. Asbestos fibres derive essentially from two groups of silicates which can generate a fibrous crystalline form: serpentine and amphiboles groups (Table 1).

Figure 1 shows the asbestos fibre of Chrysotile in 100 x zoomed optical microscopy image. The silicate microscopic needle structure indicates that pretreatment should be carried out with great care.

Analysis techniques

Various asbestos analysis techniques are available, such as microscopic methods, with optical or electronic techniques including PCM (Phase Contrast Microscopy), PLM (polarized light microscopy) and TEM (transmission electron microscopy). Another common technique is the X-ray diffractometry method (XRD) which is able to detect elements other than crystalline structures.

Another known method is IR spectrometry represented by FTIR, Fourier Transformed Infra Red spectroscopy. This technique detects and identifies asbestos fibres independently of subjective evaluations such as the visual method.

In comparison with the microscope sample preparation technique, a procedure is shown which isolates the fibres and results in a precise identification.

The suggested procedure for FTIR is:

1. dissolve organic solvent (acetone suitable for mixed esters membranes) in a glass test tube;
2. add KBr in the test tube, stir and centrifuge it and remove the supernatant
3. repeat item 2 to eliminate the dissolved polymer
4. dry and grind the solid residue and prepare a 13 mm KBr pellet.

Figure 2c: Sample after acid attack

Sample preparation

When approaching samples analysis, it is necessary to consider the following:

Elimination of organic interference via:

1. solvent dissolution;
2. chemical degradation (humid-nitric acid or sulphuric/nitric acid mixture or dry treatment), having a clear possibility of interaction of the degrading agent or temperature with the silicates.

Elimination of inorganic interference via:

1. acid dissolution (from acetic to hydrochloric acid);
2. specific weight separation (by means of heavy-liquid).

This last point relates to samples containing components insoluble in acids: grinding, sifting, suspending the mixture and separating insoluble components by means of centrifuging with heavy-liquid. The separation will occur based on difference of the specific weight among phases (suggested: bromoform $CHBr_3$-D≈2,85-, diiodmethane CH_2I_2-D≈3,31-; it is possible to obtain different densities while diluting the heavy-liquid with 1,1,2-trichloroethene C_2HCl_3 or 1,1,2,2-tetrachlorethene C_2Cl_4.

Once the fibres have been separated, ground in an agate capsule with a vibrating mill and mixed with 200 mg of IR grade KBr (around 1 % of pellet weight), a KBr pellet is formed.

Groups	Name	Formula
Serpentine	Chrysotile (white asbestos)	$Mg_3Si_2O_5(OH)_4$
Amphiboles	Amosyte (brown asbestos)	$(Fe,Mg)_7Si_8O_{22}(OH)_2$
	Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$
	Anthophyllite	$Mg_7Si_8O_{22}(OH)_2$
	Aktinolite	$Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$
	Crokydolite (blue asbestos)	$Na_2(Fe_{++3}Fe_{+++2})Si_8O_{22}(OH)_2$

Table 1: Asbestos materials

Analytical conditions

The Shimadzu IRPrestige-21 spectrophotometer and KBr-Pellet holder are required for the analysis in transmission mode. Identification is carried out using the decision table (Figure 3) or a reference spectrum as in Figures 4A to 4D on Page 16. The reference spectrum is from Chrysotile and prepared from certified reference material. Infrared spectra are presented in absorbance scale.

Interpreting asbestos IR spectra

A sample, an Eternit based profile sheeting was analysed using FTIR measurement technique. The measured infrared spectra show the separation steps between original material, solvent and acid treatment and the isolation of the fibres. Chrysotile was positively identified in parts of this sample. The influence of the treatment method used is significant. When stronger purification techniques are used, the presence of asbestos in the sample may no longer be apparent as it was found when using dry ashing.

Separation with heavy-liquid shows the benefit of the treatment: see result of the top right spectra in comparison with the SRM Chrysotile (lower right). Chrysotile fibre has been isolated and identified. The related peaks at 3690, 1080, 605 and 440 cm^{-1} are detected.

Future developments

Whereas inhalation of asbestos fibres is considered to be extremely dangerous for the respiratory system, medical science is currently studying the danger of ingestion of fibres in the digestive tract.

We will gladly send you further information. Please note the appropriate number on your reply card. **Info 324**

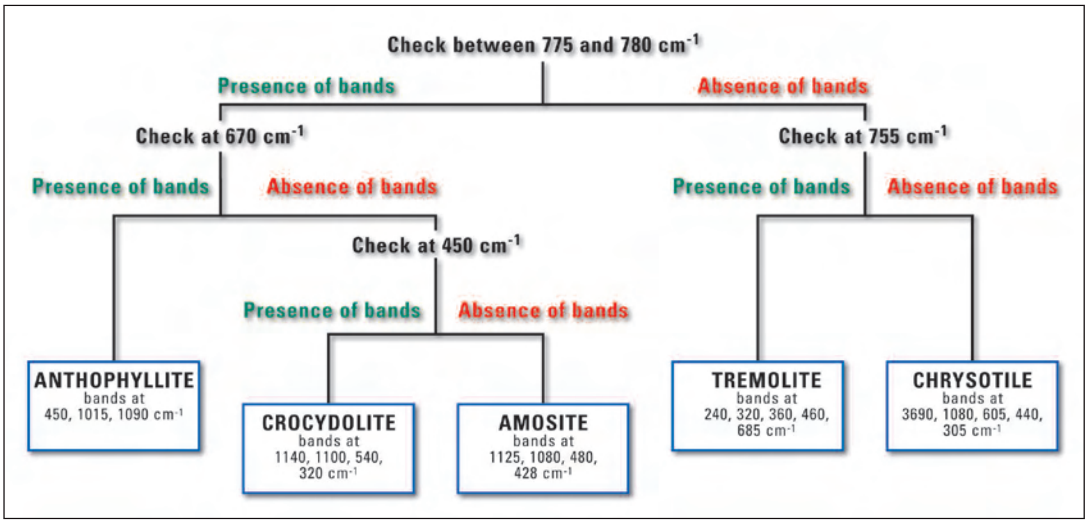

Figure 3: Typical band patterns confirm the asbestos type (Canadian Norm, NEN-Norm)

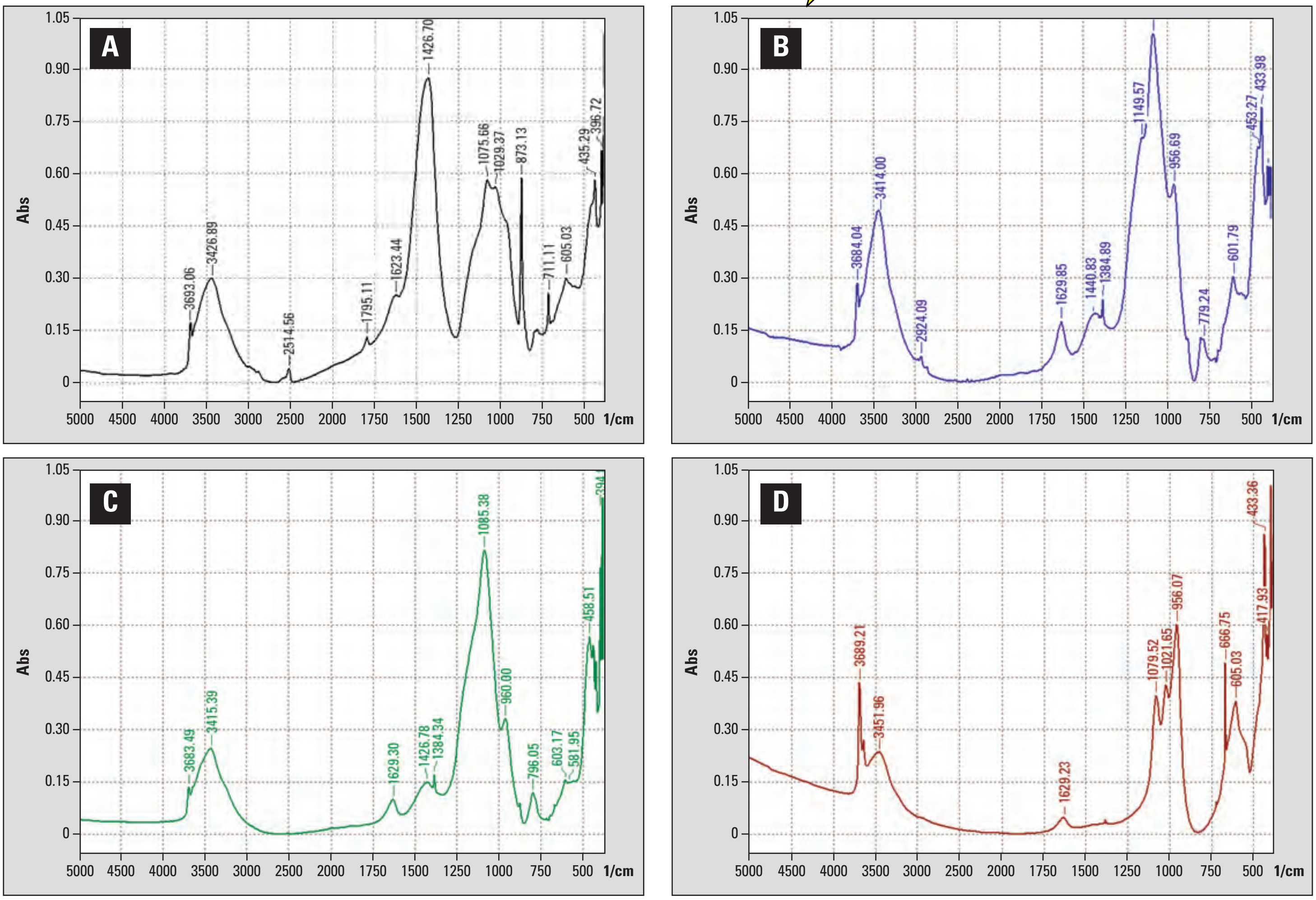

Figure 4A: Untreated Eternit sample

4B: Organic acid purification and separation with heavy-liquid

4C: Mineral acid purification (sulphuric-nitric acid mixture)

4D: Standard reference material Chrysotile SRM1866a

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New developments in column technology and HPLC hardware have stimulated new demands. The same applies to environmental aspects and adaptations of possible MS detection in order to attain improved detection sensitivities. With the famous-

Figure 1: Solvent selection or quaternary gradient switching valve integrated in the pump