

# Solid analysis

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

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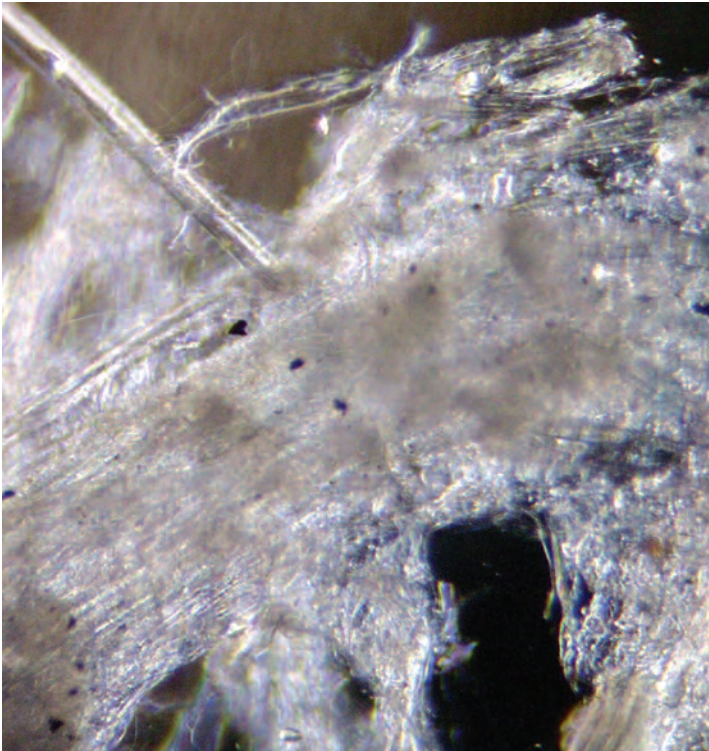


Figure 1: 100 x zoomed optical microscope image of Chrysotile

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



Figure 2a: Untreated sample



Figure 2b: Sample after solvent purification

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

#### 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  $\text{CHBr}_3$ -D $\approx$ 2,85-, diiodmethane  $\text{CH}_2\text{I}_2$ -D $\approx$ 3,31-; it is possible to obtain different densities while diluting the heavy-liquid with 1,1,2-trichloroethene  $\text{C}_2\text{HCl}_3$  or 1,1,2,2-tetrachloroethene  $\text{C}_2\text{Cl}_4$ .

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)	$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$
Amphiboles	Amosite (brown asbestos)	$(\text{Fe},\text{Mg})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$
	Tremolite	$\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$
	Anthophyllite	$\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$
	Aktinolite	$\text{Ca}_2(\text{Mg},\text{Fe})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$
	Crokydolite (blue asbestos)	$\text{Na}_2(\text{Fe}^{+3},\text{Fe}^{+2})\text{Si}_8\text{O}_{22}(\text{OH})_2$

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  $\text{cm}^{-1}$  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.  $\blacktriangleright$

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Figure 2c: Sample after acid attack

- 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.

#### Sample preparation

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

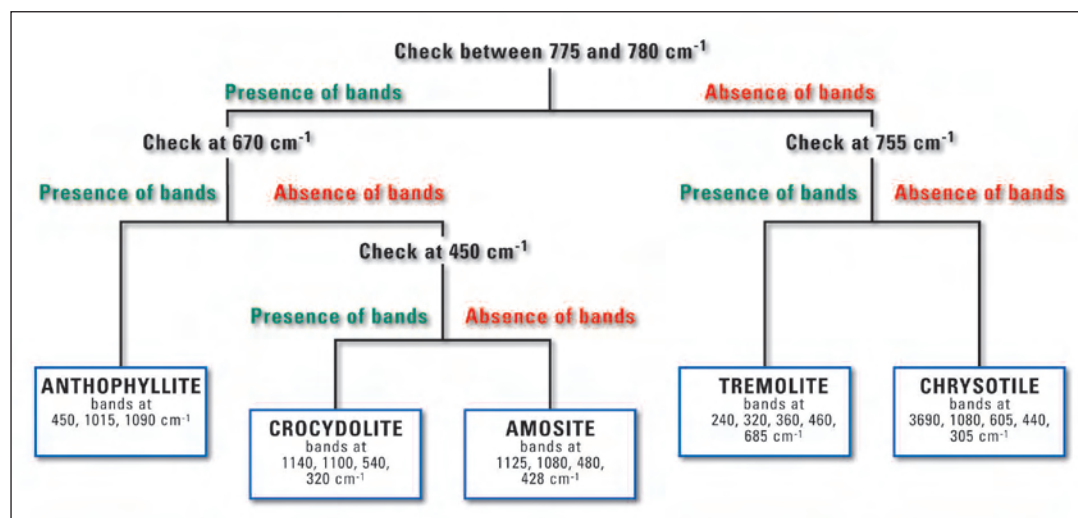


Figure 3: Typical band patterns confirm the asbestos type (Canadian Norm, NEN-Norm)

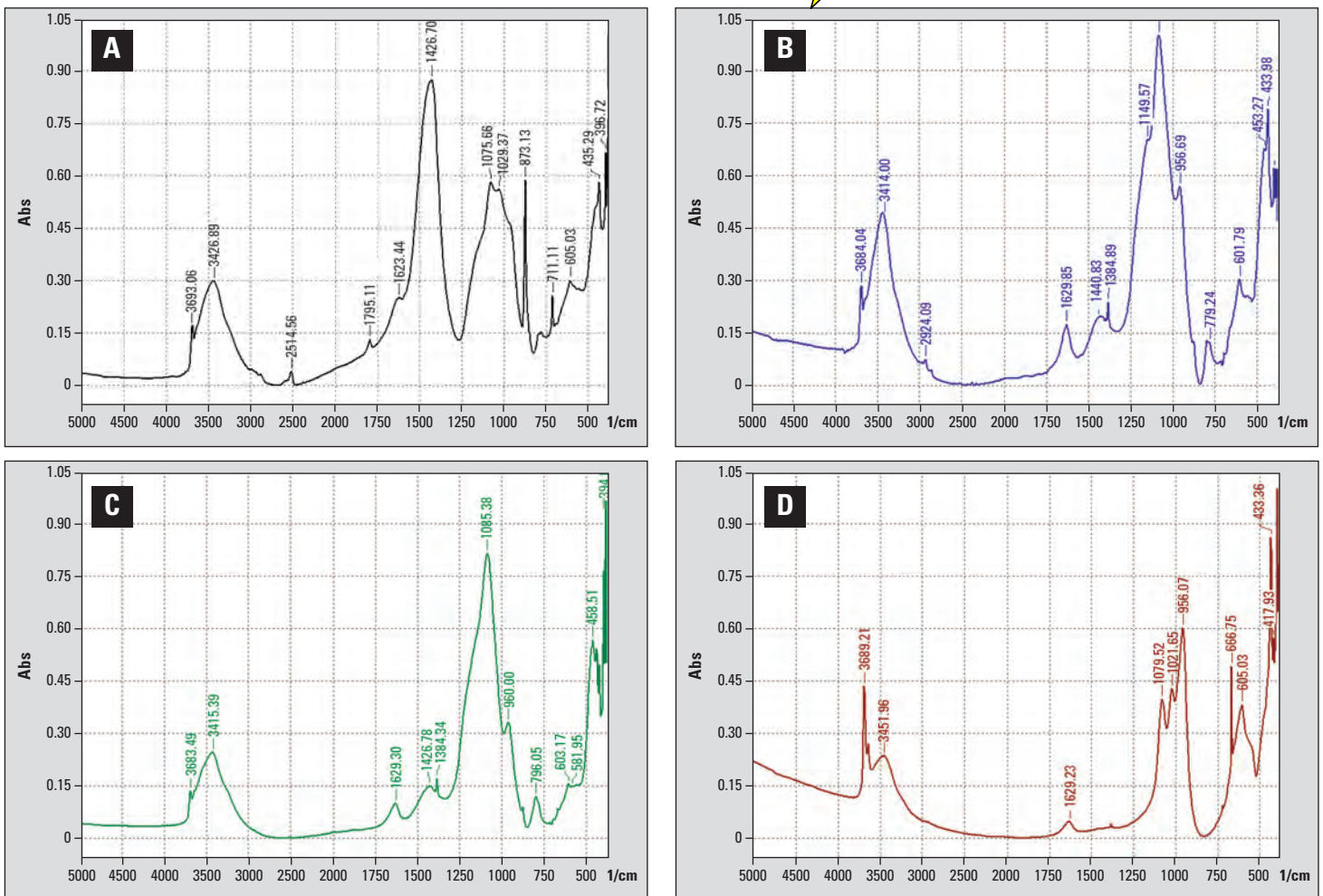


Figure 4A: Untreated Eternit sample

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

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

4D: Standard reference material Chrysotile SRM1866a

## PRODUCTS

# “Everything flows” – literally

## Method development and optimization using the *prominence* HPLC

The times when nothing changed in HPLC as an established method are over. After a relatively long phase without large change, methods are now being challenged; existing HPLC methods are being optimized while others are being redeveloped from scratch. In addition, faster and simpler separations are being considered. Or, depending on the particular application area, even more complex solutions are called for.

All of this within laboratory environments which for many years have been working with standard validated methods allowing no alteration.

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-

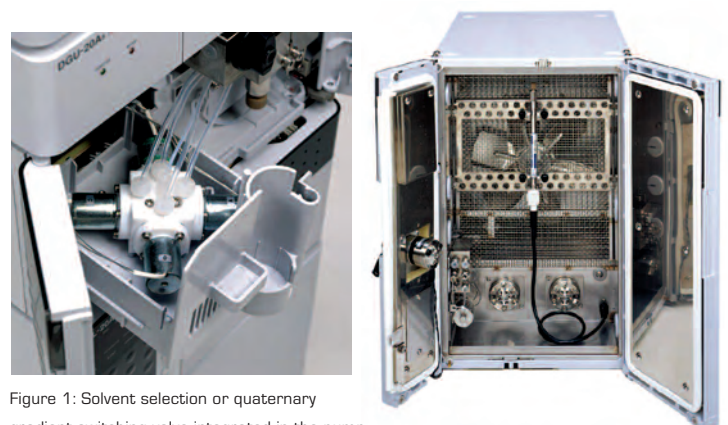


Figure 1: Solvent selection or quaternary gradient switching valve integrated in the pump