Plastics Identification & Asbestos Analysis By FTIR
Rapid Development in the Electrical and Electronics Industries
- Waste generated increased significantly
- New materials or chemicals from such waste may be harmful to humans
- In 2003 EU published two directives to control the disposal of waste and restrict their use from electrical and electronic equipment
  - Waste Electronics and Electrical Equipment - WEES
  - Restriction of the use of certain Hazardous Substance in electrical and electronic equipment - ROHS 2002/95/EEC
- Testing requirements for many materials and chemicals
Infrared and infrared microscopy an excellent tool for materials identification and contamination checking.

FTIR technique uses unique fingerprint of materials for identification and is sensitive and well documented.

Requirements to identify type of plastics in plastic material, ink, coating, paper, fabric, leather, PCB products using infrared technique.

Similarly for confirming the contamination of asbestos in plastics, ink, coating, paper, fabric, leather, PCB products using infrared and infrared microscopy.
Testing limits

- Identification of Plastic
- Permissible Limit: N/A
- Source of Legislated Limit: N/A
- Possible Method: FTIR
- Test item: Polyvinyl Chloride (PVC)

- Chemicals/Compounds: Asbestos
- Permissible Limit: Not detectable
- Source of Legislated Limit: 91/659/EEC
- Possible method: Microscope/FTIR/XRD
- Criteria/Scope: Chrysotile, crocidolite, amosite, actiolite, anthophyllite, tremolite
- Requirements: All products in this E&E category. Exemption for chrysotile (under 91/659/EEC), which is a totally banned in a limited number of products, but still allowed in a component if the products is labelled according to Annex 2 of 76/769/EEC. According to 99/77/EC a total ban, to include chrysotile will be in force by 1-1-2005.


......for Dangerous Substances
Mid-Infrared

- Spectra are well understood - high confidence
- Well supported in the literature
- Good legislative acceptance
- Reliable finger print - good diagnostic tool
- Very versatile technique
- Skilled sample preparation
Infrared Signatures of PVC and additives

PVC RESIN

Semi rigid PVC

DEHP (Di-Ethylhexyl Phthalate)

DINP (Di-Isononyl Phthalate)
Why PVC?

- Polyvinyl Chloride (PVC, or Vinyl) is one of the most commonly used materials in the consumer marketplace.
- Found in packaging, construction and automotive material, all categories of products, including toys, and medical equipment.
- PVC contains phthalates, which accumulate in body tissues, and can damage liver, lungs, and have been shown in lower mammals to damage reproductive organs.
- Phthalates show almost no toxicity in adult humans even at high doses, however the cumulative nature of phthalate toxicity results in toxic effects even at very low dosage when ingested over a long period of time.
- Very young infants may be at greater risk of harm.
- The common availability of phthalates in the consumer products causes inevitably chronic ingestion for almost all modern industrial consumers.
Phthalates

- The PVC polymer is a very rigid plastic. When a soft or flexible plastic is required, a plasticizer is added. Phthalates esters are the most commonly used in PVC.
  - DEHP (Di-Ethylhexyl Phthalate) has been the most commonly used, and is still used as a plasticizer for all PVC medical products. DEHP in children's products was replaced during the past ten years by DINP (Di-Isononyl Phthalate) due to concerns about its toxicity. Semi-rigid PVC contains about 10 percent phthalates; flexible PVC, as much as 50 percent by weight.

Phthalates migrate easily and are also given off freely by PVC. DEHP is nearly insoluble in water, but highly soluble in fats and oils. When used in medical tubing, it has been found to accumulate in blood, lung, and liver tissue, as well as in fat. In fatty foods products packaged in PVC, significant amounts of DEHP or DINP have been found in surface layers. Under relatively slight pressure, phthalates will exude from PVC. (PVC Handbook, from C. P. Hall, plasticizer manufacturer).
Simplest techniques are

- Film making
- Abrasive pad sampling followed by diffuse reflectance measurements
- Universal ATR measurement
**Film Making**

**The Process**

| Powder or Solid Piece | Heat + Pressure | Film ~30um | Cool & Remove from press | Spectrometer + Film Accessory |

15-30 minutes

- **Process Difficulties**
  - Sample sticking
  - Surface contamination
  - Sample degradation
  - Interference fringes

- **High Operational Cost**
  - High skill
  - Not routine handling
  - Slow
Specac Integrated Film Maker

- Up to 400 deg C
- Water Cooling
- 2 tons pressure
- Estimated expert preparation time:
  - 15 minutes
Spectrum One - Intelligent Sampling
Diffuse Reflectance

- Automatic accessory recognition
- Auto focus to adjust sample height and on-screen adjustment
- Powder cups, proprietary coated abrasive pads, ordinary uncoated pads, and diamond sticks
- Full multimedia tutorial
Sampling with Abrasive Pad

Diamond or SiC coated pad

Particles of sample
Spectrum One - Intelligent Sampling Drifts
Normally Difficult Samples

Floppy Disk, DRIFT Abrasive sampling, 8 Scans

Electrical Connector, In Situ, DRIFT Abrasive Sampling, 8 Scans

On-screen display of beam path and accessory
Schematic Diamond ATR

Pressure

Sample

Diamond

0 1 mm
The ATR Experiment

Index $n_s$

ATR CRYSTAL

$\theta \theta$

SAMPLE

$nc > ns$

$nc$

MIR

DEPTH OF PENETRATION

ELECTRIC FIELD STRENGTH

$ns$

PerkinElmer precisely
Advanced Sampling in Mid-IR Diamond ATR

The Process

- Powder or Solid Piece
- Clamp Optical Contact
- Spectrum

<3 minutes

- Low Operational Cost
  - Low skill
  - Routine handling
  - Fast

- Process Difficulties
  - Control of path length
  - Control of pressure
Spectrum One - Intelligent Sampling
Universal ATR

- Automatic accessory recognition
- Automatic recognition of top-plate
- On-screen display of force applied to sample
- Diamond crystal
- Choice of trough and flat plate versions
- Choice of 1, 3, or 9 reflections
- Full multimedia tutorial
Universal ATR – PVC ATR Spectrum

On-screen display of force applied to sample
Spectrum identification

- **COMPARE** Simple, intuitive, fast method development, with unique filters
- **Euclidean Search** Full spectrum comparison for large product libraries
- **Verify** SIMCA (Soft Independent Modeling by Class Analogy)
  - chemometric approach
  - comprehensive statistical information
One approach:

- Use 1 reference spectrum per class
- Full spectrum comparison
- Scores are listed 0-1
- Filters designed to minimize influence of common problems

**Compare**
Using the Compare algorithm

- Simple library development
- Intuitive
- Filters improve discrimination between similar materials and improve robustness
- Most often the 1st choice for materials verification

N.B
Not easy to include expected sample variability
Filters excellent for emphasising chemical differences, not always good for physical differences.
Polymer Verification

Graph #2

File: pvc polymer.ep
Correlation: 1.0000
Factor: 1.0000
Comments: AP0074 POLY(VINYL CHLORIDE) INHERENT VISCOITY

Status: Ready for next command...

cm-1
Materials verification using Euclidean Search

- Full spectrum comparison for large product libraries
- Can use 100’s of spectra
Euclidean Search for rapid i.d

Spectrum Search

- Full spectrum matching
- Hits are rated by scores 0-1
- Single binary library
- Can exclude interferences
Why Asbestos?

Asbestos is a mineral fiber. There are several types of asbestos fibers. In the past, asbestos was added to a variety of products to strengthen them and to provide heat insulation and fire resistance.

How Can Asbestos Affect My Health?

1) Breathing high levels of asbestos fibers can lead to an increased risk of: lung cancer
2) mesothelioma, a cancer of the lining of the chest and the abdominal cavity
3) asbestosis, in which the lungs become scarred with fibrous tissue.

The presence of these materials is usually directly or indirectly associated with the manufacture and production of industrial and consumer products. The maintenance of legislation to help protect the general public, places a burden on the analytical chemist to develop simple and reliable methods for the determination and control of these materials.

A fibre of asbestos or related substance is coated by an iron-protein complex and surrounded by macrophages - NIOSH
Where is it prohibited?

The placing on the market and the use of products containing these fibres shall be prohibited for:
(a) toys;
(b) materials or preparations intended to be applied by spraying;
Member States may, however, allow on their territories butiminous compounds containing asbestos intended to be applied by spraying as vehicle undersealing for anti-corrosion protection;
(c) finished products which are retailed to the public in powder form;
(d) items for smoking such as tobacco pipes and cigarette and cigar holders;
(e) catalytic filters and insulation devices for incorporation in catalytic heaters using liquefied gas;
(f) paints and varnishes.'
Asbestos is a collection name to a number of naturally occurring complex, crystalline, fibrous silicates.

- Chrysotile
- Amosite
- Anthophyllite
- Crocidolite
- Tremolite

**Approximate formulae**

- **Chrysotile**: $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$
- **Amosite**: $(\text{Fe}(\text{II})/\text{Mg})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$
- **Anthophyllite**: $(\text{Mg}/\text{Fe}(\text{II}))_7\text{Si}_8\text{O}_{22}(\text{OH})_2$
- **Crocidolite**: $\text{Na}_2\text{Fe}_3(\text{II})\text{Fe}_2\text{III}\text{Si}_8\text{O}_{22}(\text{OH})_2$
- **Tremolite**: $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$
Analysis of asbestos

Analytical procedure is dependable on the physical form of the sample and the information required.

For confirming the contamination of asbestos in plastics, ink, coating, paper, fabric, leather, PCB products using infrared and infrared microscopy.

The information we can obtain is characterization of asbestos type, quantity of asbestos present and/or relative proportion of individual asbestos types present in mixed forms.
Polarized Light Microscopy - P.L.M. is the most commonly used method for the analysis of bulk samples, using 450 to 800 power magnification. This method is performed by dropping acids on samples which results in a change of color enabling the analyst to determine percent and the type of asbestos.

Phase Contact Microscopy - P.C.M. is a less expensive method that is commonly used for the analysis of air samples. During P.C.M., the sample material is magnified from 450 up to the 800th power.

Transmission Electron Microscopy - T.E.M. analytical method is 100% accurate in either a bulk or air sample but also very expensive. The method utilizes an electron microscope, magnifying the sample material up to 50,000 times.

Infrared Spectroscopy /Microscopy – With careful sample preparation and in certain cases with computer processing, it is possible to satisfy the requirements for the different sample categories and to define well defined IR analytical methodologies.
Spotlight - An IR Imaging Tool to provides the complete picture of molecular distribution rapidly

AutoIMAGE - Complete PC control of the microscope with Auto Focus, Auto Aperture and other automated features

MultiScope - A practical, low-cost tool for tackling everyday analytical problems with speed and accuracy
APPLICATIONS OF FT-IR MICROSCOPES

What can an FT-IR microscope study?

- Small samples down to about 10 x 10 µm: fibers, particles, crystals
- Small inhomogeneities in a larger matrix: contaminants in paper, polymers, electronic components
- Surface studies: defects on coatings, painted surfaces
- Microscopic changes of composition across a sample: additives in polymers, purity of materials
- And ....

Asbestos fibres
Simplified flow diagram of IR peaks of asbestos

Present Absent

Present IR band at 670 cm⁻¹

Absent IR band at 775 to 780 cm⁻¹

Present IR band at 755 cm⁻¹

Absent

Anthophyllite
also at 450, 1015 and 1090 cm⁻¹

Bands at 450 cm⁻¹

Tremolite
also at 240, 320, 360, 390, 460 and 685 cm⁻¹

Chrysotile
also at 1080, 605, 440, 305 and 3690 cm⁻¹

Crocidolite
also at 1140, 1100, 540 and 320 cm⁻¹

Amosite
also at 1125, 1080, 480 and 428 cm⁻¹
General appearance and interpretation of the asbestos spectrum

- All asbestos exhibit intense absorptions in the 1200-900 cm\(^{-1}\) and 600-300 cm\(^{-1}\) regions
- Weaker but characteristic bands are observed between 850-600 cm\(^{-1}\).
- Maximum information for qualitative identification of asbestos type is gained by recording the spectrum to 200 cm\(^{-1}\).
- There are weak absorptions around 3700-3200 cm\(^{-1}\) and 1700-1400 cm\(^{-1}\).
- Broad absorptions centred around 3400 cm\(^{-1}\) and 1620 cm\(^{-1}\) are due to absorbed water from hygroscopic halide disk matrix.
- Chrysotile is significantly different from the amphiboles since it exhibits an intense double hydroxyl groups at 3693/3648 cm\(^{-1}\) produced between layers of hydroxyl groups sited between the main silicate layers of the lattice.
- This band is used for characterisation and quantitative estimation of the fibres in samples collected from the dust, or liquids subjected to asbestos filtration.
- This band is sensitive to interference from other mineral silicates such as talc, kaolinite and montmorillonite which are also used in other industrial processes.
Sample preparation procedure

- Selected method is strongly dependent on the type of sample
- Using FTIR instrument
- Airborne samples is deposited on a filter material, ashed and made into a halide disk preferably CsI
- Groups of fibres in a composite matrix can be prepared as a CsI/KBr disk.
- For resins - removing individual fibres at fracture points in the sample with tweezers or dissolve the sample with organic solvent if it is not highly cross-linked and then prepare a CsI disk
- Fibres can also be placed on a diamond ATR crystal and scanned
- Using Infrared Microscope – preferable for individual fibres
- Groups of fibres in a composite matrix can be prepared as a micro CsI/KBr disk with a quick press
- Removing individual fibres in the sample with tweezers. Place sample on a KBr disk and analyse by transmission or place sample on a gold mirror and analyse by reflection
KBr Disk Sampling
Method for making micro KBr disk

KBr Disks

Quick Press for micro KBr disk
Chrysotile, Amosite, Anthophyllite and Crocidolite forms of asbestos can be identified individually by infrared spectroscopy.

Chrysotile may be determined quantitatively using its absorption at 3690 cm\(^{-1}\) provided anthophyllite is absent.

Anthophyllite may be measured using its absorption at 670 cm\(^{-1}\) in the absence of talc.

The absorption bands at 775 cm\(^{-1}\) common to amosite, crocidolite and anthophyllite may be used for quantitatively analysis of these asbestoses mixed with chrysotile.

Many of the other bands in the flow diagram of IR peaks of asbestos can be used to identify and quantify the different type of asbestos.
Comparison of Chrysotile and Amphibole Asbestos

3690 cm\(^{-1}\)

1080 cm\(^{-1}\)

605 cm\(^{-1}\)

440 cm\(^{-1}\)

305 cm\(^{-1}\)
Comparison of Chrysotile, Amosite and Crocidolite

**Chrysotile**
- 1125 cm⁻¹
- 780 cm⁻¹ (Amosite)
- 428 cm⁻¹
- 1080 cm⁻¹

**Amosite**
- 780 cm⁻¹
- 450 cm⁻¹
- 540 cm⁻¹
- 320 cm⁻¹

**Crocidolite**
- 1140 cm⁻¹
- 780 cm⁻¹
- 540 cm⁻¹
- 320 cm⁻¹
- 450 cm⁻¹
- 1100 cm⁻¹
Comparison of Chrysotile, Crocidolite, Anthophylite and Talc

![Graph comparing Chrysotile and Crocidolite](image1)

![Graph comparing Anthophylite and Talc](image2)

- **Chrysotile**
  - $1015\text{ cm}^{-1}$
  - $1090\text{ cm}^{-1}$
  - $450\text{ cm}^{-1}$

- **Crocidolite**
  - $780\text{ cm}^{-1}$

- **Anthophylite**
  - $450\text{ cm}^{-1}$
  - $670\text{ cm}^{-1}$

- **Talc**
  - $1015\text{ cm}^{-1}$
  - $450\text{ cm}^{-1}$
Frequently asbestoses occur as minor component in a non-asbestos silicate matrix. A typical example is the amphibole tremolite (and sometimes anthophylite) which occasionally occurs in similar rock strata as talc. For this reason, batches of talc are analysed for the possible presence of the amphibole.