FTIR and Raman Spectroscopy of Asbestos Minerals

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Introduction

Asbestos is a collective technical and commercial term for 6 naturally occurring fibrous minerals from the serpentine and amphibole group (EU, 2003, 2006). The term "fibrous" is quite essential, because these hydrous silicates can occur both in asbestos (fibrous) and non-asbestos form. Both forms have the same chemical composition, but differ significantly in their habitus. Therefore, in addition to the mineralogical, respectively chemical aspect, the asbestos must also meet relevant shape criteria. A "fibre" is defined as a particle that is more than 5 µm in length, has a length-to-width ratio of at least 3:1, and must be less than 3 µm wide (WHO, 1985). Due to the formation of fibres of microscopic dimensions, asbestos remains in the air column for a relatively long time, which is associated with the risk of inhalation and deposition of these fibrous particles in the human respiratory system. The presence of asbestos fibres in the respiratory tract can then lead to serious diseases, such as asbestosis, lung cancer or malignant mesothelioma. For this reason, all asbestos are classified as a Category 1 of human carcinogens (WHO, 1986). Although there are other "fibrous" minerals with similar health risks, since they have not been used for industrial applications in the past, they are not classified as asbestos.

Table 1 *Asbestos minerals and their non-asbestos equivalents*

Asbestos form	Chemical composition	Non-asbestos form
	Serpentine group	
Chrysotile „white asbestos“	$Mg_3Si_2O_5(OH)_4$	Antigorite
		Lizardite
	Amphibole group	
Actinolite asbestos	$Ca_2(Mg,Fe^{2+})_5Si_8O_{22}(OH)_2$	Actinolite
Anthophyllite asbestos	$Mg_7Si_8O_{22}(OH)_2$	Anthophyllite
Tremolite asbestos	$Ca_2Mg_5Si_8O_{22}(OH)_2$	Tremolite
Amosite „brown asbestos“	$Fe^{2+}{}_7Si_8O_{22}(OH)_2$	Grunerite
Crocidolite „blue asbestos“	$Na_2(Fe^{2+},Mg)_3Fe^{3+}{}_2Si_8O_{22}(OH)_2$	Riebeckite

- EU, 2003. Directive 2003/18/EC of the European Parliament and of the Council of 27 March 2003 amending Council Directive 83/477/EEC on the protection of workers from the risks related to exposure to asbestos at work. Official Journal L097, 15/04/2003, 48–52.
- EU, 2006. Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC. Official Journal L 396, 1–*849.*
- WHO, 1985. Reference methods for measuring airborne man-made mineral fibers (MMMF). WHO/EURO Technical Committee for Monitoring and Evaluating MMMF. World Health Organization Regional Office for Europe, Copenhagen, Denmark.
- WHO, 1986. Asbestos and other natural mineral fibres. Environmental Health Criteria 53. World Health Organization, Geneva, Switzerland.

Samples

The rock samples were purposefully collected at locations in the Czech Republic in such a way that they represented rocks potentially containing asbestos and included a wider spectrum of asbestos minerals, for more details see a map web portal https://www.ugn.cas.cz/other/map/azrock/mapa.html

Table 2 *Characterization of selected rock samples*

Locality	Region	Part of the region	Type of rock	XRD
Loužnice	Lugicum	Krkonoše - Jizera Unit	serpentinite	tremolite, antigorite chlorite, augit
Orlovice	Bohemicum	Domažlice Unit	peridotite	olivine, Mg-hornblend, anthophyllite, enstatite, magnetite
Šebířov	Moldanubicum	Moldanubicum of Šumava and Southern Bohemia	serpentinite	antigorite, chrysotile, chlorite, chromite

Methods

Within the testing a suitable procedure for determining the presence of naturally occurring asbestos (NOA) in rocks, a wide range of analytical methods was applied - optical microscopy in polarized light (OPM), X-ray diffraction (XRD), vibrational spectroscopy (FTIR, Raman), scanning electron microscopy (SEM, SEM-EDX) and transmission electron microscopy (TEM).

FTIR and Raman spectroscopy was applied as a complementary method to X-ray diffraction for rapid characterization of the chemico-mineralogical composition of rock samples.

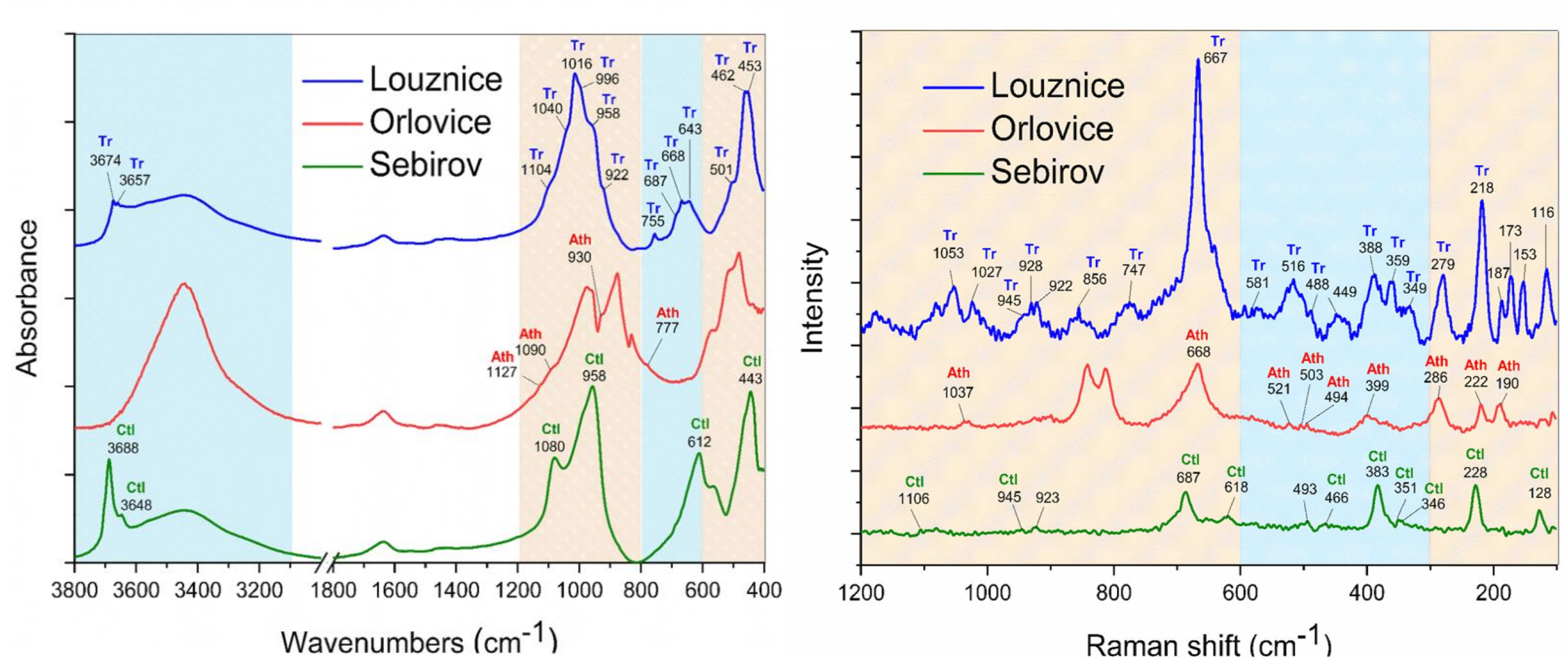
FTIR analysis was carried out using the conventional KBr pellet technique on a Nicolet 6700 FTIR spectrometer (Thermo Scientific, USA). The spectra were recorded in a range from 4000 to 400 cm^{-1}, with a resolution of 2 cm^{-1} and 64 scans.

Raman measurements were performed on a DXR SmartRaman dispersive spectrometer (Thermo Scientific, USA). The Raman data were collected in a back-scattering geometry on a powder sample using a 780 nm excitation laser in the spectral range of 3000–100 cm^{-1}. The sample surface was exposed a 20 mW laser power under the aperture (50 µm slit). To equalize signal to noise, 150 scans were measured over 1 second at a resolution of 4 cm^{-1}.

Results and discussion

The combination of FTIR and Raman spectra can significantly help in the characterization of asbestos minerals. Based on the similarity with all hydrous silicates, the vibrational spectrum of asbestos minerals can be divided into two basic parts: the higher wavenumber region (4000–3000 cm^{-1}), where OH–stretching vibrations of hydroxyl molecules dominate; the lower wavenumber region (<1200 cm^{-1}), where internal vibrations of the tetrahedral skeleton Si-O-Si, cation-oxygen polyhedral (M-O), or bending/libration modes, are found. To reveal the presence of Fe^{2+}, Mg^{2+} or other cations in octahedral positions, spectral bands from two regions of the vibrational spectrum are suitable: OH–stretching region (3700–3600 cm^{-1}); the low-wavenumber region of cation-oxygen polyhedral (M-O) mode (450–300 cm^{-1}). The vibrational spectra of amphibole asbestos are more complex compared to serpentine asbestos due to their wide variability in chemical composition. In the case of asbestos rocks, it is necessary to take into account the presence of accompanying mineral phases, which may overlap some important spectral features of the investigated asbestos minerals.

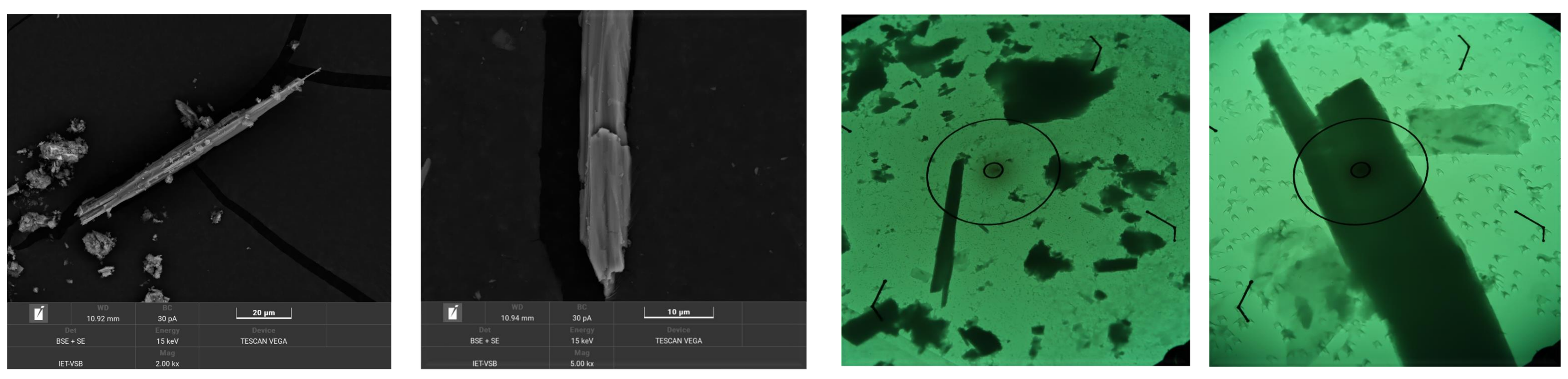
FTIR and Raman spectroscopy can provide the first information about the potential risk of the presence of asbestos. To assess the risk of carcinogenicity based on the morphology of individual asbestos fibres, it is necessary to use SEM (SEM+EDX) or TEM analysis. The reason is the a spatial resolution of both spectral methods - traditional FTIR microscopy having a typical resolution of 5-15 microns, compared with Raman at typically around 1 micron.



tremolite (Tr); **athophyllite (Ath)**; **chrysotile (Ctl)**

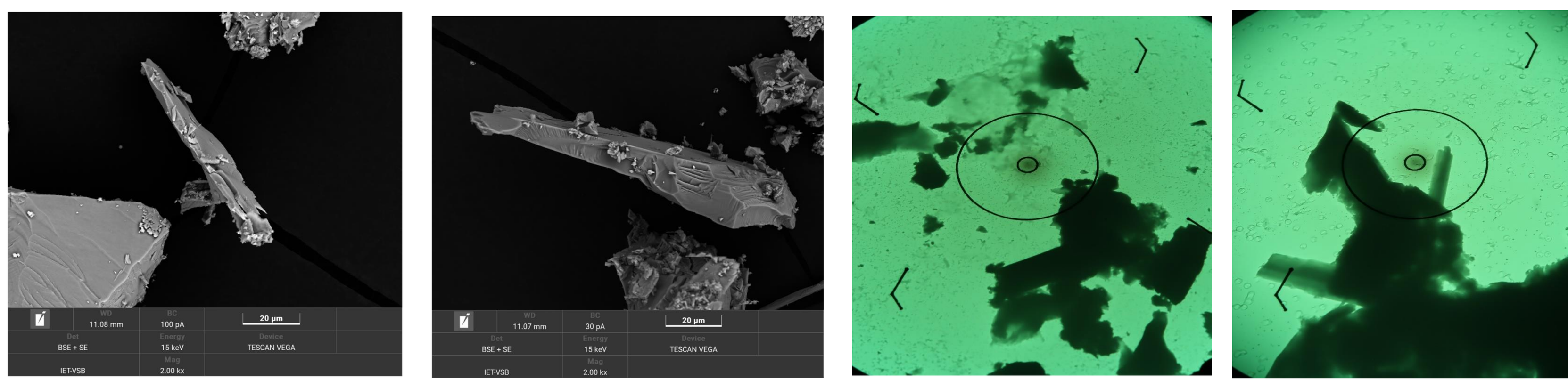
Abbreviations according to Evans, Am. Min. (2010) 95, 185-187.

Loužnice (tremolite)



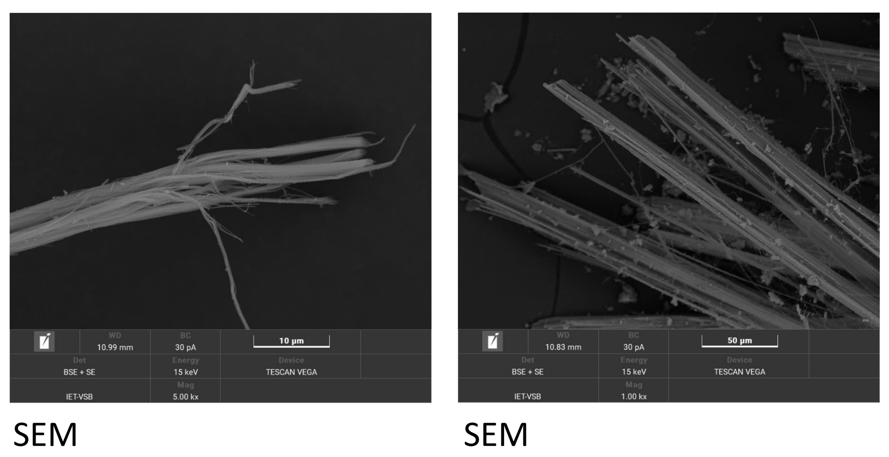
SEM SEM TEM (2500x) TEM (13500x)

Orlovice (anthophyllite)

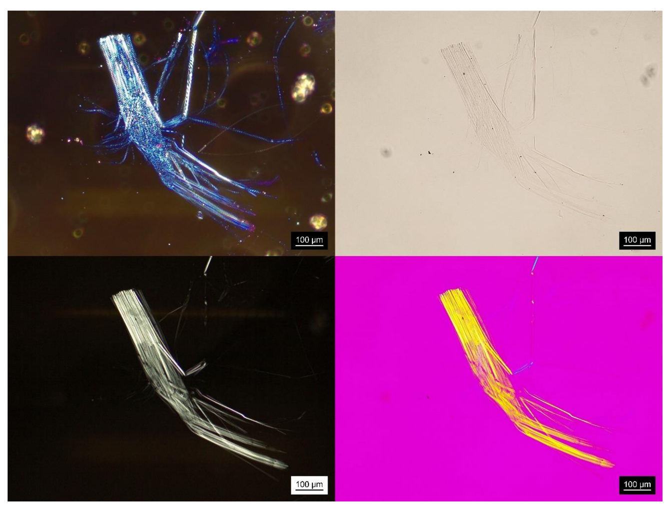


SEM SEM TEM (2500x) TEM (13500x)

Šebířov (chrysotile)



SEM SEM



OPM

Acknowledgement

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