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Case Report: Forensic Chemistry Analysis in Asbestos Litigation

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Abstract. Chrysotile asbestos, a naturally occurring fibrous silicate mineral, is extensively used in various industries due to its advantageous properties, including low cost, thermal insulation, mechanical strength, and resistance to chemical and biological degradation. However, its usage is associated with significant health risks, including mesothelioma and lung cancer, and environmental concerns due to its slow degradation and widespread contamination. Despite legislative efforts, asbestos remains a prevalent issue, particularly in countries like Brazil with significant asbestos deposits. Legislation addressing chrysotile asbestos has led to its prohibition in many countries, including Brazil. In forensic chemistry, the identification of materials suspected of containing asbestos is crucial for compliance with regulations. This study aims to showcase chemical and physical analyses conducted on samples from a real investigation involving a metallurgical company accused of using asbestos-containing materials. Various analytical techniques, including FTIR, Raman spectroscopy, SEM-EDS, XRF, and XRD, were employed, consistently identifying chrysotile asbestos in the samples despite its banishment. This case underscores the importance of forensic chemistry in identifying hazardous materials and ensuring compliance with regulatory standards.

Keywords: chrysotile asbestos; forensic chemistry; FTIR; Raman spectroscopy; SEM-EDS; XRD; XRF.

1. Introduction

Chrysotile asbestos – [$Mg_3Si_2O_5(OH)_4$] – is a naturally occurring fibrous silicate mineral widely used in the industry due to its various advantages, such as its low cost, low thermal conductivity, high mechanical strength, resistance to chemical and

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biological attacks, and its ability to withstand heat, fire, acids, and friction. Consequently, it finds numerous applications, including use in construction materials (roofs, water tanks, pipes), thermal insulation, heat-resistant materials in buildings, industrial processes, and the manufacture of various products for household and environmental use. It is also utilized in the automotive industry in clutches, brakes, and transmission parts[1].

Despite all these advantages, there are also numerous health-related disadvantages associated with chrysotile asbestos, including various diseases such as malignant mesothelioma, lung cancer, laryngeal cancer, ovarian cancer, asbestosis, and pleural disease. Additionally, it can also pose environmental problems, as the construction, demolition, mining, and production of asbestos can release it into the environment, contaminating air, water, and soil, potentially traveling long distances and persisting for extended periods due to its extremely slow degradation[1,2].

Studies have revealed that an important factor directly related to the harmful effects of chrysotile asbestos is the dimensions of their fibers[3,4]. In Brazil, Annex 12 (Tolerance Limits for Mineral Dust) of Regulatory Standard 15 (NR-15) is an important reference for protecting workers exposed to mineral dust in the workplace. It defines "breathable asbestos fibers" as those with a diameter less than 3 micrometers, length greater than 5 micrometers, and a length-to-diameter ratio exceeding 3:1[5].

Concerns about the various harms caused by asbestos have led to its prohibition in approximately 66 countries[6,7]. However, it is still widely used in construction materials in countries such as Brazil, China, Russia, India, and Indonesia, which together account for 85% of the world's asbestos consumption[8]. Brazil, which ranks among the top three asbestos suppliers globally, has the largest asbestos deposit in Latin America, located in the city of Minaçu. This deposit has been operational since the 1960s and has supplied asbestos not only to Brazil but also to countries like Colombia, India, and Indonesia[6,7].

In Brazil, regarding legislation, the issue of chrysotile asbestos was extensively discussed in direct actions of unconstitutionality (ADI) 3356, 3357, 3937, 3406, 3470, and in the claim of non-compliance with a fundamental precept (ADPF) 109. In August 2017, the Brazilian Supreme Court (STF) deemed constitutional a law from the State of São Paulo banning asbestos use and declared Article 2 of Federal

Law 9.055/1995 unconstitutional, which previously permitted its use. Similar decisions were made regarding laws in Pernambuco, Rio Grande do Sul, Rio de Janeiro, and the Municipality of São Paulo. Finally, in November 2017, ruling on the Rio de Janeiro case, the Court gave broad and binding effect to the decision, prohibiting the extraction, manipulation, industrialization, and commercialization of chrysotile asbestos throughout Brazilian territory[9].

It´s natural whenever a substance becomes prohibited or regulated, materials suspected of being or containing such substance may be subject to analysis in investigations aimed at their unequivocal identification. Thus, forensic chemistry is one of the important areas aiming to achieve this goal. Forensic chemistry encompasses various subareas considered more typical, more common, which are those most present in the routine of forensic chemistry laboratories, such as drugs, medications, fuels, explosives, pesticides, among others. However, less common cases may often occur. In these cases, the disclosure of the approaches used, so that they can serve as a reference for any future similar cases in laboratories facing this demand, is relevant. The characterization of chrysotile asbestos is one such case. Therefore, the aim of this study is to present some chemical (and physical) analyses conducted on samples from a real investigation case in which employees of a company claimed to have been handling materials containing asbestos while the company denied the use of this material. Some of the workers developed related illnesses after decades of service to the company.

2. Materials and methods

2.1 Materials

In this study, samples of insulating material suspected to be composed of chrysotile asbestos were collected and seized during a forensic examination conducted at a metallurgical company. Five fragments were taken from the piece of insulating material, with each fragment assigned to one of the five instrumental analysis techniques described in section 2.3 Instrumentation presented below. Figure 1 presents a fragment to illustrate the analyzed material.

Figure 1. Part of the suspected sample that comprised the thermal insulation.

2.2 Sample preparation

Except for the XRD analyses, all the analyses were performed directly on the material without the need for sample preparations. For the XRD analyses aiming to obtain the material in powder form, a small portion of the material was subjected to grind, subsequently ethyl alcohol was added and filtered through a 60 μm sieve. After drying, the obtained solid material was subjected to the XRD analyses.

2.3 Instrumentation

The analytical instrumental techniques listed below were selected to obtain comprehensive results based on different chemical principles. Fourier-transform infrared (FTIR) spectroscopy and Raman spectroscopy provide detailed structural information by analyzing the molecular vibrations of substances, allowing for the identification of functional groups and chemical bonds. On the other hand, scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM/EDS) and X-ray fluorescence (XRF) offer insights into the elemental composition of the materials. SEM is particularly relevant for measuring the dimensions of fibers, which is an important parameter according to the previously mentioned legislation. Additionally, X-ray diffraction (XRD) provides information regarding the crystalline structure of the materials, thus consolidating robust and unequivocal identification.

2.3.1 Fourier transform infrared (FTIR)

FTIR analyses were conducted using a Thermo Scientific Nicolet iS10 FTIR Spectrometer equipped with an ATR (attenuated total reflectance) accessory and a

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DTGS detector operating at room temperature. Spectra collection and analyses were performed using OMNIC 8.1.0.10 software (Thermo Fisher Scientific, Waltham, MA, USA).

2.3.2 Raman spectroscopy

The Raman analysis was conducted using a HORIBA XploRATM Plus confocal Raman microscope, with an excitation wavelength of 785 nm, a spectral range of 200-3500 cm^{-1}, using a 20X objective lens. The data were processed with LabSpec 6 software.

2.3.3 X-ray diffractometry (XRD)

The X-ray diffraction pattern was performed using an X-ray diffractometer (Bruker AXS D2 Phaser) with CuKα radiation (40 kV, 40 mA) and General Area Detector Diffraction System (GADDS). The data were processed with EVA software.

2.3.4 X-ray fluorescence (XRF)

Analyses were conducted using an X-Ray Fluorescence Analyzer Niton XL3t GOLDD+ from Thermo Scientific. The data were processed with NITON Data Transfer (NDT) software (Version 8.5.1; Thermo Scientific Portable Analytical Instruments, Inc).

2.3.5 Scanning electron microscopy with energy-dispersive x-ray spectroscopy (SEM/EDS)

Analyses were conducted using an FEI scanning electron microscope, model QUANTA 200 3D, coupled with an Energy Dispersive Spectrometer (EDS) for X-ray analyses. The data were processed with INCA energy software.

3. Results

FTIR analysis is an excellent choice as a starting technique because it is simple and fast, requiring, in general, no sample preparation. Figure 2 shows the FTIR results, revealing that despite the spectrum being simple with few bands, it is a good indicator of chrysotile asbestos when compared to the standard spectrum available in the NIST electronic library. The main bands are at 943 cm^{-1}, 1066 cm^{-1}, 3643 cm^{-1}, and 3680 cm^{-1}. The signals at 3640–3680 cm^{-1} are associated with inner and outer OH stretching vibrations, while the signals at 900–1100 cm^{-1} can be attributed to Si–O–Si stretching vibrations[10].

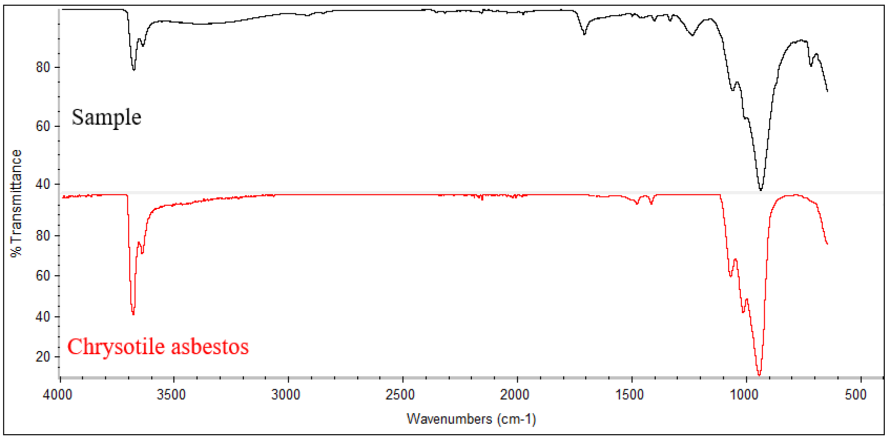

Figure 2. FTIR spectra of suspected sample (black line) compared to the Chrysotile asbestos from the NIST library (red line).

Another vibrational spectroscopic technique, Raman spectroscopy, was also applied to identify the material. The results are presented in Figure 3, showing the similarity between the spectrum of the analyzed sample and the standard spectrum suggested by the Bio-Rad's Raman Spectral Database. The main observed bands are at the following wavenumbers: 235 cm^{-1}, 388 cm^{-1}, 694 cm^{-1}, and 1106 cm^{-1}. The band in the SiO$_4$ region observed at 1106 cm^{-1} arises from the antisymmetric stretching vibrations of Si–O$_{nb}$–Si groups (nb – non-bridging oxygen); the signal at 694 cm^{-1} probably originates from the symmetric stretching mode of Si–O–Si groups; the signal at 388 cm^{-1} arises from bending Si–O–Si vibrations; and the signal at 235 cm^{-1} is due to the vibrations of O$_{nb}$···H–O groups[10].

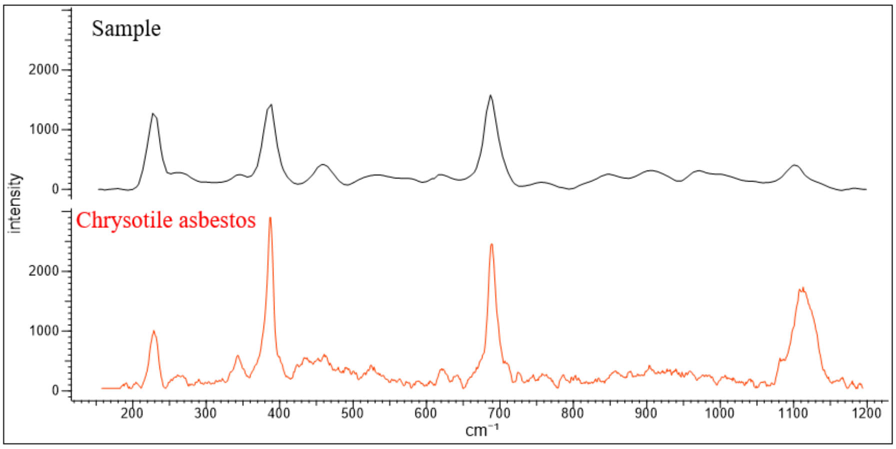

Figure 3. Raman spectra of suspected sample (black line) compared to the Chrysotile asbestos from the Bio-Rad's Raman Spectral Database (red line).

Regarding the analyses using X-ray diffractometry, the results obtained were found to be compatible with chrysotile asbestos when compared with the literature [11]. Figure 4 shows the obtained diffractogram, where the main peaks (d-values) can be observed at 7.33 Å, 4.47 Å, 3.66 Å and 2.45 Å. The most intense peaks at 7.33 Å, 3.66 Å, and 2.45 Å correspond to the diffraction of the basal planes (001), (002), and (003), respectively, which are characteristic of chrysotile asbestos and confirm its crystalline structure[12].

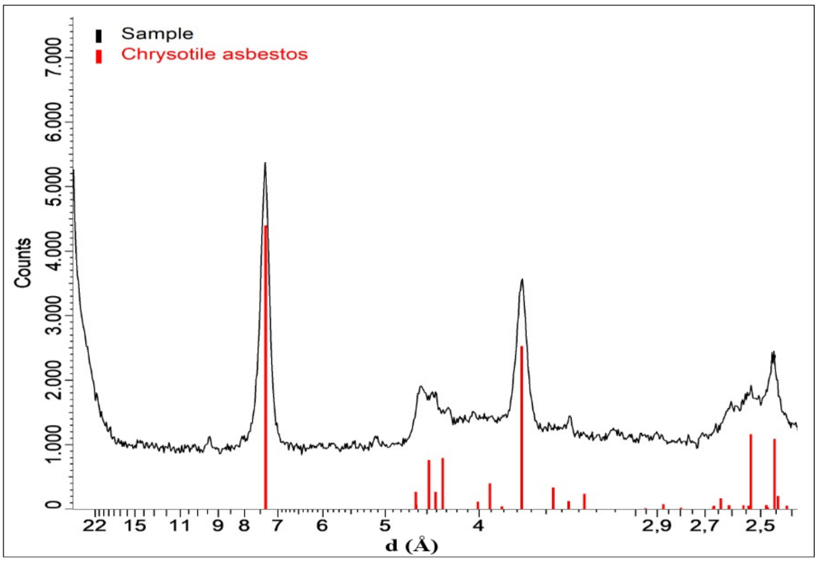

Figure 4. X-ray diffractogram of the suspected sample (black line) compared to chrysotile asbestos from the EVA software database (red line).

Analyses were also conducted using scanning electron microscopy coupled with energy-dispersive spectroscopy (SEM-EDS). The analyses identified the expected elements for chrysotile asbestos - [$Mg_3Si_2O_5(OH)_4$]. Figure 5 displays the EDS spectrum obtained with the main peaks corresponding to the elements magnesium (Mg), silicon (Si), and oxygen (O), consistent with those presented in the literature, further confirming the composition of chrysotile asbestos[11] XRF analyses were also performed, confirming the presence of the elements magnesium and silicon.

As mentioned earlier, studies have revealed that an important factor directly related to the harmful effects of chrysotile asbestos is the dimensions of its fibers. Therefore, some fibers were randomly selected to measure their dimensions, revealing several fibers that fit the definition of "breathable asbestos fibers." Figure 6 shows, on the left, an image of a part of the sample, and on the right, some of the fibers with their measured diameters indicated (0.26 µm, 1.32 µm, 1.64 µm, and 1.88 µm).

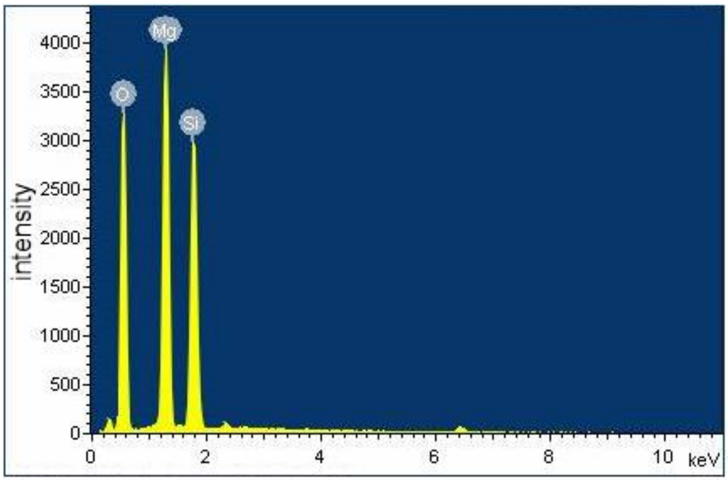

Figure 5. EDS spectrum of the sample.

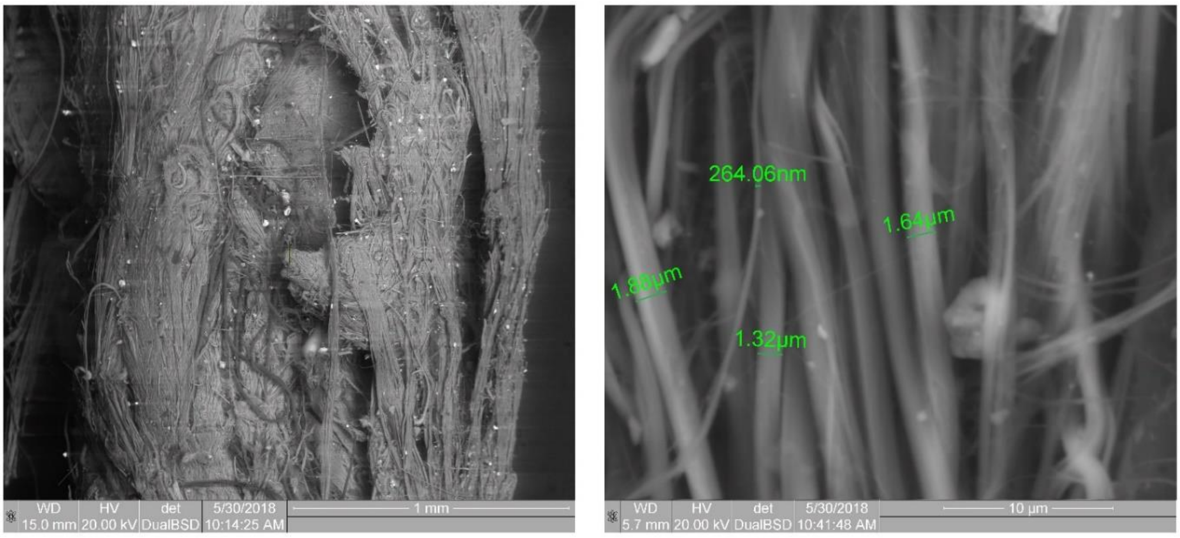

Figure 6. SEM photomicrograph of the sample. (Left) Amplification providing a more general view of a part of the sample and (Right) higher magnification and measurements of some randomly selected fibers.

4. Conclusions

This case report details the identification of a thermal insulation sample collected from a surveyed site associated with a metallurgical company facing a lawsuit from workers. The workers alleged that they had handled chrysotile asbestos materials for decades, including several years after its ban due to its potential harm. Various analytical techniques were employed for this investigation, including FTIR, Raman spectroscopy, SEM-EDS, XRF, and XRD. The results from all these methods were consistent with those expected for chrysotile asbestos and can serve as a valuable reference for forensic chemistry analysts, given that such cases are not very common in this field.

Additionally, these findings have legal implications, as they directly support claims regarding the use of banned hazardous materials in the workplace. The methodologies applied in this study can play a critical role in similar future investigations, where the identification of banned substances such as asbestos may be pivotal in litigation cases. The integration of robust, multi-technique analytical approaches strengthens the reliability of forensic evidence, which can be essential for legal proceedings. This work not only contributes to the body of knowledge in forensic chemistry but also highlights the importance of analytical methods in ensuring compliance with regulations and safeguarding public health. By presenting these results, this case can serve as a reference for forensic investigations involving asbestos and similar hazardous materials, potentially influencing future legal actions and policy developments.

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