Monte Carlo simulation of the effect of shape and thickness on SEM-EDS microanalysis of asbestos fibres and bundles: the case of anthophyllite, tremolite and actinolite

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Abstract. Asbestos is a generic term used for six types of silicate minerals that are found in fibres or bundles of fibres, which can be easily cleaved into thinner ones. Scanning electron microscopy energy-dispersive X-ray spectrometry (SEM-EDS) quantitative microanalysis of asbestos mineral fibres still represents a complex analytical issue because of the variable fibre shape and small thickness (< 5 µm) compared with the penetration depth of the incident electron beam. Following previous work on chrysotile, crocidolite and amosite, here we present a study by means of Monte Carlo simulations of the thickness and shape effect on SEM-EDS microanalysis of anthophyllite, tremolite and actinolite asbestos. Realistic experimental conditions, such as sample geometry, SEM set-up and detector physics were taken into account. We report the results obtained on 100 µm long fibres and bundles of circular and square section and thicknesses from 0.1 µm to 10 µm, for electron beam energies of 5, 15 and 25 keV. A strong influence of the asbestos mineral fibres and bundles shape and thickness on the detected EDS X-ray intensity was observed. In general, the X-ray intensities as a function of fibre thickness showed a considerable reduction below about 0.5 µm at 5 keV, 2 µm at 15 keV, and 5 µm at 25 keV for all the elements and minerals, with a non-linear dependence. Correction parameters, k-ratio, for the thickness effect were calculated and proposed.

1. Introduction

Asbestos is a generic term used for six types of silicate mineral fibres that are or have been widely exploited in many types of technology. They belong to two mineral groups: serpentines and amphiboles. Chrysotile is the only asbestiform member of the serpentine group. The amphibole group contains five asbestiform members: crocidolite (asbestos variety of riebeckite), amosite (asbestos variety of grunerite), anthophyllite, tremolite and actinolite. They are found in fibres or bundles of fibres, which can be easily separated into thinner ones. Accurate chemical analysis of asbestos mineral fibres is of paramount importance for their identification and in depth mineral characterisation. Fibre composition is related to the minerals’ environmental and health impact and potential toxicological effects [1-3].

Asbestos fibres toxicity was demonstrated by in vitro and in vivo studies to be associated to the chemical composition, and there have been suggestions that the Fe content and its oxidation state may
play a role [4]. In addition, the generation of reactive oxygen species and other radicals, which are catalysed by iron ions at the fibre surface, is also thought to be a mechanism of cytotoxicity and genotoxicity [5]. The mineralogical composition of fibres with bonded metal ions induces a strong biochemical reaction. Techniques able to accurately quantify the chemistry of mineral fibres in situ at the micrometre- and sub-micrometre scale will make important contributions to fundamental cell biology research on the interaction of cells with fibres containing highly reactive chemical species [6].

Among the microanalytical techniques, scanning electron microscopy equipped with energy-dispersive X-ray spectrometry (SEM-EDS) has proven to be of great importance for minerals, materials and biomaterials characterisation, and furthermore in evaluating the phenomena and possible mechanism of interaction between materials and bio-entities [7-9]. In particular, EDS is by far the most routine method for asbestos chemical analysis [1]. Nevertheless, SEM-EDS quantitative micro-analysis of asbestos fibres may be subjected to systematic errors due to the variable shape of the fibre and small thickness (< 5 µm) with respect to the penetration of the incident electron beam. The classical correction methods for the correction of matrix effects (e.g., ZAF or $\phi(\rho_z)$ procedures) used in quantitative microanalysis of bulk samples assume both standard and sample to have flat polished surfaces and be infinitely thick compared to the penetration of the electron beam.

The size and shape of micrometric and sub-micrometric particles may cause large errors in the quantification because of particle effects on the generation and measurement of X-rays from the sample. These effects are associated with the elastic scattering of electrons in the finite size (mass) of the particle, which is strongly influenced by the average atomic number. The particle thickness is key, for a given mean atomic number, with a shape component affecting both the absorption and fluorescence contributions to the correction routine. X-ray absorption path length and emergence angle cannot be determined as for flat polished samples in the case of micrometric and sub-micrometric particles analysis [10, 11]. Furthermore, since EDS systems are often set to normalise the results, they are prone to hide poor analytical results like high or low totals, which in turn hide any problem in the analytical protocol. Empirical methods were developed to overcome these issues, however they are cumbersome and need characterised standards for thickness, geometry and composition [11-13].

The Monte Carlo method is an effective tool for examining the basis, the reliability and the limitations of quantification procedures. In the context of asbestos fibres analysis, Monte Carlo simulations can be of paramount importance for analysing the electron transport and X-ray generation under unconventional measurement conditions or in samples with complex geometry [14-16].

We recently proposed a study by means of Monte Carlo simulations to investigate the effect of thickness and shape on SEM-EDS microanalysis of the three asbestos with the highest industrial exploitation: chrysotile, crocidolite and amosite asbestos [17]. Here, we further extend this work to the investigation of anthophyllite, tremolite and actinolite asbestos. The Monte Carlo programme NIST DTSA-II [18, 19] was used to simulate electron transport, X-ray generation and detection in cylindrical fibres and bundles of square section.

Although about 95% of asbestos used in commercial products was chrysotile, amphibole exposure in the natural environment is greater than chrysotile, since amphiboles are more widespread than chrysotile [20-24]. Furthermore, anthophyllite, tremolite and actinolite may be found as a contaminant in other fibres or in other industrial minerals. In addition, amphiboles generally contain higher levels of iron than chrysotile.

2. Methods and simulation models

2.1. Methods

The Monte Carlo simulations were performed using the programme NIST DTSA-II Jupiter 2017-2-28 revision [18], which simulates electron transport, X-ray generation and transmission in complex sample geometries. Accurate quantitative analysis by X-ray spectroscopy is possible through the
understanding of electron scattering, X-ray generation, absorption and fluorescence. The Monte Carlo method applied to electron and X-ray transport allows one to simulate electrons trajectories and X-rays through the asbestos mineral fibre and to the X-ray detector.

NIST DTSA-II carries out a single scattering model to track the trajectories of electrons as they interact with matter. It implements three elastic scattering models: a basic screened Rutherford model [25], the Mott scattering cross-section of Czyzewski and co-workers [26], and the Mott cross-section of Jablonski and co-workers [27]. The energy loss is modelled using the Joy-Luo expression [28] that is an empirical modification of the Bethe energy loss equation [29]. The ionisation cross-section is modelled using the expression of Bote and Salvat [30]. The mass absorption coefficients are those of Chantler and co-workers [31], and the fluorescence yields are tabulated experimental values [32].

The electron source is defined as a Gaussian beam. A response function that mimics the energy resolution of an EDS detector is convolved with the emitted X-ray events. The effect of shape and thickness was evaluated by simulating EDS spectra of single cylindrical asbestos fibres and of bundles of fibres. Peak intensities were integrated and compared as a function of thickness, shape, and beam energy for all minerals, after background subtraction.

Finally, correction factors, $k$-ratios, for the asbestos fibre thickness effect are calculated and proposed.

2.2. Simulation models

Fibres and bundles of fibres of variable thickness and shape placed on a pure carbon holder were simulated taking into account realistic experimental conditions, such as sample geometry, detector physics and SEM set-up.

We investigated anthophyllite, tremolite and actinolite asbestos with chemical formulae as specified in Table 1, and mass density of 3.21, 3.00 and 3.23 g/cm$^3$, respectively. This is an average chemical formula since there can be a range of Mg to Fe ratio within each species of amphibole.

| Mineral name  | Chemical formulae               |
|---------------|--------------------------------|
| Anthophyllite | $\text{Mg}_{5.25}\text{Fe}^{2+}_{1.75}\text{Si}_8\text{O}_{22}(\text{OH})_2$ |
| Tremolite     | $\text{Ca}_2\text{Mg}_{4.75}\text{Fe}^{2+}_{0.25}\text{Si}_8\text{O}_{22}(\text{OH})_2$ |
| Actinolite    | $\text{Ca}_2\text{Mg}_{3.5}\text{Fe}^{2+}_{1.5}\text{Si}_8\text{O}_{22}(\text{OH})_2$ |

Each mineral was modelled taking into account both a three-dimensional fibre of circular section and a three-dimensional bundle of square section, deposited on a flat graphite support (see figure 1 for a 2D view of the different geometries). For both models the mineral was 100 µm long and with thicknesses ranging from to 0.1 µm to 10 µm. The influence of thickness and shape on the simulated spectrum was investigated for electron beam energies of 5 keV, 15 keV and 25 keV.

An electron probe of 40 nm in diameter was considered. The probe was focussed in parallel illumination onto the surface of the bundle or fibre, in a mid position with respect to the edges. The modelled EDS detector used to generate the spectrum had an ultra-thin polymer window (Moxtek AP 3.3 film), a gold layer of 7 nm, a dead layer of 10 nm, a detector diode thickness of 3 mm, a sample-to-detector distance of 45 mm, a detector area of 10 mm$^2$, 4,096 channels each of 10 eV and a resolution of 130 eV (FWHM at Mn Kα). The detector elevation angle was set to 40°, with an azimuthal angle of 0°. The bundle or fibre was oriented with its long axis in the same direction as the detector.
3. Results and discussion

The size of the electron beam interaction volume and X-ray generation volume in conventional SEM-EDS microanalysis (with beam energy between 10 keV and 30 keV) are of the order of several $\mu$m$^3$ in most materials. When the primary electron beam penetration depth is greater than the particle size, a fraction of the electron beam escapes the particle before exciting X-rays (finite size effect). As a consequence, a portion of the electron beam scatters out of the particle volume and can excite X-rays from adjacent particles or the substrate. Furthermore, the standard is typically a much larger size and so there are more X-rays generated in the standard. Thus the $k$-ratio is additionally diminished because the intensity of the element X-ray in the standard (denominator of the $k$-ratio) is larger. These phenomena can affect the analytical results.

The simulated trajectories of electrons for a 25 keV electron beam focussed onto the surface of a tremolite cylindrical fibre (figure 1a) and onto the surface of a tremolite bundle of fibres of square section (figure 1b) in a mid position with respect to the edges are shown in figure 1. The fibre and the bundle have a diameter and a thickness of 2 $\mu$m, respectively, and are assumed deposited on a graphite substrate. The primary electrons (green vertical beam) interact with the mineral as visualised by the green trajectories. At this energy level (25 keV) a fraction of the electrons (> 40 %) penetrates into the graphite substrate (blue trajectories) for several micrometres, eventually exiting (red lines). Furthermore, a fraction of the electrons (> 40 %) scatters out of the mineral volume from its sides, both toward the substrate, black trajectories, and leaving the mineral, red lines.

We report in table 2 some reference values for anthophyllite, tremolite and actinolite bulk mineral samples: the nominal range value of electron penetration depth and X-ray intensity (generated and emitted) for the three beam energies considered in this work (5 keV, 15 keV, 25 keV). The calculation was performed with the same detector physics and SEM set-up reported in section 2.2 considering 1,000 electron trajectories and a probe dose of 60 nA s. Table 2 reports for each X-ray line the absolute magnitude of generated and emitted X-ray intensity calculated on bulk samples, in arbitrary units as reported by Ritchie [33].
Table 2. Electron penetration depth (e.p.d., in µm) and absolute magnitude (in arbitrary units, as reported by Ritchie [33]) of generated (g) and emitted (e) X-ray intensity for each X-ray line calculated on bulk samples. Fe L = Lα+Lβ+Lγ.

|                  | Anthophyllite   | Tremolite   | Actinolite   |
|------------------|-----------------|-------------|--------------|
|                  | 5keV 15keV 25keV | 5keV 15keV 25keV | 5keV 15keV 25keV |
| e.p.d. [µm]      | 0.26 1.74 4.11  | 0.26 1.74 4.55 | 0.26 1.81 3.85 |
| Ca Kα            | — — —          | (g) 1 (g) 87 (g) 247 | (g) 1 (g) 85 (g) 238 |
|                  | (e) 1 (e) 81 (e) 207 | (e) 1 (e) 80 (e) 200 |
| Ca Kβ            | — — —          | (g) 0 (g) 9 (g) 26 | (g) 0 (g) 9 (g) 25 |
|                  | (e) 0 (e) 9 (e) 23 | (e) 0 (e) 9 (e) 22 |
| Mg Kα            | (g) 61 (g) 410 (g) 848 | (g) 56 (g) 367 (g) 776 | (g) 61 (g) 410 (g) 848 |
|                  | (e) 57 (e) 240 (e) 276 | (e) 52 (e) 230 (e) 276 | (e) 57 (e) 240 (e) 276 |
| Fe Kα            | (g) 0 (g) 31 (g) 129 | (g) 0 (g) 4 (g) 19 | (g) 0 (g) 26 (g) 107 |
|                  | (e) 0 (e) 31 (e) 125 | (e) 0 (e) 4 (e) 18 | (e) 0 (e) 26 (e) 102 |
| Fe Kβ            | (g) 4 (g) 16 | (g) 0 (g) 1 (g) 2 | (g) 0 (g) 3 (g) 13 |
|                  | (e) 4 (e) 15 | (e) 0 (e) 1 (e) 2 | (e) 0 (e) 3 (e) 12 |
| Fe L             | (g) 23 (g) 107 (g) 204 | (g) 3 (g) 15 (g) 29 | (g) 19 (g) 88 (g) 170 |
|                  | (e) 17 (e) 23 (e) 16 | (e) 2 (e) 3 (e) 2 | (e) 14 (e) 18 (e) 12 |
| Si Kα            | (g) 65 (g) 588 (g) 1291 | (g) 65 (g) 582 (g) 1304 | (g) 63 (g) 570 (g) 1253 |
|                  | (e) 62 (e) 422 (e) 615 | (e) 62 (e) 435 (e) 662 | (e) 61 (e) 424 (e) 632 |
| O Kα             | (g) 353 (g) 1503 (g) 2802 | (g) 354 (g) 496 (g) 948 | (g) 345 (g) 486 (g) 910 |
|                  | (e) 300 (e) 581 (e) 476 | (e) 281 (e) 418 (e) 292 | (e) 276 (e) 421 (e) 298 |

3.1. Anthophyllite asbestos

A bundle of square section and a fibre of circular one with a composition and mass density as reported in table 1 were taken into account to investigate the significance of the thickness and shape effects on anthophyllite asbestos. See section 2.2 for further details on the simulation model. Figure 2 shows the trend of the integrated intensities (counts) obtained from the simulated EDS spectra of a bundle of fibres of square section as a function of bundle thickness for each element (Mg, Fe, Si, O) at beam energies of 5 keV, 15 keV and 25 keV (see the legend in figure 2f). The simulations refer to a bundle thickness from 0.1 µm to 10 µm.

Generally speaking, for all the elements of both models (circular and square) a strong dependence of the simulated X-ray intensity on the mineral thickness was observed. The intensity values reported for thickness of 10 µm can be considered as a reference value valid for a bulk sample (infinite thickness). Indeed, by comparing the intensity values for a 10 µm thick sample with those calculated for a massive one, we verified that a thickness of 10 µm represents, at our simulated experimental conditions, a bulk sample for all energies and minerals here considered. Table 3 reports the reference intensity values for massive samples calculated at an electron beam energy of 25 keV. In general, the integrated intensity starts to have a reduction for thickness below 5 µm. Specifically, for all the considered elements, Mg, Fe, Si and O, and both fibre and bundle geometry, the integrated intensity strongly decreases starting from thickness of 0.5 µm at 5 keV, 2 µm at 15 keV and 5 µm at 25 keV.
Figure 2. Simulated SEM-EDS X-ray intensity as a function of thickness for an anthophyllite bundle of fibres of square section with beam energy of 5 keV, 15 keV and 25 keV; see legend in (f).
Table 3. Reference intensity values for a bulk sample at 25 keV in our experimental set up (§ 2.2).

|                | CaKα | CaKβ | MgKα  | FeKα  | FeKβ  | FeL  | SiKα  | Oα  |
|----------------|------|------|-------|-------|-------|------|-------|-----|
| Anthophyllite  | —    | —    | 6.82×10⁴ | 3.43×10⁴ | 4.18×10³ | 2.51×10³ | 1.60×10⁵ | 7.40×10⁴ |
| Tremolite      | 5.45×10⁴ | 6.04×10³ | 7.08×10⁴ | 4.75×10³ | 5.91×10² | 3.29×10² | 1.73×10⁵ | 5.09×10⁴ |
| Actinolite     | 5.35×10⁴ | 5.94×10³ | 4.23×10⁴ | 2.80×10³ | 3.43×10² | 1.85×10² | 1.63×10⁵ | 4.61×10⁴ |

3.2. Tremolite and actinolite asbestos

A fibre of circular section and a bundle of square one were also simulated for tremolite and actinolite asbestos, with a composition as reported in table 1. See section 2.2 for further details on the simulation model. Figure 3 reports the results for a single cylindrical fibre. It shows the trend of the integrated intensity (counts) calculated from the simulated EDS spectra, as a function of fibre diameter (thickness), for each element (Ca, Mg, Fe, Si, O) at beam energies of 5 keV, 15 keV and 25 keV (see legend in figure 3h). Fibres were simulated with a diameter from 0.1 µm to 10 µm. Bundles with a thickness from 0.1 µm to 10 µm were also simulated (data not shown, but available on request).

Generally speaking, for all the elements of both the models (circular and square) a strong dependence of the simulated X-ray intensity on the mineral thickness was observed. Intensity values calculated for thicknesses of 10 µm were found to be very close to those calculated for a bulk sample. Table 3 reports, as an example, the reference intensity values for massive samples calculated at an electron beam energy of 25 keV. In general, the integrated intensity starts to have a reduction for thickness below 5 µm. In particular, for all the considered elements, Ca (Kα), Ca (Kβ), Mg (Kα), Fe (Kα), Fe (Kβ), Fe (L), Si (Kα), O (Kα), and both fibre and bundle, the integrated intensity strongly decreases starting from thickness of 0.5 µm at 5 keV, 2 µm at 15 keV and 5 µm at 25 keV.

Both the square and circular section models present a similar effect of intensity enhancement before the reduction starting point. In terms of the previously cited finite size (thickness) and reduced absorption (shape component) effects, the reduced absorption effect initially prevails on the finite size one, which in turn becomes predominant for smaller thicknesses. Generally, in the case for “soft” X-rays, when there is high absorption, the magnitude of the reduced X-ray absorption effect is largest, in agreement with the experimental results of Paoletti and co-workers, and Small [10, 11].

3.3. Correction factors, k-ratios

Our investigation was performed to develop specific thickness correction parameters for SEM-EDS quantitative analysis of asbestos minerals. We report in table 4 the k-ratios (intensity ratio of X-rays emitted by the asbestos mineral fibre to those produced by a massive sample) calculated for single cylindrical fibres of anthophyllite, tremolite and actinolite with diameter of 0.1 µm, 0.5 µm, 1 µm and 2 µm, in the case of an electron beam energy of 15 keV.

Figure 4 shows the trend of k-ratios calculated in the case of anthophyllite asbestos as a function of some specific parameters. Figure 4a shows the k-ratios calculated for the Kα X-ray lines of a cylindrical fibre of anthophyllite with diameter of 1 µm, as a function of the electron beam energies considered in this work (5 keV, 15 keV, 25 keV). The k-ratios have specific values depending on the X-ray line and electron beam energy. At a beam energy of 5 keV, the intensity of X-rays emitted by the asbestos mineral fibre is comparable to those produced by a massive sample, for the excitable lines. As a comparison, figure 4b shows the results of the same calculations in the case of an anthophyllite bundle of fibre of square section. In general, a higher value of the k-ratios calculated for the bundle of square section compared to the circular fibre can be noted (from percentage fractions to several % depending on the beam energy). In figure 4c the trend of the k-ratios for an anthophyllite cylindrical fibre at an electron beam energy of 15 keV is reported as a function the fibre diameter in
Figure 3. Simulated SEM-EDS X-ray intensity as a function of thickness for a single tremolite cylindrical fibre with beam energy of 5 keV, 15 keV and 25 keV; see legend in (h).
Table 4. $k$-ratios calculated at 15 keV for cylindrical fibres of different thickness.

| Mineral     | Thickness | X-ray lines |
|-------------|-----------|-------------|
|              | $Ca_{K\alpha}$ | $Ca_{K\beta}$ | $Fe_{K\alpha}$ | $Fe_{K\beta}$ | $Fe_{L}$ | $Mg_{K\alpha}$ | $Si_{K\alpha}$ | $O_{K\alpha}$ |
| Anthophyllite | 2.0 µm | — | — | 0.99 | 0.99 | 1.06 | 0.99 | 0.98 | 1.02 |
|              | 1.0 µm | — | — | 0.88 | 0.88 | 0.83 | 0.71 | 0.70 | 0.73 |
|              | 0.5 µm | — | — | 0.50 | 0.50 | 0.53 | 0.36 | 0.34 | 0.39 |
|              | 0.1 µm | — | — | 0.10 | 0.10 | 0.15 | 0.07 | 0.07 | 0.09 |
| Tremolite    | 2.0 µm | 0.98 | 0.98 | 0.99 | 0.99 | 0.98 | 0.97 | 0.97 | 0.98 |
|              | 1.0 µm | 0.73 | 0.73 | 0.86 | 0.86 | 0.81 | 0.67 | 0.67 | 0.76 |
|              | 0.5 µm | 0.36 | 0.36 | 0.49 | 0.49 | 0.52 | 0.33 | 0.32 | 0.45 |
|              | 0.1 µm | 0.07 | 0.07 | 0.09 | 0.09 | 0.15 | 0.06 | 0.06 | 0.11 |
| Actinolite   | 2.0 µm | 0.96 | 0.96 | 0.98 | 0.98 | 1.04 | 0.97 | 0.96 | 1.01 |
|              | 1.0 µm | 0.76 | 0.76 | 0.88 | 0.88 | 0.84 | 0.71 | 0.70 | 0.78 |
|              | 0.5 µm | 0.38 | 0.38 | 0.51 | 0.51 | 0.55 | 0.36 | 0.34 | 0.46 |
|              | 0.1 µm | 0.07 | 0.07 | 0.10 | 0.10 | 0.16 | 0.07 | 0.06 | 0.12 |

Figure 4. Calculated $k$-ratios. a) Anthophyllite cylindrical fibre with a diameter of 1 µm. b) Anthophyllite bundle of fibres of square section and thickness of 1 µm. c) Anthophyllite cylindrical fibres at 15 keV in function of thickness.
the thickness range (0.1 – 5 µm) which is affected by the lowering of the X-ray intensity. The calculated data are highlighted by markers, whereas an exponential fit is shown by a solid line for each element. It should be remembered that the k-ratios were calculated for data simulated in our specific experimental conditions for the mineral chemistries presented in table 1, taking into account the detector characteristics and SEM experimental set-up.

4. Conclusions
The calculation of detected EDS X-ray intensity in the case of anthophyllite, tremolite and actinolite asbestos bundles and fibres revealed a strong influence of the mineral thickness and shape. In particular, the mineral fibre thickness was found to be the main factor affecting the variation of the simulated X-ray intensity. It should be noted that an X-ray intensity enhancement (reduced absorption effect) was often observed before the X-ray intensity reduction starting point, with a magnitude that depends on the mineral type, shape, specific element and beam energy. A non-linear dependence of the X-ray intensity trends as a function of thickness was observed for all the elements and minerals. In general, the X-ray intensity showed a considerable reduction for thicknesses below about 5 µm at 25 keV, 2 µm at 15 keV and 0.5 µm at 5 keV, as the excitation volume is greatly reduced by using low accelerating voltages. The Monte Carlo simulation method has proved to be an effective tool to demonstrate the effects related to the size and shape of micrometric and sub-micrometric particles in SEM-EDS microanalysis allowing the calculation of correction k-ratios factors and functions. The simulation approach appears less complex and cumbersome than experimental ones.

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