# Optimization of Parameters in Electron Probe Microanalysis

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**Abstract**

A method for refinement of atomic and experimental parameters is presented, applicable to several spectroscopic techniques. This kind of procedure, previously used in x-ray diffraction, is shown as a powerful tool in Electron Probe Microanalysis (EPMA). This method consists of minimizing the differences between an experimental x-ray spectrum and a function proposed to account for the bremsstrahlung and characteristic peaks from the corresponding sample, as well as for detection artifacts. This complicated function involves several parameters related to different sources (x-ray production, x-ray attenuation, sample composition, x-ray detection, etc.). Initial values must be supplied for them, and after a numerical iterative procedure is performed, improved values are achieved. Depending on the particular situation, certain parameters may be known *a priori*, so that they can be fixed allowing the others to vary. In this way, the method can be used for different purposes: determination of atomic parameters such as fluorescence yields, transition rates or photoelectric cross-sections; quantitative standardless analysis; determination of detector characteristics, etc. This work is intended to present the general aspects of the method for refining EPMA parameters, as well as to give some examples of its application to the aforementioned issues. Even when only EPMA spectra are included in this work, the method can be applied to different spectroscopic techniques, such as x-ray fluorescence, particle-induced x-ray emission, etc.

## 1 Introduction

Parameter refinement using the whole spectra is a very well spread technique in the frame of powder x-ray diffraction, and has widely been used in crystalline structural analysis. In this area, Rietveld [1, 2, 3] implemented the method for the first time. At present, the applications cover many different aspects, running from the refinement of parameters in simple structures to more complicated situations, which include the refinement of parameters in complex structures, high-temperature superconductor structures, structural changes determined in real time, etc. (see, for example, Ref. [4] and references therein). As an additional important advantage, the method can be used for quantifying multiphase mixtures. However, the refinement methodology has not been yet extended to other spectroscopic techniques, as electron probe microanalysis (EPMA) or x-ray fluorescence (XRF). In these areas, accuracy in different parameters is continuously searched for in order to improve the state of general scientific knowledge, as well as to obtain better

determination of sample composition. To this end, interesting results may be achieved by means of the optimization of atomic parameters poorly known, such as attenuation cross-sections for energies below 1.5 keV or for ultra light elements, atomic transition rates, fluorescence yields, etc.

Since suitable standards for performing conventional analysis are not usually available, standardless analysis is always in continuous development. For this reason, the implementation of parameter refinement for standardless quantitation appears as an important tool in materials characterization.

The method consists in performing least-squares fitting of the entire observed spectrum. Although it may be applied to different spectroscopic techniques, this work is restricted to EPMA spectra acquired with an energy dispersive system. An iterative procedure is carried out in order to minimize the differences between the experimental and the calculated spectra. The expressions used for the predicted spectrum are based on fundamental parameters for characteristic lines and bremsstrahlung emission, and take into account detection artifacts.

If $I_i$ and $\tilde{I}_i$ denote respectively the experimental and calculated intensities measured for the energy $E_i$, the quantity to be minimized can be written as:

$$\chi^2 = \frac{1}{N-P} \sum_i \frac{(\tilde{I}_i - I_i)^2}{I_i} \tag{1}$$

where the summation runs over all $N$ data points and $P$ is the number of parameters adjusted. Thus, $\chi^2$ will depend on the parameters to optimize through the expressions chosen for $\tilde{I}_i$. Since these are complicated functions, the procedure involves a non-linear least-squares fitting, and the risk of falling in local minima is not negligible. In order to reduce this risk, the initial guess for the parameters must be quite close to the correct values. An alternative way to overcome the problem is to begin with different estimates and check that the same minimum is achieved.

It is worth to emphasize that the procedure proposed here is devoted to the refinement or optimization of parameters, and it is not *per se* a method for determining them. Nevertheless, it may become a fundamental tool when associated to a quantitation routine. For example, as shown in Sec. 3.3, this procedure allows to improve the mass concentrations given by the program MULTI [5] for standardless peak-to-background quantitation.

The outline of this paper is as follows: in Sec. 2 theoretical support is given for the prediction of whole spectra in EPMA, as well as a description of the method proposed for parameter optimization. Some applications are presented in Sec. 3; these include the characterization of detector properties, the refinement of atomic transition rates and the optimization of sample compositions. Finally, in Sec. 4, some conclusions are drawn, and

a discussion about potential applications of the method is given.

# 2 Development of the method

The structure of the method is supported on two different bases. On the one hand, a full theoretical description is given for spectra acquired in EPMA. On the other hand, a numerical procedure is used to minimize the differences between experimental and calculated spectra.

## 2.1 Prediction of spectra

In order to predict a spectrum, a complete knowledge of the x-ray bremsstrahlung production, characteristic radiation emission and detection artifacts is required.

According to a previous work [6], the continuum spectrum corresponding to the emission of bremsstrahlung can be expressed as an analytical function of photon energy $E$, mean atomic number $\bar{Z}$ and incident energy $E_o$ of the electron beam impinging on the sample:

$$B = \alpha\sqrt{\bar{Z}}\,\frac{E_o - E}{E}\left[54.86 - 1.072E + 0.2835E_o + 30.4\ln\bar{Z} + \frac{875}{\bar{Z}^2 {E_o}^{0.08}}\right]\mathbf{A}\,R\,\epsilon\,\frac{\Delta\Omega}{4\pi} \quad (2)$$

where $\alpha$ is a constant proportional to the number of incident electrons, $\mathbf{A}$ corrects for x-ray absorption, $R$ takes into account intensity losses due to electron backscattering, $\epsilon$ is the detector efficiency at energy $E$ and $\Delta\Omega$ is the solid angle subtended by the detector. This simple analytical function has shown a very good performance for a wide set of experimental spectra as compared to other models.

The spectral peaks have a strong dependence on mass concentrations $C$ and therefore they are the basis of any quantitative approach. The detected characteristic intensity $P_{j,q}$ of the line $q$ from element $j$ in the sample can be written as [7]:

$$P_{j,q} = \beta\, C_j(\mathbf{ZAF})_{j,q}\, Q_j\, \omega_j f_{j,q}\, \epsilon_{j,q}\, \frac{\Delta\Omega}{4\pi} \quad (3)$$

where $\beta$ is a constant proportional to the number of incident electrons; $\mathbf{Z}$, $\mathbf{A}$ and $\mathbf{F}$ indicate the atomic number, absorption and fluorescence matrix corrections, respectively; $Q_j$ is the ionization cross section for element $j$ at the energy $E_o$, $\omega_j$ is the fluorescence yield for the considered atomic (sub)shell and $f_{j,q}$ is the transition rate related to the observed line $q$. The so-called $\mathbf{ZAF}$ corrections depend on the sample concentrations in a complicated way, and a number of different models has been proposed for them [8].

A description of the interaction between electrons and matter involving an ionization distribution function $\phi(\rho z)$ with mass depth $\rho z$ was considered for this work to account for both **Z** and **A** correction factors. Packwood and Brown's [9] description of $\phi(\rho z)$ was taken as a basis for the more realistic model [10] used in the present method. The first applications of the method presented in this work do not include the **F** correction factor, since it is not very important in the samples studied. The fluorescence yield coefficients were taken from Hubbell [11], whereas transition rates are usually optimized (see Sec. 3).

Once bremsstrahlung and characteristic emission are taken into account, a number of effects produced during x-ray detection must be considered. In different x-ray analytical techniques, the most commonly used detectors are solid-state based, particularly lithium-drifted silicon detectors, Si(Li). For this kind of detectors, the basic detection process involves a proportional conversion of photon energy into electrical signal, which is shaped and amplified, and then passed to a multichannel analyzer. A relationship between the channel number in which photons are registered and the corresponding energy must be supplied. Usually, a linear calibration is implemented in the detection systems by means of two parameters, namely the *gain* and the *zero*. These two parameters depend on the detection chain settings, and they are known at least to a first approximation.

The detector system response for photons of energy $E$ is a more or less broadened peak, whose distribution can be considered as Gaussian to a first approximation; its standard deviation $\sigma$ being a function of photon energy [12]:

$$\sigma \;=\; \left(n^2 + \varepsilon F E\right)^{1/2} \tag{4}$$

where $n$ is the uncertainty due to the electronic noise of the amplification process, $F$ is the Fano factor and $\varepsilon$ is the mean energy required for a single electron-hole pair formation —in Si(Li) detectors at 77°K, 3.76 eV.

Another important feature of the registered spectrum which must be accounted for is the detector efficiency. In a Si(Li) detector, the efficiency is close to 100% above 3 keV, but falls at lower energies owing to absorption in the isolation window (except for windowless detectors). Typically, three different thicknesses must be known: a thickness specific of the window (usually made of beryllium), a gold layer contact evaporated onto the front surface, and a dead silicon layer.

An additional artifact of spectra collected with Si(Li) detectors is a spurious Si peak due to the photoelectric absorption of the photon to be detected, within the dead Si layer of the detector. When this process occurs, the Si-$K$ photon may enter the active region and be registered, whereas Auger and photoelectrons are much more likely to be absorbed in the dead layer [13]. As a result, a photon of only 1.739 keV, corresponding to the Si-$K$

peak is registered instead of the one actually emitted by the sample. The height of this spurious peak is difficult to estimate and it may lead to a wrong quantitation when silicon is present in the sample.

Finally, some of the charge carriers produced by a photon arriving at the detector may be "trapped" before being collected. Thus, the output sent to the amplifier corresponds to an energy lower than the original one. This effect is manifested in asymmetrical peaks with low energy tails, departing from the assumed Gaussian shape. Since the highest concentration of traps occurs in a transient region close to the detector surface, between the active volume and the dead layer, peaks appear to be more asymmetric for soft x-ray lines. Therefore, a modification to the Gaussian function is necessary in order to account for this effect.

There are two further artifacts which have not been considered in this first stage, since they would not influence the results. First, there is a finite probability that Si-$K$ photons produced in the detector following absorption of an incident photon will escape from the detector. In this event, the energy of the escape photon is not deposited in the detector, and the height of the consequent pulse is correspondingly reduced, i.e., an "escape peak" occurs 1.739 keV below the main peak. Second, two pulses may reach the main amplifier within a very short time interval, resulting in the appearance of a spurious peak in the spectrum, corresponding to the sum of the energy of the two original pulses.

## 2.2 Optimization of parameters

The functional behaviour of the whole spectrum can be achieved following the description of the previous paragraphs. However, some parameters may not be precisely known *a priori*; the challenge is therefore to find the set of parameters which best fits the general shape of the proposed function to the experimental spectrum:

$$\tilde{I}_i \;=\; B(E_i) + \sum_{j,q} P_{j,q}\, H_{j,q}(E_i) + P_{\mathrm{Si}}\, G_{\mathrm{Si}}(E_i) \tag{5}$$

where $E_i$=*zero*+$i\cdot$ *gain* is the energy corresponding to channel $i$, $H_{j,q}$ is a modified Gaussian function (see Sec. 3.1.3) associated to the peak intensity $P_{j,q}$ and $P_{\mathrm{Si}}$ is the internal fluorescent Si peak, spread by means of a Gaussian distribution $G_{\mathrm{Si}}$. The parameters which may be optimized are: the scaling factors $\alpha$ and $\beta$ of Eqs. (2) and (3), the *zero* and *gain* of the detection chain, the peak-width factors $n$ and $F$ of Eq. (4), the transition rates $f_{j,q}$, the fluorescence yields $\omega_j$ and the mass concentrations $C_j$ of Eq. (3), the three parameters involved in the function $H_{j,q}$ for each peak, the three thicknesses associated to the detector efficiency, the amplitude of the $P_{\mathrm{Si}}$ peak, the transition energies for the involved decays, etc.

Since $\tilde{I}_i$ of Eq. (5) is involved in Eq. (1), the algebraic complexity of the expression for $\chi^2$ requires a numerical procedure for its minimization. Even when no perfect minimization procedure exists, certain characteristics of a given routine make it suitable for a particular application. Among the different possibilities (see, e.g. Ref. [14]), the downhill simplex algorithm [15] was chosen because, besides being a robust routine, it requires only function evaluations, not derivatives. This fact is particularly important since it is often necessary to deal with functions whose computed derivatives do not accurately point the way to the minimum, usually because of truncation error in the method of derivative evaluation.

It must be kept in mind that minimization methods can lead to a local minimum instead of the desired global minimum. A good way to overcome this problem is to start from a reasonable initial guess for the parameters to optimize; in addition, it is frequently a good idea to restart the minimization routine at the point where it claims to have found the minimum, reinitializing certain ancillary scale factors [14]. Another solution for confirming that the minimum found is the global one, is trying to get it by starting from widely varying initial values for the parameters.

Usually, it is helpful to carry out the procedure by choosing one or two parameters at a time; once their values have been achieved, they are set fixed and other reduced group of parameters is allowed to vary. When all the chosen parameters are refined, the procedure may be restarted with the obtained values as initial guesses, varying all of them simultaneously. Sometimes, a visual examination of the intermediate results is required in order to make an appropriate decision for the strategy to adopt. For this purpose, it is useful to plot the predicted and experimental spectra, as well as their differences, after the criterium of convergence is fulfilled.

The optimization method described above was implemented in the computer program POEMA —an acronym for Parameter Optimization in Electron Microprobe Analysis. The applications shown in next section have been carried out by means of this program.

# 3 Some applications

In order to show the capabilities of the proposed method, several spectra of standard samples were used, measured in a CAMECA SX-50 microprobe with a Si(Li) detector. Depending on the parameter to be refined, different spectral regions were considered, since the influence of each parameter shows up at different energy ranges.

The program developed allows to modify the input file, in order to choose the parameters to be optimized. As explained in Sec. 2.2, the best choice is to begin with the

refinement of a few parameters; for the examples presented below, the first refinement is always performed on the overall scale factors $\alpha$ and $\beta$ for the continuum spectrum and the characteristic lines, respectively. Typically, after this first step, an additional refinement of the calibration and detector response parameters is necessary, particularly when experimental conditions are changed. As an example, Figure 1 shows the spectrum fitted for a pure cobalt sample, as well as the set of optimized parameters. Logarithmic scale is used in this and next plots, in order to emphasize relative differences between experimental and predicted values. For this case, the value for the transition rate was taken from Salem [16]. As can be seen, the whole predicted spectrum shows a very good agreement with experimental data, with $\chi^2 = 1.79$. The Fano factor achieved is in agreement with typical values [17]. The good performance of this application of the method implies that the models used for the different processes involved are correct, specially those related to the generation and absorption of bremsstrahlung and fluorescent lines.

## 3.1 Detector characteristics

### 3.1.1 Detector thicknesses

As mentioned in Sec. 2.1, three thicknesses must by supplied in order to know the detector efficiency at low photon energies (less than 3 keV). These thicknesses are usually provided by the detector manufacturer, but their values may change with time due to different reasons. The beryllium window often gets stained, usually because of the presence of oil molecules coming from the vacuum pump. On the other hand, the cooling system may favour the nucleation of water molecules, resulting in the growth of ice crystals on the gold surface layer. Finally, the dead silicon layer may be modified because of the migration of lithium atoms within the crystal. Since it is very difficult to measure each of these thicknesses, the method of parameter optimization is proposed as a tool to solve this problem.

For the sake of simplicity, each thickness is assumed to remain monoelemental after contamination. Bearing this hypothesis in mind, the efficiency curve of a Si(Li) detector at low energies was characterized. The "effective" thicknesses were optimized by using four different pure samples. According to the results shown in Table 1, reasonable values were found, showing an acceptable agreement among the different samples used. The mean values obtained for each thickness have been used for all the spectra fitted in the present work.

Table 1: Characteristic detector thicknesses determined by using four pure samples.

| Sample | Be ($10^{-4}$ cm) | Au ($10^{-6}$ cm) | Si ($10^{-5}$ cm) |
|---|---|---|---|
| Ti | 9.6 | 1.9 | 2.9 |
| V | 9.1 | 2.1 | 2.9 |
| Mn | 9.0 | 1.6 | 2.7 |
| Co | 8.9 | 2.0 | 2.5 |
| Average | 9.2 | 1.9 | 2.8 |

### 3.1.2 Internal fluorescent peak

As can be seen from Fig. 1, a small peak appears below 2 keV. This spurious Si peak has been mentioned in Sec. 2.1 as inherent to the detection process. Its height is difficult to predict because it depends in a complicated way on the detector geometry and on the photon spectrum itself. For this reason, it is a parameter typically refinable by the optimization process, starting from an initial value estimated by visual observation of the spectrum. When silicon is present in the sample, it is necessary to determine previously the internal fluorescent peak height in a sample of similar composition, but without silicon. The good fit achieved for the Si peak illustrated in Fig. 1 shows the usefulness of the method for this application.

### 3.1.3 Incomplete charge collection

As explained above, when not all charge carriers reach the detector electrodes, a reduction on the registered pulse height results in "tailing" in the low energy side of the peak. For this reason, an asymmetrical correction to the ideal Gaussian peak is required. In the present work, the Hypermet [18] function was chosen:

$$H_{j,q}(E_i) = M[G_{j,q}(E_i) + S_{j,q}(E_i) + T_{j,q}(E_i)]$$

where $M$ is a normalization factor, $G_{j,q}(E_i)$ is a Gaussian function centered at the characteristic energy $E_{j,q}$:

$$G_{j,q}(E_i) = \frac{1}{\sqrt{2\pi}\,\sigma_{j,q}}\,\exp\left[-\frac{(E_i - E_{j,q})^2}{2\,\sigma_{j,q}^2}\right],$$

$S_{j,q}(E_i)$ is the step function of height $s_{j,q}$ convoluted by the Gaussian:

$$S_{j,q}(E_i) = s_{j,q}\,\mathrm{erfc}\left(\frac{E_i - E_{j,q}}{\sqrt{2}\,\sigma_{j,q}}\right)$$

and $T_{j,q}(E_i)$ is an exponential tail of width $\beta_{j,q}$ and height $t_{j,q}$ convoluted by the Gaussian:

$$T_{j,q}(E_i) = t_{j,q}\, e^{(E_i - E_{j,q})/\beta_{j,q}}\ \mathrm{erfc}\left(\frac{E_i - E_{j,q}}{\sqrt{2}\,\sigma_{j,q}} + \frac{\sigma_{j,q}}{\sqrt{2}\,\beta_{j,q}}\right).$$

In these functions, the parameters $s_{j,q}$, $t_{j,q}$ and $\beta$ are not known *a priori* and must be refined if peak asymmetries are taken into account. Figure 2 shows a clear example in which peak-shape corrections for Ca $K$-lines are unavoidable, in a dolomite sample.

## 3.2 Transition rates

Inner shell transition probabilities have extensively been dealt with. The reason for which special attention has been paid to transition rates is mainly because reliable experimental values can be used as a straight test for theoretical atomic models. Particularly, separate relativistic Hartree-Fock solutions for atoms in their initial and final states have been used for calculating radiative decays of $K$ or $L$ vacancy states [19, 20]. On the other hand, spectroscopic techniques based on x-ray emission analysis have largely evolved during the last decades. This is mainly due to its non-destructive nature —which enables the reproducibility of results—, as well as to the low detection limits achieved (ppm and ppb levels). The adequate knowledge of transition rates allows to improve the analyses, since peak overlaps between e.g. $K\alpha$ and $K\beta$ lines of neighbouring elements are frequently a problem for the analyst.

The spectra selected for this example were first fitted to find adequate values for scale factors and detector response, as explained above. Once the proper values for these parameters have been achieved, they are fixed and the line fractions are refined instead. In this particular case, it is convenient to perform the refinement along with the peak scale factor $\beta$ of Eq. (3), since changes in the intensity ratios may influence its value.

Table 2: Transition rates for $K$ decays determined by the method proposed in this work compared with values from the literature.

| Element | This work | Ref.[19] | Ref.[21] |
|---|---|---|---|
| Ca | 0.890 | 0.884 | 0.887 |
| Ti | 0.886 | 0.881 | 0.884 |
| V | 0.883 | 0.880 | 0.883 |
| Cr | 0.883 | 0.882 | 0.883 |
| Fe (in siderite) | 0.884 | 0.878 | 0.882 |
| Co | 0.880 | — | 0.881 |

The values obtained for transition rates are compared with theoretical [19] and experimental [21] data from the literature in Table 2. These line fractions are taken as the ratios between $K\alpha$ intensities and total $K$ ($K\alpha + K\beta$) intensities. As can be seen, a good agreement is achieved, following the general trend of experimental and theoretical data.

The good performance of this method for $K$ ratios encourages to study relative transitions involving decays to different inner atomic shells, for which measurements and theoretical predictions are more difficult.

### 3.3 Sample composition

Most analytical techniques are based on the determination of characteristic intensities detected from the sample of interest and from reference standards. The method presented here allows the refinement of concentrations in the irradiated material by means of the best fit of a unique spectrum. With the purpose of showing the capabilities of this method in this kind of application, several samples of known composition have been analyzed.

The first example involves a cobalt oxide, for which nominal mass concentrations are 78.65% Co and 21.35% O. Despite its simplicity, this is a very interesting situation, since neither a characteristic peak is observed for oxygen nor standards are used. In addition, the stoichiometric relationship is assumed to be unknown, although the information that there is no further element is taken into account by normalizing to 100%. As mentioned above, initial values for the parameters should not be too different from the correct ones, since the risk of falling in local minima for $\chi^2$ must be avoided. Nevertheless, in this case the respective inital values were set as 83% and 17%, rather apparted from the true values. The strategy followed was to refine only the cobalt concentration and the overall scale factors. After a first iteration, both concentrations were renormalized to 100% and given as input for a further iteration. This strategy has been repeated until convergence. The final values achieved were 78.14% Co and 21.86% O, which are in very good agreement with the nominal composition.

The next specimen considered is a siderite sample, whose nominal concentrations are shown in Table 3. In this case, the specimen composition was first estimated by means of the standardless peak-to-background algorithm of Trincavelli and Van Grieken [7], as included in program MULTI [5]; to this end, stoichiometric relationships were considered for determining carbon and oxygen. For the refinement of concentrations by means of the method presented here, normalization to 100% was used as in the previous example. The good fit achieved for this example is shown in Fig. 3. As can be observed, the problem of peak overlapping is adequately overcome —in this case, Mn-$K\beta$ and Fe-$K\alpha$. Table 3 shows how the good estimates obtained by means of MULTI are improved, particularly

Table 3: Mass concentrations calculated by program MULTI and optimized by this work, as compared to nominal values for a siderite sample.

| Element | MULTI | This work | Nominal |
|---|---|---|---|
| Fe | 46.35 | 45.36 | 45.93 |
| Mn | 2.98 | 2.27 | 2.28 |
| O | 40.71 | 42.08 | 41.45 |
| C | 9.96 | 10.29 | 10.34 |

for minor elements.

It is worth noticing that when input values are very close to the nominal concentrations, the stability of the method must hold. This condition is fulfilled only if a good theoretical description of the whole spectrum is given, and a robust numerical minimization routine is provided. This fact is illustrated in Table 4, in which a dolomite sample is characterized: the predictions given by program MULTI are very good, and consequently, the present method slightly improves them.

Table 4: Mass concentrations calculated by program MULTI and optimized by this work, as compared to nominal values for a dolomite sample.

| Element | MULTI | This work | Nominal |
|---|---|---|---|
| Ca | 21.63 | 21.68 | 21.75 |
| Mg | 13.58 | 13.56 | 13.13 |
| O | 51.82 | 51.75 | 52.12 |
| C | 12.96 | 12.94 | 12.93 |

# 4 Conclusions

A versatile method for parameter optimization has been presented, which allows the refinement of different magnitudes of interest in the frame of atomic physics as well as analytical and physical chemistry. Although in this work only EPMA spectra have been used, the scope of the proposed method includes other spectroscopic techniques, such as X-Ray Fluorescence, Particle Induced X-Ray Emission, etc., for which the corresponding theoretical description of Sec. 2.1 should be supplied.

An important feature of this methodology is the capability of refining atomic parameters such as radiative decay rates, Coster-Kronig yields, fluorescence yields, mass attenuation coefficients for low photon energies, etc. Some examples of $K$-shell transition rate refinement have been given here, showing a very good performance. In view of these results, work is being done in the study of $L$-shell transition rates. Additional applications may be carried out in the refinement of some of the parameters involved in modelling characteristic lines and bremsstrahlung spectrum. Alternatively, the effect of chemical bonds on transition rates and energies can also be faced by means of the procedure of parameter optimization proposed.

The method implemented in this work achieves a very good description of whole spectra in Electron Probe Microanalysis. The good performance shown in the examples given above, with $\chi^2$ values less than 2, is reflected in values for the parameters optimized very close to the corresponding expected ones. This fact suggests that the methodology proposed here may become a powerful tool for the refinement of fundamental atomic magnitudes, as well as an essential stage for standardless quantitation routines.

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FIGURE CAPTIONS

Figure 1: Fit for a pure Co spectrum irradiated at 20 keV. Dots: experimental; solid curve: fitted spectrum. The values for the refined parameters are also shown.

Figure 2: Spectral region including Ca $K$-lines fitted for a dolomite sample. Dots: experimental; dashed curve: best fit using a Gaussian distribution for the peaks; solid curve: best fit using the Hypermet function.

Figure 3: Spectral region fitted for a siderite sample. Dots: experimental; solid curve: fitted spectrum.