Study of the provenance of *Terra sigillata* by Mössbauer spectroscopy

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Summary. Mössbauer spectroscopy has been applied to the characterization of archaeological potsherds and has been found to be able to provide information on the provenance of *Terra sigillata*. Spectra and parameters are described in detail.

Introduction

The introduction of Mössbauer spectroscopy in the study of archaeological artifacts is one of the additions to physical analytical techniques that have been widely used in the elucidation of archaeological problems [4, 7]. The importance of these techniques is based on the presumed elimination of subjectivity in criteria used by archaeologists to classify and extract information from ancient objects.

In the past few years, Mössbauer spectroscopy has been applied to the characterization of archaeological potsherds and has been found to be able to provide information on the provenance and manufacture of ancient pottery; the greater part have been devoted to *57*Fe studies [2, 3, 6, 9, 12].

Pottery wares are of prime importance in archaeology as cultural items, indexes of artistic and technological skill, and objects of extensive trade in the ancient world.

Ceramic pastes consist of combinations of several clay minerals together with lesser amounts of iron oxides and hydroxides (typically *α*-Fe2O3, *α* and *β*-FeOOH) and organic materials. Of the clay minerals, illite and chlorite contain the largest concentration of iron, which may be up to a few percent, either as ferrous or ferric ions substituted in octaedral sheets [11].

A *57*Fe Mössbauer study of archaeological potteries has been used in research of the provenance of *Terra sigillata* (fine tableware of the Roman Era), whose ceramic paste is made with aluminosilicates with a high content of iron.

These fragments were found in the archaeological site of *Victrix-Iulia-Celsa*, Zaragoza, Spain; whose origins of manufacture are Italic and Gaulish.

Experimental

**Apparatus**

A constant acceleration drive system and a 512-multichannel analyzer.

- A 20 mCi *57*CoRh source.
- Perkin-Elmer, Plasma 40 spectrophotometer.
- Perkin-Elmer, model 2380, atomic absorption spectrophotometer.
- Digital equipment VAX 8300 Computer.

**Procedure**

Mössbauer spectra were recorded at room temperature. The calibration was done by using an *α*-Fe absorber. All experimental isomer shift values are given with respect to *α*-Fe.

The powdered ceramic samples were prepared with the optimal thickness given by the expression [5]:

\[ t = \frac{2}{\sum f_i \mu_{e,i}} \]

where:
- \( t \): optimum sample absorber thickness (g · cm\(^{-2}\)).
- \( \sum f_i \mu_{e,i} \): electronic mass absorption coefficient for the Mössbauer γ-rays of the *i*-th element (cm\(^2\) · g\(^{-1}\)).
- \( f_i \): mass fraction of the *i*-th element.
- \( i \): number of elements in the sample.

For these samples, \( t = 150 - 200 \text{ mg} · \text{ cm}^{-2} \).

The spectra were evaluated by a standard least-square fitting procedure.

Results and discussion

The five chosen samples of *Terra sigillata* have different place of manufacture. They are calcareous, their chemical compositions (Al, Ca, Fe, Mg, K, Ti, Mn and Sr) have been studied with atomic spectrometry (flame-AAS and ICP-AES) (Table 1) [1].

The shape of Mössbauer spectra is shown in Figs. 1 - 5. For fragments of *Terra sigillata*, a non-magnetic component (a doublet, due to structural iron, Fe\(^{3+}\)) and a magnetic sextet (it can be attributed to iron oxides, *α*-Fe2O3) are observed in room temperature spectra; this is because of...
Table 1. Chemical composition in percentage of oxide of the elements of the samples

<table>
<thead>
<tr>
<th>Element</th>
<th>S-191</th>
<th>S-194</th>
<th>S-192</th>
<th>S-241</th>
<th>S-10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>19.24</td>
<td>18.44</td>
<td>18.32</td>
<td>18.68</td>
<td>23.89</td>
</tr>
<tr>
<td>CaO</td>
<td>9.17</td>
<td>10.55</td>
<td>11.07</td>
<td>7.48</td>
<td>12.00</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>7.73</td>
<td>7.24</td>
<td>7.30</td>
<td>5.56</td>
<td>5.87</td>
</tr>
<tr>
<td>MgO</td>
<td>4.61</td>
<td>4.55</td>
<td>4.71</td>
<td>5.71</td>
<td>3.05</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.99</td>
<td>1.12</td>
<td>0.91</td>
<td>1.40</td>
<td>1.07</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.93</td>
<td>0.90</td>
<td>0.89</td>
<td>0.65</td>
<td>1.11</td>
</tr>
<tr>
<td>MnO</td>
<td>0.174</td>
<td>0.165</td>
<td>0.160</td>
<td>0.077</td>
<td>0.114</td>
</tr>
<tr>
<td>Sr⁶⁺</td>
<td>527.1</td>
<td>540.1</td>
<td>600.4</td>
<td>629.9</td>
<td>609.1</td>
</tr>
</tbody>
</table>

*a μg·g⁻¹

Fig. 1. Mössbauer spectrum of sample S-191

Fig. 2. Mössbauer spectrum of sample S-194

Fig. 3. Mössbauer spectrum of sample S-192

Fig. 4. Mössbauer spectrum of sample S-241

Fig. 5. Mössbauer spectrum of sample S-10

the oxidizing firing atmosphere used for this pottery (a special firing method, oxidizing-oxidizing, at 900—1100°C) [10]. Their parameters: isomer shifts (IS), quadrupole splittings (QS) and magnetic hyperfine fields (HF), and ratios of the area of the magnetic subspectrum to the total spectrum (Table 2) gave interesting differences and they helped to the identification of potsherds.

The variation of Mössbauer parameters and relative areas of the magnetic subspectra with the different samples (represented by their percentages of CaO) can be observed in Figs. 6—8.

In some samples (S-10 and S-241), the hyperfine magnetic field is smaller than for a pure α-Fe₂O₃ (515 K G) and this could suggest that the iron would be partially substituted by various impurities, probably aluminium (Fe₁₋ₓAlₓ)₂O₃ or other substitutional impurities, and it may be due even to other factors like vacancies, small particles sizes, etc.

Because of the firing temperature (900—1100°C) and the parameters of the quadrupole doublet (IS and QS), we could say that it is a doublet typical of Fe³⁺ in octahedral coordination, in the place of Al³⁺ in the lattice.

The smaller quadrupole splittings (QSD) are due to the crystallographic rearrangement of kaolinite to form mullite and cristobalite near 980°C, though the final value of QSD is dependent on the firing temperature and the firing sequence.

The value of quadrupole splitting of the doublet is also dependent on the nature of the original clay: calcareous or non-calcareous [8]. The QSD of the calcareous clays fired at 900—1100°C is higher than that of the non-calcareous, due to the high content of small-particle oxides of the former.