Micro-analysis of Artists’ Pigments by Grazing-Emission X-ray Fluorescence Spectrometry

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Abstract

The potential of a prototype Grazing-Emission X-ray Fluorescence (GEXRF) instrument for analyzing artists’ pigments is described in terms of elemental sensitivity, absolute detection limits, peak-to-background ratio, time of analysis and range of detectable elements. Artificial paint layer samples and pigments sampled from the 17th century painting “Madonna with child”, attributed to the Antwerp Baroque painter Pieter Thijs, were used in this study. GEXRF is a new analytical X-ray fluorescence technique using the same advantages of the total reflection phenomenon as the related TXRF technique. Its sensitivity for light elements and the experimental simplicity can make GEXRF suitable to analyze pigments in a virtually non-destructive way. GEXRF will not replace but rather complement other techniques used for pigment analysis. A characterization of the different present coloured paints and pigments can be performed by such analysis. Micro-analysis of artists’ pigments is valuable in art history studies.
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and authentication, conservation and restoration of paintings.

1. Introduction

Several instrumental techniques are nowadays applied to pigment analysis; one of the most popular is X-ray fluorescence spectrometry (XRF). The *in situ* XRF mode of application requires a particular large-scale mechanical construction in order to reach any point of a painting, and, unfortunately, the method is not specific to the analysis of the upper pigment layer since it ambiguously incorporates the ground layer and even the support [1]. A major drawback of conventional XRF is the requirement that pigment samples need to be removed from the paint by means of a scalpel or needle to be analyzed in a laboratory instrument; this involves taking sample amounts of about 0.5 mg or more, leaving visible marks on the painting [2]. Using total reflection X-ray fluorescence (TXRF), a variant of XRF, the required sample mass can be reduced to 0.5 µg or less, by applying a unique ultra-microsampling technique, primarily introduced by Moens et al. [3]. Such sampling by means of a cotton-wool bud (Q-tip) is virtually non-destructive. A restriction of the TXRF technique is the insensitivity for elements with atomic number below 11, mainly due to absorption in the Be-window of the energy-dispersive (ED) detection system. Using a wavelength-dispersive (WD) detection system in the TXRF set-up could resolve this instrumental limitation; however, in practice this is not feasible due to intensity losses that occur during the monochromatization and collimation of the primary X-ray beam. An alternative experimental arrangement with the use of a WD-detection system is to employ an incident beam that impinges perpendicularly to the surface and to detect the fluorescent radiation at grazing emission angles. It has been demonstrated that X-ray emission at grazing angles is also surface sensitive [4]. This has led to the development of the Grazing-Emission mode of XRF (GEXRF) [5,6]. Because GEXRF can be combined with a wavelength-dispersive form of
detection, an improved spectral resolution for the radiation of light elements can be realized. In this paper, the analytical characteristics of GEXRF and TXRF (detection limits, sensitivity and peak-to-background ratio) will be compared. The purpose of this investigation is to establish whether GEXRF can be applied in this area of analysis and to obtain a clear idea of the limitations and/or advantages this novel variety of XRF may have in comparison to conventional XRF and to TXRF.

2. Experimental

Instrumentation

The experimental configuration of GEXRF is illustrated in Figure 1. An optically flat carrier is irradiated vertically with an uncollimated, polychromatic X-ray beam. The fluorescent radiation is detected at grazing angles (mrad) in such way that scattered radiation generated in the support material cannot reach the detector, leading to a reduction of the scatter background. Further principles and applications of this method are described elsewhere [7-10].

![Figure 1: Instrumental set-up of GEXRF](image)

In this study, a prototype GEXRF module, inserted in a commercial Philips PW2400 WD-XRF spectrometer (Philips Research Laboratories, Almelo, The Netherlands) was used. Samples were
placed onto polycarbonate carriers and were excited by means of an unfiltered rhodium tube, operating at a voltage of 40 kV and a current of 70 mA. Typical counting times of 1000s for each element (including measurement of the background next to the peak) were applied. Alignment of the fluorescence beam is performed with a double-slit collimator. The slit width can be adjusted to reach the most profitable compromise between angular resolution and detected intensity; two GEXRF modules, one with fixed collimation slits of 50 μm and one with an adjustable slit pair (up to 500 μm opening) were applied to investigate the advantage of the latter. To obtain the lowest absolute detection limits, one should sacrifice angular resolution for intensity, i.e. use wider slit settings in the collimator. Measurements for each element were performed under the "isokinetic angle" [11], where equal responses for particle and film sample deposits on a sample carrier are obtained.

TXRF analyses were performed with a commercially available Extra II instrument (Rich. Seifert & Co., Ahrensburg, Germany), equipped with both molybdenum and tungsten tubes, and a Si(Li) detector (Oxford Analytical/Link Systems Ltd., Abingdon, England) and multichannel analyzer. A voltage of 50 kV and a current of 5-38 mA were applied for excitation. Samples were measured on quartz glass carriers for about 100 s.

Furthermore, the analytical characteristics of a conventional EDXRF spectrometer were measured with a TN-Spectrace 5000 XRF analyzer. The instrument was operating at a voltage of 40 kV and a current of 0.2 mA.

**Specimen preparation**

In order to collect the pigment samples from the 17th century painting, the sampling
method for pigment analysis described by Moens et al. [3] for TXRF analysis, was used. This procedure involves rubbing a dry and clean cotton wool bud over a spot of the pigment layer and afterwards tapping/rubbing the bud on the surface of a quartz or polycarbonate substrate [7], so that a number of pigment particulates previously removed from the painting, are deposited onto the substrate. This sampling method can only be employed during restoration of the painting since varnish or other protective layers must be removed before sampling. Only relative elemental concentrations can be assessed since the mass of the pigment particulates on the support cannot be determined in its entirety (typically less than 100 ng of pigment is present) [12].

Next to pigment samples from a 17th century painting, samples were also taken from artificially made paint layers. These consisted of pieces of hard board, coated with a chalk-glue mixture (as is usually the case in Baroque paintings on wooden backing) on top of which a layer of oil paint (usually prepared by mixing a single pigment with either linseed or walnut oil) was applied. Test plates of vermilion (red), azurite (blue), smalt (blue) on a chalk glue (white) base layer were prepared.

In order to establish the elemental yields for the three spectrometers which were employed, NIST SRM 1832 and NIST SRM 1833 “thin-glass film” standards (for regular EDXRF), a self prepared mixture (1 µg/g) of the following elements Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Sr, Ba, Tl, Pb, Bi (for TXRF) and a multi-element solution of 1 µg/g (Merck, ICP solution IV, Darmstadt, Germany) (for GEXRF) were used. For TXRF and GEXRF analysis, standard solutions were pipetted directly onto their respective substrates and were dried on a hot plate or under an IR-lamp.
The painting

Samples were taken from the painting of the 17th century "Madonna with Child" (property of the city of Antwerp, Belgium), probably from the hand of a pupil of Antoon Van Dijck, called Pieter Thijs. A particular interest of the restorer concerned the sites shown in Figure 2. Six sampling sites were selected on the various coloured parts of the painting so that the largest variety in the sampled pigment material was obtained. The sampling sites were located in the coat (M1, blue), the dress (right breast, M2, red), the veil (M3, dark brown), the peach (M4, yellow/orange), the pomegranate (M5, green/yellow) and the background (M8, brown/dark blue).

3. Results and Discussion

3.1 Comparison of analytical characteristics

As TXRF and GEXRF, variants of the common XRF technique, are directed towards reducing the spectral background, it is useful to determine the peak-to-background ratio and the absolute detection limits achievable with these three techniques. Furthermore, it is of interest to know the elemental yield of the applied techniques in order to perform pigment sample analysis. The elemental yield (sensitivity) is determined by using the following formula [13]:

$$S(Z) = \frac{N(Z)}{t(s) \cdot m(Z)}$$

with $S$ expressed in counts/s/ng and where $Z$ is the atomic number, $N$ is the net peak intensity, $t$ the measuring time and $m$ the mass deposited on the carrier. Figure 3 shows the elemental yields obtained for the EDXRF and TXRF spectrometers and for the GEXRF spectrometers with fixed...
Figure 2: Painting "Madonna with Child" by Pieter Thijs (17th century, Antwerp)
slits of 50 µm and adjustable slits sizes up to 500 µm. TXRF sensitivities (between 10-100 counts/s/ng) are two orders of magnitude lower than obtained with a conventional XRF technique.

![Elemental yield](image)

Figure 3: Elemental yield, expressed in counts/s/ng, of GEXRF, using 50 µm and 500 µm slit width, compared to TXRF and EDXRF.

The elemental yield for the GEXRF system is in the region of 0.3 to 16 counts/s/ng, when the module equipped with the adjustable slits is used. As can be expected, the use of a 500 µm wide slit opening results in an improvement of about a factor of 100 compared to the GEXRF module applying a fixed (50 µm wide) double-slit collimator. Due to the total reflection phenomenon and/or the instrumental arrangements, TXRF and GEXRF are characterized by a reduced background and thus have better detection limits compared to conventional EDXRF.
limits (DL) are calculated according to:

\[ DL = \frac{3\sqrt{N_b}}{N_{net}} m_{sample} \]

where \( N_b \) is the peak background area, \( N_{net} \) is the net peak area and \( m_{sample} \) is the sample mass [13]. In all cases, the measuring time was normalized to 100 s for each element. The absolute detection limits, obtained by means of matrix-free standard solutions, are shown in Figure 4 and are situated at the low-picogram level (Cr: 60 pg) for TXRF and in sub-nanogram level (Cr: 300 pg) for GEXRF using the adjustable slits. Detection limits in GEXRF are improved by a factor of 100 when the wide slit settings are applied, although the latter result in a worse angular and energy resolution, which however is still below 50 eV.

![Detection limit (pg)](image)

Figure 4: Absolute detection limits, expressed in pg, of GEXRF, using 50 µm and 500 µm slit width, of TXRF and of EDXRF. Measuring time is normalized to 100 s for each technique.
The peak-to-background ratio indicates even more the difference between EDXRF, TXRF and GEXRF. Although EDXRF has the highest elemental yield, a significant background signal still exists. The low background signal leads to a peak-to-background ratio in between 6 and 60 for TXRF, and between 1 and 40 for GEXRF, as shown in Figure 5. The main drawback of the present GEXRF instrument is the time-consuming aspect: for each sample, the measuring time is 10 times longer than for the corresponding multi-element TXRF measurement.

![Graph showing peak-to-background ratio](image)

**Figure 5:** Peak-to-background ratio of GEXRF, using 50 μm and 500 μm slit width, and TXRF.

### 3.2 Test samples

Test samples, made of a single inorganic pigment, were primarily prepared to investigate whether GEXRF lends itself to the analysis of artist pigments. The obtained intensities and absolute amounts of each element, detected in each test sample are shown in Table 1. Analyses were performed with a fixed slit width of 50 μm; background intensities are obtained from a
blank polycarbonate substrate. Some data in Table 1 are missing because the elemental sensitivities were not available. Since the tests plates are coated with a chalk glue base layer, Ca and Fe are present in all the samples. Furthermore, smalt is characterized by the following elements, Al, K, Si, Co and Pb. This pigment, commonly used in the 17th century, is a moderately finely to coarsely ground potassium glass of blue colour. The blue is due to small (<5%) but variable amounts of cobalt added as cobalt oxide during manufacture. Azurite (2CuCO₃.Cu(OH)₂) is a natural blue pigment, found in many parts of the world in the upper oxidized portions of copper ore deposits. Vermilion is a standard name given to artist’s red synthetic pigment, made by a dry process based on mercuric sulfide (HgS). From the relatively good peak-to-background ratio values, it is obvious that pigment analysis can be performed with GEXRF. As mentioned above, the GEXRF technique is sensitive enough to apply also the ultra-microsampling technique used earlier in TXRF. Even inorganic pigments characterized by light elements, such as smalt, can be identified in minor sample amounts. It should be pointed that test samples are more roughly coated than (previously varnished) paintings and more material will be deposited on the substrates. So higher intensities and a high absolute elemental amount will be obtained for test samples, compared to pigment samples obtained from paintings. Nevertheless, the technique is sensitive enough to examine the latter, when using the module with the adjustable slit opening.
Table 1: Elemental intensities and amounts of detected material derived from test samples analyzed with GEXRF using a 50 µm slit width.

<table>
<thead>
<tr>
<th>A)</th>
<th>Chalk glue</th>
<th>Element</th>
<th>Ca</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Peak intensity (counts/s)</td>
<td>156</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Background intensity (counts/s)</td>
<td>0.9</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Peak to background ratio</td>
<td>173</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Detected amount (ng)</td>
<td>14 800</td>
<td>35</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>B)</th>
<th>Smalt</th>
<th>Element</th>
<th>Al</th>
<th>Si</th>
<th>K</th>
<th>Ca</th>
<th>Fe</th>
<th>Co</th>
<th>Pb</th>
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<tbody>
<tr>
<td></td>
<td>Peak intensity (counts/s)</td>
<td>0.5</td>
<td>4.2</td>
<td>0.8</td>
<td>156</td>
<td>3.6</td>
<td>5.5</td>
<td>47</td>
<td></td>
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<tr>
<td></td>
<td>Background intensity (counts/s)</td>
<td>0.3</td>
<td>0.9</td>
<td>0.6</td>
<td>0.9</td>
<td>0.9</td>
<td>0.5</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Peak-to-background ratio</td>
<td>1.7</td>
<td>4.7</td>
<td>1.3</td>
<td>173</td>
<td>4</td>
<td>11</td>
<td>53</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Detected amount (ng)</td>
<td>72</td>
<td>-</td>
<td>17</td>
<td>14 800</td>
<td>137</td>
<td>-</td>
<td>1.7</td>
<td></td>
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<table>
<thead>
<tr>
<th>C)</th>
<th>Azurite</th>
<th>Element</th>
<th>Si</th>
<th>Ca</th>
<th>Fe</th>
<th>Cu</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Peak intensity (counts/s)</td>
<td>1.3</td>
<td>1.4</td>
<td>2.6</td>
<td>14</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Background intensity (counts/s)</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.7</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Peak-to-background ratio</td>
<td>1.4</td>
<td>1.5</td>
<td>2.9</td>
<td>20</td>
<td>56</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Detected amount (ng)</td>
<td>-</td>
<td>48</td>
<td>86</td>
<td>-</td>
<td>1.9</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>D)</th>
<th>Vermilion</th>
<th>Element</th>
<th>Mg</th>
<th>S</th>
<th>Ca</th>
<th>Fe</th>
<th>Cu</th>
<th>Sr</th>
<th>Hg</th>
<th>Pb</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Peak intensity (counts/s)</td>
<td>0.7</td>
<td>8</td>
<td>15</td>
<td>9.4</td>
<td>23</td>
<td>90</td>
<td>428</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Background intensity (counts/s)</td>
<td>0.3</td>
<td>1.2</td>
<td>0.9</td>
<td>0.9</td>
<td>0.7</td>
<td>1</td>
<td>0.7</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Peak-to-background ratio</td>
<td>2.3</td>
<td>6.7</td>
<td>17</td>
<td>10</td>
<td>33</td>
<td>90</td>
<td>611</td>
<td>61</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Detected amount (ng)</td>
<td>58</td>
<td>-</td>
<td>1348</td>
<td>430</td>
<td>962</td>
<td>-</td>
<td>2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.3 Analysis of painting

In the present study, only qualitative analyses are performed with TXRF and GEXRF since the primary aim of the investigation was to establish to what extent pigment identification is possible with GEXRF. However, some quantification is possible by a normalization to 100% [14]. Qualitative statements are presented in Table 2. Different colours were identified in the painting “Madonna with Child” by Pieter Thijs (Antwerp, 17th century, Rubenianum, Belgium). The blue coat did not contain any Co or Cu, indicating that smalt (Co-glass) or azurite (2CuCO₃·Cu(OH)₂) could not have been used. Probably the organic pigment indigo was utilized to obtain the blue colour. The red parts of the dress of the madonna were painted with vermilion (HgS), mixed with an amount of Fe, probably red ochre. High amounts of Fe together with Mn (very small amounts), on the dark brown veil, could indicate the use of umber besides vermilion, to obtain the dark brown colour, but this is not a conclusive indication. The high intensities of Sn and Pb derived from the yellow-orange pigment used to paint the peach, show, next to Hg and Cu signals, that the painter applied lead-tin yellow (Pb₂SnO₄), mixed with the red pigment, vermilion (HgS) and a green pigment (Cu-green). The pomegranate contains a green Cu-pigment, possibly malachite (CuCO₃·Cu(OH)₂) or verdigris (Cu(CH₃COO)₂·nCu(OH)₂). The background of the painted scene consists of a dark blue colour. Analysis shows besides a large amount of Mn and Fe (probably due to the use of umber), also significant Na, Si and Al signals, which may point to the presence of ultramarine blue (Na₈·₁₀Al₆Si₄O₂₄S₂·₄) are present in smaller amounts. However, ultramarine was very expensive in the 17th century and normally only used for a madonna not for the background.
Table 2: Characteristics of sampling sites

<table>
<thead>
<tr>
<th>Sample site</th>
<th>Description</th>
<th>Colour</th>
<th>Elements detected with TXRF</th>
<th>Elements detected with GEXRF</th>
<th>Attributed pigments</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>blanket</td>
<td>blue</td>
<td>Fe, Zn, Pb</td>
<td>Fe, Sr, Si</td>
<td>indigo (?)</td>
</tr>
<tr>
<td>M2</td>
<td>dress (right breast)</td>
<td>red</td>
<td>Fe, Hg, Ca</td>
<td>Fe, Hg, S, Ca, Sr</td>
<td>red ochre (?)</td>
</tr>
<tr>
<td>M3</td>
<td>veil</td>
<td>dark brown</td>
<td>Fe, Hg, Ca, Zn, Pb</td>
<td>Mn, Fe, Hg, S, Mg, Ca</td>
<td>umber (?)</td>
</tr>
<tr>
<td>M4</td>
<td>peach</td>
<td>yellow/orange</td>
<td>Pb, Hg, Ca, Fe</td>
<td>Sn, Pb, Hg, S, Ca, Fe, Cu</td>
<td>lead-tin yellow vermilion</td>
</tr>
<tr>
<td>M5</td>
<td>pomegranate</td>
<td>green/yellow</td>
<td>Cu, Ca, Fe, Ti, Pb</td>
<td>Cu, S, Cl, Fe, Pb</td>
<td>Cu-green</td>
</tr>
<tr>
<td>M8</td>
<td>background</td>
<td>brown/dark blue</td>
<td>Mn, Fe, Si, Co, Ni, Cu, As, Pb</td>
<td>Mn, Fe, Na, Si, Al, K, Ca, Sr</td>
<td>umber ultramarine blue (?)</td>
</tr>
</tbody>
</table>

Conclusions

The new GEXRF method is suitable for the determination of individual and mixed pigments and screening of paintings under restoration. Sample preparation is easy and non-destructive. The method was proven to be sensitive, also for light elements. However, with the present sequential prototype, analyses are prohibitively very time-consuming. It is obvious that the GEXRF method will not replace (for this application), but rather complement other existing techniques, especially when low Z-elements are to be determined as the key elements in a pigment.

Acknowledgment

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paintings; we also are indebted to Dr. A. Balis and N. Van Hout for their assistance and device during the sampling.

References


