


Pigment particles analysis with a total reflection X-ray fluorescence spectrometer: study of influence of instrumental parameters

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Received: 14 July 2016 / Accepted: 17 November 2016 / Published online: 26 November 2016
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Abstract Total reflection X-ray fluorescence (TXRF) analysis is an excellent tool to determine major, minor and trace elements in minuscule amounts of samples, making this technique very suitable for pigment analysis. Collecting minuscule amounts of pigment material from precious works of art by means of a cotton swab is a well-accepted sampling method, but poses specific challenges when TXRF is to be used for the characterization of the unknown material.

1 Introduction

The technique of TXRF is based on irradiating material that was applied on a flat sample carrier, e.g. a quartz disc, with grazing incidence conditions obtained with a 0°–90° excitation geometry, causing total reflection of the incident monochromatic X-ray beam [1, 2]. As a result, the spectral background is dramatically reduced so that trace elements down to ppb level of concentration can be detected [1, 3]. Quantification is greatly simplified, as the thin layer approximation can be applied [4, 5]. Major, minor and trace elements concentrations can be obtained in minute amount of samples [3, 6]. Typical fields for application of TXRF are environmental, geological, biological and medical sciences, and the semiconductor industry [7, 8]. Since

more than two decades, TXRF is also being used for archaeometrical investigations [4, 5, 9–20].

Elemental analysis of inorganic pigments helps in a better understanding of the painter's palette, as regards both pure pigments and complex mixtures; later interventions could be identified thanks to the presence of key elements related to pigments which are incoherent with the chronological attribution of a work of art (some examples are zinc and titanium white [18]). As a result of correct pigment identification, more detailed chronological information can be achieved, as well as a deeper insight into potentially harmful degradation processes [9, 14, 18].

Various elemental and molecular analytical techniques are now established in the field of archaeometry. Portable instruments for non-destructive analysis are now available for many techniques [21–23]. For TXRF analysis, however, only a minuscule sample is required. Pigment sampling for dry TXRF analysis of particles can be carried out in a virtually non-destructive way, by means of carefully rubbing with a dry cotton swab on a non-varnished surface [5, 18]. This sampling is different from the traditional scalpel-, or needle, based acquisition. It can only be performed on unvarnished surfaces to ensure that pigment material is actually collected, leaving no visible trace on the object [9]. Collecting only micrograms amount of material on the cotton swab, even lower amounts (ng) are then transferred on the sample carrier in a next step [5, 14]. Von Bohlen and Klockenkämper et al. [4, 14] report that a simple and accurate quantification is possible, as long as the deposited weight of the particles does not exceed 50 µg in total and the particle size is only a few µm. Sampling with a cotton swab allows for multiple sample collection, improving the representativity of the analysis [5, 9]. Curators accept such sampling, but still these rare samples are very precious in that respect.

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Obtaining microscopic pigment particles on a cotton swab poses some specific challenges, when characterizing the used pigments and mixtures using the TXRF methodology [3, 5, 6, 9, 11]. Considering the very small amounts of material to be characterized with the TXRF method, one needs to take extra care to prepare the necessary “clean” sample carriers. In this respect, the determination of instrumental (spectroscopical) artefacts was necessary. During this period of study, the manufacturer of the used G.N.R. TX2000 TXRF spectrometer altered its sample chamber, so that the influence of this instrumental change could also be evaluated. In addition to the qualitative identification of the pigments, (semi)quantitative information can be obtained as well from the spectroscopical data. In order to verify the commercial quantification software SinerX delivered with the G.N.R. TX2000 spectrometer, a quantification scheme was set up for convenience, as reported by [5]. The peak and background intensities for these calculations were obtained by means of AXIL [24]. The transfer of the precious material from the cotton swab to the sample carrier right at the correct position on the sample carrier, so that the incoming X-rays can optimally excite it, is of major concern. Because the actual physical deposition of particulate material from the cotton swab to the sample carrier is not physically fully controllable, the imperfect positioning on the sample carrier was subject to study, in order to better understand the influence it may have on the TXRF results.

The final goal of the evaluation of all the steps described above will help to better understand the influence of the different experimental parameters when performing TXRF investigation of pigment particles sampled with cotton swabs, especially when the traditional liquid sample preparation methods conventionally used in TXRF analysis are not applicable [25].

2 Experimental and methods

The TXRF measurements were performed with a state-of-the-art G.N.R. TX2000 total reflection X-ray fluorescence spectrometer. The selected monochromatic X-ray source is the result of monochromatizing (Si/W multilayer reflector) the Mo-K α line from a long fine-focus (0.4 \times 12 mm) high-power (3 kW) Mo/W anode. The characteristic radiation induced in the sample is collected using a Peltier-cooled silicon drift detector (SDD) with 30-mm² active area. The energy resolution for Mn-K α is 140 eV. A sample carousel allows automated batch measurements of 12 samples. All measurements were performed operating the tube at 40 kV/30 mA, with 1000 s measurement time. It should be noted that during the period of this study, G.N.R. replaced the measurement chamber in order to

improve the measurement conditions. The software package SinerX, delivered with the instrument, was used for data processing of TXRF spectra.

The availability, and use, of “clean” sample carriers seems trivial for a TXRF methodology, but the delivery of batches of effectively clean sample carriers may not be such a trivial task in practice for an instrument that promises ppb levels of limit of detection. In order to reveal the power of detecting trace elements, the NIST SRM 1640a (trace elements in natural water) was measured.

The procedure to obtain clean quartz sample carriers used in this work is described by Klockenkämper for the cleaning of digestion vessels [3]. The use of a subboiling device (vessel cleaner by ANALAB Sàrl, France) allows the preparation of vast numbers of carriers in an unsupervised way, and with reduced reagent consumption. The preparation steps are as follows: (1) any residue of previous analysis is removed with paper and Disinfectol[®]; (2) the sample carriers are inserted in a specifically designed 24-slot Teflon holder [3, 6], which is suited for use in combination with a perfluoroalkoxy alkanes (PFA) subboiling device; (3) the sample carriers are exposed to supra pure nitric acid vapours, obtained by setting the heating unit to 145 °C; (4) the sample carriers are rinsed with MilliQ water; (5) the sample carriers are exposed to MilliQ water vapours, obtained by setting the heating unit to 115 °C; (6) same as step 4; (7) the sample carriers are vacuum dried on their support; (8) finally, they are transferred to Petri dishes for temporary storage. For each batch, one sample carrier was prepared with a 10 μ L droplet of a diluted multielement standard and measured together with the batch.

The influence of the cleaning procedure duration was investigated by cleaning batches of sample carriers with varying treatment times for steps 3 and 5 (12, 2 or 1 h each, for a total cleaning time of, respectively, 24, 4 or 2 h). After this procedure, each batch of sample carriers was measured five times each for 1000 s.

When preparing multielement standard solutions (Multi Element Standard Solution IV, Merck, Germany), and the NIST SRM 1640a (trace elements in natural water) samples, a surfactant (Triton) was added to prevent the 10 μ L drop from running on the sample carrier and to ensure it will dry in a circular shape (ca. 8 mm in diameter) in the centre of the sample carrier [6, 26–28]. A blank solution containing Triton was prepared and studied to check it was not adding unwanted elements to the samples under study.

Lower limits of detection (LLD) were calculated from a 1 ppm multielement standard solution and the NIST SRM 1640a measured for 1000 s (5 repetitions), according to the following formula [3]

$$\text{LLD}_j = 3 \times \frac{C_j \sqrt{I_{\text{bkg},j}}}{I_j}$$

where C_j is the concentration of the selected element j , with $I_{bk,g,j}$ and I_j , respectively, the background and the net peak area, as obtained by AXIL [24].

Next to the use of the commercial SinerX software, delivered with the TX2000 instrument, the following quantification calculations were performed. Instrumental relative sensitivities ($R_{j,IS}$) needed to be calculated from multielement standard analysis. $R_{j,IS}$ were obtained from the known elemental concentrations C_j in the multielement standard and the measured peak intensities I_j for each element j , referred to an internal standard element (IS), for example, Fe or Ga, according to the formula [3]

$$R_{j,IS} = \frac{I_j \times C_{IS}}{I_{IS} \times C_j}$$

From the derived sensitivity curves for K and L lines, the relative sensitivities for elements not present in the multielement standard could be obtained by simple interpolation. Once the $R_{j,IS}$ are calculated, quantification was performed by applying the following formula, as reported by Klockenkämper [3]

$$C_j = \frac{I_j \times C_{IS}}{I_{IS} \times R_{j,IS}}$$

where C_{IS} can be either the concentration of the added internal standard (e.g. Ga) or the arbitrary concentration given to a present element, which acts as an internal standard (e.g. Fe = 1 ppm). This latter approach, referred to in this work as *Qcalc*, was used in this study both for the NIST SRM 1640a and for pigment particles, to obtain semiquantitative information. In order to be able to compare the results of the SinerX processing, and of *Qcalc* with the certified values of NIST SRM 1640a water sample, concentration ratios to Fe were calculated.

The correct positioning of microscopic particles on the sample carrier for TXRF analysis is not trivial, and it seemed interesting to study. Conventional liquid samples, when added of a surfactant, or when applied on adequately prepared sample carriers, can be easily positioned in the centre of the sample carrier and dry in a circular shape [6]. On the contrary, particles suitable for TXRF analysis pose some issues, and it seemed relevant to investigate the measured area of the sample carrier. The sampled pigment particles are not visible by naked eye, and they are trapped between the fibres of the cotton swab. Also, because the size of a droplet of surfactant-containing multielement standard as small as 10 μ L is extremely hard to control, even after correct pipetting on centre of the sample carrier, it was decided to use a material, such as a commercial felt-tip eyeliner (Cosnova, Frankfurt, Germany), with which samples of controllable size (ca. 1 mm dots) and position (0, 2 and 4 mm from the centre of the round sample carrier) could be achieved. Each prepared

sample carrier was also rotated in four steps of 90° ($n = 3$ for each position), to take into account instrumental geometry effects. As a final test, samples of Kremer (Germany) pigment particles were prepared by means of dry cotton swabs (Deltalab, Spain), transferred on a clean sample carrier and immediately analysed. Following the data presentation commonly reported in archaeometrical literature regarding TXRF analysis of pigments, the obtained concentration values as ppm from SinerX and *Qcalc* were easily converted into percentages to the total of detected elements by normalization to 100%, as no internal standardization can be performed in the case of pigment particles analysis [3–6, 10, 11, 14, 15].

3 Results and discussion

After applying the cleaning procedure based on the use of a subboiling device, contaminants such as K, Ca, Fe, Ni, Cu, Zn, Pb might still appear. Ni, Cu and Zn are of instrumental origin, while the other elements come from external contamination/handling. Multiple sets of sample carriers cleaned for 24, 4 or 2 h in total (step 3 + step 5) were measured before chamber replacement, and the obtained intensities are shown in Fig. 1. The results of the shortest cleaning procedure are comparable with the longest one, on the condition that sample carriers showing potential contamination are removed from the calculations and from further use. Contaminated sample carriers appear

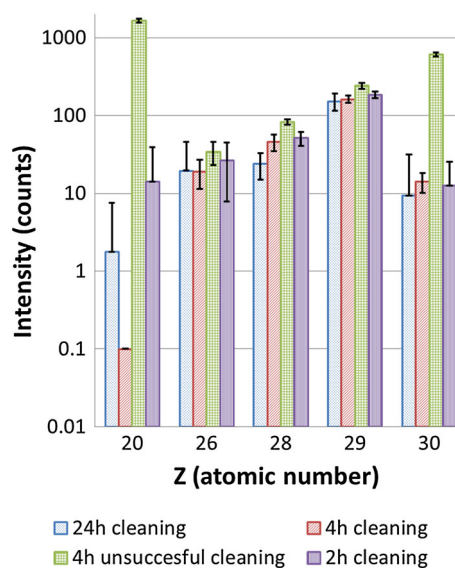


Fig. 1 Effect of duration of cleaning time. Observed intensity of residual elements after cleaning for different times (step 3 + step 5 = 24, 4 or 2 h), measured 1000 s, as a function of cleaning time, versus the atomic number. The standard deviation s_j is shown for each cleaned batch, measured five times. All the measurements were performed before chamber replacement. One standard deviation s_j is indicated

Table 1 Effect of chamber replacement on the intensity of some elements on cleaned sample carriers (five repetitions, 1000 s), for 4 and 2 h total cleaning time

	Ni-K α		Cu-K α		Zn-K α	
	Average counts	s_j	Average counts	s_j	Average counts	s_j
4 h, before chamber replacement	78	15	251	64	5	6
4 h, after chamber replacement	409	93	63	8	122	10
2 h, before chamber replacement	42	16	180	28	19	23
2 h, after chamber replacement	266	12	68	24	136	24

randomly, independently to the total cleaning time, in all the cleaned batches, and are most likely related to inaccurate handling of the sample carriers after cleaning and/or dust particles accidentally deposited. A selection procedure was still needed, as no cleaning procedure could ensure a 100% success rate in giving clean sample carriers. Figure 1 shows as well the unsuccessful cleaning of a sample carrier cleaned for a total of 4 h (Ca contamination estimated to approximately 2 ppm). During this study, the measurement chamber was replaced, causing a decrease in Cu interference and the simultaneous slight increase in the signals of Ni and Zn (Table 1), related to the detector's design. No further tests were performed in the old setup, i.e. prior to chamber replacement. In the present conditions, Ni, Cu and Zn remain stable and can be considered as instrumental background, corresponding to contamination levels of approximately 50–100 ppb of Ni. Ca and Fe are, on the other hand, related to the cleaning procedure or to handling. As regards the cleaned sample carriers, Fig. 2 shows the intensities (A) and spectra (B) of sample carriers cleaned for a total of 2 h. The iron concentration on a sample carrier showing contamination could be estimated in the range of few hundreds ppb. LLD below 10 ppb are observed for elements between Cr and Sr ($24 < Z < 38$), both in a 1 ppm multielement standard and for the NIST SRM 1640a, LLD = 2 ppb are achieved for Sr-K and 4 ppb for Bi-L lines (1 ppm multielement, 1000 s, Fig. 3). As an example of the selection of clean sample carriers, being the LLD for Fe = 7 ppb, the contaminated sample carrier shown in Fig. 2a, b has to be discarded from further use, being its estimated Fe content approximately few hundreds ppb. From a 10-ppm multielement standard spectrum, it was also possible to calculate the relative sensitivities values (K and L lines, Fig. 4a, b, respectively) to Fe and Ga for the elements of interest ($19 < Z < 38$; $48 < Z < 95$) based on their concentration in the standard and on the recorded net intensities [3, 6]. Interpolation was performed to obtain information on the elements not present in the multielement standard.

Based on the *Qcalc* method, spectra of the NIST SRM 1640s water sample were processed to obtain the concentration values of the elements of interest, based on a given

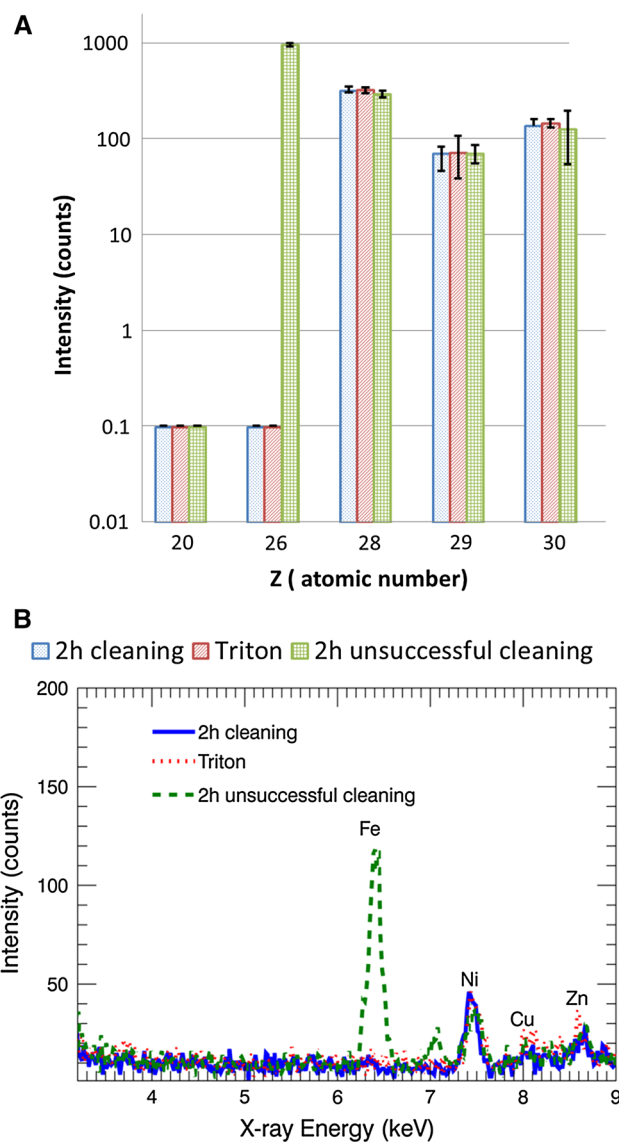


Fig. 2 a, b Study of the effect of surfactant (Triton). Observed intensity of residual elements after cleaning for 2 h (step 3 + step 5), and of a blank solution of surfactant (Triton). A clean sample carrier (full line), a cleaned sample carrier showing Fe contamination (dashed line), and a blank (Triton, dotted line) are compared in terms of elemental intensity (a), and of spectral data (b). The standard deviation s_j for five repeated measurements of 1000 s is given. One standard deviation s_j is indicated

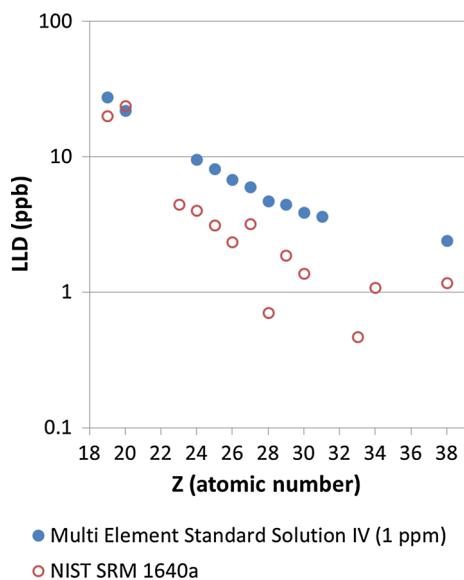


Fig. 3 Calculated LLD (ppb) for 1000 s measurement time. The given data correspond to the calculated LLD from a 1 ppm multielement standard solution (*full circles*), and to the calculated LLD for the studied NIST 1640a water sample (*empty circles*). For the multielement standard elements not shown (L lines), the LLD are: Cd = 52 ppb, Ba = 24 ppb, Tl = 5 ppb, Pb = 4 ppb, Bi = 4 ppb. For the NIST SRM 1640a elements not shown (L lines), the LLD are: Ba = 36 ppb, U = 2 ppb

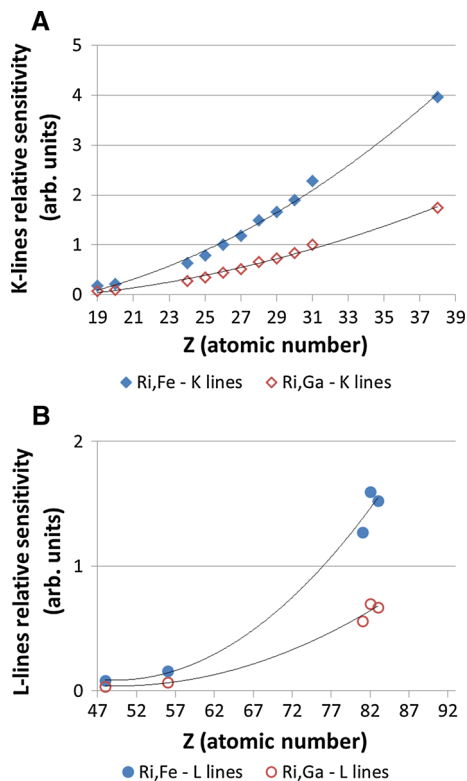


Fig. 4 *a, b* Calculated relative sensitivities (to Fe and Ga, *full* and *empty symbols*, respectively) for elements of interest present in a 10 ppm multielement standard solution (1000 s measurement time): *a* K lines, *b* L lines

value of 1 ppm for Fe. Figure 5 shows the quantification results for both methods, when no internal standard is added, and Fe, originally present in the sample, is given a value of 1 ppm in order to perform the calculations. The SinerX-based quantification overestimates strongly all the present elements, except potassium, while *Qcalc* yields results closer to the expected values, with some exceptions. Ca is not optimally estimated, as expected from its low relative sensitivity to Fe. V is not considered, as it is present at the LLD level. For Ni, Cu and Zn, it is important to remember that some instrumental background contributes to their signal, making their quantification inaccurate when they are present at the tens of ppb level, as in the present case. However, when using the *Qcalc* method, it would be possible to correct for such a problem, so that the correct concentration is calculated. As regards the quantification of elements whose L lines are present in the spectrum, Cd is not quantified, as it is present below LLD. Ba quantification is problematic with both methods. Pb, although present in detectable concentration levels, could not be identified in the spectra processed with AXIL. Finally, both methods overestimated the content of U. It appears that the standardless analysis gives better results when *Qcalc* is used. In general, a different excitation source (for example, W) and the selection of a multielement standard containing different elements might be successfully used to improve the

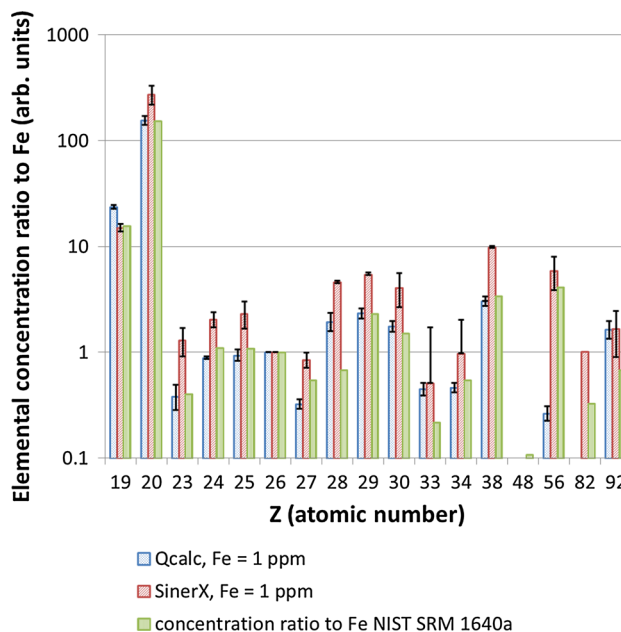


Fig. 5 Comparison of elemental concentration ratios to Fe for NIST 1640a water sample. Fe was used as internal standard (1 ppm). Dotted bars refer to *Qcalc*, slant lines to SinerX, vertical lines to the NIST SRM 1640a. The calculated elemental ratios via both methods are compared to the reference material data. One standard deviation s_j is indicated

results of quantification for elements such as Cd, Ba and for other elements $Z > 80$.

As regards the effect of sample positioning on the quantification results, Fig. 6 shows the elemental counts ratio between Fe and Mn, used to evaluate the measured area of the sample carrier. The lowest relative standard deviation of the ratio $s_{\text{Fe/Mn}}$ ($n = 3$) is observed for centred samples (4%), while it increases to 14% at 2 mm and to 17% at 4 mm from the centre. On the other hand, the effect of rotations (0° , 90° , 180° , 270°) is not clear. Elemental ratios are still acceptable for samples placed in an 8-mm \varnothing area in the centre of the sample carrier, even though the relative standard deviation increases with distance from the centre.

Thanks to the small particles' size and the low density of pigment particles on the sample carrier surface, it can be considered that matrix effects are strongly reduced. No internal standardization can be applied to such pigment samples, as the exact weight of the analysed sample cannot be determined [5, 6, 9, 11, 14]. However, a relative quantification is possible. This is an approximation, as matrix effects are absent only for very fine ($0.1 \mu\text{m}$) grains and for little amounts of material on the sample carrier surface ($<10 \mu\text{g cm}^{-2}$). Moreover, the quantification excludes the low- Z elements, as they are not detected, and the given results will be relative to the total of detected elements [3–6, 10, 11, 14, 15]. Si is also excluded from the calculations, as the quartz sample carrier contributes to the signal, and elements such as Sn and Sb, which are relevant for the study of pigments, are also not considered at this

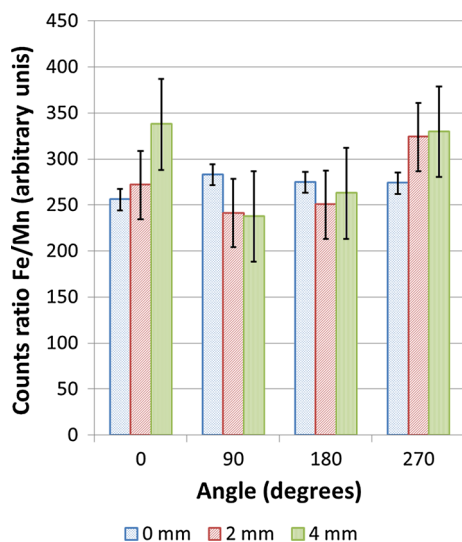


Fig. 6 Study of the effect of distance from the centre and angle. Fe/Mn intensity ratio of commercial eyeliner when measuring ca. 1-mm-diameter dots at angles of 0° , 90° , 180° , 270° (from a reference position) as a function of distance from the centre of the sample carrier. The standard deviation s_j was obtained by three repeated measurements of the same sample carrier

point, based on the results of multielement standard analysis with the Mo source, as explained in the previous paragraph. In the case of pigment analysis, the quantification can only rely on relative quantification of detected elements based on one selected element as internal standard (i.e. Fe), which are then normalized to 100%, and finally converted to percentages of detected elements [3–6, 10, 11, 14, 15]. Also, no certified values from the producer are available regarding the minor and trace elements in the selected pigments (<http://kremer-pigmente.com/>, last visited on 23 May 2016), so the comparison here regards three different samples for each selected pigment, processed via *Qcalc* or via the commercial software SinerX. The results (in percentages of detected elements) are summarized in Tables 2, 3 and 4. The results of quantification on the studied pigment samples are comparable for both the *Qcalc* and the SinerX calculations, the greatest discrepancy between the results being ca. 5.5% on the main element (Pb in lead tin yellow I). For the minor and trace elements, differences could be observed, for example, Ca in yellow ochre, which is quantified by SinerX as twice the amount resulting from calculations, or of many impurities in magnetite, not identified by the commercial software. The qualitative identification of pigments based on the presence of key elements can successfully be performed, on the condition that conclusive identification is well supported by complementary analysis, especially in the case of lead-containing yellow pigments, arsenic- and copper-containing pigments, and lapis lazuli/ultramarine.

As already pointed out in the previous paragraph, as some elements of relevance in pigment analysis are not successfully excited by the Mo tube, the obtained elemental composition on some yellow pigments such as lead tin yellow types I and II and Naples Yellow is limited to lead, and to other detectable minor elements. In that case, as well as for arsenic-based pigments, a different approach (molecular techniques, such as Raman spectroscopy [29]) could be more suitable and give better results. Among the iron-based pigments, yellow ochre and green earth showed a more varied composition, including K and Ca as well, as expected from the mineralogy of these materials. For the ultramarine and lapis lazuli blue pigments, as expected, no specific key elements can be identified by means of XRF-based techniques. Misidentification of green pigments based on copper, or of mixtures of Cu-containing blue pigments with (organic) yellow materials, is very likely to happen, when only using elemental analytical techniques. The TXRF analysis is anyway fast and does not consume material, which allows for further analysis, such as microscopy and micro-Raman spectroscopy [4, 11–13, 15], preferably done after TXRF measurement, in order to minimize the exposure of the sample to airborne contamination and unnecessary handling.

Table 2 Analysis of Kremer pigment particles sampled with a cotton swab, processed by *Qcalc* and SinerX. Results of pigment analysis (white and yellow/orange)

Pigment	Lead white		Lead tin yellow I		Lead tin yellow II		Naples yellow		Realgar		Orpiment		Yellow ochre	
	2PbCO ₃ ·Pb(OH) ₂		Pb ₂ SnO ₄		PbSn _{1-x} Si _x O ₃		Pb ₂ Sb ₂ O ₇		As ₄ S ₄		As ₂ S ₃		Fe ₂ O ₃ ·H ₂ O + clay + SiO ₂	
Z	%	<i>s_j</i>	%	<i>s_j</i>	%	<i>s_j</i>	%	<i>s_j</i>	%	<i>s_j</i>	%	<i>s_j</i>	%	<i>s_j</i>
19	<i>Qcalc</i>	0.0	0.0										6.9	0.6
	SinerX												5.9	0.4
20	<i>Qcalc</i>	0.2	0.0	0.6	0.1	0.5	0.1				0.2	0.0	0.4	0.2
	SinerX	0.0	0.0	2.2	0.1	0.4	0.0				0.1	0.1	0.9	0.0
22	<i>Qcalc</i>			0.0	0.0								2.0	0.0
	SinerX												3.5	0.0
24	<i>Qcalc</i>	0.0	0.0			0.0	0.0			0.0	0.0	0.0	0.0	
	SinerX			0.0	0.0	0.0	0.0			0.0	0.0	0.0	0.0	
25	<i>Qcalc</i>			0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
	SinerX			0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
26	<i>Qcalc</i>	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.1	0.0	0.0	0.0	90.0
	SinerX	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	88.0
27	<i>Qcalc</i>													
	SinerX													
28	<i>Qcalc</i>	0.1	0.0	0.0	0.0	0.1	0.0	0.1	0.1	0.2	0.0	0.2	0.0	0.1
	SinerX	0.1	0.0	0.1	0.0	0.2	0.0	0.2	0.0	0.1	0.0	0.1	0.0	0.0
29	<i>Qcalc</i>	0.1	0.0	0.0	0.0	0.1	0.0	0.1	0.1	0.1	0.0	0.1	0.0	0.2
	SinerX	0.1	0.0	0.1	0.0	0.2	0.0	0.2	0.0	0.1	0.0	0.1	0.0	0.9
30	<i>Qcalc</i>													0.1
	SinerX													0.0
33	<i>Qcalc</i>									99.6	0.0	99.5	0.0	
	SinerX									99.7	0.0	99.7	0.1	
37	<i>Qcalc</i>													
	SinerX													
38	<i>Qcalc</i>	0.0	0.0					0.0	0.0					0.0
	SinerX	0.2	0.0			0.3	0.0	0.3	0.0					0.0
48	<i>Qcalc</i>	7.1	0.8	0.4	0.1	6.4	0.3	6.1	3.9					
	SinerX	3.6	0.3	3.5	0.3	1.9	0.4	1.9	0.8					
80	<i>Qcalc</i>	0.2	0.0	0.0	0.0									
	SinerX	0.3	0.0	0.4	0.1									
82	<i>Qcalc</i>	92.1	0.7	99.0	0.1	92.8	0.3	93.6	4.0					0.2
	SinerX	88.3	0.6	93.5	0.3	97.0	0.4	97.5	0.8					0.9
83	<i>Qcalc</i>	0.2	0.0											
	SinerX	7.2	0.9											

The given values are calculated based on a given concentration of Fe = 1 ppm and are expressed in percentage of detected elements. The standard deviation *s_j* is calculated on three measurements per sample

The rows in italic refer to results obtained via the *Qcalc* method. The main element(s) for each pigment are marked in bold

4 Conclusions

The G.N.R. TX2000 instrument is a highly performing TXRF spectrometer, showing LLD as low as 2 ppb for Sr (K lines). The detection power of the instrument was demonstrated by analysing trace elements in natural water (NIST SRM 1640a). For the study of microscopic

particles sampled on a dry cotton swab, the effect of positioning is of primary importance, as deviation of the results because of mispositioning is to be expected. Elemental count ratios (Fe/Mn) of a sample deposited in a controlled way, as regards both size and position on the sample carrier, show a relative error of 4% for centred samples, increasing to 17% at 4 mm from the

Table 3 Analysis of Kremer pigment particles sampled with a cotton swab, processed by *Qcalc* and SinerX. Results of pigment analysis (red and blue)

Pigment	Fe oxide red		Cinnabar		Vermillion		Co blue		Lapis lazuli		Ultramarine		Azurite	
	Fe ₂ O ₃		HgS				CoO·Al ₂ O ₃		Na ₈ [Al ₆ Si ₆ O ₂₄]S _n				2CuCO ₃ ·Cu(OH) ₂	
Z	%	s _j	%	s _j	%	s _j	%	s _j	%	s _j	%	s _j	%	s _j
19	<i>Qcalc</i>		1.2	0.4					0.2	0.4	3.2	0.1	0.7	0.1
	SinerX		0.4	0.0							2.1	0.1	0.2	0.0
20	<i>Qcalc</i>	0.1	0.0				4.4	3.3	96.8	0.7	92.7	0.1	0.7	0.1
	SinerX	0.0	0.0				4.2	0.2	95.3	0.5	94.0	0.1	0.4	0.0
22	<i>Qcalc</i>		0.2	0.1					0.4	0.2	0.7	0.0	0.4	0.0
	SinerX		0.2	0.0					1.0	0.2	1.0	0.0	0.3	0.1
24	<i>Qcalc</i>	0.3	0.0	0.0	0.0	0.0	0.0	0.0	3.7	2.7	0.0	0.0		
	SinerX	1.0	0.0	0.0	0.0	0.0	0.0	0.0	5.5	0.0	0.1	0.0		
25	<i>Qcalc</i>	0.2	0.0			0.0	0.0	0.2	0.0	0.0	0.1	0.1	0.1	0.0
	SinerX	0.6	0.5			0.0	0.0	0.4	0.2	0.0	0.0	0.1	0.0	0.0
26	<i>Qcalc</i>	99.1	0.1	1.1	0.0	0.1	0.0	2.1	1.8	1.0	0.1	3.2	0.1	2.6
	SinerX	97.4	0.4	0.6	0.1	0.1	0.0	0.1	0.0	0.8	0.1	2.3	0.1	1.2
27	<i>Qcalc</i>							84.4	11.7					
	SinerX							80.0	0.4					
28	<i>Qcalc</i>	0.0	0.0	0.1	0.0	0.1	0.0	0.3	0.2	0.3	0.1	0.0	0.0	0.1
	SinerX			0.1	0.0	0.1	0.0	0.7	0.3	0.5	0.2	0.0	0.0	0.1
29	<i>Qcalc</i>	0.2	0.0	0.1	0.0	0.2	0.0	0.4	0.3	0.9	0.1	0.1	0.0	95.8
	SinerX	1.0	0.0	0.1	0.0	0.1	0.0	0.7	0.2	1.5	0.1	0.2	0.0	96.7
30	<i>Qcalc</i>	0.0	0.0	0.1	0.1			4.6	3.4	0.1	0.0	0.0	0.0	0.3
	SinerX	0.0	0.0	0.3	0.1			7.8	0.2	0.2	0.0	0.0	0.0	1.0
33	<i>Qcalc</i>	0.0	0.0	0.1	0.1	0.2	0.0	0.0	0.0					
	SinerX	0.0	0.0	0.1	0.0	0.3	0.3	0.2	0.1					
37	<i>Qcalc</i>											0.0	0.0	
	SinerX											0.0	0.0	
38	<i>Qcalc</i>									0.0	0.1	0.0	0.0	
	SinerX									0.2	0.0	0.1	0.0	
48	<i>Qcalc</i>													
	SinerX													
80	<i>Qcalc</i>			98.1	0.2	99.4	0.0							
	SinerX			98.1	0.1	99.4	0.3							
82	<i>Qcalc</i>									0.1	0.0	0.0	0.0	0.0
	SinerX									0.4	0.2	0.1	0.0	0.0
83	<i>Qcalc</i>													
	SinerX													

The given values are calculated based on a given concentration of Fe = 1 ppm and are expressed in percentage of detected elements. The standard deviation s_j is calculated on three measurements per sample

The rows in italic refer to results obtained via the *Qcalc* method. The main element(s) for each pigment are marked in bold

centre. The cleaning procedure using a subboiling device, which allows for the cleaning of vast numbers of sample carriers, requiring limited human intervention and little reagent consumption, still cannot ensure for a cleaning success rate of 100%. This requires the checking of the sample carriers, to identify possible contaminated ones, to be discarded based on the instrumental LLD. Moreover, from the cleaned sample

carriers analysis, it appeared that instrumental interferences of Ni, Cu and Zn occur, causing overestimation of such elements at the moment of quantification. The final quantification test performed on Kremer pigments by means of *Qcalc* and SinerX showed that both approaches correctly quantify the samples, the greatest uncertainty being related to the correct positioning of the microscopic pigment particles. The present study allowed a

Table 4 Analysis of Kremer pigment particles sampled with a cotton swab, processed by *Qcalc* and SinerX. Results of pigment analysis (green and black)

Pigment	Malachite		Verdigris		Cu resinate		Green earth		Viridian		Magnetite	
	CuCO ₃ ·Cu(OH) ₂		Cu _x (CH ₃ COO) _y (OH) _z ·nH ₂ O		Cu salts of abietic acid		K[(Al,Fe)(Fe,Mg)], (AlSi ₃ ,Si ₄)O ₁₀ (OH) ₂		Cr ₂ O ₃ ·2H ₂ O		Fe ₃ O ₄	
Z	%	<i>s_j</i>	%	<i>s_j</i>	%	<i>s_j</i>	%	<i>s_j</i>	%	<i>s_j</i>	%	<i>s_j</i>
19 <i>Qcalc</i>							2.7	0.1				
SinerX							1.7	0.1				
20 <i>Qcalc</i>			0.0	0.0			82.2	0.1	0.5	0.8	0.67	0.10
SinerX			0.0	0.0			84.1	1.0	0.1	0.1	0.00	0.00
22 <i>Qcalc</i>							0.9	0.1				
SinerX							0.8	0.1				
24 <i>Qcalc</i>	0.0	0.0	0.0	0.0					99.0	0.0	0.12	0.01
SinerX	0.0	0.0	0.0	0.0					99.3	0.1	0.00	0.00
25 <i>Qcalc</i>							0.5	0.0			0.43	0.00
SinerX							0.9	0.1			0.99	0.00
26 <i>Qcalc</i>	0.1	0.0	0.1	0.0	0.4	0.1	13.0	0.3	0.9	0.0	99.34	0.02
SinerX	0.0	0.0	0.0	0.0	0.2	0.0	10.7	0.7	0.4	0.0	99.01	0.00
27 <i>Qcalc</i>	0.1	0.0	0.0	0.0								
SinerX	0.0	0.0	0.0	0.0								
28 <i>Qcalc</i>	0.2	0.0	0.1	0.0	0.4	0.0	0.0	0.0	0.0	0.0	0.01	0.00
SinerX	0.2	0.0	0.2	0.0	0.3	0.1	0.1	0.0	0.0	0.0	0.00	0.00
29 <i>Qcalc</i>	99.5	0.1	99.6	0.1	99.0	0.1	0.3	0.0	0.1	0.0	0.06	0.01
SinerX	99.4	0.1	99.2	0.1	98.6	0.2	0.5	0.0	0.1	0.0	0.00	0.00
30 <i>Qcalc</i>	0.2	0.0	0.1	0.0	0.3	0.1	0.0	0.0	0.0	0.0	0.04	0.00
SinerX	0.3	0.1	0.6	0.1	0.6	0.1	0.0	0.1	0.0	0.0		
33 <i>Qcalc</i>												
SinerX												
37 <i>Qcalc</i>												
SinerX												
38 <i>Qcalc</i>							0.3	0.0				
SinerX							1.1	0.1				
48 <i>Qcalc</i>												
SinerX												
80 <i>Qcalc</i>												
SinerX												
82 <i>Qcalc</i>					0.3	0.1	0.0	0.0				
SinerX					0.3	0.1	0.1	0.0				
83 <i>Qcalc</i>												
SinerX												

The given values are calculated based on a given concentration of Fe = 1 ppm and are expressed in percentage of detected elements. The standard deviation *s_j* is calculated on three measurements per sample

The rows in italic refer to results obtained via the *Qcalc* method. The main element(s) for each pigment are marked in bold

better understanding of the effects of some specific instrumental parameters on the obtained TXRF results on pigment particles.

Acknowledgements The authors thank Ghent University for its financial support through the concerted research actions (GOA) programme. Sylvia Lycke is also acknowledged for the support in the laboratory.

References

1. Y. Yoneda, T. Horiuchi, Rev. Sci. Instrum. **42**, 169 (1971)
2. H. Aiginger, P. Wobrauschek, Nucl. Instrum. Methods **114**, 157 (1974)
3. R. Klockenkämper, *Total Reflection X-ray Fluorescence Analysis* (Wiley, New York, 1997)
4. A. von Bohlen, E-Preserv. Sci. **1**, 23 (2004)

5. R. Klockenkämper, A. von Bohlen, L. Moens, W. Devos, *Spectrochim. Acta B At. Spectrosc.* **48**, 239 (1993)
6. R. Klockenkämper, A. von Bohlen, *Total-Reflection X-ray Fluorescence Analysis and Related Methods*, 2nd edn. (Wiley, New York, 2014)
7. P. Wobrauschek, *X-Ray Spectrom.* **36**, 289 (2007)
8. L. Ying, *Adv. X-Ray Chem. Anal.* **46**, 13 (2015)
9. L. Moens, W. Devos, R. Klockenkämper, A. von Bohlen, *Trends Anal. Chem.* **13**, 198 (1994)
10. A. von Bohlen, F. Meyer, *Spectrochim. Acta B At. Spectrosc.* **52**, 1053 (1997)
11. G. Van Hooydonk, M. De Reu, L. Moens, J. Van Aelst, L. Milis, *Eur. J. Inorg. Chem.* **1998**, 639 (1998)
12. P. Vandenabeele, B. Wehling, L. Moens, B. Dekeyzer, B. Cardon, A. von Bohlen, R. Klockenkämper, *Analyst* **124**, 169 (1999)
13. B. Wehling, P. Vandenabeele, L. Moens, R. Klockenkämper, A. von Bohlen, G. Van Hooydonk, M. De Reu, *Microchim. Acta* **130**, 253 (1999)
14. R. Klockenkämper, A. von Bohlen, L. Moens, *X-Ray Spectrom.* **29**, 119 (2000)
15. N. Civici, O. Demko, R. Clark, *J. Cult. Herit.* **6**, 157 (2005)
16. R. Fernández-Ruiz, M. García-Heras, *Spectrochim. Acta B At. Spectrosc.* **62**, 1123 (2007)
17. R. Fernández-Ruiz, M. Garcia-Heras, *Spectrochim. Acta B At. Spectrosc.* **63**, 975 (2008)
18. C. Vázquez, A. Albornoz, A. Hajduk, D. Elkin, G. Custo, A. Obrusky, *Spectrochim. Acta B At. Spectrosc.* **63**, 1415 (2008)
19. I. Domingo, P. García-Borja, C. Roldan, *Archaeometry* **54**, 868 (2012)
20. L. Bonizzoni, A. Galli, M. Gondola, M. Martini, *X-Ray Spectrom.* **42**, 262 (2013)
21. D. Lauwers, A. Hutado, V. Tanevska, L. Moens, D. Bersani, P. Vandenabeele, *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **118**, 294 (2014)
22. L. Van De Voorde, J. Van Pevenage, K. De Langhe, R. De Wolf, B. Vekemans, L. Vincze, P. Vandenabeele, M.P.J. Martens, *Spectrochim. Acta B At. Spectrosc.* **97**, 1 (2014)
23. B. Brunetti, C. Miliari, F. Rosi, B. Doherty, *Top. Curr. Chem.* **374**, 10 (2016)
24. B. Vekemans, K. Janssens, L. Vincze, F. Adams, P. Van Espen, *X-Ray Spectrom.* **23**, 278 (1994)
25. M. Dargie, A. Markowicz, A. Tajani, V. Valkovic, *Fresenius J. Anal. Chem.* **357**, 589 (1997)
26. E. Towett, K. Shepherd, G. Cadisch, *Sci. Total Environ.* **463–464**, 374 (2013)
27. H. Stosnach, *Spectrochim. Acta B. At. Spectrosc.* **61**, 1141 (2006)
28. E. Marguá, A. Marques, M. Prisal, M. Hidalgo, I. Queralt, M.L. Carvalho, *Appl. Spectrosc.* **68**, 1241 (2014)
29. P. Vandenabeele, A. Von Bohlen, L. Moens, R. Klockenkämper, F. Joukes, G. Dewispelaere, *Anal. Lett.* **33**, 3315 (2000)