e-PS, 2004, **1**, 23-34
ISSN: 1581-9280

www.e-PreservationScience.org
www.Morana-rtd.com

e-PRESERVATIONScience

published by MORANA RTD d.o.o.

FULL PAPER

REVIEW

SHORT COMMUNICATION

TOTAL REFLECTION X-RAY FLUORESCENCE SPECTROMETRY - A VERSATILE TOOL FOR ULTRA - MICRO ANALYSIS OF OBJECTS OF CULTURAL HERITAGE

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Abstract

A short introduction into total reflection X-ray fluorescence spectrometry (TXRF) is given. Some aspects of development, including theory, technical advances and publications covering the last 30 years are summarised. The main fields of TXRF applications, trace analysis of elements, micro analysis of solids and surface analysis are presented. A special section describes in detail a gentle micro-sampling method that can be used for the analysis of objects of cultural heritage. The versatility and efficiency of TXRF combined with the micro-sampling of solids for restoration, preservation and art historical tasks are demonstrated using new applications. These examples concern pigment analysis of paintings, analysis of iron gall inks in ancient manuscripts and historical violin varnishes. References are given for further examples. More than 50 references, mainly dedicated to TXRF analysis of art objects, are included.

1. Introduction

Since the discovery of X-rays by Wilhelm Conrad Röntgen in 1895, the development of spectrometers for materials analysis has a notable history. Several of these developments are associated with the names of famous scientists of the last century.

After the introduction of solid-state detectors and computers for the simultaneous acquisition of X-ray spectra – energy dispersive X-ray fluorescence (EDXRF) - a stagnation in instrumental development occurred. The introduction of Total Reflection X-Ray Fluorescence (TXRF) - a special variant of EDXRF - in 1971 by Yoneda and Horiuchi[1], and some years later the introduction of capillary X-ray optics for focussing the primary beam in spectrometers by Rindby et al.[2], are the milestones in X-ray spectroscopy of the last thirty years of the 20th century. Nowadays these two developments show that X-ray fluorescence spectrometry (XRF) is an attractive and competitive method of atomic spectroscopy. All XRF techniques are working without consuming the samples and give full quantitative analysis of many elements over a large concentration range from 100% down to some ng/g. TXRF requires only micro amounts of sample for a com-

received: 03.03.2004
accepted: 06.07.2004

key words:
TXRF, Total Reflection X-Ray Fluorescence Spectrometry, Pigments, Iron Gall Ink, Medieval Manuscripts, Archaeology

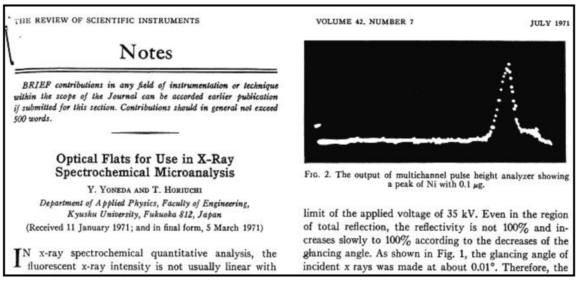
plete analysis and combines all of the excellent features of XRF. Thus, it is ideal for the analyses of objects of cultural heritage.

2. Brief History of TXRF

Total reflection of X-rays at an optically flat surface for spectrochemical analysis was first mentioned in the journal ‘The Review of Scientific Instrument’ (Figure1). The note was presented by Y. Yoneda and T. Horiuchi, Japan, in 1971[1]. Some years later this promising idea was picked up by Aiginger and Wobrauschek, Austria, in 1975[3]. They studied the phenomenon in a more extensive experimental way and gave a first evaluation of its potential and illuminated theoretical aspects. However, the status of the instrumentation at that time was simply that of laboratory experiments. Knoth and Schwenke, Germany[4], were the first to produce a more or less technically perfected prototype, which was produced some months later by Seifert & Co, Germany, as the first commercially available TXRF spectrometer in 1982/83. Since 1984 TXRF instruments had been improved continuously. The most impressive developments are related to the excitation by means of powerful X-ray tubes, by using new monochromator systems for the primary beam and by the use of synchrotron radiation instead of radiation from an X-ray tube. Additionally, special software packages with all imaginable options have become available.

Directly coupled to the instrumental development of TXRF, the spectrum of analysable samples increased rapidly and the absolute detection limits were improved from some ng down to a few pg for commercially available instruments. The detection of some fg using TXRF with excitation by means of synchrotron radiation (Table 1) has been reported. Nowadays synchrotron TXRF is state of the art and is available at nearly all dedicated synchrotron facilities.

Several techniques of sample preparation in analytical chemistry used for atomic spectroscopy were adapted for TXRF analysis. Sample digestion procedures, matrix separation and trace preconcentration methods were described in papers presented in the years following 1978. The relative detection limits for several elements in a great variety of samples could be improved and the ng/L region was attended for simultaneous multi-element analysis. However, the sensitivity of other methods such as inductively coupled plasma mass spectromerty (ICP-MS) is superior in several cases compared with that of TXRF.



THE REVIEW OF SCIENTIFIC INSTRUMENTS VOLUME 42, NUMBER 7 JULY 1971

Notes

BRIEF contributions in any field of instrumentation or technique within the scope of the Journal can be accorded earlier publication if submitted for this section. Contributions should in general not exceed 500 words.

Optical Flats for Use in X-Ray Spectrochemical Microanalysis

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(Received 11 January 1971; and in final form, 5 March 1971)

In x-ray spectrochemical quantitative analysis, the fluorescent x-ray intensity is not usually linear with

Fig. 2. The output of multichannel pulse height analyzer showing a peak of Ni with 0.1 μg.

limit of the applied voltage of 35 kV. Even in the region of total reflection, the reflectivity is not 100% and increases slowly to 100% according to the decreases of the glancing angle. As shown in Fig. 1, the glancing angle of incident x rays was made at about 0.01°. Therefore, the

Figure 1. First paper on TXRF for spectrochemical analyses.

Authors	**Year**	DL	Comment	Ref.
Yoneda & Horiuchi	**1971**	1 - 5 ng	for Ni	1
Knoth & Schwenke	**1978**	< 50 pg	more than 10 elements	4
Knoth & Schwenke	**1980**	< 10 pg	more than 11 elements	5
Reus et al.	**1989**	< 2 pg	more than 11 elements	6
Wobrauschek et al., Synchrotron TXRF	**1997**	13 fg	for Ni	7
Roentec, portable TXRF	**2000**	~ 10 pg	for 10 elements	8

Table 1. Development of the absolute detection limits (DL) achieved by TXRF for chemical analysis from 1971 until now. DL has improved five orders of magnitude in about thirty years.

Nevertheless, the fast and economic multi-element micro-analytical capability of TXRF remains unequalled.

TXRF can be classified according to the application of the technique:
- TXRF is used for the chemical analysis. In combination with a more or less extensive chemical pre-treatment and/or a pre-concentration of the traces present in the sample, TXRF shows its real potential. In certain cases, simply evaporating the solvent containing the sample leads to detection limits at ppt levels. Many papers have been published dealing with these topics, they were reviewed previously[9-12].
- TXRF as a micro-analytical method. If we are looking at only minute quantities of sample, e.g. some pigment grains, dust particles or small tissue samples, we can use TXRF as a micro-analytical method. This technique is a very useful for the analysis of the smallest amounts of solid samples and has been applied many times[9, 15, 16].
- TXRF for surface analysis. If we are looking only at the uppermost layers of a flat surface, we can use TXRF for surface analysis. This, after it has been recognised by Huber et al. in 1988[17] as well as in combination with a chemical decomposition of the uppermost layer of a Si-wafer, the VPD-TXRF procedure introduced by Neumann and Eichinger[18], are today the most prominent methods for the control of wafer surfaces[19].

In the years shortly after 1971 only a few publications concerning TXRF can be found. The number of published papers per year increased drastically after the second international congress dedicated to the method. It was held in Dortmund, Germany,

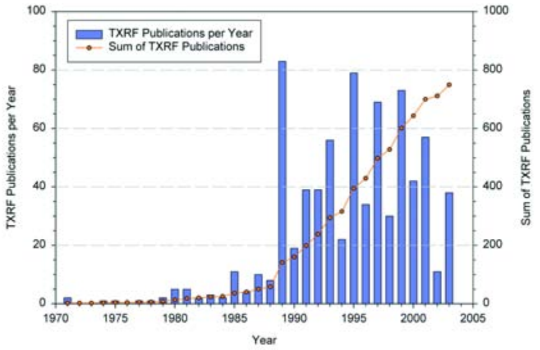

Figure 2. Number of TXRF publications in refereed journals starting from 1970 until 2003.

in 1988. A graphical representation of the development of publications dealing with TXRF is given in Figure 2. The periodical structure of two years is due to publications after each congress. Until now, about 780 original papers including some reviews has been published, whereas about 30 of them concern the analysis of objects of cultural heritage.

This overview focuses on the micro-analytical capabilities of TXRF for the direct analysis of the smallest samples taken from objects of cultural heritage. The first application of TXRF to the analysis of some pigment grains was mentioned in 1987[14].

3. Principle

X-rays, as other electromagnetic waves, exhibit total reflection for a particular angle of incidence when passing from a material with a higher refractive index to a material with lower refractive index. This is fulfilled for X-rays when they pass from vacuum (or air) to any other material. For absorptive media the refractive index is given by a complex quantity:

$$n = 1 - \delta - i \times \beta \qquad (1)$$

where

$$i = \sqrt{-1}$$

The real component δ, called the decrement, is a measure of the dispersion and is for X-rays is of the order of 1×10^{-6}. The imaginary component β is a measure of the absorption and is even smaller than 10^{-6} for many media. Both, δ and β can be reduced to physical parameters[9,12]. Total reflection of X-rays occurs at very small glancing angles. For transparent media, for which $\beta/\delta \sim 0$, there exists a very distinct limit, the critical angle Φ_c. Below this angle total reflection occurs and this can be calculated according Snell's law:

$$\Phi_c = \sqrt{2\delta} \qquad (2)$$

For Mo-Kα X-rays passing from vacuum to quartz glass $\delta = 1.5\times10^{-6}$, $\beta = 4.6\times10^{-9}$ and hence Φ_c = 5.9 minutes of arc[9,12].

This indicates that for X-rays to be totally reflected at a flat quartz surface, or any other similar material, the angle of incidence must be very small, i.e. less than 6 min of arc. In the intersection field of incoming X-rays and totally reflected X-rays standing waves can be observed (Figure 3)[10]. Interference of X-rays during total reflection at a flat surface has important consequences for X-ray fluorescence spectrometry. The first consequence is that small grains of material deposited onto the reflector are efficiently excited into X-ray fluorescence. On average the excitation is double compared with conventional XRF for particle sizes larger than 300 nm[10].

A second consequence of total reflection is that the waves penetrate only 2 or 3 nm into the material on which they are totally reflected. Hence the sample support acts like a virtual foil of 2 or 3 nm thickness. This means that in TXRF analysis the sample support contributes little to the spectral background.

In Figure 4, a schematic representation of a simple set-up of an energy dispersive X-ray spec-

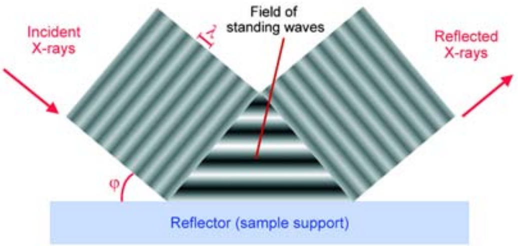

Figure 3. Field of standing waves in the intersection of totally reflected X-rays upon a flat surface. Adapted from Klockenkämper et al.[40].

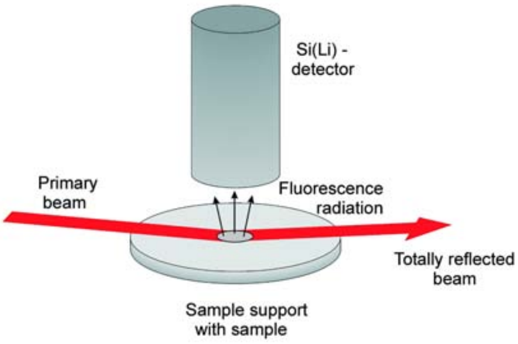

Figure 4. Schematic representation of an energy dispersive X-ray fluorescence spectrometer using the total reflection of the primary beam from an optically flat reflector.

trometer with total reflection of the primary beam is shown. This basic arrangement was expanded and completed by adding different kinds of filters / monochromators[3, 6, 12, 20] according to the monochromatization of the primary beam. Commonly TXRF spectrometers are operated at normal atmospheric conditions. This limits the detection to elements with atomic numbers higher than 14 (Silicon). For the detection of lighter elements, down to Carbon and Oxygen, TXRF spectrometers with vacuum chambers were developed[21].

A well designed and configured spectrometer operating in air under total reflection of the primary beam can achieve absolute detection limits of less than 2 pg for numerous elements. These amounts are about 1000 times smaller than those detectable by conventional XRF methods.

If we only apply some small grains of material for analysis, the conditions of total reflection are not disturbed and the sample material appears as it infinitely thin for the X-rays. That means that no matrix effects – such as secondary excitation, absorption, etc. common to all other X-ray spectrometric methods - can occur and a simple and reliable quantification of the detected elements becomes possible[9,12]. However, upper margins of operation depending on the sample composition must be taken into account. These are shown for organic tissue, for mineral powders and for metallic smears in Figure 5[22]. Large grains as well as too much sample will disturb the conditions of total reflection and erroneous results may be obtained.

Two TXRF spectra are shown in Figure 6. The left is a typical spectrum of a clean quartz glass support. Counts are plotted versus the photon energy of the fluorescence radiation given in keV. Only system imminent signals were detected: Si from the quartz glass of the reflector, Ar from the air gap between detector and reflector, and Rayleigh and Compton signals of Mo from the scattered primary beam. The interval between these peaks from 4 to 16 keV shows a very low spectral background. The right spectrum shows signals from the residuum of 10 µl of a multi-element standard solution containing 13 elements. Each element has the same concentration in the multi-element solution. The absolute amount after evaporation of the solvent directly onto the TXRF sample support is of 0.1 µg for each element. The different sensitivities for elements with identical concentration are immediately obvious: V is less sensitive than Cr, Cr less than Mn, etc.

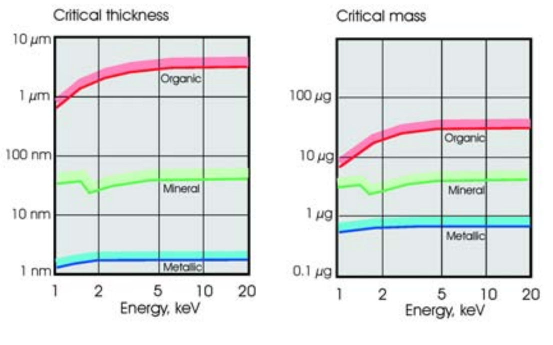

Figure 5. Critical mass and critical thickness of relatively rough and 'infinitely thin' samples of different composition for the analysis using TXRF[22].

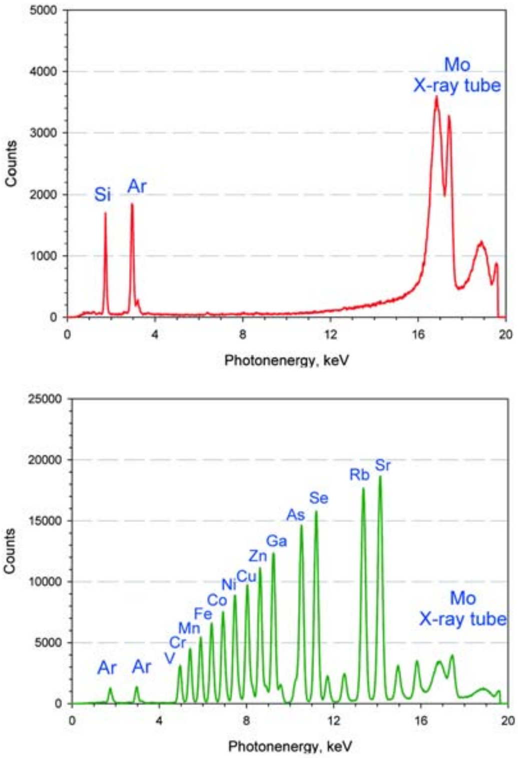

Figure 6. TXRF spectra of a clean quartz glass sample support (above) and of the residuum of 10 µL multi-element standard solution after evaporation of the solvent (below).

The choice of adequate sample amounts is of crucial importance for TXRF. The absence of matrix effects for any thin sample, which may be regarded as infinitely thin for X-rays, permits the determination of relative sensitivities for all detectable elements. This means that we can use a single set of relative sensitivities for the quantification of all elements detected in any type of sample material.

4. Sampling

Sampling µg amounts of pigments or inks is a simple procedure and can be carried out anywhere. The request for single ended clean cotton wool buds (Q-tips) which can be placed in clean containers to prevent contamination is the only prerequisite[16, 23-40].

For succesful sampling, a clean surface of the object to be sampled is needed. The first step of the sampling procedure is to rub off carefully with the cotton swab some grains from the area of interest. Normally, small, abraded quantities of sample adhere to the cotton wool and are invisible to the naked eye. If they are visible, an unecessarily large sample was taken and the amount collected will be of the order of some hunderd µg. The second step is to save the Q-tip immediately after sampling in a container to prevent contamination. In fact, if only a few µg of sample were collected, some grains of airborne particulates or simply dust can seriously disturb the original chemical composition of the sample. Therefore, careful handling of such micro-samples must to be emphasized. A schematic representation of the sampling procedure is given in Figure 7.

Depending on the sampling area different types of Q-tips are recommended. For larger areas, e.g. of paintings on canvas or on wood, polychromed sculptures, etc., normal Q-tips for hygiene can be used. They can be obtained in an excellent clean quality in every supermarket. Usually, we cut them into two pieces and place each half with the cotton wool end down in a clean poly propylene container 11×55 mm with a top (Merck, Qualilab®). For smaller areas, e.g. miniatures or single iron gall ink letters, we use slightly modified STD-PEN for Male (# 69-5018/R11, Abbott Laboratories, IL USA 60064) regularly applied in urology and ophthalmology for sampling chlamydiazyme/gonozyme (Figure 7).

After sampling the containers with Q-tips can be sent for analysis by normal post to the laboratory. There, the samples are prepared in a similarly simple way as the sampling itself. The sampled grains adhered to the cotton wool of the Q-tips must be knocked out or struck off and deposited onto a clean TXRF sample support (Figure 7, no. 5). A clean support means that the surface contamination must be below 1 pg mass (1×10^{-12} g) for about 50 elements. These amounts are below the detection limits of conventional laboratory TXRF devices. The transferred sample mass ranges between 0.1 ng (1×10^{-10} g) for small samples and about 3µg (3×10^{-6} g) for big samples. This upper restriction is necessary to prevent matrix effects as described before (Figure 5).

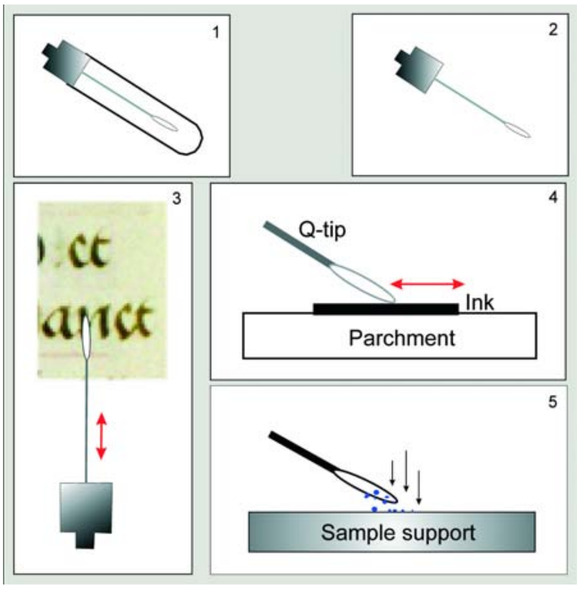

Figure 7. Sampling small particles of iron gall ink written letter from a medieval manu-script: 1 - Protected clean “Abbott Q-tip”, 2 - Q-tip ready for sampling, 3 - sampling ink of the letter “n”, 4 - schematic representation of the procedure shown in no. 3, 5 - sample preparation onto the TXRF sample support, sampled particles are deposited onto the support

5. Quantification

Following the a.m. conditions for infinitely thin samples, it can be assumed that the intensities are proportional to the mass fractions c_i for the respective element i. Intensities I_i for all elements i obtained from TXRF spectra can be used for a simple and reliable quantification when combined with the relative sensitivities S_i. These sensitivities are constants of proportionality, they must be determined only once and are in general well known (relative standard deviation < 2%) for each individual TXRF spectrometer. Thus, the relative mass fraction c_x of an element x can be determined by referring to the sum of all elements i detected in the spectrum[9, 12, 22, 41].

$$c_x = \frac{I_x / S_x}{\sum I_i / S_i} \cdot 100\% \qquad (3)$$

This method of quantification gives only relative mass fractions of the detected elements and is applied usually for very small samples without any special assumption. For an absolute quantification two further quantities are needed: a) the sample mass and b) a known amount of an element not present in the sample, which must be added to the sample as an internal standard element. Then absolute mass fractions of elements present in a sample can be calculated from[9, 12, 22, 41]:

$$c_x = \frac{I_x / S_x}{I_{\mathrm{int}} / S_{\mathrm{int}}} \cdot \frac{m_{\mathrm{int}}}{m_{sample}} \qquad (4)$$

c = mass fraction, I = intensity, x = element to be determined, int = added element (internal standard), m = mass.

The sample masses provided by a micro-sampling method such as that of Q-tips are too small to be weighed reliably. For this reason only a quantification using equation (3) is possible, and only relative mass fractions of the detected elements are accessible. However, these relative mass fractions are sufficient for the elemental characterisation of many inorganic pigments as well as of mixtures of pigments contained in paints, historical varnishes, iron gall inks, glass, etc.

6. Examples

Many analyses of micro samples have been made for resolving questions concerning objects of cultural heritage. In certain cases more than simple analyses of the elemental composition were performed. The results were used for dating tasks, for detecting fakes, for the comparison of objects and for the detection of unknown materials. Selected examples will be highlighted in the following pages.

6.1 Pigments and Paintings

The chemical composition of a great variety of inorganic pigments can be characterised by applying the described method. A list containing some of them is presented in Table 2. Most of the pigments listed can be recognised by their key-elements[16] in combination with the additional information of the colour of the sampled paint. However, some of them, e.g. some Cu containing green pigments, cannot be differentiated by TXRF analysis. In such cases an additional method for the characterization of the molecular composition (e.g. micro-Raman spectroscopy) of the pigments is required[34-40].

Historically, looking at analyses of art works, pigments of old paintings were the first samples sys-

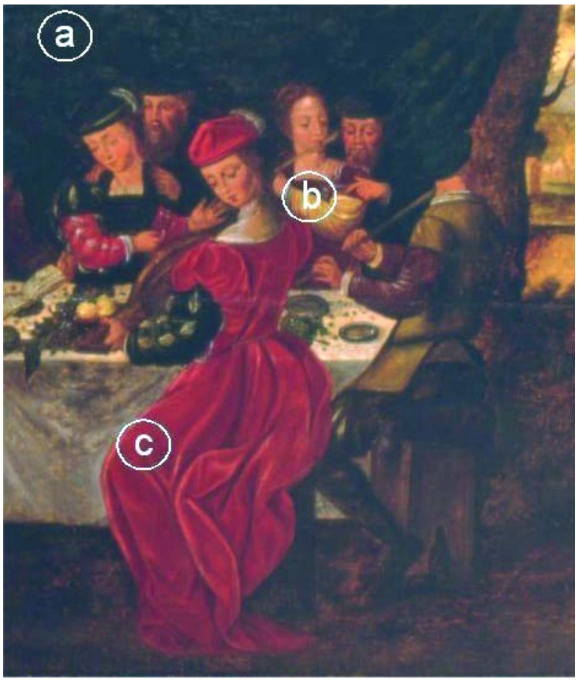

Figure 8 . Anonymous 16th century Flemish painting 'The Concert after Dinner' (detail).

White Pigments	
Antimony white	Sb_2O_3
Lithopone	$ZnO + BaSO_4$
Permanent white	$BaSO_4$
Titanium white	TiO_2
White lead	$2PbCO_3 \times Pb(OH)_2$
Zinc white	ZnO
Zirconium oxide	ZrO_2
Chalk	$CaCO_3$
Gypsum	$CaSO_4 \times 2H_2O$
Yellow Pigments	
Auripigmentum	As_2S_3
Cadmium yellow	CdS
Chrome yellow	$2PbSO_4 \times PbCrO_4$
Cobalt yellow	$K_3[Co(NO_2)_6] \times 1.5H_2O$
Lead-tin yellow	Pb_2SnO_4 / $PbSn_2SiO_7$
Massicot	PbO
Naples yellow	$Pb(SbO_3)_2$ / $Pb_3(SbO_4)_2$
Strontium yellow	$SrCrO_4$
Titanium yellow	$NiO \times Sb_2O_3 \times 20TiO_2$
Yellow ochre	$Fe_2O_3 \times nH_2O$ (20% - 70%)
Zinc yellow	$K_2O \times 4ZnO \times 4CrO_3 \times 3H_2O$
Red Pigments	
Cadmium red	$CdS + CdSe$
Cadmium vermilion	$CdS + HgS$
Chrome red	$PbO \times PbCrO_4$
Molybdate red	$7PbCrO_4 \times 2PbSO_4 \times PbMoO_4$
Realgar	As_2S_3
Red lead	Pb_3O_4
Red ochre	Fe_2O_3 (up to 90%)
Vermilion	HgS
Green Pigments	
Basic copper sulfate	$Cu_x(SO_4)_y(OH)_z$
Chromium oxide	Cr_2O_3
Chrysocolla	$CuSiO_3 \times nH_2O$
Cobalt green	$CoO \times 5ZnO$
Emerald green	$Cu(CH_3COO)_2 \times 3Cu(AsO_2)_2$
Guignet green	$Cr_2O_3 \times nH_2O + H_3BO_3$
Malachite	$CuCO_3 \times Cu(OH)_2$
Verdigris	$Cu(CH_3COO)_2 \times nCu(OH)_2$
Blue Pigments	
Azurite	$2CuCO_3 \times Cu(OH)_2$
Cerulean blue	$CoO \times nSnO_2$
Cobalt blue	$CoO \times Al_2O_3$
Cobalt violet	$Co_3(PO_4)_2$
Egyptian blue	$CaO \times CuO \times 4SiO_2$
Manganese blue	$BaSO_4 \times Ba_3(MnO_4)_2$
Prussian blue	$Fe_4[Fe(CN)_6]_3$
Smalt	Co-glass ($K_2O + SiO_2 + CoO$)
Ultramarine	$Na_{8..10}Al_6Si_6O_{24}S_{2..4}$
Black Pigments	
Antimony black	Sb_2O_3
Black iron oxide	$FeO \times Fe_2O_3$
Carbon black	C (95%)
Cobalt black	CoO
Ivory black	$C + Ca_3(PO_4)_2$
Manganese oxide	$MnO + Mn_2O_3$

Table 2. Some pigments used for the preparation of paints. By means of the elements contained (key-elements) most of pigments can be distinguished from each other when analysing only ng-amounts by TXRF.

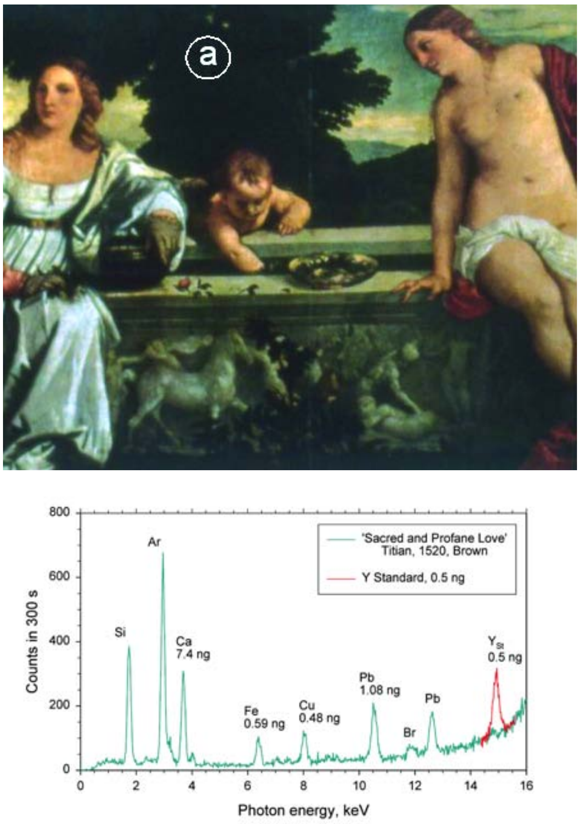

Figure 9. Detail of ‘Sacred and Porfane Love’ by Titian, 1520. Galeria Borghese, Rome. Below: TXRF spectrum of (a). Absolute amounts of elements given in ng, Yttrium as an internal standard.

tematically characterised by TXRF[16, 24-30]. Several questions, mostly related to restoration or of an art historical nature, could be elucidated until now using TXRF. Two paintings will be discussed as examples, demonstrating TXRF capabilities in this field of application.

A detail of an anonymous Flemish painting of the 16th century called ‘The Concert after Dinner’ presented in Figure 8, shows a dark greyish brown cloth acting as a curtain in the background (a)[27]. What pigment was used here? And, is the yellow paint (b) in agreement with the dating of the painting? Is the red colour (c) of the dress Vermilion?

The red parts (c) of the painting were painted, as deduced from TXRF spectra, with a mixture of Vermillion and White Lead, mostly a ratio of 100/107. Some minor constituents e.g. K, Ca, Fe, and Zn were detected, too.

The yellow pigment of the dress (b) contains abundance of Pb and Sn. The actual ratio of Pb/Sn is 100/25, which is close to the ratio of Pb and Sn in Lead-Tin Yellow, Pb_2SnO_4 (Pb/Sn = 100/29). This finding is in good agreement with the use of the older Lead-Tin Yellow until 1750 and the use of more modern Naples Yellow ($Pb_2Sb_2O_7$ or $Pb_3(SbO_4)_2$) starting around the year 1720.

A brown pigment was expected for the curtain (a), but the results of the TXRF investigation indicate a paint containing high amounts of a Cu containing pigment. The curtain was probably green, so that pigments like Verdigris and Copper Resinate might have been used. These pigments were prepared with copper acetate. Chemical degradation, including light and air pollution, of the pigments leading to the formation of black or brown pigments has been reported[42, 43].

A similar discoloration of a famous painting on canvas from 1520 by Titian was observed[27, 31]. The leaves of trees as well as the scrubs are dull brown. Experts disagree on the intentions of Titian in his painting „Sacred and Profane Love“. Figure 9 shows a detail of the painting and a spectrum of the brown (a). There Ca, Fe, Cu, and Pb can be found and, after quantification with Y as internal standard, a total mass of the detected elements is below 10 ng. This ultra-micro analysis of pigments shows that probably the trees and bushes were painted in a lively green before discoloration completely changed the appearance of the painting.

6.2 Medieval Manuscripts, Inks and Pigments

Flemish manuscripts of the end of the 15th century are of outstanding beauty. However, they keep some secrets and some mystery in the handwritten texts and hand coloured miniatures. Art historians ask for the chemical composition of selected inks and pigments used for the production of those manuscripts. Additional information, independent from art historical sources, may give hints for better understanding the production of those manuscripts. Moreover, the information can be used for restoration and preservation tasks. Applying the gentle sampling technique described above (Figure 5) and a subsequent TXRF analysis and / or a micro-Raman spectroscopy, some of these questions could be elucidated.

Results of the analyses of several manuscripts of the collection ‘Raphael de Mercatellis’ from Ghent University Library, Belgium, and of the famous Cat. No. 946 ‘Breviarium Meyer van den Bergh’ from Meyer van den Bergh Museum, Antwerp, Belgium have been previously published[32-39].

6.2.1 ‘Breviarium Meyer van den Bergh’

Questions concerning paints used in miniatures:
- special or unique colours[32, 38, 39]
e.g. orange from David’s tunic, in the miniature ‘David and Goliath’ f°20v
- the blue of the cloak of the Madonna in the dif-

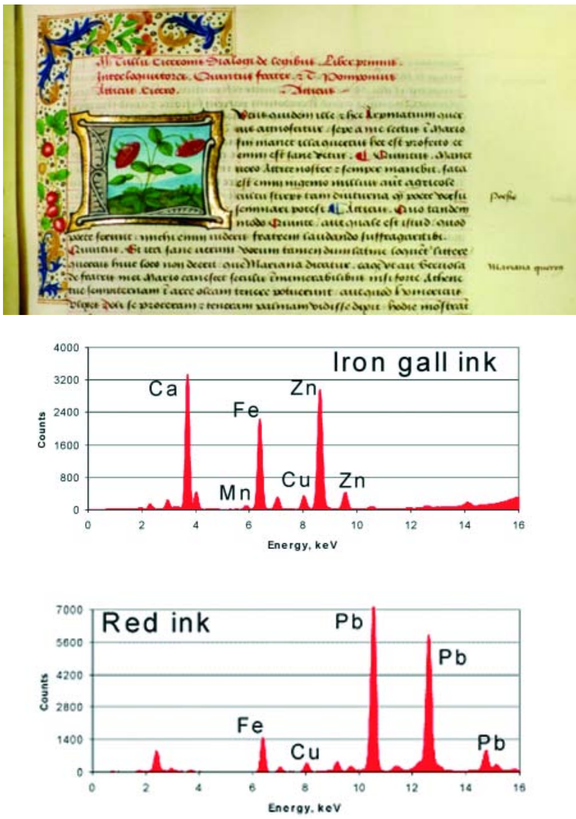

Figure 10. Capital letter L with miniature, HS 109, Collection 'Raphael de Mercatellis' at University Library of Ghent, Belgium. Below TXRF spectra of iron gall ink and of red ink.

ferent representations[32, 38, 39] only two pigments were used, Lapiz Lazuli and Azurite

- colours used in f°522v and f°536v, attributed to the same miniaturist[32, 38, 39], green was confirmed to originate from the same batch

6.2.2 Collection 'Raphael de Mercatellis'

Questions concerning pigments, inks, and dating

- additional 'chemical sorting criteria' used for different manuscripts[36-39]
using the blue paragraph marks like a 'C' as shown in Figure 10
- iron gall inks, characterisation[32, 33]
typical spectra of iron gall ink and of red ink are shown in Figure 10
- blanks of the used parchments containing high amounts of K, Ca, Sr[39]
- an unknown green pigment was detected and could be synthesised[35, 38, 39]

The most impressive result of these analyses was that the sampling procedure by means of 'Abbott' Q-tips could be made by using only a single Q-tip for both analytical methods. That means that only one sample could be used for determining the elemental composition by TXRF and for the molecular characterisation by micro-Raman spectroscopy. These complementary information of the same sample obtained by two excellent micro methods of instrumental analytical chemistry gave a deep insight into the materials and techniques used at the end of the Middle Age for the production of these finest manuscripts.

6.3 Violin Varnishes

Historical varnishes, especially those of musical instruments have been of the subject of many investigations. Tiny flakes of several historical varnishes have been studied and their content of heavier metals characterised by TXRF[44-48]. The following two examples demonstrate the capability of TXRF in this field of application.

Figure 11 shows the scroll of a cello made by L. Maugin, Paris, in the 19th century. The instrument shows several scratches on the varnish which is normal for an instrument regularly used for concerts. The violin-maker had some doubts about

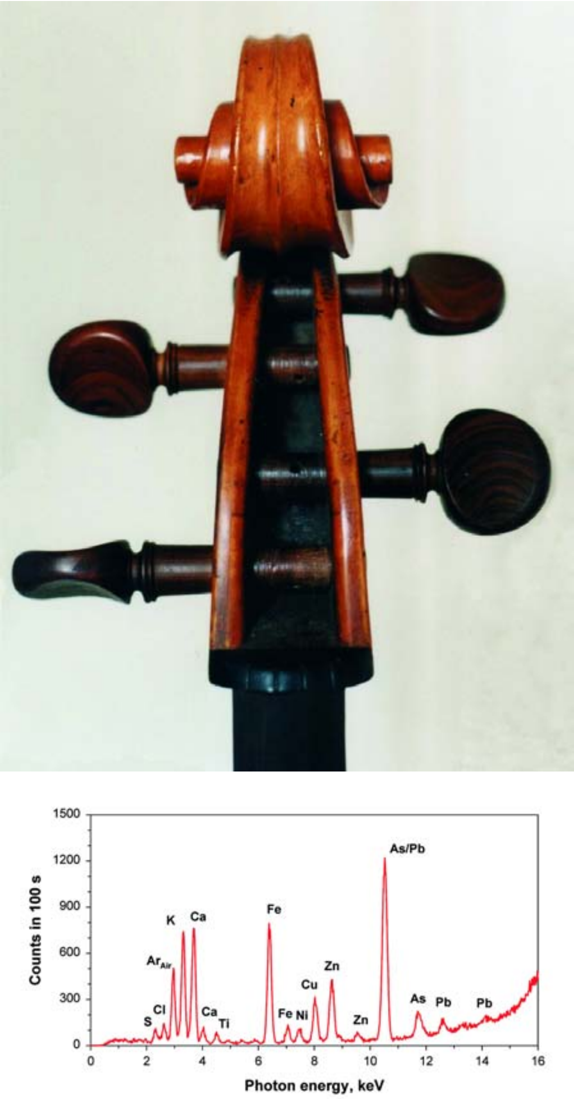

Figure 11. Scroll of a Cello made by L. Maugin, 19th century and TXRF spectrum of the original varnish.

	Scroll % rel.	Side % rel.
S	13.4	8.4
Cl	16	20.7
K	30.1	29.7
Ca	24.3	22
Ti	1.3	0.8
Mn	0.2	0.5
Fe	6.2	11
Ni	0.5	0.1
Cu	1.4	0.5
Zn	1.8	2
As	3.7	3.8
Ag	0.5	-
Pb	0.7	0.5

Table 3. TXRF results of varnish analysis from Cello Mangin.

the originality of the neck and the scroll of the instrument, so that two small samples of less than 20µg each were extracted with a clean scalpel and the flakes were analysed by TXRF. The first sample was taken of the scroll and the second of the side of the cello, which was supposed to be in original condition since the instrument had been finished by Maugin. A spectrum of the varnish of the scroll as well as the results of TXRF analysis are shown in Figure 10 and Table 3, respectively.

The varnish flake taken from the scroll and the piece taken from the side are of similar elemental composition. The varnish from the side of the cello contains significantly higher amounts of Mn, Fe, and Pb. These elements are commonly connected to some additives: e.g. earth pigments such as Ochre, Terra di Sienna, Kassler Brown, etc. or are connected to Pb containing pigments or siccatives such as Massicot, White Lead or Red Lead. However, the elements Ni, Cu, and Ag are significantly higher in the varnish of the scroll. This finding can be attributed to metal abrasion of the strings in the close vicinity of the scroll leading to a contamination of the varnish. However, all these elements are present in small amounts. The main elements such as Cl, K, Ca, Ti, Zn, and As are present in similar amounts (their sum is 77.2 % and 79.0 % respectively) and lead to the conclusion that both varnishes are from the same original batch.

In contrast to the cello made by Maugin, the original varnish from the back and the retouched neck of a violin made by Ch. & S. Thompson, London ca. 1780, show clear differences. The superimposed TXRF spectra (Figure 12) of both varnishes illustrate the results of the micro-analyses using only some µg samples. Clear differences for nearly all elements can be observed except for S, Cl, and Ni. Some modern chromium containing pigments seem to have been added to the varnish used for retouching to obtain a similar hue to the original varnish.

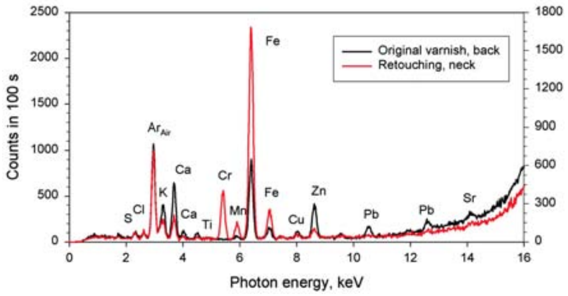

Figure 12. TXRF spectra of an original and retouched violin varnish from a violin made by Th. & S. Thompson, London, about 1780.

6.4 Metals

Samples were taken by means of Q-tips from a polychrome late 17th, early 18th century wooden bust of St. Liborius, from St Anna Imperial Chapel, Antwerp. The sculpture is not only covered with different paints, it is also gold leaved. The gilding of the mitre lappets show different colours of gold leave varying from a warm orange hue to a more yellowish-white tone. Quantitative analyses could be carried out because all elements of the alloys in question were detected. TXRF analysis gave a composition of 74% Au, 3% Ag and 23% Cu for the warmer colour, and 76% Au, 22% Ag and 2% Cu for the yellowish-white colour[31]. However, metal objects are by far the most difficult samples for the Q-tip sampling procedure. Experiments made on certified standard reference material (SRM) using Q-tips for sampling do not reflect accurately the composition of the standards. Sometimes, intolerable large deviations from the certified values of major and minor constituents are determined. Additionally, low repeatability, as expressed by high RSD values of more than 15% were observed. According to these unpublished results[49], the abrasion of the elements of an alloy is not uniform. For example, the amount of Pb obtained form a brass standard is much higher than the certified value and the TXRF value for the abraded Cr of a stainless steel is below the detection limit.

A simple characterisation of metals using Q-tips for sampling and TXRF for analysis can only be recommended for a rough estimation of the elemental composition. A more detailed differentiation of alloys will not be free of risks.

6.5 Glass

European glasses, especially a Bohemian 'Reichsadlerhumpen' and a Flacon, were subject of TXRF studies[50]. Using a destructive sampling procedure, in contrast to those presented up to now, fine glass powder was ground form the objects by means of a diamond dentist driller. Some grains of these powders, mostly taken from the bottom of the objects, were analysed directly by TXRF. Ratios of different element combinations were calculated (Ca : K, Fe : Mn) and minor constituents like Ba, Rb, Sr, Zn, and Ti were compared with the composition of known historical glasses. However, a destructive sampling is not necessary having in mind, that glass objects can be easily analysed in-situ using portable EDXRF devices[51].

6. Soils

Also soils of historical relevance have been analysed. Due to the lack of other historical sources of information, earth from archaeologically dated levels of the city of Dortmund was collected. The distribution of the medieval population and of the medieval trade inside the city wall should be reflected in the elemental distribution/contamination of the soils. The impact of human activities on the medieval environment should be accessible when analysing soluble or mobile elements present in the soils. These elements of anthropogenic origin were extracted by means of *aqua regia* from more than 90 different soil samples. The local distribution of contaminations could be recognised combining TXRF analysis of the extracted elements and multivariate analysis of the data. Two different sites could be isolated from all others by their outstanding elemental composition. In one case the extremely high amounts of Cu, Zn, Sn, and Pb corroborate the contemporary street name 'Eisenmarkt'. In the other case, an early Pb melting area, known to have been used before the foundation of Dortmund, was clearly identified[52] by the extraordinary amounts of extractible Zn and Pb present in the soil samples.

Evaluation

TXRF has been successfully used for more than 15 years for extreme micro-analyses. Among others, TXRF has been used for the analysis of pigments, inks, metals, glass and varnishes of historical relevance. Therefore, a gentle micro-sampling technique using cotton wool buds (Q-tips) for the collection of only µg-amounts of samples for a complete elemental characterization was combined with a modern method of instrumental analytical chemistry. However, some limitations of the method have to be mentioned. Only elements with atomic numbers higher than 14 (Silicon) can be detected with excellent sensitivity. This limits the number of detectable key-elements used for the characterisation of historical inorganic pigments. Further, small samples are not necessarily representative for the characterization of a painted area. On the other hand some advantages cannot be neglected. A fast and non-consumptive analysis combined with a simple and effective sampling can be used to characterize many objects of cultural heritage without moving them form their location to the laboratory. This gentle procedure is safe and inexpensive. The presented examples confirm the advantages of the method.

A last question might be allowed: "*How much of natural sciences might an object of art endure?*" This philosophical question appeals to our conscience to act in a responsible manner. We have to discuss and answer this question before starting with our work. Nevertheless, the results obtained by chemical analyses increase our knowledge about objects of cultural heritage and might help in better understanding of how to preserve them for the next generations. This, and not the satisfaction of our curiosity, should be the maxim.

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