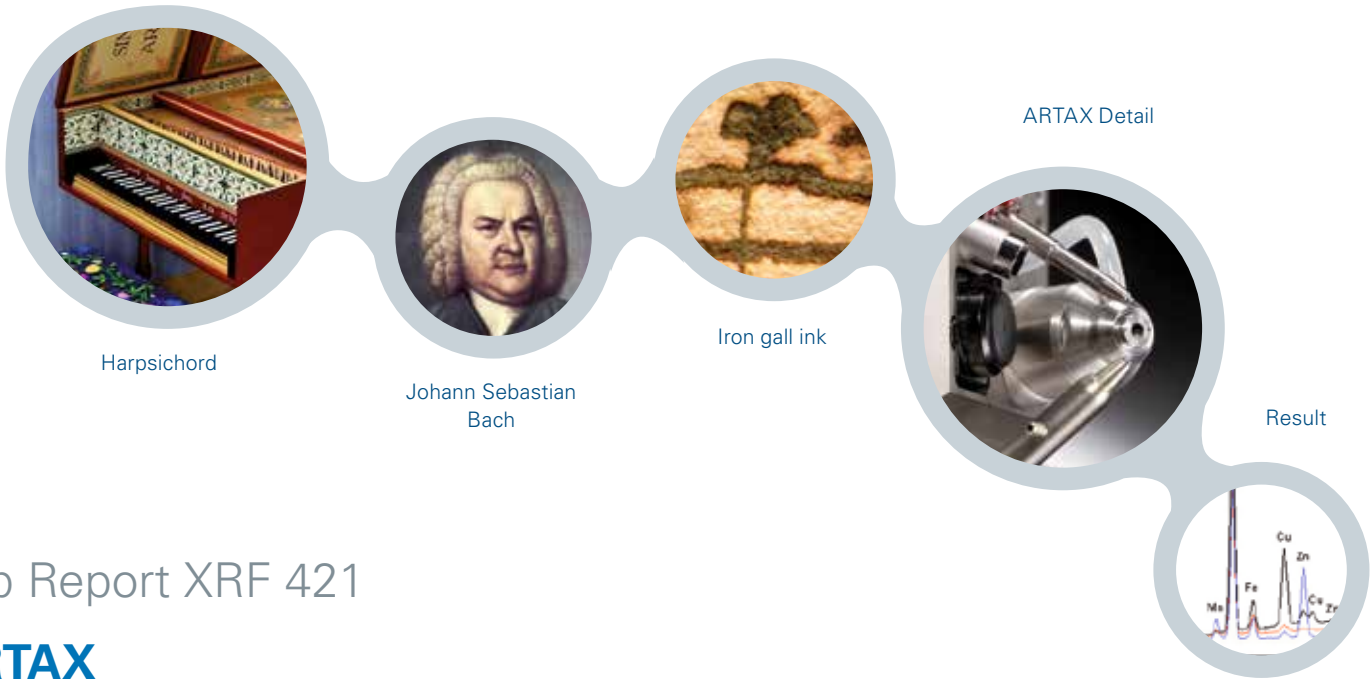


Lab Report XRF 421

ARTAX
Non-Destructive Characterization of Historical Inks using Micro X-ray Fluorescence Analysis

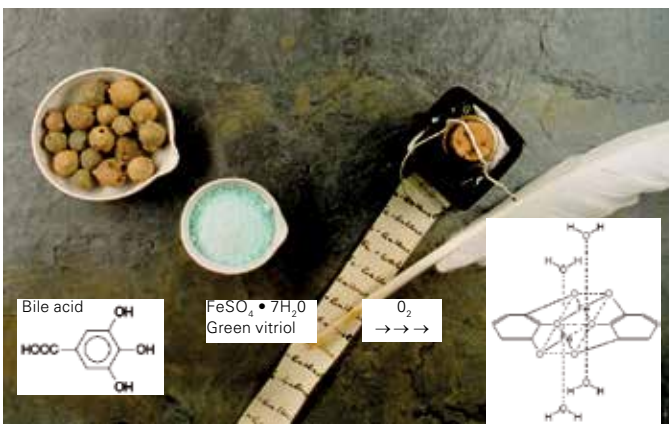
Introduction

X-ray fluorescence analysis (XRF) is highly suitable for the characterization of inks. Non-destructive analysis has shown itself to be necessary when tests are carried out on priceless originals or serve as evidence in criminal investigations. This paper describes the successful use of the Micro-XRF system ARTAX in the area of historical inks.

Iron Gall Inks

From the 16th to 18th century manuscripts were written in iron gall ink. This ink was made by mixing iron vitriol (iron (II) sulphate) with gallnut extract. The black, indelible iron (III) gallet complex was created following oxidization upon exposure to air (Fig. 1).

Fig. 1: Raw materials for the production of iron gall ink



Iron pyrogallol complex

Because of the use of naturally occurring raw materials, the composition of the ink has variable amounts of main and side components and contaminations. The analysis of the components consequently allows a definite characterization and chronological ordering of the inks.

Handwritten Manuscripts by Mozart, Bach, Goethe

Alongside the chronological order, the analysis of the iron gall inks is necessary for the selection of correct measures for conservation. To a large extent historical handwriting has been subject to damage, such as, for example, ink-erosion (Figs. 2, 3).

On the one hand ink-erosion occurs through the oxidization of excess iron (II), which also releases sulphuric acid. On the other hand ink erosion occurs through the catalytic degradation of the paper due to metal ions, which contaminate the ink.

Depending on the composition of the ink, the writing appears stained (Fig.3) or brown in color (Fig. 2). Only a few handwritten manuscripts have remained "perfectly" black (Fig.4).

Methods

The ARTAX was set up with the following test parameters:

- X-ray tube, 30 W, Mo target
- U =45 KV, I = 600 µA

Line scans with 10 measuring points (each of them with 15 seconds duration) were carried out. The spectra were added, in order to balance inhomogeneities in the distribution of the pigment.

Results

The various components of vitriols other than iron are known (Table 1). The X-ray spectra of iron gall ink from the 18th century are shown in Fig. 5.

There always is a problem in the measurement of ink samples with varying layer thickness. Therefore an absolute quantification is not possible!

During the examination of iron gall ink the main component Fe was standardized (≡ 1) for that reason. The other components could then be quantified relative to iron

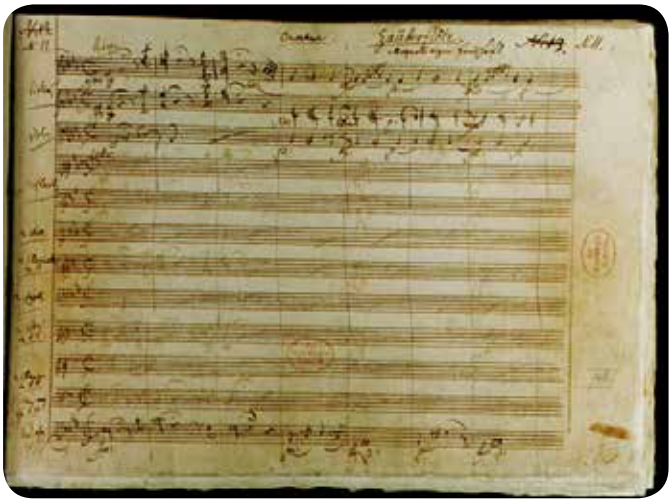


Figure 2: W.A. Mozart, The Magic Flute

Figure 3: Johann Sebastian Bach
Serenade for Leopold of Saxony-Koethen

Figure 4: J.W. von Goethe, Faust II

(Table 2). As a result of the XRF-spectra, characteristic "fingerprints" of the various iron gall inks could be obtained. This permits characterization and chronological classification of various inks used by an artist. In turn, this facilitates dating works of art, which previously couldn't be chronologically categorized in an artist's work.

Future Developments

It took Goethe many decades to write his drama Faust II. Details of the writing process will be clarified in the near future with the aid of the Micro-XRF spectrometer ARTAX.

Bibliography

O. Hahn, W. Malzer, B. Kanngiesser and B. Beckhoff (2004): Characterization of Iron Gall Inks in Historical Manuscripts and Music Compositions using X-Ray Fluorescence Spectrometry, X-Ray Spectrometry, 33, 234-239.

Table 1: Concentrations of metallic salts in vitriols

Parts in %	Cu	Zn	Mn	Al	K	Mg
Vitriolum romanum	2	--	--	10	10	--
Vitriolum goslariensis	7	11	9	12	--	8

Table 2: XRF-results of the composition of iron gall inks

	Mg	K	Mn	Cu	Zn
early 18th cent.	0.015	0.056	0.020	0.582	0.103
mid 18th cent.	0.017	0.055	0.054	0.025	0.020
late 18th cent.	0.025	0.153	0.115	0.010	0.140

1) Early 18th cent. (black)

2) Mid 18 th cent., J.S. Bach (red)

3) Late 18th cent. (blue)

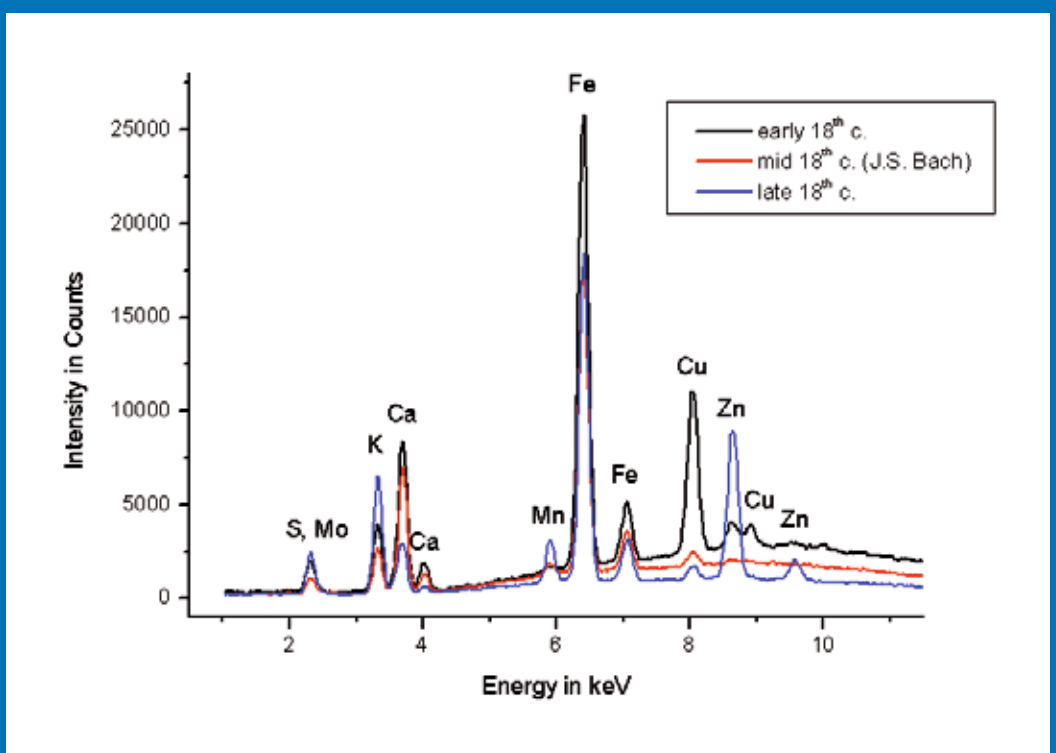


Figure 5: XRF spectra of various iron gall inks

Acknowledgements

The tests on historical inks were carried out by Dr. Oliver Hahn, BAM, Berlin.

The figures were made available by kind permission of the Goethe-Schiller Archives, Weimar (Goethe) and the State Library in Berlin (Mozart).

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