**Introduction**

Historical manuscripts, ancient printed books made of paper or parchment as well as thin wooden objects like musical instruments and cloth materials had been studied by applying several methods of instrumental analytical chemistry [1-7]. Sometimes these studies were performed in-situ, sometimes after gentle sampling of µg amounts of material. The applied methods cover a great variety, among others PIXE, TXRF, Raman spectroscopy, IR spectroscopy, LIPS, SR-XRF, and SEM-EDX. Mostly, the results could only be presented as qualitative evaluation of the analyses. Advantages of full quantitative analysis are the direct comparability with those obtained by other methods, the possibility of trace back to origin and they reflect in a certain manner the (historical) production process.

PIXE with an extracted beam is predestined for in-situ analyses of many objects of cultural heritage, especially manuscripts and books, and also objects made of wood or cloth are suitable. In combination with a powerful quantification procedure, results of microanalyses will become comparable to those obtained by other independent methods.

The quantitative evaluation of X-ray spectra is normally performed applying methods using fundamental parameter calculation. Mostly they are designed for infinitely thin or infinitely thick samples. For thick samples often the option is used to calculate all sample components to match up 100 wt%, including so called depending invisible elements as e.g. oxygen in oxides (the oxygen is not seen in the PIXE spectra). By using this option the knowledge of the actual particle fluency is not necessary, which is only estimated with difficulties by in air analyses of insulating samples. However this option is not available to determine contents of elements in an organic matrix, since this matrix is not seen in the spectra. More modern methods are based on Monte-Carlo simulations fitted to standard reference materials and afterwards to unknown samples. A third possibility for a reliable quantification of element concentration in thin samples, based on the absence of matrix effects, on the determination of relative sensitivities for each element and on the use of an internal standard, will be presented below.

Basically, it means that the influence of the matrix can be nearly neglected and a set of relative sensitivities can be used for at least a semi-quantitative analysis. The relative mass fractions of each detected element can be calculated in relation to another element by

\[
c_x = \frac{I_x}{I_{Ei} S_{Ei}} \cdot 100 \text{ a.u.}
\]

Here \(c_x\) is the mass fraction of the element \(x\), \(I_x\) is the net intensity obtained from the element \(x\), \(S_x\) is the respective relative sensitivity and \(E_i\) is any element present in the sample. A further evaluation can be made by relating the mass fraction of any element \(x\) to the sum of all detected elements \(x\):
\[ c_x = \frac{I_x}{\sum I_{El}/S_{El}} \cdot 100 \% . \]

In contrast to these approaches, the internal standardization with known amount of an internal standard element \( S_t \) and known sample mass \( M \) provides a full quantitative method. The absolute mass fractions \( c_x \) of each element present in the sample can be calculated according to [8]:

\[ c_x = \frac{I_x}{I_{S_t}/S_{S_t}} \cdot \frac{m_{S_t}}{M} \]

The necessary effort for the determination of the sensitivities, in view of the lack of homogeneous standard reference material at the 10 \( \mu \)m scale for microanalyses, seem to be reasonable.

If the determination of relative sensitivities and a homogeneous distribution of the internal standard over the sample can be obtained, a versatile tool for the quantitative evaluation of element concentrations in different matrices will be available. Many questions concerning books, manuscripts, thin cloth and wooden artefacts will be easily accessible. For the analyses of historical violin varnishes a comparison with the results of micro-digestion of tiny samples and analysis by total reflection X-ray fluorescence [9] will give additional information to understand the techniques used in former centuries to varnish musical instruments.

**Experimental**

\( \mu \)-PIXE measurements, accompanied by SEM-EDX investigations on known organic materials will be carried out to investigate the following:

- Different matrices, paper, parchment, wood or cloth, will be doped with standard solutions of selected elements and presented to \( \mu \)PIXE for analysis in order to record EDX spectra.
- Starting from these spectra relative sensitivities were calculated on the basis of net intensities derived from the X-ray emission lines.
- Multi-element analyses of samples loaded with several standard solutions were analysed.
- The dynamic range of the proposed method was assessed by doping material with different amounts of elements.
- The detection limits according to IUPAC’s definition as well as the upper ranges of content, shown by a non-linearity of the calibration curves, will be elucidated.
- The homogeneity was be controlled exemplary for each matrix by recording line-scans over a wide range in the mm scale.

The proposed method will be applied later to the quantitative analysis of varnishes on wood, to printed matter on paper and to handwritten documents on parchment.
Results and Discussion

As expected the proposed method shows the above mentioned capability for some typical applications. The analysed samples, mostly small droplets of iron gall ink doped with single element standard solutions, were applied to modern drawing paper, parchment and canvas. The ink itself serves as coloured liquid for the optical alignment. The dry residues were analysed by external µPIXE. In a first run the element homogeneity in the residues were controlled. The line-scans preformed with this purpose on the three materials are presented in Fig. 1. A trace produced by the 3 MeV protons at 1-2 nA current is clearly visible. Thus, these kind of analyses on valuable artefacts have to be carried out at much lower current even if some trace elements cannot be detected. The results obtained from the line scans across the residua of the 2µL droplets confirm the expected non-homogeneous distribution of the elements. An interesting observation concerns the added standard solutions. The distribution shows enrichment at the centre and borders of the residue. Their distribution is very similar when comparing the added elements and are also similar to Fe of the ink (cf. Fig.2). In view of the determination of relative sensitivities for the elements this observation leads to the conclusion that for the analysis the whole area of the residue has to be covered, otherwise a disproportion may give wrong sensitivity values. For that purpose the droplet volume was reduced to a minimum, i.e. some nL were deposited and dried. On the other hand the proton micro-beam was enlarged to an ellipse of 750 µm x 500 µm. This area covers the residual trace of the smallest droplets (Fig. 3).

Figure 1. Samples of iron gall ink applied to paper, parchment and canvas.

Figure 2. Element distribution across a residue of iron gall ink doped with Tl and Pb.

Figure 3. Blue nL droplets covered by the proton beam.
A spectrum of the residue of a doped iron gall ink is shown in Fig. 4. High concentrated liquid standard of Cr, Ni, As, Se and Sr (stock each 1000 µg/mL) were added to the ink.

![PIXE spectrum of doped iron gall ink on parchment.](image)

Based on these measurements, mostly on three to five replicates, sensitivities for some elements were calculated. The relative standard deviation obtained for these sensitivities are of the order of 2.5 % or better. A graphical representation of the obtained sensitivities (Fig. 5) suggests a smooth function, so some missing values might be interpolated until their determination. For an absolute relation “counts/s/ng” the exact amount of standard applied should be known. Unfortunately, the nL-droplets could not be generated with exact volumes, thus the standard amount has to be determined by chemical dissolution and analysis via total reflection X-ray fluorescence of the residues. This will be done in the near future.

![Relative sensitivities for some elements on paper and parchment for the µPIXE at C2RMF, Paris.](image)
References


