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Symposium on "Material investigations of Limoges painted enamels"

– Introduction –

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At May 21st/22nd 1999 a symposium was held at the Museum of Applied Arts in Berlin on scientific investigations of painted enamels from Limoges (France). Most of the 22 participants – art-historians and enamel restorers, archaeometrically working scientists and builders of analytical devices from France, Great Britain and Germany – are experts in this special field. The lectures and dicussions were held from very different points of view thus enlightening what experiences were already made and what questions are still to be solved.

Reason for this meeting has been the start of a new 3-year project on this topic at the Institute of Inorganic and Analytical Chemistry of the Technical University Berlin which is financed by the German Federal Ministry for Education, Research and Science (BMBF).

The two most important German collections of Limoges school painted enamels at the Herzog Anton Museum Brunswick and at the Museum of Applied Arts in Berlin will be in focus of the research work. Co-operation partners in science and industry are the Rathgen Research Laboratory Berlin, the Federal Institution for Material Research and Testing Berlin, the Research Centre in Rossendorf and Fa. IfG-Institut für Gerätebau Berlin.

Painted enamels from Limoges belong to the most significant creations of French applied art of the Renaissance. The pictorial world of these polychrome or *grisaille* glass fluxes on a carrier of pure copper include religious and profane themes, portraits as well as scenes from antique mythology. To imitate precious stones small sheets of gold or silver foils (*paillons*) were laid under a translucent enamel, flesh tones (*incarnations*) were painted with iron oxide, as final decoration ornaments were carried out by gilding.

The city of Limoges was an important centre of enamel manufacturing since the Middle-Ages. Painted enamels, a development of the late 15th century, needed highly-skilled and experienced workshops that kept their profitable knowledge as an arkanum within the enameller's families. During the 19th century – a period when Medieval art and architecture saw a strong revival – Limoges painted enamels became desired for private collections. For this reason damaged pieces were restored, missing ones copied or completely new created by specialised enamel manufacturers. To recognise these high-quality replicas is nowadays a problem which is intensely discussed under art-historians.

Beside stylistic examination the composition of the material itself may reveal information about the manufacturing time because of technological changes and the usage of new, formerly unknown raw materials. As the experiences of other working groups showed, especially the glass fluxes seem to be very promising in that question.

A suitable analytical method for the investigation of these objets d'art has to fulfil three requirements:

- Non-destructivity – the good conservation state of most of the pieces makes sampling only justifiable in a few cases, by far not enough for the necessary systematic investigations
- Mobility – a transport of the fragile enamels is not desirable, so the measurements should be carried out in the museum
- High lateral resolution for the investigations of small painting details.

Micro X-Ray Fluorescence Spectrometry (Micro-XRF) - which as comparably young method is subject of technical and analytical research within this project itself – avoids the possibility of combining these qualities in an ideal way. Micro-XRF is a further development of the well-established "classic" XRF, a non-destructive method which allows qualitative and quantitative determination of a wide elemental range down to trace amounts. During the last years there has been a rapid development in the field of X-ray technology: Total-reflecting capillary optics are able to focus the primary X-ray beam to spot sizes below 100 µm with low loss of intensity, furthermore the invention of detector systems working without liquid nitrogen cooling and the common trend of miniaturization of hard- and software make a transport possible.

The first, technical goal of the project will be the construction of a portable Micro-XRF spectrometer for the determination of elements with an atomic number $Z > 11$ (Na). Element analysis will be combined with the imaging of the sample surface. The new tool will be especially fitted to the analysis of silicate materials but undoubtedly it will be highly valuable for a lot of archaeometrical applications like the material analysis of pigments, ceramics, metals and alloys, too.

To overcome the method's limitation of restricted depth sensitivity as well as for reference purposes Micro-XRF will be supplemented by Electron Probe Microanalysis (EPMA) and other methods for which their main advantages and restrictions are compared in table 1.

Method	Sampling?	Mobile?	Spatial resolution	Information	Problems
X-Ray Fluorescence Analysis (XRF)	No (limited sample chamber)	No	ca. 1cm	Qualitative and quantitative determination down to trace elements	No depth information
Micro-XRF (portable)	No	Yes	ca. 50 µm	See above + painting details, inhomogenities, elemental distributions	No depth information, surface irregularities, corrosion
Scanning Electron Microscopy (SEM/EDX, EPMA)	Yes	No	min. 5-6 µm	Qualitative and quantitative determination of main and minor elements (detection limit ca. 0.2%)	
Laser-Microanalysis (LMA, Laser-OES)	Yes	No	ca. 50 µm	Qualitative detection of boron	
Proton-Induced X-Ray Emission (PIXE)	No	No	ca. 1 mm	Depth information, Quantitative analysis of metals & alloys	Quantification of light elements

Table 1: Comparison of the used analytical methods for enamel investigations

An illustration of the "analytical strategy" for the investigation of the Limoges painted enamels is given in Fig. 1. Finally the results yielded by stylistic research, by optical examinations and those regarding the peculiarities of manufacturing technology, by archival studies on treatises and technological literature and last but not least by the determination of the chemical

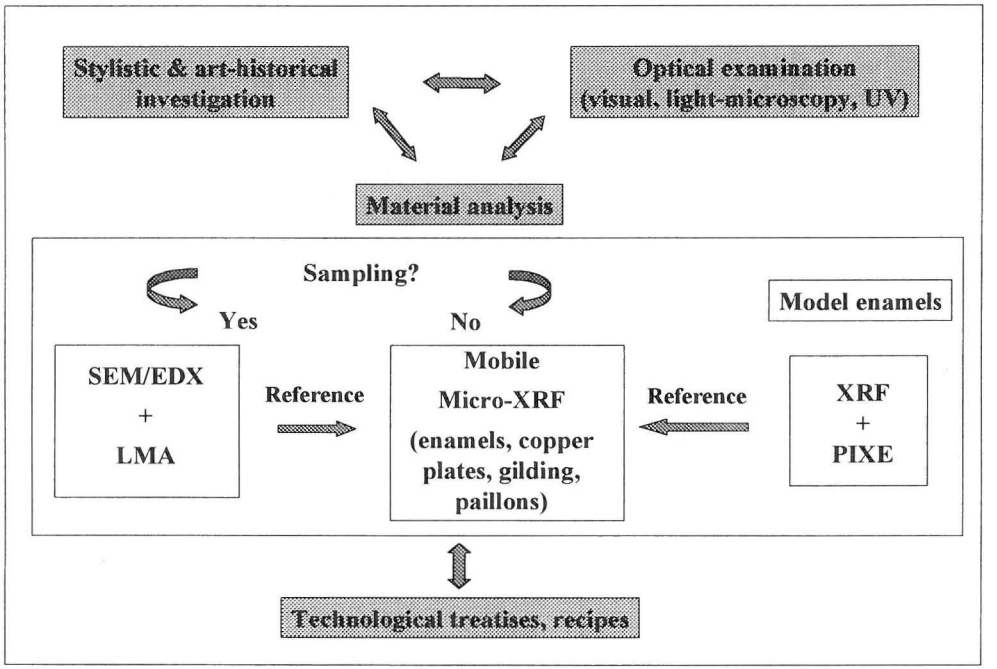

Fig. 1: Analytical strategy for the enamel investigations

composition will be evaluated in coherence. This lets expect broadest information on chronology and dating questions, first of all the recognition of 19th century replicas, possibly a characterisation of different artists/workshops and of significant technological changes.

The following contributions were held as lectures at the symposium giving an introduction in the collections of painted enamels in Berlin and Brunswick and reflecting the most relevant questions the art-historians are confronted with as well as describing the so far existing scientific and technological knowledge and our first experiences in this field.