

# An Odyssey Through Time at EMPA

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**Abstract:** For years EMPA has made many contributions to research on historical materials and their manufacture and conservation in archaeology, restoration and the preservation of historical monuments; areas that are somewhat exotic for a materials testing and research institute. This involves complex, preferably non-destructive investigations on objects that are often very valuable by means of organic and inorganic analysis methods. The emphasis is on investigations of paints and varnishes on paintings and metals such as gold, silver, copper, bronze and iron. The analysis of various materials and the associated problems are illustrated by a range of examples.

**Keywords:** Archaeometallurgy · Archaeometry · Art conservation · Artists' pigments

## 1. Introduction

Archaeology belongs to the humanities, whereas the restoration and conservation of cultural heritage also includes craft and scientific components. In many areas, all three are now dependent upon scientific support in order to be able to conduct research. As a result, archaeometry has developed as a bridge between these subjects. The questions raised are often basic, such as the determination of organic and inorganic materials, their state of preservation, their conservation, production, and provenance. It is sometimes also a matter of determining an object's authenticity. With a metal object, for example, interest is primarily in its form and thus function, which are often hidden under corrosion, and then in its production and processing and, if possible, its provenance, so that quality features and the age of the object may be ascertained.

The artistic impact of a work of art remains only as long as it is physically intact. All objects are subject to ageing of one kind or another depending upon the material composition and environment and upon handling or use. If the ageing

process is to be understood, it is essential to carry out a careful examination of the individual factors, such as climatic conditions, pollutant content of air and soil, presence of microorganisms and, of course, the material composition of the object itself. Once any interrelationships have been identified, it is often enough to make slight changes to these factors in order to retard the ageing process. However, if ageing has progressed so far that the continued existence of the object is in question, conservation measures are also required.

Reference is made to such findings when selecting the materials used for carrying out restoration. Where appropriate, traditional materials are used. However, this is often impossible and 'modern' products are used instead. In this case, thorough knowledge of the composition of the products used and their chemical, physical and biological characteristics is vital, especially with regard to possible interactions with the original materials into which they are incorporated.

State authorities together with university departments, the art trade and museums thus depend upon being able to collaborate with a research laboratory which not only has experience of characterising and testing inorganic and organic materials and of the destructive influence of microorganisms, but is also able to carry out such complex investigations on a routine basis. EMPA has a long tradition of developing exotic applications for material-testing methods and research results. Combining the skills of scientific re-

searchers with comprehensive facilities and an efficient service infrastructure, EMPA is in an ideal position to use its know-how to devise elegant solutions to tricky problems.

## 2. Organic Materials

Organic materials are often the subject of restoration work, but are of less significance in relation to archaeology and the conservation of cultural heritage because investigating such materials is complex and costly. Moreover, they have a shorter life than inorganic and metallic materials because they can be broken down substantially faster by environmental conditions such as heat, moisture, light, pollutants and microorganisms.

In works of art, on the other hand, organic materials such as wood, paper and textiles play an important part because they are generally protected from weathering and may consequently often be preserved for centuries. Considerable time and money are devoted to restoring and conserving works of art.

Which analytical methods are suitable for investigating works of art, thus making it possible to answer complex questions? Over the last decade, various techniques have been refined and combined in such a way that powerful analyses can be carried out non-destructively or using only very small samples. However, tried and trusted techniques, such as optical microscopy, still provide valuable assistance.

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Two examples from the Chemistry Section of EMPA St. Gallen illustrate this point. When restoring furniture, the question always arises of the identity of the materials that the craftsman used to produce the piece. The first question is to identify the species of wood, which defines the strength, structure, and colour of the furniture. The restorer faces a difficult task in identifying and acquiring these often rare woods and specialist assistance is required. The next question is to determine how the piece of furniture has been surface-treated. This entails the use of analytical methods, such as infrared spectrometry, gas chromatography, and X-ray fluorescence spectrometry, to identify the coatings and stains that have been applied. In the present case (Fig. 1), it was a matter of identifying the varnish on the wooden secretary shown in the figure and determining the materials to be blended in order to replicate the varnish as accurately as possible. The test results revealed that the varnish was a complex mixture of natural raw materials, specifically a resin from an unidentified species of tree which had been boiled and dissolved in linseed oil.

Selecting the correct analytical strategy and evaluating the results demands considerable experience. The analyses rarely reveal complete formulations, but they do provide valuable partial results which make it possible for the experienced restorer, using his or her craft



Fig. 1. Wooden intarsia from a secretary.

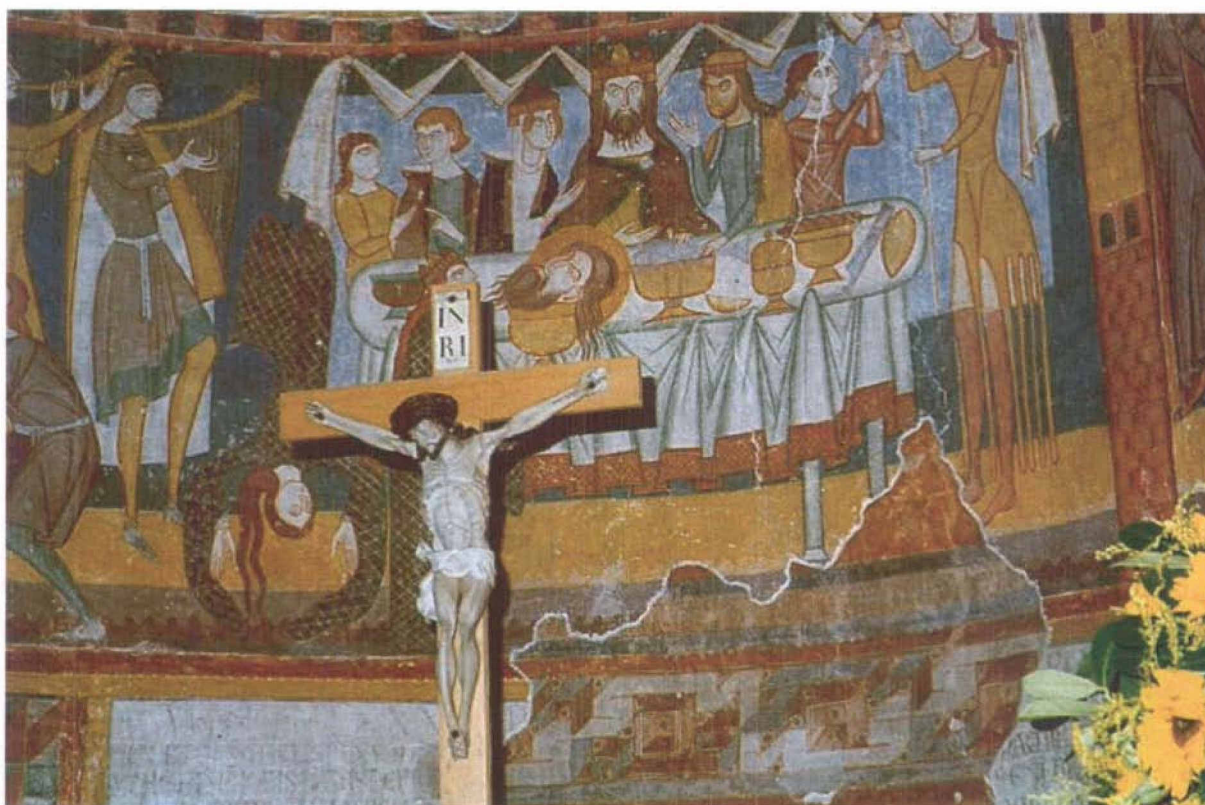


Fig. 2. Chancel of the monastery church at Müstair with Romanesque frescoes over Carolingian wall paintings.

skills, to test replicated formulations under practical conditions in the workshop.

The Münstair monastery complex, classified as a World Heritage Site, is under the protection of UNESCO. Wall paintings have been uncovered in the church of St. Johann which go back to Carolingian times (9th century AD), when the monastery was founded. During the Romanesque period, these were covered with new paintings. The original, Carolingian painting can be seen at the bottom right of the picture of the chancel (Fig. 2), while the upper painting is Romanesque. Methods of analytical chemistry are being used in an attempt to identify the materials used in creating these frescoes. Material is being lost from the wall paintings due to flaking of the paint layer and microbial decay. The presence of protein residues on the surface was revealed by means of gas chromatography/mass spectrometry (amino acids) and plasma emission spectrometry (phosphates). They are attributable to the casein frequently used in tempera. In this project, analytical chemistry assists the microbiologist and acts as a decision-making tool for the restorer. The investigations are still underway. Knowledge of the paint formulations makes it possible for the restorer to replicate similar formulations in the workshop. Laboratory and outdoor weathering tests then reveal whether the replicated formulations are stable over the long term. At present, tempera paints are being tested and artificially aged on sample plates. This approach ensures that our descendants will be able to enjoy the original Romanesque and Carolingian paintings for as long as possible.

EMPA Dübendorf's Corrosion/Surface Protection Section is currently investigating a product which should be useful for art conservation. Tests are being carried out on a plant-derived consolidation agent named *funori* (polysaccharide) which is obtained from red seaweed of the genus *Gloiopeltis* and has been used in Japan for centuries in paper restoration. Preliminary tests in the conservation and restoration workshop for paintings and sculptures of the Swiss National Museum have shown that chalky, matt paintings on various substrates can successfully be consolidated with *funori* without the optical surface changes, such as unwanted gloss, fogging or darkening, which occur with other consolidation agents.

In the project, tests were conducted on models to investigate ageing and the risk of possible salt efflorescence. Testing was performed using an accelerated

weathering device with exposure to UV radiation and a condensing atmosphere, which is normally used to test industrial coatings such as automotive paints, but which was modified and adapted to the requirements of these much more sensitive specimens. The Biology Section at EMPA St. Gallen has tested *funori*'s susceptibility to attack by microorganisms and established that it bears comparison with other consolidation agents. In summer 1999, a collaborative field test with restorers working on the decorative painting of the St. Andreas charnel house chapel at Kerns in the canton of Obwalden confirmed the positive laboratory and workshop findings [1]. In order to get a clearer picture of the various products that are available under the name *funori*, materials from various suppliers were included in the investigation. The variations in quality revealed by this investigation make it difficult to introduce this consolidation agent in its current form in conservation work, despite its very good performance. This variability encouraged us to pursue the production of a standardised seaweed-based product. A high quality seaweed-based product would be a valuable addition to the conservator/restorer's toolbox for consolidating matt paintings.

### 3. Inorganic materials

Since metals are the principal inorganic materials investigated in an archaeological context at EMPA, the following discussions focus on them. Other materials such as slags and pigments are investigated only occasionally. The Inorganic Analytical Chemistry/Characterization of Solids Section has a long tradition of research in metals. Apart from the detection of forgeries, most analytical work on metals relates to elucidating manufacturing processes, determining provenance, and to restoring and conserving metal artefacts.

#### 3.1. Iron

Various individual studies address all the above issues in relation to iron.

EMPA has long been helping to determine the shape of iron finds which its X-ray experts have systematically radiographed on behalf of the Swiss National Museum prior to restoration and conservation.

Corrosion experts have contributed to conservation matters, e.g. with an investigation into the passivation of chlorides in the corrosion layer of iron in the 1980s [2]. They discovered that the most important component in rusting is the iron hydroxide akaganéite ( $\beta\text{-FeO(OH)}$ ), which is only formed in the presence of chlorine. It has a catalytic effect on the rate of corrosion of iron even in the presence of low levels of humidity and cannot be completely removed from the corrosion layer. It was concluded that no restoration or conservation method is capable of totally reducing the chloride content over the long term and that only storage at low atmospheric humidity after conservation can, to a certain extent, guarantee long-term preservation. In the 1990s, metallurgists investigated the behaviour of certain steel microstructures during plasma conservation. The investigation revealed that microstructure, whether obtained by hardening or by cold working, is not destroyed by plasma conservation as applied today because it proceeds at a temperature below the microstructure transformation temperature.

The history of iron goes far back into antiquity; the oldest finds dating back to the 4th millennium BC in Asia Minor, where the production of iron became established in the 2nd millennium BC, as in Africa. In the 1st millennium BC, iron production spread to Europe and China.

In the 1980s, metallurgists at EMPA investigated one of central Europe's oldest swords (Fig. 3) dating from the 8th century BC [3]. The metallographic investigation revealed that the sword blade was produced by piling (Fig. 4), a technique in which the layers are additionally folded or twisted. Carbon dispersion is irregular, showing that the technique of carburisation had not yet been mastered. In the 1990s, further iron objects were in-

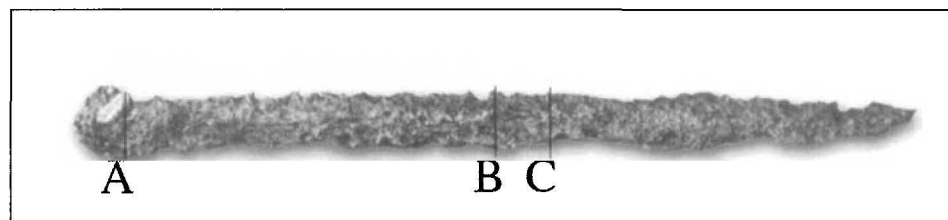
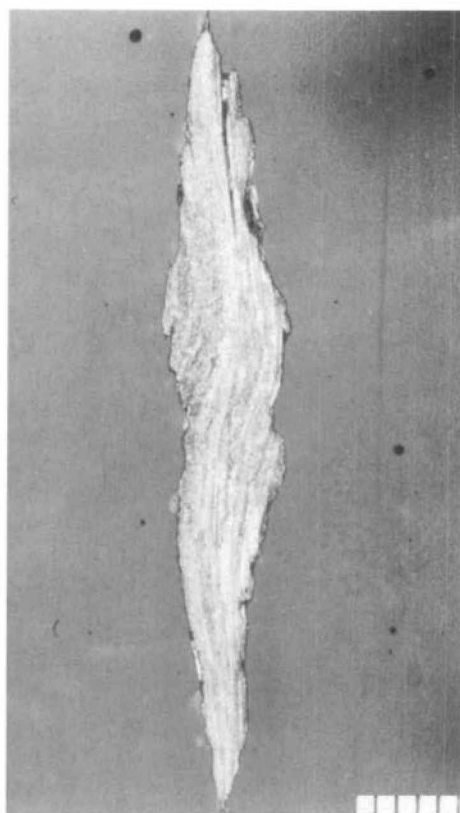


Fig. 3 Sword from Singen, Germany, 8th century BC, with marks of areas for metallographic sections. Length 53 cm.

Fig. 4. Optical micrograph of the cross section etched by Nital of the mark B on the sword from Singen. At the top the partially opened principle welding. The sword is constructed by edge-to-edge banding. The carbon content varies between 0.0 and 0.8 %. Darker parties are carbon richer.



investigated in a collaborative project with the Department of Prehistory at the University of Zürich and the Swiss National Museum, one of which was a spear from the Iron Age hoard from Wartau Ochsenberg in the canton of St. Gallen [4]. The metallographic investigation revealed that this likewise piled object had been exposed to thermal change after its production, a finding which confirmed the archaeologists' suspicion that this hoard was a burnt offering.

At around the same time, archaeometallurgists began to seek out methods of chemically characterising historic iron, with its high content of inclusions, so as to be able to determine its provenance. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) proved to be an ideal method as it can be used for selectively measuring small portions of a surface (in this case 80–100  $\mu\text{m}$  across, 35–45  $\mu\text{m}$  deep, ablated mass estimated around 0.5–1  $\mu\text{g}$ ). Craters of a smaller size could be obtained, but smaller craters would decrease the relative sensitivity and are considered to be less representative of the iron composition [5][6]. EMPA's development of the capabilities of its instrumentation opened up a new application in the form of archaeometallurgy, providing archaeologists with the answer to a burning question. Although it has not yet been possible to use this method to determine elements such as nitrogen and sulfur, which are important to the material characteristics of iron, it has proved possible in the case of the early medieval, now abandoned hamlet of Develier-Courtételle in the canton of Jura to determine which iron objects were produced locally (an example is shown in Fig. 5 and 6). Develier-Courtételle was a settlement which specialised for a time in smithing. Excavations have uncovered one of Europe's largest quantities of smithing slags. EMPA has been investigating waste and products from this smithy for four years in a joint research project with the canton of Jura. A thesis relating to the material characteristics and the manner of fabrication of iron objects from the Iron Age to the early medieval period will shortly conclude this research [7].

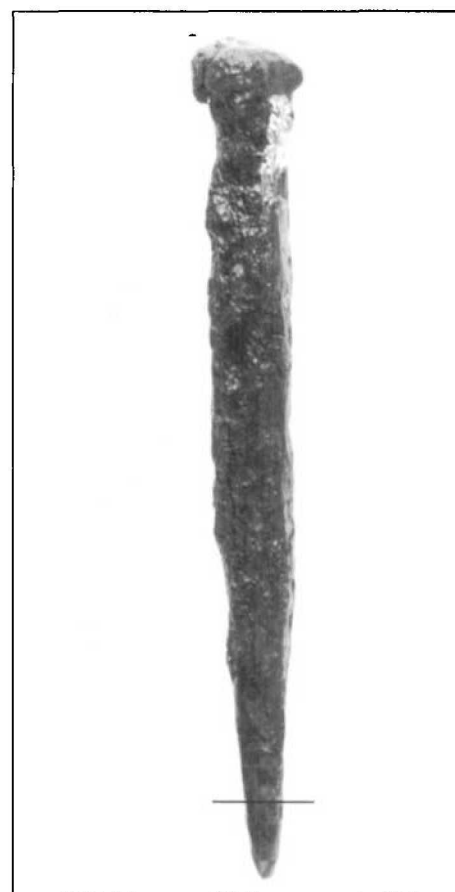


Fig. 5. Early medieval, locally produced chisel from Develier-Courtételle, canton of Jura. Length 9.3 cm (Photo Office du patrimoine historique jurassienne, Section d'archéologie).

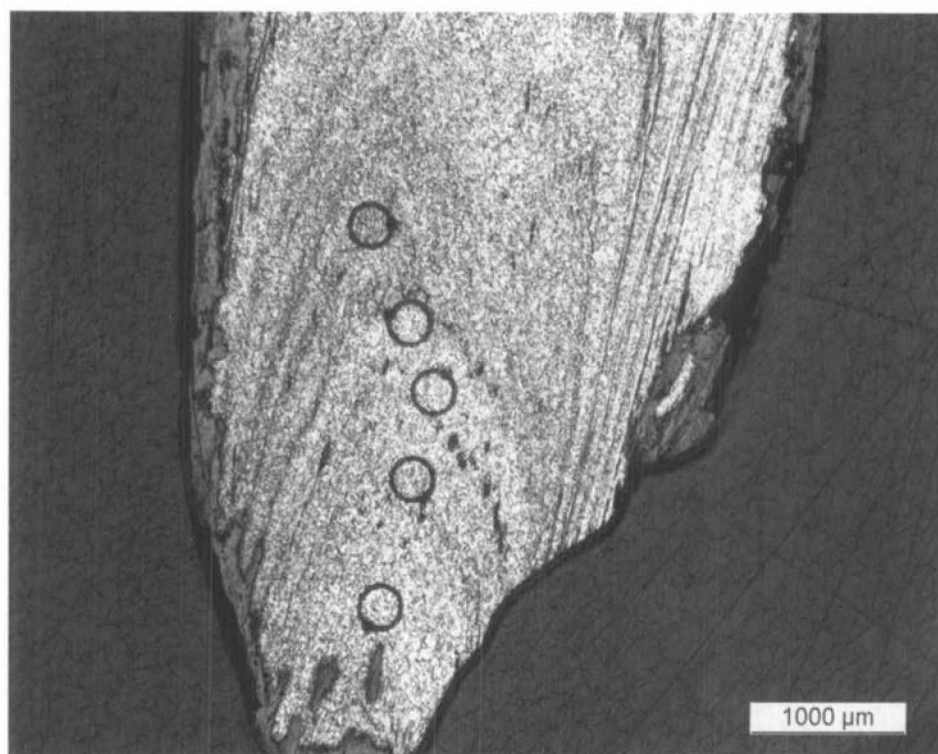


Fig. 6. The optical micrograph of the cross section etched by Nital shows the welded-on tip of hypoeutectoid steel from the chisel. The tip is constructed by surface-to-surface banding. The circles mark the areas to be analysed by LA-ICP-MS.

### 3.2. Copper and Bronze

Since the mid 1980s, EMPA has been actively involved in a first major project using plasma emission spectrometry (ICP-OES) to characterise chemically a thousand archaeological bronze objects from Switzerland. Analysis of the major and minor elements revealed the development of copper alloys over an entire millennium from 1800–800 BC [8]. 1993 saw a collaborative investigation with the Swiss National Museum and the archaeology department of the canton of Zurich into the composition of Roman and medieval bronze taps. Analysis by ICP-OES and metallography revealed that the materials were of moderate quality corresponding to an everyday, mass-produced article. No criteria for distinguishing between Roman and medieval nonferrous metals could be identified. EMPA's first foray into the experimental archaeology of nonferrous metals involved X-ray fluorescence (XRF) and metallographic analyses of an experimentally recast Bronze Age sword to investigate possible gravity segregation.

1997 saw the beginning of intensive collaboration with archaeological institutions researching copper smelting in antiquity. The first step involved analysis of ancient copper smelting slags from Cyprus. Variations in the composition of the major elements of individual slag flows within the same furnace batch were identified [9]. As a follow-up, ores, slags and metals from prehistoric copper smelting at Oberhalbstein in the canton of Grisons were investigated in collaboration with the archaeology department of the Swiss National Museum for their trace element composition by XRF. As a result of this

investigation, it was possible to rule out the hypothesis that fahlores (compounds of copper with arsenic, antimony and sulfur:  $(\text{Cu, Ag})_{10}(\text{Fe, Zn})_2(\text{Sb, As})_4\text{S}_{13}$ ) were smelted at Oberhalbstein and to conclude firmly that the prehistoric copper was produced by smelting chalcopyrite (copper, iron and sulfur:  $\text{CuFeS}_2$ ) [10]. The same year saw the beginning of investigations into metallic materials and waste products from the archaeological excavations at the monastery complex of St. Johann at Müstair, canton of Grisons. The aim was to provide a comprehensive chemical and metallographic characterization of these materials. Only once the investigations were under way did the focus move to the bronze wastes with a high tin content, which indicate systematic recycling and reuse of broken bells.

A year ago, a project was started as part of a thesis in archaeometallurgy to evaluate the excavations of the only completely recorded site of ancient copper production on the 'copper island' of Cyprus [11]. Analyses of ores, slags, furnace residues and metals are currently underway at EMPA.

One example which may be mentioned is the ICP-OES analysis of raw copper finds from two sites on Cyprus. The significant difference in the concentrations of minor elements (Fig. 7) proves that two different ore bodies were being exploited: the purer metal was obtained from unaltered chalcopyrite in a stockwerk mineralisation deposit. The less pure metal with a higher content of silver, arsenic, lead, antimony, tin and zinc indicates the exploitation of zones of secondary enrichment in a massive sulfide ore body. Investigations into possible frac-

tionation of the lead isotopes in all the materials of the production chain are to be carried out in cooperation with various laboratories. Experimental reconstruction of the smelting furnaces is intended to elucidate the production process [12]. By using the most authentic raw materials and tools possible for the experiment and then subjecting the products of the experiment to the same series of analyses as the archaeological finds, the intention is to test the archaeological hypotheses against the results of the experiment.

### 3.3. Silver and Gold

The question of authenticity frequently arises with noble metals. Art experts have various criteria at hand to assess the authenticity of silver or gold antiquities. Forgeries or stylistic copies may often be identified as such solely by a thorough visual inspection of the method of production, on the basis of stylistic features, by hallmarks or traces of wear. Faithful copies or forgeries of high quality may, however, appear deceptively authentic even to a practised eye. It is, on the other hand, very difficult to reproduce the characteristic composition of the trace element contaminants present in old silver or gold. The contents of these trace elements are in fact mainly dependent upon the metallurgical refinement process used for the noble metal.

In the early 1990s, EMPA was commissioned to examine four gold dishes prior to an auction of pre-Columbian works of art. A trace analysis by plasma mass spectrometry of tiny chips of gold taken from these objects revealed elevated mercury contents, indicating that the gold was obtained using the amalgama-

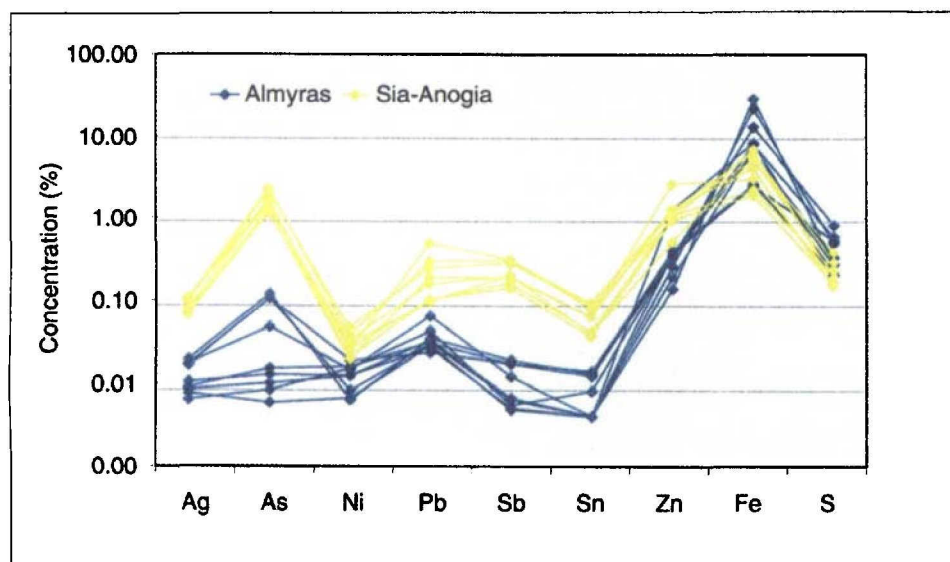


Fig. 7. Distribution of minor elements in copper, determined by ICP-OES (plasma emission spectrometry), from the two Cypriot copper smelting sites Almyras and Sia-Anogia.

tion process which was unknown to the pre-Columbian Indians. As a result, the four objects were withdrawn from the auction.

In recent years, an antiques dealer has commissioned tests of the authenticity of various silver statuettes and drinking vessels, mainly dating from the 16th and 17th centuries. The 19th century saw the introduction of new metallurgical processes which substantially altered the trace element composition of silver alloys. Thanks to the LA-ICP-MS method mentioned above in relation to iron, it is possible to carry out virtually non-destructive tests to verify whether the trace element contents of a silver alloy correspond to the period before or after the 19th century [13] (Fig. 8). To this end, the trace sample is compared with a constantly growing, in-house database of European silver artefacts from the 16th to 20th centuries. This method has made it possible to detect various forgeries, which could have damaged the dealer's good reputation had they been sold on.

The same analytical method was also used to investigate fragments of a spiral ring from a grave in Sion, canton of Valais, which dates back to 2400 BC [14]. To date, this is Switzerland's most ancient noble metal find. In this case, the purpose of the analysis was not to determine the authenticity of the object, as this was not in question, but instead to determine whether it was made from natural, native silver or from smelted, cupelled silver. The metal's relatively high content of the companion element lead

(0.2%) in comparison to native silver (0.001–0.01% Pb) would tend to indicate production by a cupellation process from a lead ore. During cupellation the lead-silver mixture smelted from ore is heated in a flat hearth (cupella) into an oxidising atmosphere. Lead changes in lead oxide (litharge) and silver remains as unaltered, fluid metal.

### 3.4. Determining the Provenance of Lead Pigments

Natural lead consists of the four stable (non-radioactive) isotopes  $^{204}\text{Pb}$ ,  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$  and  $^{208}\text{Pb}$ . In terrestrial lead, the latter three isotopes are partly the end product of the radioactive decay series of thorium and uranium, whereas  $^{204}\text{Pb}$  is not radiogenic in origin. The relative abundances of the lead isotopes in a lead-bearing ore deposit and in the products derived from that ore depend on the initial U and Th concentrations in the parent ore and on the age of the ore body. Hence, the lead isotope composition of natural ore deposits shows regional variations, which can be used to determine the geographical provenance of artefacts containing lead.

It is possible, for instance, to trace the geographical origin of historical lead paints on works of art by lead isotope analysis. In combination with the determination of naturally occurring trace impurities, e.g. silver, manganese and antimony, the origin of the lead in white lead paint can be pinpointed almost exactly.

Using EMPA St. Gallen's multicollector inductively coupled plasma mass

spectrometer (MC-ICP-MS), isotope ratios can be determined with great accuracy and precision ( $s_{\text{rel}(1)} = 0.002 - 0.01\%$ ) and trace impurities can be measured down to a concentration of about one  $\mu\text{g/g}$  of material. This method has been used to analyse  $\mu\text{g}$  amounts of lead white on renaissance and baroque paintings. In this way, it has been possible to distinguish historical white lead paint from Flanders from Italian white lead and modern white lead from historical white lead. Fig. 9 shows a scatter plot of lead isotope ratios in four white lead samples from renaissance paintings and three modern white lead samples. The lead isotope pattern in white lead from the sampled renaissance paintings differs significantly from the pattern in modern white lead because modern white lead comes from other ore sources than historical lead; a fact which can be used to detect modern additions and forgeries.

## 4. Conclusions

The various investigations clearly demonstrate that archaeology and the conservation and restoration of cultural heritage derive great benefit from the sciences, with close collaboration being essential to mutual understanding. This work is of course not the daily bread and butter of a materials testing and research laboratory. This is an example of how disciplines such as analytical chemistry and the characterization of solids must always be ready to tackle new areas by

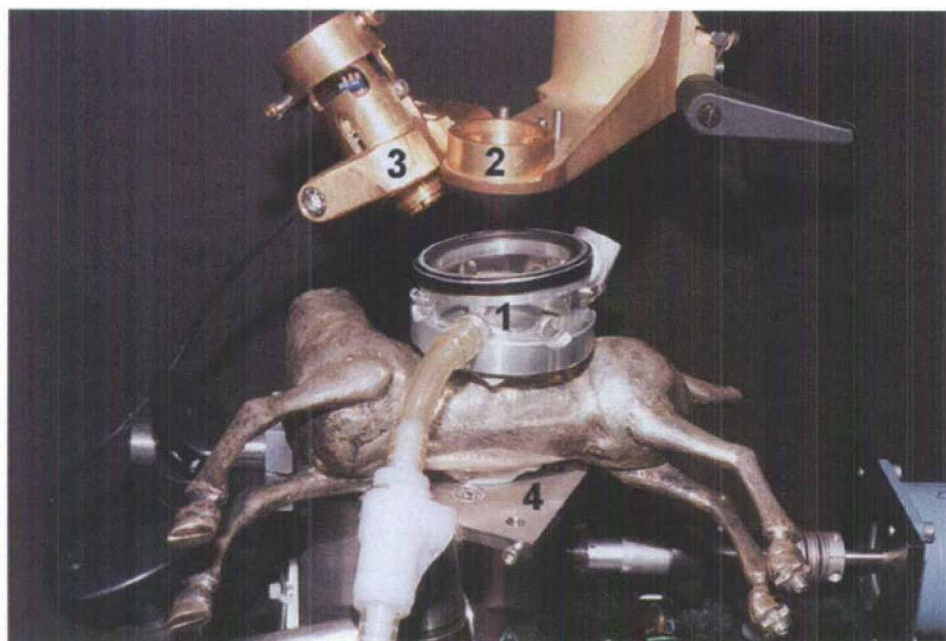


Fig. 8. The alternative laser ablation cell used in this work, placed upon a silver statuette: 1, laser ablation cell; 2, focussing lens, 3, auto-focus; 4, supporting platform.

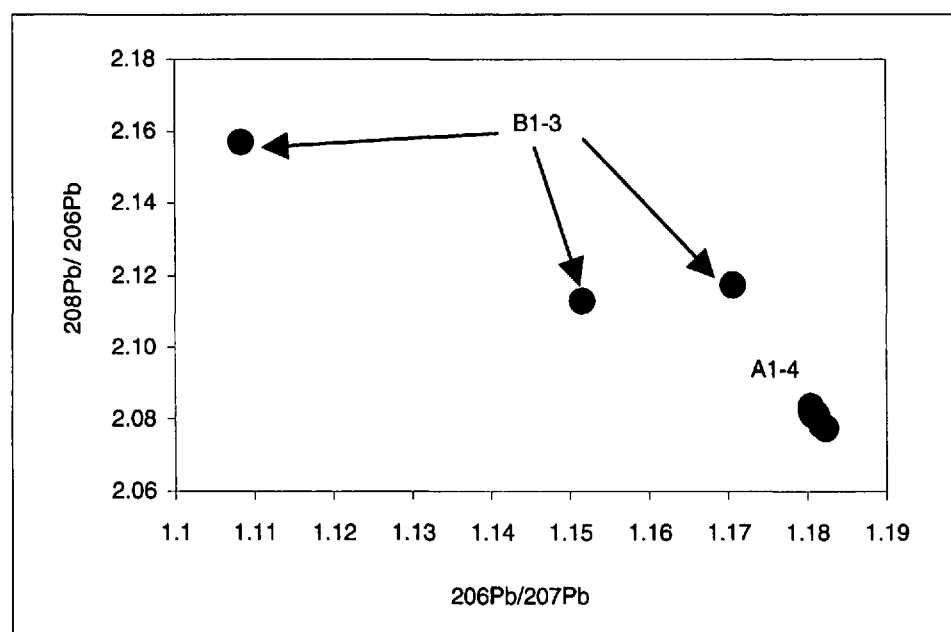


Fig. 9. Scatter plot of the ratios  $^{208}\text{Pb}/^{206}\text{Pb}$  versus  $^{206}\text{Pb}/^{207}\text{Pb}$ : A1-4 = historical white lead pigment, B1-3 = modern white lead pigment.

seeking dialogue with other scientific disciplines, helping to find common terms of reference.

In an extended understanding of the science of materials it is thus desirable to know about the history of materials production and that this knowledge will take its place in researching modern materials with regard to sustainability.

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