Chimia 55 (2001) 915–922
© Schweizerische Chemische Gesellschaft
ISSN 0009–4293

Archaeometry – Analyzing the Cultural Heritage

Willem B. Stern*

Abstract: Archaeometry is an interdisciplinary field of research, where the studied object stems from archaeological, cultural or historical domains whereas the approach of investigation is based on (natural) science. In the present overview the main focus is on case studies and non-destructive techniques. X-ray fluorescence and diffraction studies on ceramics, coin alloys, glass, man-made and natural gemstones, and objects of fine art prove that material analysis may contribute to insights in questions of authenticity and origin, but also in ancient technologies *e.g.* of coinage.

Keywords: Ancient glass · Archaeometry · Authenticity in art · Non-destructive analysis · Numismatics

Archaeometry is a relatively recent term. It came into use around 1950 in England, and soon infiltrated many languages. Periodicals bear the term, like '*Archaeometry*' since 1958 in the UK, '*Berliner Beiträge für Archäometrie*' since 1976, or '*Revue d'Archéométrie*' in France since 1977. Nevertheless, it has not been included in many encyclopedias or dictionaries. It is missing *e.g.* in Collins/Pons (1997), Wahrig (1989), Webster's (1993).

Archaeometry is an interdisciplinary topic, where the studied object stems from historical science or the cultural domain, but the method of investigation is from (natural) science. Meaning in the beginning merely 'measuring/determining the age of a historical object by physical methods like isotope dating' it adopted later a more general meaning of 'performing scientific measurements on objects of art, culture and history', or shortly 'analyzing the cultural heritage'.

The objects of investigation cover a wide range from alloys, over bone, ceramics and coins, paper, pigments and postage stamps to teeth and textiles. Because many objects represent not only cultural, but commercial value as well, investigations are preferably performed by non-destructive methods. This was not possible in the early days of analytical chemistry, when *e.g.* Klapproth executed the first analyses of Roman glass and Greek silver coins in the late 18th century, a 150 years before the term Archaeometry came into use.

For certain material groups like ceramic or glass shards, conventional destructive methods of chemical and physical analysis are still used in practice, when the mass of available shards allows consumption of a selected quantity.

The following case studies, however, deal solely with the challenging task of non-destructive analysis. Its aim is not only the correct labeling of *e.g.* museum exhibits – alabaster is not onyx, brass not bronze, silica not necessarily quartz, a white pigment not necessarily chalk, limestone not marble *etc.* – but also more complex targets like questions of authenticity, or of ancient trade, to mention only two.

The present outline is not intended to be comprehensive. It rather reports archaeometric fact-finding as it may occur in a laboratory specialized in instrumental analysis and material science.

Analytical methods are non-destructive when neither preparation steps nor the analysis itself cause detectable alterations or long-lasting radioactivity of the studied object. In general, no (sub-) sampling is allowed, nor any polishing or scratching of the object's surface.

The analytical techniques in the following case studies belong to the group of instrumental analysis and deal with chemical aspects of solids, but also with their physical-mineralogical aspects. X-ray fluorescence (XRF) spectrometry performs an elemental analysis of roughly 95% of all elements in the periodic system, whilst X-ray diffractometry (XRD) detects elemental assemblages provided that they represent physically ordered compounds or minerals.

Both aspects of solid matter are of importance in archaeometry: a Babylonian cylinder seal described as 'white stone' may chemically consist of calcium as main component besides carbon and oxygen, which suggests a compound of $CaCO_3$, and excludes *e.g.* gypsum (containing also sulfur) or bone (containing phosphorous). But the chemical analysis does not tell us whether the seal is made of chalk (chemically $CaCO_3$, mineralogically calcite) or of shell (chemically also $CaCO_3$, but mineralogically aragonite). A similar case may be a white pigment consisting chemically of titanium (and oxygen), hence being TiO_2. But mineralogically different species with the same composition occur, such as anatase, brookite and rutile. Natural TiO_2 minerals are black or brown due to impurities, but two of them have been synthesized

---

*Correspondence: Prof. Dr. W.B. Stern
Geochemical Laboratories
Institute for Mineralogy and Petrography
Department of Earth Sciences
University of Basel
Bernouillistrasse 30
CH–4056 Basel
Tel.: +41 61 267 36 22
Fax: +41 61 267 28 81
E-Mail: willem-b.stern@unibas.ch

and commercialized in known, but different time spans, and belong today to the most widespread white pigments. Hence, the chemical proof of titanium white may represent a first hint in a question of authenticity, but the mineralogical proof of either anatase or rutile gives further insight in the question of dating.

XRF and XRD are based upon the same physical principles, namely Bragg's equation and Moseley's law of 1914. For a deeper insight, the reader may consult the comprehensive textbook of Potts (1993) [1]. A schematic overview on X-ray applications used during the past 100 years is given in Fig. 1.

Instrumental analysis is *in general* based upon an often unspoken, but essential prerequisite: the object of investigation has to be chemically and structurally homogeneous. Analytical data from heterogeneous objects will always be problematic when the investigated area, volume or mass is smaller than the entire object. The analytical quality may be outstanding, the data nevertheless meaningless because of lacking representativity. The topic seems simple but is a permanent point of discussion between analysts and archaeologists.

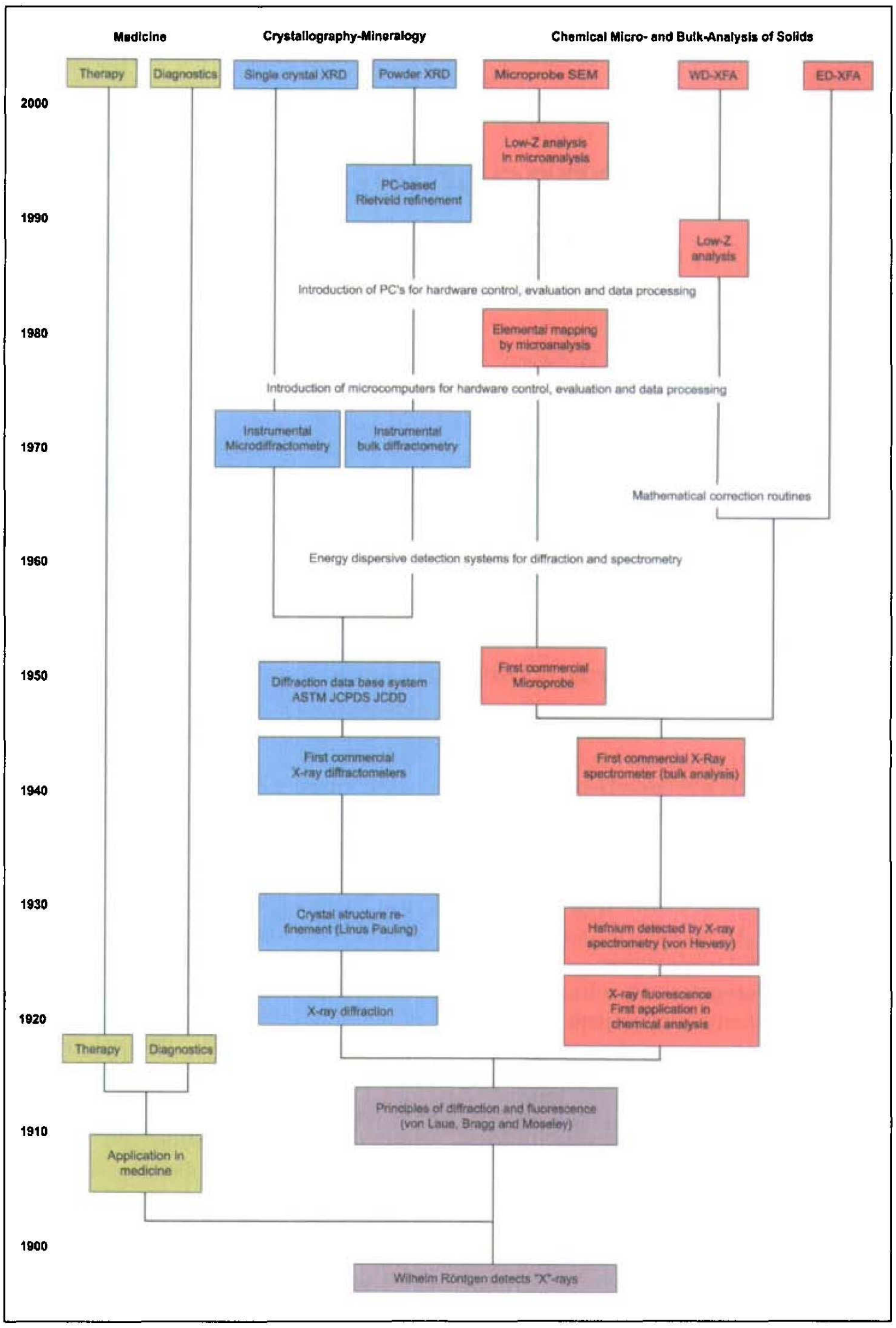

Fig. 1. The application of X-rays in material science over the past 100 years. Although X-ray diffraction (XRD, blue boxes) and X-ray fluorescence (XFA, red boxes) have a relatively long history, their worldwide application only became important after the second world war. XFA with its wave-length dispersive/sequential (WD-XFA) and its energy dispersive/simultaneous options (ED-XFA) belong today to the most frequently used instrumental techniques for the analysis of inorganic solids in spite of the relatively high investment of 50'000 to 150'000 € [1].

Case Studies

1. Terra Sigillata – Is the Red Gloss a Clue to Production Origin?

Terra sigillata is one example of industrial large-scale pottery production in Roman time. Terra sigillata was manufactured at different sites in Italy but also in what is today France and elsewhere. The manufacturers can, in favorable cases, be identified by stamps of origin on the underside of ceramic bowls, dishes, plates. Sometimes not only the production place is identified but also the name of the craftsman involved.

Terra sigillata is a quite spectacular type of pottery, easy to identify by means of its characteristic orange-red gloss ('engobe', slip), a very fine grained and thin cover on the ceramic body. This cover is believed to consist of originally a clay-mineral enriched slip which turned by oxidative firing to a glaze- or enamel-like, quite scratch-resistant coating. One may expect that its chemical composition reflects roughly 'clay' with silica and alumina as the main detectable components, and additional elements in variable amounts, like potassium, calcium, titanium, manganese, iron *etc.* The relative proportions of these elements – or some of them – may vary according to the origin of the clay, and therefore from one production plant to another geographically remote site.

From four different production sites twelve fragments from museum collections were chosen, each fragment bearing a stamp of origin, and some also the mark of the potter Sentius, known to have worked in Italy and France as well.

The chemical composition from the pottery surface, *i.e.* the coating, was determined non-destructively by means of Energy-Dispersive X-ray Fluorescence Spectrometry (ED-XFA), and the concentrations of TiO_2, MnO, Fe_2O_3, and K_2O found were plotted as elemental ratios in a XY graph (Fig. 2). Although the projection points from the surface, and of the different shards from each origin do scatter, the individual production centers Arezzo (A, Italy), La Graufesenque (G, France), Lezoux (X, France) and Lyon (L, France) occupy, however, distinctively different chemical fields. This means that an individual unknown fragment without a stamp of origin could most probably be attributed correctly to one of the four production sites, or possibly to an additional not yet studied origin.

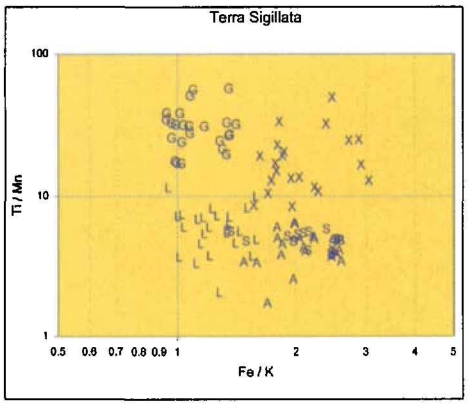

Fig. 2. Non-destructive analysis (ED-XFA) of the red slip on Roman terra sigillata of known origin. Pottery from Arezzo (A, Italy), La Graufesenque (G, France), Lezoux (X, France) and Lyon (L, France) display distinct elemental ratios such that the products of a certain potter Sentius (S) working in Lyon and Arezzo can be traced back by the respective chemical fingerprints [2].

Stamps referring to the potter Sentius (S) are present twice in the Lyon group, and seven times in the Arezzo 'population' (Fig. 2).The shards stem from excavations in Augusta Raurica, and Vindonissa (Switzerland). Hence, by means of 'fingerprinting' the glossy surface we not only conclude that sigillata of different origin can indeed be chemically distinguished, but it confirms also that a certain potter Sentius did work in Italy and France as well [2]. The chemical fingerprint of red gloss is indeed a possible clue to the provenance of terra sigillata.

2. Legal Cheating and Criminal Coin Forgery

It is common knowledge that the first coins were minted in western Anatolia, today Turkey, in the 7th century BC. These early coins consisted of electron, a natural compound of gold and silver, occurring in placer deposits of Asia Minor/ Lydia. Not much later the first silver coins were minted in continental Greece, in Athens, most probably from ore of the famous Attica lead mines. The small silver content in lead ore was enriched by means of mineral dressing and early large-scale cupellation technologies making possible an enrichment of originally less than 1 wt.% silver in the ore to 99% silver which was used for coinage. Silver coins from Greece became tender not only in Greece, but in many places of the Mediterranean where Greek traders were active, notably in Spain and in the Rhône valley then inhabited by Celtic tribes. They used Greek coins since the 4th century BC and since the 3rd century BC imitated them by creating a 'barbarian' Greek-based coinage which was produced and in use until Augustan times.

Gold and silver coins from Greece were soon 'treated', *i.e.* legal tender was forged by individuals producing plated coins. On top of bronze (seldom iron or lead) flans a thin foil of gold or silver was fixed, and struck with a die. This technique has allegedly never been used by official mints. In ancient Greece the falsification was tested by official controllers slicing or cutting suspicious coins at least since the 4th century BC [3]. Although Archimedes' density determination was known at that time, it was not used in coin testing. The large density difference of gold (19.3 g/cm^3) and bronze (around 8.5 g/cm^3) reveals plating easily, and is today one of the easiest and fastest non-destructive methods to detect plated coins. It is obvious also that plating causes a reduction in weight; if the coin size is kept constant, lower weights could be easily detected.

Since early times mint offices tried to debase coins in order to produce more pieces out of a given mass of noble metal. Changing the weight or metrics would have been noticed. But changing the silver or gold content by adding a small percentage of copper does not change color or luster noticeably. If, however, larger amounts are added, the aspect of a coin will change. In order to reduce this effect, debased (and even 'good') coins were surface-treated. In a first step the planchets are annealed at several hundred centigrade in order to oxidize the copper present. Metallic copper at the surface is transformed to black cuprite (Cu_2O), with an increase in volume. Cuprite is dissolved in a second step by boiling the planchets in acid. This process is called blanching in case of silver alloys. The surface is now bright-silvery and consists of nearly pure, but to a certain extent spongy, silver; the core remains unchanged. Striking the planchet in a next step compacts the thin (thickness of a few micrometers) spongy 'noble' layer. This technique was in use in ancient and modern times as long as noble metal was coined, even when the fineness was fixed by law. Blanching acted in such a case as an improvement of the aspect. Depending on different factors, the circulation of coins leads to slower or faster wearing-off of the noble layer.

Since blanching transforms an initially homogeneous alloy into a heterogeneous, onion-shaped body, any instrumental analysis of such a coin will lead to possibly doubtful results. But also strike tests, used since antiquity, will possibly give erroneous information as long as the noble layer is still present, and sampled for quality control.

Over the past 15 years some 10 000 Celtic, Roman, Greek and Central-Asian coins have been analyzed by XFA [4-9]. Surface treatment, *i.e.* blanching, was widely applied at all times as can be demonstrated by comparing the specific weight (ρ, measured experimentally) with the density calculated from surface analysis. The density difference 'delta-ρ' is informative (Fig. 3). The data suggest also that a second phenomenon influences the overall specific weight of a coin. Many Roman and Islamic coins display a low experimental density with reference to the analyzed alloy.

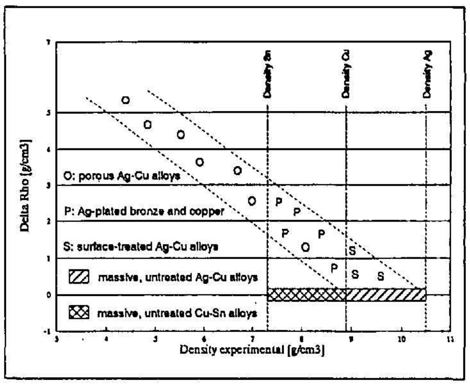

Fig. 3. Non-destructive analyses (ED-, WD-XFA) and experimental density determination of Roman silver coins, schematic overview. Binary alloys of silver and copper should display an Archimedes density between ρ_{Ag} (10.5 g/cm^3) and ρ_{Cu} (8.9 g/cm^3) in case of solid, homogeneous alloys. Plated coins will be specifically lighter when the core consists of bronze or iron. The X-analysis reflects mainly the chemical composition of the surface and the layer close to the surface. If the coin is homogeneous and solid, the density calculated from surface analysis and the experimental Archimedes density will be identical, their difference Delta Rho equal to zero. Surface treated ('blanched', *i.e.* copper-depleted), silver plated bronze or iron, and porous coins will, however, display a Delta Rho with positive values. Hence, the combination of two independent, non-destructive methods like experimental density determination and XFA enables an insight in details of coin production and technology [4].

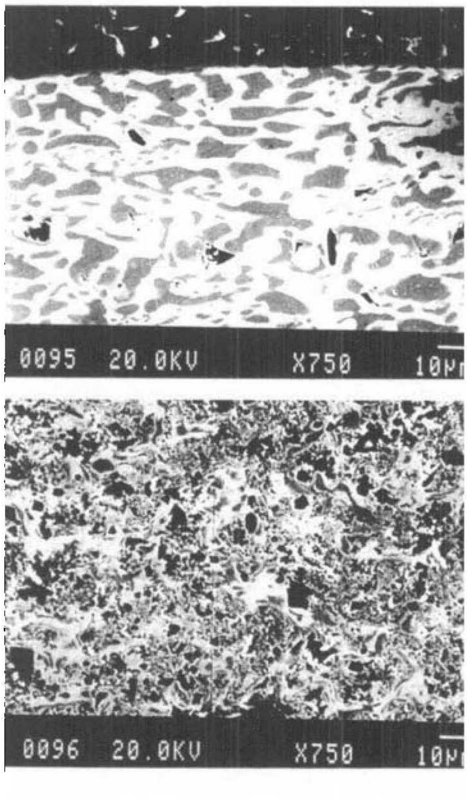

Fig. 4. Destructive analysis of a cut and polished silver dirham by electron microprobe. The upper image displays the outer zone, compacted by striking, with its unmixing structures of Ag94/Cu06 (white) and Ag06/Cu94 (gray). The lower micrograph shows the core with roughly 24% of pores, black [7].

To take an extreme example: a binary alloy of silver-50 and copper-50 may be surface treated which leads to a measured silver content greater than 50% and a copper content accordingly lower than 50%, the density being theoretically around 9.8 g/cm^3. The experimentally determined density, however, may be as low as 8.9, which is lower than ρ_{Cu} and hence impossible for a binary Ag-Cu alloy. One explanation would be to assume some kind of small-scale porosity of the coin body.

Since surface treatment was common practice, the core of silver coins is shielded by the impact of striking, producing a thin and compact layer of noble metal on top of the debased alloy. Hence no direct microscopical evidence for small-scale porosity is possible. In seldom cases, however, destructive measures are allowed. By cutting the coin body, or by grinding off the surface and polishing the exposed core, analysis is possible by electron microprobe [7] (Fig. 4). The compacted rim zone is nearly free of pores, but the core displays a complex system of pores with a diameter of 2 to 5 micrometers and less. The total amount of pores is well above 20 vol.%. This porosity reduces the specific weight accordingly. Porosity, however with channel-like structure, was also found in Celtic gold [8]. The explanation for this porosity is not yet understood, it may be connected with degassing, expulsion of oxygen during the smelting process. Its effect was probably welcome for it enables large coin volumes with a low amount of noble metal. It is clear, however, that the weight of these porous coins is also reduced. Since the phenomenon has to be studied by destructive means, only a restricted number of coins can possibly be investigated, and biased results may therefore result.

Another insight taken from coin analysis is the development of fineness as a function of minting time. Whether debasing at a given time interval took place in a specific minting place only, or in a merely regional or larger scale, is easy to pinpoint by surface analysis, provided that sufficiently large, numismatically well-documented coin series are available [9]. In case of Central Asia we clearly see strong debasing of silver coins in a relatively short time span of roughly one century affecting all investigated minting places between 300 and 400 PH (around 900–1000 AD). Most of the investigated silver (N = 2700, Fig. 5, top) is surface treated, *i.e.* blanched, but plated pieces are rare. Gold coins also lost their fineness gradually, but slightly later, between 350 and 500 PH (around 950–1100 AD), and not in all minting places (Fig. 5, bottom).

Plated gold coins are practically absent in the investigated set of 466 coins. Either the collectors screened carefully, or plating was rare in Central Asia between 250 and 650 PH (around 850–1250 AD). From density considerations it seems also that surface manipulations are not as common as in the case of silver. And indeed, improving the surface of ancient gold alloys is somewhat more difficult than blanching silver. Although ancient gold is very often a binary alloy, as is modern gold, an essential difference exists. Ancient gold coins consist of gold and silver resembling electron, whereas modern gold coins consist of gold and copper. Modern gold can be treated much

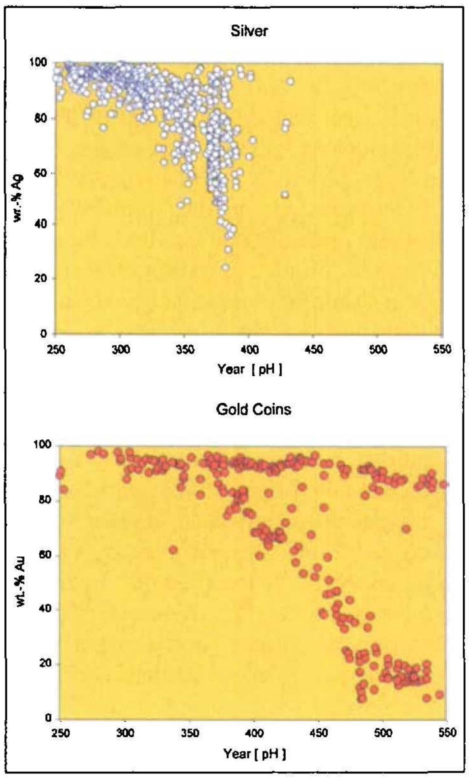

Fig. 5. Non-destructive analyses (ED-XFA) of Central Asian silver (upper) and gold coins (lower graph). The fineness in wt.% is plotted *versus* the minting year (years post Hedjra). It is evident that around 350 PH a debasing of silver at all investigated mint offices begins, whereas the debasing of gold starts some 50 years later and is not observed for all mints. The debasing of silver coins coincides in time with the disappearance of Central Asian coin import to Northern Europe, and the onset of silver mining in medieval Europe [8].

like silver in order to obtain a copper-free surface layer. Ancient gold, however, cannot be 'improved' in the same way. Silver is removed only by a tedious cementation process, where long heating at high temperatures between 850 to 1100 °C in presence of rock salt (NaCl) is essential.

Some additional, fairly exotic facts were also observed. In certain narrow time spans additional elements occur which are otherwise rare in silver coins. Around 190 PH high mercury concentrations of up to 20 wt.% Hg are common in Central Asian pieces, as is arsenic around 370 and 600 PH with peak concentrations up to 2 wt.% As. Extraction of silver from the raw ore by amalgamation might have been applied; mercury was certainly available at the relevant time and place. But it is not easy to understand how mercury can survive the process of smelting. On the other hand surface improvement by fire silvering is possible, but then it would be applied on debased alloys with accordingly low specific weight – but the density of the mentioned 190 PH Hg-rich coins do not display conspicuous values. Also, the presence of arsenic in narrow time spans cannot be explained so far.

The Central Asian coins stem from a museum collection where a quality screening reduced or eliminated obviously forged, *i.e.* plated, pieces. Accordingly, published analyses *e.g.* from Roman silver coins from British collections [10] display plated coins only rarely. Again, silver hoards practically never contain plated coins.

In contrast the percentage of plated coins stemming from provincial excavations is relatively high [4]. From 630 silver coins from the Augusta Raurica/Switzerland excavations, 28% were plated. This may imply that plating was not necessarily considered forgery in imperial Roman provincial money, but the insight of the numismatic specialists is called for this question.

As a conclusion one may state that surface manipulations were common practice in mints at all documented time periods, and hence 'legal cheating' was usual business. Plating, however, was considered to be against the law at least at certain times and in certain places, but possibly not everywhere and at all times. Again, the opinion of numismatic specialists is required.

3. Glass Making Far from the Sea

Natural glass (volcanic glass, obsidian) has been used for making tools, like knives, since prehistoric times. Because not too many sources of obsidian exist, and the chemical composition of obsidian may vary, the chemical fingerprint of obsidian artifacts can be applied for the study of trade *e.g.* in the Mediterranean stone age (Fig. 6). Neolithic obsidian artifacts from Lipari (Aeolian Islands, Italy) do not most probably originate from the well known and spectacular, and today exposed, lava flows (Forgia Vecchia, Rocche Rosse) but from older, presently widely covered flows. The artifacts are also chemically different from examined obsidian of Vulcano, Sardinia and Anatolia. Volcanic glass is, in general, potassium-rich and poor in calcium; the K/Ca ratio is therefore high. The method of plotting elemental ratios is selected because of two reasons: more variables can be presented in a x/y graph and morphology effects (influence of surface geometry on measured X-ray intensities) are reduced.

Man-made glass has been known for at least 3.5 millennia. Glass pearls, vials, flasks, bowls, plates were widely used in the Mediterranean area and in northern Europe. Glass-making workshops, documented today in archaeological excavations, were present all over the Roman empire, although certain ingredients for glass making are found only at rare sites.

There are three prerequisites for glass making: a suitable silicate sand, a flux, and thermal energy. Additional ingredients may be colorants, bleaching agents, additives for viscosity reduction *etc.* Whilst suitable sand and wood are relatively ubiquitous, flux is not. Natural soda (Na_2CO_3) is known from Egypt (Wadi Natrun) and it is believed that glass making started in Egypt or Palestine due to the presence of this essential ingredient. Soda may also be produced on a technical scale by calcination of certain sodium-incorporating plants like salicornia, and subsequent washing and refining of the ash. Because salicornia grows on many sea shores in the tidal zone, soda may be produced at many places along the coast. But would soda be traded to *e.g.* central Europe for glass making? Or would the glass be transported to the customers in central Europe either as a final product, or as glass ingots? Or would used glass be recycled? Or would soda glass only be produced along the coast, and in the interior potash glass, since potash can be produced from many kinds of wood, which is used for energy production in any case?

Different study groups are working worldwide on this topic; a comprehensive overview was presented by Bezborodov that represents the state of the art of the late 1960s [11]. A later extensive technological and historical overview was compiled by Wedepohl in 1993 and 1998 [12][13].

Early glass analyses tend to be incomplete, since only the expected chemical elements were searched for, the applied methods being sequential. This means that before starting the analysis, an *a priori* assumption was made as to which main chemical component would be important, and these elements would then be analyzed in a sequential order. Since the analytical procedure – gravimetric, or spectrometric – was destructive, repetitions to check the homogeneity of the investigated object, and representativity of the obtained analysis were seldom performed. Certain elements like phosphorous and chlorine were often supposed to be absent and hence not analyzed.

Ancient glass nowadays often displays a heterogeneous structure. The surface and the adjacent parts are often

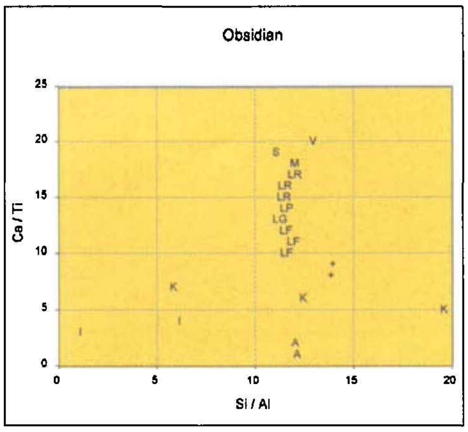

Fig. 6. Non-destructive analyses (ED-XFA) of obsidian from different sources. Key: A Anatolia; I industrial obsidian-like scories; K Mt. Kibo, Tanzania; M obsidian arrow, Mexico; S Sardinia; V Vulcano, Eolian Islands/Sicily; LF Lipari Forgia Vecchia flow; LG Lipari Gabelotto flow; LP Lipari Pumice; LR Lipari Rocche Rosse flow. The crosses represent obsidian artifacts from Lipari with a chemical fingerprint different from the currently exposed obsidian lava flows of Lipari (unpublished data).

leached out; alkalis are replaced by water, which induces the well-known mother-of-pearl luster, and finally a puff-pastry shape of the glass surface when the process has proceeded far enough. The leached layer may vary from between a few micrometers to over 0.2 mm. Non-destructive bulk analysis of such leached glass tends to give biased values for the alkali content: the surface analysis by X-ray fluorescence spectrometry (XFA) will possibly detect no alkalis at all because of the low energies of Na and K spectral lines (1.0 and 3.3 KeV, respectively) and hence weak penetrative power. Other techniques like neutron activation analysis [NAA] will reflect the entire glass body, the measured alkali content then depends on the ratio between layer- and core thickness.

Tempering the glass prior to analysis may have a 'healing' effect by causing a redistribution of the alkalis, but the procedure is risky and rarely allowed for objects of value.

Roman glass-making workshops with kilns are known *e.g.* from the early imperial site of Aventicum-Avenches/Switzerland [14], where not only kilns were excavated, but also large quantities of broken glass. Shards of different colors were analyzed by ED-XFA, and some, for comparison, also by destructive WD-XFA. It was found that colorless glass contains very little iron and was hence manufactured with selected, pure raw materials, *i.e.* quartz- and feldspar sand. The latter is proven by the presence of alumina. Red glass contains elevated concentrations of manganese, whilst green and blue glass has elevated CuO contents. The conspicuous opaque white and blue shards are rich in antimony which acted as darkener. Phosphorous was not present as a main component, and hence bone ash was not used. Traces of flux material were not found in the excavated area, but their solubility makes preservation over longer periods of time unlikely.

Our own investigations on Celtic, Roman, Greek and medieval glass confirm that Roman glass is principally sodium glass and hence produced with soda as a flux at all production sites, and never with potash. Roman glass contains in general an elevated percentage of chlorine, suggesting the use of rock salt (NaCl) as a 'softener', *i.e.* viscosity reducing agent [15][16]. Medieval glass is either potash or soda glass and occasionally contains chlorine [17].

A problematic observation is the presence of phosphorous as a main chemical constituent in many glass shards analyzed to be of Roman and medieval age. Whether bone ash was added as a raw material is not clear, nor is its influence on glass quality, but it possibly acts as a stabilizer, making the glass more resistant to chemical attack. Bone ash has probably been widely used as a raw material for glassmaking, for white coatings on ceramic, and also for ceramics ('bone china'). It may be added that bone was most certainly also used for the production of glue and of tallow. But not very much is known from literature.

4. Decorative- and Gemstones

The study of decorative- and gemstones is normally done by means of microscopical techniques, usually on isolated crystals or gem stones, and not on set stones. The *identification* is often possible with considerable certainty, but the chemical composition as a clue to *origin* or *authenticity* also became important when appropriate non-destructive methods were developed.

Colored minerals, stones, animal products (antlers, bone, tuskers, but also coral) have been used for millennia for decorative purposes. Their cultural and commercial importance makes them a cherished object of study. As far as questions of authenticity are concerned, not much is published, however. If genuine and falsified objects are clearly discernible by certain published methods, cunning readers will possibly try to avoid mistakes in future, and get away with undetected fraud. To mention an example: Soon after publication [18] of the observation that gallium is an essential trace element in *natural* corundum (ruby, sapphire), but missing in *man-made* stones (manufactured with pure alumina), the first synthetic 'ruby' with spiked gallium appeared on the market. Hence an important criterion is, in principle, now no longer applicable.

Great efforts have been made to correlate the chemical fingerprint (trace element pattern) of certain gemstones with their genesis and origin (mining site, country of production). According to genesis, this fingerprint may vary considerably for one and the same mineral species. If the source of a given stone is known, and a statistically representative set of specimens stemming from that source has been analyzed, and if, furthermore, as many as possible different sources/origins are documented accordingly, a specimen of unknown origin may be compared chemically, and possibly identified by means of the reference sets.

A specimen of unknown or questionable origin may *e.g.* display an entirely different fingerprint, and hence stem from an additional, not yet documented source. It may, however, display a similar trace element pattern as a documented case, *e.g.* mine NM, and therefore originate from NM. It may, in contrast, be different from mine NN, and this 'falsification' is a strong criterion in question of origin, whereas 'verification' (similarity with a reference group) is a weaker one, because not all mining sites worldwide can be known or documented.

From 1979 to 1999 well over a thousand gemstones (ruby, sapphire, alexandrite) of known origin have been tested for their respective trace element pattern ('fingerprint') by non-destructive methods (ED-XFA), and their fingerprints and variation documented. This data base is used for the study of origin and questions of genuineness; an example is shown in Fig. 7.

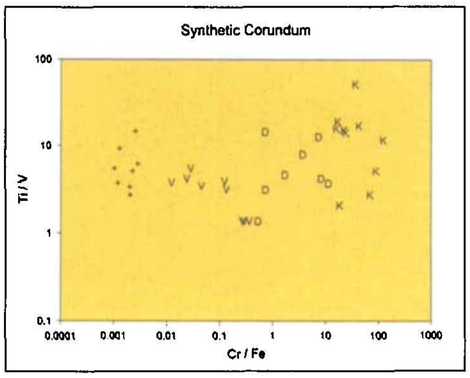

Fig. 7. Natural and man-made gemstones of different provenance may display distinct chemical fingerprints. V represents synthetic Verneuil, D synthetic Douros, K synthetic Kashan corundum of ruby type, whilst the crosses stand for natural corundum from Viet-Nam (sapphire), unpublished data.

5. The Question of Authenticity in Art

One and the same masterpiece of art may be labeled 'certainly false' by an art historian, and 'possibly authentic' by a scientist; both opinions put down in a report on behalf of a court of justice. The authenticity of a masterpiece of art is by tradition not merely based upon the signature and/or year of creation, but upon its 'pedigree', *i.e.* its documented line of owners back to the artist's workshop. If such a pedigree is missing, the evidence of authenticity has to rely either upon stylistic, iconographic and/or comparison studies, or else upon scientific arguments.

The stylistic approach is probably the most common one, but also the most controversial, because a high degree of personal 'feeling' enters the final judgment. More objective, but time-consuming is the iconographic and comparative approach, where authentic masterpieces of the artist in question are studied for comparison in art galleries, musea and respected collections. The art historian will finally give a statement as to the authenticity of a questioned masterpiece in terms of 'certainly authentic', or 'certainly false'.

The scientific approach is relatively seldom used, mainly for two reasons: first, the scientific analysis has to be nondestructive, which was not easily possible in the past, and second because the evidence for authenticity or non-authenticity may not be present in a given masterpiece of art. Physical age determinations by isotope analysis, or thermoluminescence dating are not suitable for objects created after *ca.* 1500. The evidence has hence to rely upon time-conform or time-inconsistent parts of the questioned object, like paint, pigment, canvas/cardboard/wood, working material. If a scientist analyzes pigments in objects of art that were created allegedly in the 19th century, but which contain pigments which were commercialized after the second world war only, his statement will be 'certainly false'. If the questioned objects, however, do not contain any time-inconsistent materials whatsoever, he will state 'possibly authentic', since by lack of arguments he has to plead in favor of at least possible authenticity. The scientific approach is hence by nature able to falsify, but not to verify with same certainty.

In the example mentioned above, the statement of the art historian 'certainly false', and of the scientist 'possible authentic' are not contradictory, but have to be explained to the court of justice involved.

One of the latest important cases of art forgery known to the public (Drew/Myatt) could have been rapidly and easily solved simply by examining the paint: masterpieces by Braque, Chagall, Dubuffet, and Giacometti were claimed to have been painted in the 1920s, but were actually painted with acrylic paint, which only came into use in the 1950s. These paintings are clear forgeries even if they are signed and dated, and even when cunning forgers have fabricated 'authentic' pedigrees, and even when famous experts of contemporary art have attested authenticity, relying on stylistic arguments. The Drew/Myatt case ended 1998/99 in London with a prison sentence for the relatively careless forger and his manager [19], but only after a lengthy court case.

The chance to find time-inconsistent arguments is relatively small because many paints and pigments have been in use for centuries, if not millennia [20]. If, however, a masterpiece of art, supposed to be painted, say, in the mid-19th century, contains so-called titanium white in the original painting material, the entire piece is a forgery – titanium white, chemically TiO_2, only came into use as an artist pigment after the first world war. This commercially produced titania consisted mineralogically of anatase. Later commercial developments led, after the second war, to an improved titania, mineralogically rutile. It is hence not only the mere presence of titania of importance, but also its mineralogical character when the question of dating is concerned.

The presence of titania, anatase or rutile, in artist pigments is obviously of importance. The practical test is relatively difficult when it has to be carried out without any subsampling or invasive means, *i.e.* non-destructively. Titania white is furthermore extremely fine-grained (particle size below 1 micrometer) and can therefore not easily be studied with conventional optical light microscopy. One approach has been to take subsamples of a microscopical dimension and to examine them by high-resolution scanning electron microscopy (SEM-techniques). There exists, however, a problem of dimensionality: are a few grains of titania already a proof of an artist's *pigment*? And how can the presence of anatase or rutile be documented? Both minerals also occur in nature, although not as white crystals, but as black or brown grains.

Attempts have been made in our laboratory to perform a quasi-nondestructive, yet representative sampling and to do not only a chemical analysis to examine the presence of titanium by X-ray spectrometry, but subsequently (on the same specimen) also the mineralogical speciation by means of X-ray diffraction (Fig. 8).

Because microsampling is an established method in forensic and police procedures, a so-called 'criminal' adhesive tape was used to prepare specimen holders. Plexiglass frames, fitting into conventional X-ray fluorescence sample changers, were prepared with a central opening of 15 mm diameter, over which the tape is placed (Fig. 8a). Plexiglass is used because it is cheap, easy to handle and virtually free of all interfering chemical elements. Specimens taken from reference paintings, or standard materials for calibration are prepared the same way. The necessary sample mass may vary between less than 0.5 to 2 mg, spread over a surface of less than 2 cm^2, and is sufficient to perform the elemental analysis for main components and some trace elements. The analytical procedure is strictly non-destructive, the specimen therefore ready for additional tests, *e.g.* by XRD (Fig. 8b), for alternative measurements, or for storage.

The mineralogical, non-destructive speciation of microsamples is much more difficult and possible only when the minerals to be identified are present as main components in the pigment (Fig. 8c). The diffraction runs are in any case extremely time consuming (exposure time 10 to 50 h), therefore costly and not fit for large serial investigation.

This kind of microsampling for chemical fingerprinting has also become in the meantime a routine procedure for archaeological objects (alloys, bone, ceramics *etc.*), since it is easy to handle, but also to preserve for further additional examination and storage.

Received: September 19, 2001

---

[1] P.J. Potts, 'A Handbook of Silicate Rock Analysis', Blackie, Glasgow, London, **1992**, ISBN 0-216-93209-2.

[2] P.J. Ballié, W.B. Stern, 'Non-Destructive Surface Analysis of Roman Terra Sigillata: A Possible Tool in Provenance Studies?', *Archaeometry* **1984**, *26*, 62–68.

[3] G. Stumpf, 'Ein Athenisches Münzgesetz des 4.JH.v.Chr.', *JB Numismatik und Geldgeschichte* **1986**, *26*, 23–40.

[4] C.N. Zwicky-Sobczyk, W.B. Stern, 'X-Ray Fluorescence and Density Measurements on Surface-Treated Roman Silver Coins', *Archaeometry* **1997**, *39*, 393–405.

[5] A. Burkhardt, W.B. Stern, G. Helmig, 'Keltische Münzen aus Basel. Numisma-

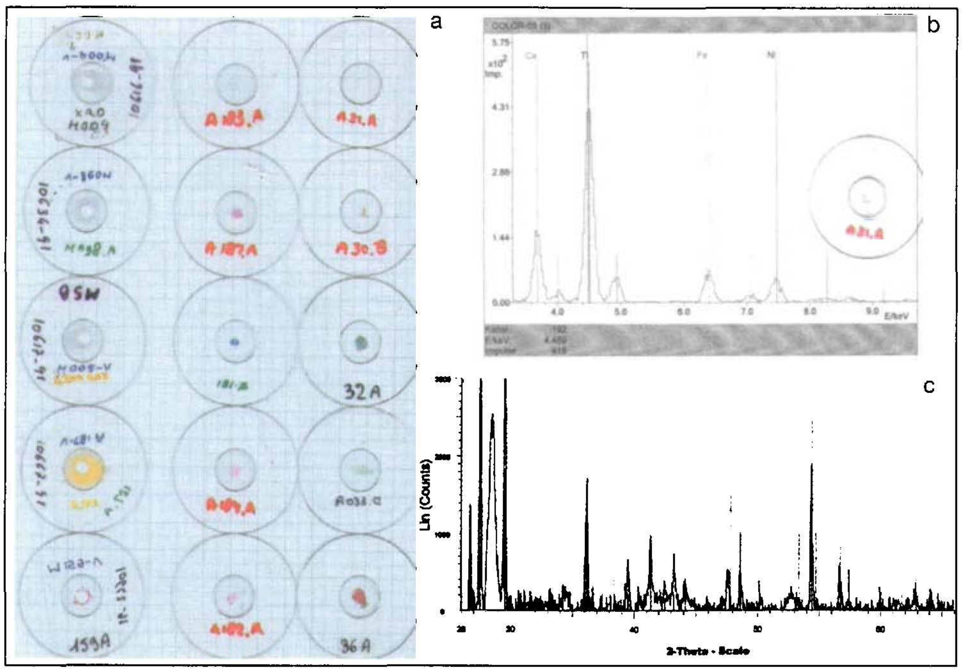

Fig. 8. Chemical fingerprinting in questions of authenticity in art: a) A set of microsamples taken from objects of fine art; the right two columns represent specimens as used for chemical investigation on pigments present, and inorganic compounds. The left column displays specimens which were first analyzed by non-destructive ED-XFA, and subsequently by destructive ICP-analysis (punched central part) for control measurements. The sample mass varies between less than 0.5 and 2 mg.

Quite small quantities of roughly 100 micrograms can be used for element identification; b) where the element titanium is clearly visible.

When mineral speciation is asked for, X-ray diffraction (Fig. 8c) is possible on microsamples on police tape, provided that a suitably large tape surface is covered by the pigment powder, and a long exposure time of 10 to 50 h is applied. The identification of the present compounds is performed by on-line data base research and reveals rutile (red bars), calcite (blue), quartz, whereas anatase (green bars) is proved to be absent.

tische und metallanalytische Untersuchungen', *Antiqua* **1994**, *25*; Schweizerische Gesellschaft für Ur- und Frühgeschichte Basel, ISBN 3-908006-17-1.

[6] A. Burkhardt, 'Quantitative Methoden zur keltischen Numismatik am Beispiel der Münzfunde aus latènezeitlichen Siedlungen der Oberrheinregion', Dissertation Basel, Paul Haupt Verlag, Bern, **1998**, ISBN 3-258-05858-X.

[7] W.B. Stern, A. Burkhardt, S. Schmidt, J. Kraut, 'Was leistet die chemische Analyse in der Numismatik?', Festschrift Ludwig Berger, *Forschungen in Augst* **1998**, *25*, 235–241.

[8] H.G. Bachmann, A. Burkhardt, R. Dehn, W.B. Stern, 'New Aspects of Celtic Gold Coinage Production in Europe', *Gold Bulletin* **1999**, *32*, 24–29.

[9] W.B. Stern *et al.*, 'Zur naturwissenschaftlichen Analyse von Edelmetallmünzen', VW-Projekt, **2001**, in press.

[10] D.R. Walker, 'The metrology of the Roman silver coinage', BAR Supplement Series London **1976-1978**, *5*, *22*, and *40*.

[11] M.A. Bezborodov, 'Chemie und Technologie der antiken und mittelalterlichen Gläser', Philip von Zabern, Mainz, **1975**.

[12] K.H. Wedepohl, 'Die Herstellung mittelalterlicher und antiker Gläser', Abhandlungen Mathematisch-Naturwissenschaftliche Klasse Nr. 3, Franz Steiner Verlag, Stuttgart, **1993**.

[13] K.H. Wedepohl, 'Mittelalterliches Glas in Mitteleuropa: Zusammensetzung, Herstellung, Rohstoffe', Nachrichten der Akademie der Wissenschaften Göttingen, II. Mathematisch-Physikalische Klasse Nr. 1, **1998**.

[14] H. Amrein, A. Burkhardt, W.B. Stern, 'Analysen von Gläsern aus der frühkaiserzeitlichen Glaswerkstatt von Aventicum (Schweiz)', *Bulletin Association Pro Aventico* **1995**, *37*,189-201.

[15] N.R.U. Gmür-Brianza, 'Chemische Untersuchungen an römischen Gläsern, Vindonissa und Eretria', Dissertation Basel, **1990**.

[16] B. Rütti, L. Berger, S. Fünfschilling, W.B. Stern, N. Spichtig, 'Die Zirkusbecher der Schweiz. Eine Bestandesaufnahme', Jahresbericht Gesellschaft Pro Vindonissa, **1987**.

[17] R. Glatz, 'Hohlglasfunde der Region Biel. Zur Glasproduktion im Jura', Staatlicher Lehrmittelverlag Bern, Paul Haupt, Bern, **1991**, ISBN 3-258-04562-3.

[18] H.A. Hänni, W.B. Stern, 'Über die Bedeutung des Gallium-Nachweises in Korunden', *Zeitschrift Deutsche Gemmologische Gesellschaft* **1982**, *31*, 255–260.

[19] P. Landesman, 'A 20th Century Master Scam', *New York Times Magazine* **1999**, July 16.

[20] E. West FitzHugh, Ed., 'Artists' Pigments. A Handbook of Their History and Characteristics', **1997**, Vol. 1-3, Oxford University Press, ISBN 0-89468-256-3.