Alchemy and Fire Assay – An Analytical Approach

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'We would call the attention of students of the history of chemistry to these early 16th century attempts at analytical chemistry; for in them lie the foundations of that science.' (Hoover and Hoover 1912, 220).

Abstract

Alchemy and fire assay use similar, often even identical ceramic vessels, tools and techniques, but have very different aims. For the interpretation of such finds from archaeological excavations it is hence often difficult to differentiate properly between these early chemical activities. The investigation of 16th century material from Cologne is used as a case study to develop valid scientific criteria to assign an archaeological complex of crucibles, ceramic and glass vessels to one specific craft. Among the possibilities discussed – glass and glaze working, alchemy, gold working – the evidence points to a goldsmith's workshop with a high degree of probability.

Introduction

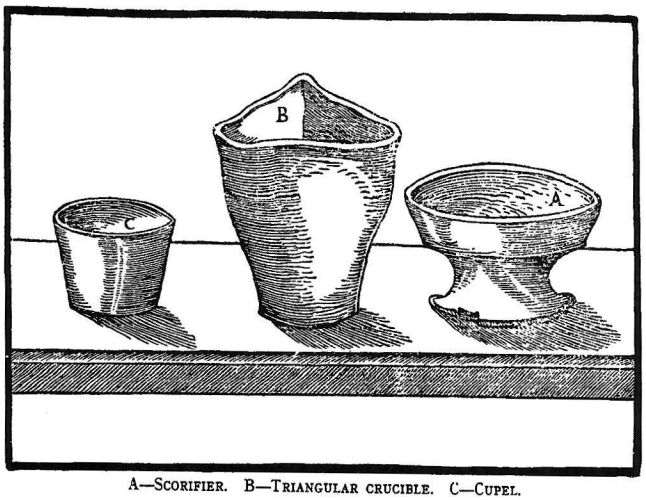
The period of the transition from the Middle Ages to Modern Times includes the beginning of modern and analytical chemistry, together with an increasing criticism of traditional alchemy. Landmarks in this development are the books *eg* by Agricola (1556) and Ercker (1580), promoting a very rational approach to metallurgical chemistry. Although rooted soundly in much older knowledge, their approach is now based on precise observations and quantitative measurements: typical for modern experimental and analytical chemistry. Hence, the roots of modern chemistry are to be found not only in the 'academic' attempts of the alchemists, but also in the practical experience of early metallurgists: that is why the research urged by the Hoovers in the quotation given above is of significance for the history of metallurgy as well. The relation between alchemists and metallurgists has often been ambiguous, their aims and approaches being quite diverse. The chemical techniques and substances used by them however were often identical, and linked them to some degree. Fire assay – and cupellation in particular – played a foremost part in this linkage, since it served both: the practical metallurgist in determining the metal content of a sample, and the theoretical (al)chemist in testing the results of his experiments on transmutation and upgrading the philosophical quality of various substances.

With the alchemists' written work being *'shrouded in an obscure cloak of gibberish and attempted mysticism'* (Hoover and Hoover 1912, 220), the aim of this paper is to illustrate the potential that lies in the scientific analysis of early laboratory remains, be they metallurgical or alchemical. The case study used for this is a set of 16th century finds from Cologne. It comprises a diversity of crucibles and heating trays, lots of glass fragments, a cupel and many other items. The material analysed here is chosen for variety, not for representativeness. It includes different slag linings from crucibles, substances treated in various vessels, the cupel and the antimonite reguli. Though the material stems from one source, we have no indication about its position within the particular laboratory, or laboratories in Cologne in general. Given the innovative character of this study, any generalisation would be premature.

The range of tools and techniques

Chemical techniques used at the end of the Middle Ages comprise a wide range of grinding, washing and mixing, of calcining, melting and fluxing, and of pickling, precipitating and distilling: the latter mainly for the preparation of mineral acids, alcohol and the purification of volatile substances. Accordingly, the inventory of a medieval laboratory included many different vessels and tools, which are well known from literary sources (*eg* Agricola, Ercker, Geber, Libavius, Paracelsus and many more) and archaeological excavations (*eg* von Osten 1992) alike (Fig 1). In this study, only finds related to dry analytical operations are considered, *ie* those covered by the term fire assay. More precisely, only the substances in the vessels are studied, not the vessels themselves.

Among the material found in 1966 at the Weyerstraße in Cologne, fragments of glass and ceramic distillation vessels were predominant. Next came, with more than ten items each, various trays, glazed cylindrical and conical crucibles, triangular crucibles, heating trays and flat circular melting trays with a spout. Other, less frequent items were mainly domestic pottery, but also a single rectangular lead vessel, one cupel, a cupel-like tray and two antimonite cakes. About 20 samples of roughly



A—Scorifier. B—Triangular crucible. C—Cupel.

Fig 1: Three typical metallurgical vessel-types: scorifier, triangular crucible and cupel (top: after Agricola; bottom from Oberstockstall (scale 5cm).

1 cubic millimetre each were mounted for metallographic investigation and analysed with an EDX system fitted to a SEM. A detailed report, giving the complete list of objects, drawings and all analyses, is currently in preparation together with Prof. Steuer, University of Freiburg.

Triangular crucibles

Triangular crucibles are known since the Early Iron Age (Tylecote 1987, 187), but went more or less out of use during the Roman and early Medieval period, when bag-shaped vessels dominated (see *eg* Bayley 1989, 1992, Rehren 1998). Only during the later Medieval period, triangular crucibles appear again and develop into a standard vessel shape for laboratory use. Now, they are generally made of a high firing, light, almost white clay, sometimes covered with a thin graphite slip. Fabrics rich in graphite exist also, particularly in Saxony (Richter 1994, Eckstein *et al* 1994) and Bohemia where graphite-containing ceramics have a long tradition. They come in various sizes, from as small as 3 cm up to vessels of more than 20 cm height (von Osten 1992). The rim forms an equilateral triangle, while the flat base is circular. Contours vary, from height equalling the upper width, to taller examples, where the height is about 1.5 times the upper width. The Cologne examples all belong to the isometric group.

The slags adhering to the triangular crucibles are mostly bright red to yellow, often in the form of a 'slag fin' sticking firmly to the ceramic. In one case, there is a smaller crucible standing in a slightly larger one, the slag penetrating from the inner crucible to the outer one, glueing the two irresolvably together. Chemically, these slags are often surprisingly clean lead silicate glasses, coloured by varying amounts of copper oxide. Some alumina, particularly close to the ceramic body, is present, but rarely exceeds a few wt%. All other elements are at or below one wt%. The slags contain frequent inclusions of quartz grains in a resorption-crystallisation equilibrium, *ie* showing both corrosion rims and precipitation of quartz on their surfaces (Fig 2). In these cases, the melt is no longer aggressive against siliceous ceramic, even though it may still contain up to 80 wt% PbO.

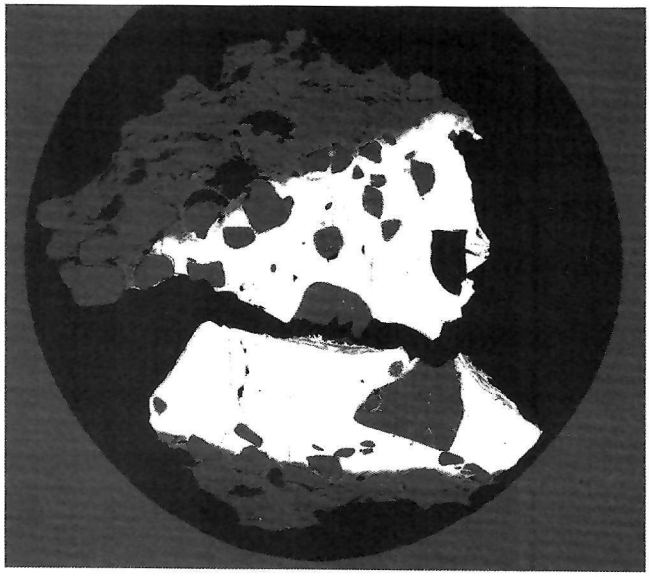


Fig 2: Lead silicate slag (bright white) with quartz grains (dark grey), adhering to crucible ceramic. Sample 18, triangular crucible from Cologne-Weyerstraße; sample size about 1 mm. SEM photomicrograph.

Apparently, these crucibles were used to melt a charge with a high lead flux under rather oxidising conditions. The morphology of the residual slag rim or fin sometimes indicates the original presence of a second, metallic melt underneath this slag. Different kinds of lead oxide dominated fluxes are listed and discussed by Agricola (Hoover and Hoover 1912, 232). Given their mutual

similarity, the small sample volume and the fact that the fluxes have already reacted with both the charge and the ceramic fabric, it is impossible to determine today with any degree of certainty which type of lead oxide was actually used. The presence of phosphorous in some cases however points to hearth-lead, *ie* lead oxide from cupellation hearth linings or used cupels.

Scorifiers

Scorifiers are shallow, open ceramic dishes used for the primary melting of a charge to remove gross impurities to an initial rough slag. Scorifiers are known at least from the later Medieval Period (Eckstein *et al* 1994, Richter 1994), and continue to be used even today. Although they are often used in close contact with lead oxide melts, they are typically made of siliceous ceramic without specific attention to other qualities than a good refractoriness.

The Cologne scorifiers differ in size and shape; one prominent example is a heavy pot, 13 cm in diameter, 6.5 cm high and with relatively step walls, increasing in thickness from 1 cm at the rim to about 2 cm at the bottom. Two different slag layers are preserved in this vessel, the older one being yellow, the younger one bright green. The latter has been highly corrosive, penetrating the wall at one side. Both slags are high lead silicate melts, contaminated mainly by alumina and some titania, indicating resorption of ceramic material. The yellow slag is coloured by finely dispersed crystals of lead antimonate, a phase commonly known as a pigment in glass production. The average antimonite content of the slag however is still below the detection limit of the EDAX system, *ie* clearly below one wt%.

Glazed Cylindrical Crucibles

Cylindrical or conical, but in every case rounded vessels with a wide opening form another important fraction of the crucibles studied. The fabric is usually glazed, its colour is dark grey to brown. The walls are often thicker than those of the triangular vessels, and the conical crucibles usually have a spout.

Two samples taken from conical vessels are presented here. One is from the metallic charge still sitting two cm thick at the bottom of a crucible that cracked during use around the base, the second one is a small metal and slag droplet from the inner wall of another vessel. The charge sample consists of heavily corroded metallic lead; the microscopic picture shows tiny patches of metallic lead in a matrix of lead carbonates. The structure is interpreted as due to oxidation during corrosion and not in the hot stage; it is hence assumed that the melting itself occurred under neutral to reducing conditions. The second sample turned out to be a heavily corroded silver drop, now mostly transformed to silver chloride (Fig 3), with a chain of primary copper oxide crystals around the edge. Only some metallic silver is still to be seen. The slag from this crucible is mostly fused ceramic material; the lead content is very low and may well stem from a residual lead fraction in the silver metal. The cuprite crystals however demonstrate that in this case, the melting was done under oxidising conditions, transforming some of the base metals into dross.

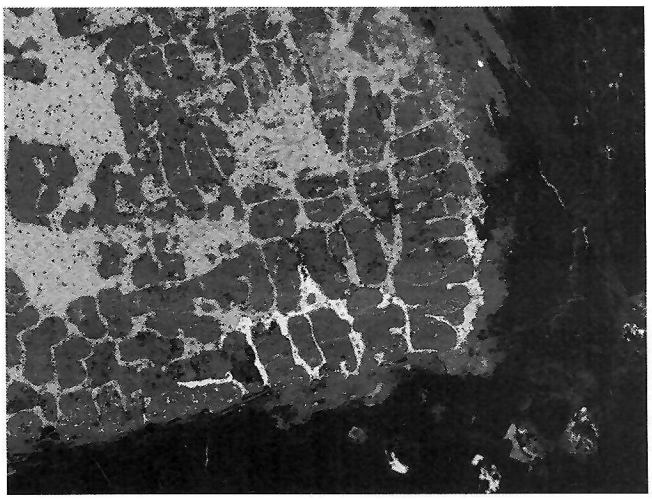


Fig 3: Corroded silver-copper droplet, now consisting of silver chloride (light grey matrix), copper oxide (dark grey cubes) and some residual silver metal (white). Sample 12, from a glazed conical crucible from Cologne. SEM photomicrograph: width 0.25 mm.

Antimonite cakes

Among the substances not adhering to ceramic vessels, a pair of plano-convex ingots attracted our attention. They are circular, with a diameter of 5.5 cm and 1.5 cm thick. The upper surfaces are covered with coarse vesicles, broken open and revealing a thin grey metallic network. The underside is spherical and covered by a thin layer of mud-coloured, glassy slag. Underneath this, a striated texture appears, pronounced by a whitish corrosion. The microscopic investigation of two samples, collected from the rim of the cakes, showed a matrix of corroded antimonite lathes, intergrown with droplets and feather-like aggregates of cinnabar (Fig 4). No other metals or metal compounds were found beside some traces of zinc and iron in the mercury sulphide.

Contemporary sources know antimonite (*stibium* in Latin, generally accepted as being not the metal antimony, but antimony sulphide, the mineral stibnite or antimonite. A recent study of the production of *stibium crudum* is given by Siebenschock *et al* 1996) as a parting agent to separate gold and silver (Hoover and Hoover 1912, 451-2), and describe this process in detail. In principle, the antimonite acts as an agent to sulphurise the silver, while the gold remains unaffected and is gained by

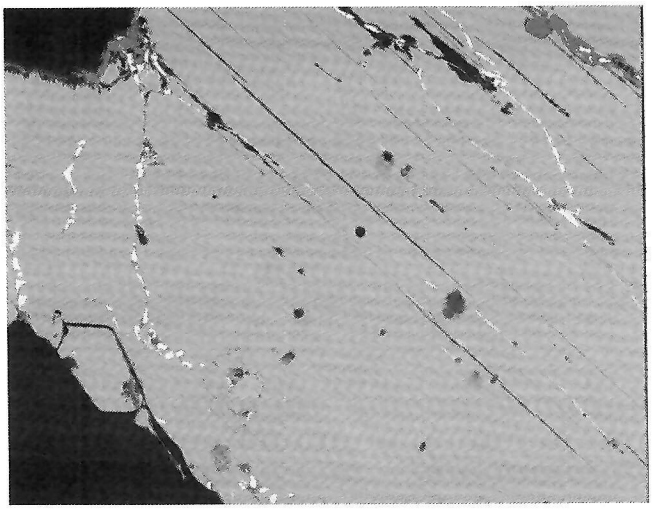


Fig 4: Matrix of stibnite (light grey), containing a network of cinnabar (white). Some corrosion is visible (dark grey). Sample 21, stibnite cake, Cologne. SEM photomicrograph: width 0.5 mm.

gravity separation in the liquid state, settling underneath the antimonite cake. Unfortunately, neither of the two cakes from Cologne shows any impression of a regulus at its bottom, and no noble elements were found in the samples taken. This however comes as no surprise, since the melting was repeated as many times as necessary to regain all the gold present. The last antimonite cake will therefore lack any impression of an underlying regulus, and only this last cake is liable to disposal for the lucky archaeologist of later centuries, if it is not remelted with lead to recover any silver present.

In our case, not silver but mercury was found as the principal contaminant in the antimonite, and it seems plausible to assume that this is not a primary mineral associate of the antimonite ore, but due to the treatment of an amalgam. The separation mechanism of gold and quicksilver in this case will be much the same as that of gold and silver, while the final step of recovering the silver of course was not applicable here.

Square lead vessel

All samples investigated so far originate from high temperature metallurgical material. This last one has not been subjected to much heat, but is a loose powder collected from a square vessel made of lead sheet. The vessel is about 2.5 cm high and roughly 5 cm wide. The thickness of the lead sheet is 3 to 5 mm. The sample is from some greenish powder found in a corner of the vessel. This powder consists mainly of corrosion products, soil material and lime; but interspersed in this secondary matrix are frequent agglomerates of cuprite and several tiny flitters of gold and silver amalgam, not exceeding a few microns in diameter.

It appears as if in this vessel either residues of fire gilding and silvering were collected, or filings or shavings from scrap gilded and silvered objects. This evidence immediately recalls the description given by Theophilus of how to separate gold from copper: 'Now if you ever break gilded copper or silver vessels or other kind of gilded work, you can recover the gold in this way. ... Then carefully scrape the gold off the copper and wrap the scrapings in lead that has been hammered flat and thin.' (Hawthorne and Smith 1963, 146). This parcel then is put in a cupel like any rich lead sample. What would make more sense than collecting the filings already in a lead sheet vessel, easy to fold up eventually?

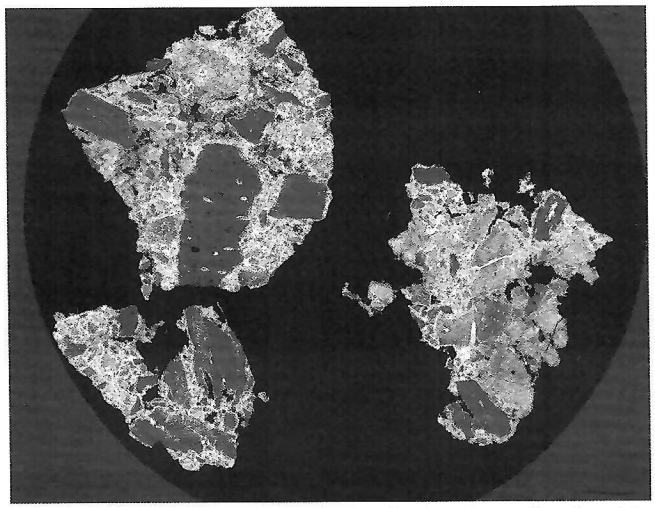


Fig 5: Fragments of a used cupel, showing a lead oxide matrix (white) around crushed bone ash particles (dark). No chemical reaction happened between the bone ash and the lead oxides. Sample 17, cupel from Cologne; sample size about 1 mm. SEM photomicrograph.

Cupel

Cupels are highly diagnostic and unmistakable finds for the working of precious metals. Characterised at least since the late Medieval period by a very typical form, even small fragments can be distinguished from almost all other substances on the basis of their unique composition and microstructure. The Cologne cupel has an upper diameter of 4 cm, decreasing to 3 cm at the bottom. It is 1.8 cm high at the rim, and 1.3 cm in the centre. Its colour is a light yellow brown. The microstructure is dominated by a porous network of finely ground bone ash, soaked in with lead oxide (Fig 5). As one would expect, there is little reaction of the bone ash material with the litharge. This is in contrast to the cupels investigated so far from Oberstockstall (Rehren 1997a), which contain a good deal of siliceous matter and hence reacted thoroughly with the lead oxide. Obviously, the Cologne cupel followed strictly the recipes given by the contemporary authorities. This is mirrored in the extremely small quantities of silver found in the sample, demonstrating nicely the benefit of using

high quality absorbent material for cupel production (Rehren and Eckstein 1996) and the deleterious effect of even small quantities of siliceous material on the stability of the cupels.

The cupellation of rich lead, *ie* the oxidising melting of lead containing precious metals in order to collect gold and silver in a regulus, while all base elements are carried away in the litharge, is a crucial operation in various steps of the treatment of the noble elements. The general versatility of this process is only recently shown by Bayley and Eckstein (1996). In our context, cupellation can be expected at the beginning of scrap recycling, when rich debris is fused with lead and than transformed into a bullion regulus. But cupellation is again necessary after the parting of gold and silver, be it by antimonite or by nitric acid, to consolidate and refine the gold, and to regain the silver which was intermediately transformed to silver nitrate or silver sulphide. Given the purity of silver found in the cupel from Cologne, and the general lack of contaminants, it is considered here as belonging to this final cupellation step.

Interpretation

The individual samples from Cologne – Weyerstraße, not only as presented above, all fit the dry chemical processes given in the contemporary literature. However, many of them can be seen either in a mundane metallurgical context or as a result of more elusive alchemical activity. Bayley and Eckstein (1996, Fig 3) gave a recent outline of small scale metallurgical activity leading to cupellation, including first the concentration of silver in a lead button by either smelting under neutral to reducing ('pot analysis') or under oxidising ('scorification') conditions, followed by cupellation. At Cologne, we have proof for pot analysis in the cylindrical and conical vessels, and for scorification in flat dishes and the triangular crucibles alike. Cupellation is evident from the cupel, while the antimonite cakes and, more indirectly, also the distillation vessels hint to the parting of gold and silver.

As briefly mentioned in the introduction, the tools and techniques used are often the same for metallurgy and alchemy. There are however some diagnostic processes or substances. The strong appearance of mercury in the antimonite cakes is taken as one such feature, pointing strongly to the recycling of fire gilding scrap, particularly when seen next to such scrap being collected in the lead sheet vessel. It is conceded however, that an alchemist may equally well have tried some transmutation here. For the time being, the author is inclined to develop from these finds an outline picture of a goldsmith's workshop, dealing with base metals like copper and brass (no tin has yet been found in the samples, but sometimes zinc) as a basis for gilding and silvering work. Further, the raffination and parting of gold and silver is attested by several finds. The diversity of methods applied and the amount of glass ware and ceramic vessels unearthed indicate the substantial size of the workshop, though one has to be cautious with this aspect since we have no idea about the length of time involved in the deposition of the material. Does it represent several decades, or was it all dumped more or less at once?

This attribution to a goldsmith's workshop implies that most fragments represent debris of small scale operations of the handling of metals rather than proper fire assay, *ie* the quantitative analysis of small samples as *eg* in a mint office. In the latter case, one would expect much more cupels among the debris, and probably less mercury. But again, this is subject to discussion, the processes themselves are identical (see Agricola's statement to this in Hoover and Hoover 1912, 220-3).

An early suggestion made in the first – unpublished – investigation of this material aimed at the production of coloured glass and glazes. This idea originated from the colourful slags visible in several crucibles, and could even gain support from the identification of yellow lead antimonate, a widespread glass pigment, in one of these slags. The alkali-deficient composition of the slags speaks clearly against glass, and, together with their undeniable relation to gold and silver working, renders this glass theory highly unlikely. More probably this antimony is due to contamination of the charge by some of the stibnite cake material.

Yet another possibility is the allocation of these finds to a pharmacy. Medieval cities of the size of Cologne had several such drugstores in their walls, and the emphasis on distillation apparatus could well point to such an interpretation for the finds. But again, the clear evidence for precious metal working rules out this possibility, and the distillation vessels will have served in the preparation of mineral acids necessary for further parting processes, or the purification of volatile ingredients.

Conclusion

The investigation focused on a limited fraction of the entire material from Cologne – Weyerstraße, namely those finds bearing traces of dry metallurgical activity. The reminder, overwhelming in quantity, was considered unapproachable with the methods available. It is recognised as being glass and ceramic laboratory and domestic ware, including heating and boiling vessels and distillation apparatus alike. Though these point to some sort of wet chemical activity, no distinction can be made as to whether this has been in an alchemical, metallurgical, iatrochemical or other context.

The various finds investigated, although presented here

only in some selection, relate all in one way or the other to dry metallurgical methods known as fire assay if used for analysis, or just reflecting small scale operations in a workshop. They all can be seen as individual pieces of a jigsaw, not necessarily coherent, but belonging to one and the same overall picture. The outlines visible – melting of base and precious metals in different crucibles and scorifiers, using lead-dominated fluxes, collecting rich scrap in a lead vessel, the cupellation of rich lead, the parting of gold and (quick)silver by antimonite – all techniques match a goldsmith's workshop. They could, admittedly, as well relate to an alchemist's laboratory, but in view of the evidence for mercury gilding scrap, preference is given to the first suggestion.

The unexpectedly wide range of substances, materials and processes recognised during this study only underlines the potential that lies in the investigation of medieval urban metal workshops. Although a wide range of apparently specialised tools could give rise to the hope that such tools are diagnostic for a narrowly defined process or practice, it becomes evident that one and the same vessel was used for different operations, and that one process could be done in different vessels. Tall conical vessels need not imply melting under reducing conditions, but may have been used for neutral or even oxidising melting also. Similarly, scorification was done both on flat open dishes and in relatively steep triangular crucibles. Further work will probably allow to assign tools and techniques more specifically, but a certain degree of uncertainty will always remain.

Only recently has the metallurgy of Medieval and early Modern periods come into focus for scientific studies, often in an urban context (Bayley 1992, Rehren *et al* 1993). This period turns out to be highly interesting, offering a wide potential to the history of technology. For many thousand years, a very limited range of metals has been available to mankind. This only starts to change in the early Modern period, when substances like zinc, bismuth and arsenic were recognised as metallic matter in their own right, and the whole concept of 'elements' is put on new ground. The impact of innovation, analysis and experimentation with new concepts and ideas on the late Medieval society is discussed *eg* by von Stromer (1995) in view of developing industries not only in metallurgy. The growth of modern chemistry from roots as different and as close as alchemy, metallurgy, and pharmacy (Weyer 1992) is only another example of the evolutionary power gaining ground at the dawn of rationalism. Urgent questions concern the first appearance of specialised crucibles and cupels; Richter (1994) and Jeanjacquot (1993) both give examples dating to the 12th to 14th century. According to Oddy (1983, 55) cupellation was mentioned in London during the 12th and 13th centuries, while the first written technical evidence appears only about two centuries later. Which processes can be related to these finds? When does proper analytical chemistry start, *ie* the quantitative analyses of a weight sample representing a larger total (Rehren 1997b)? The potential (and need) for further interdisciplinary research into all aspects of urban metallurgy is evident.

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