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today has the composition found in many museum objects. It is, however, possible to analyse bronzes by using a combination of two of the standards available. The standards used for pewter were "tailor made" for the alloy compositions expected and analysed by an independent consultant analyst. It is critical that the physical form of the standards should be the same as that for samples, *i.e.*, used drilled standards for drilled samples, filed standards for filed samples. Table 1 shows the effect of sample "form" in the analysis of pewter. Bronzes show a similar but smaller effect.

The analytical regime devised is now illustrated by considering the analysis of pewter. Brass and bronze are analysed using a similar type of regime.

Pewter Analysis

The sample is first analysed qualitatively, using the most advantageous spectrometer conditions for each part of the X-ray spectrum, for all elements having atomic numbers above 21. A background "trace" has also been recorded and a tracing made of this on transparent acetate sheet. The positions of all of the spectral lines of the elements expected are marked on this "trace." The edited background trace is then superimposed on the analytical trace, thus making it possible to evaluate without reference to 2θ tables which elements are present. The peak heights of SnK_α, PbL_α and CuK_α are measured for all samples, together with the peak heights given by a standard containing 80.7% Sn, 15.5% Pb and 1.0% Cu. The approximate composition is then calculated from these peak heights. A normalisation calculation is used to account for different sample masses, the sum of the elements measured being taken as 99.5%. This preliminary calculation indicates if the pewter is "fine metal" or "lay metal." Fine metal was defined by the Pewterers Company in the 14th Century as an alloy containing up to 26 lb of copper per 112 lb of tin, while lay metal contains up to 26 lb of lead per 112 lb of tin. The values also give a double check on the final quantitative analysis, thus making certain that the data has been correctly "fed" into the computer.

Table 2. Analysis of sample 4B

Determination number	Composition, % *m/m*					
	Sb	Sn	Bi	Pb	Cu	Fe
1	0.06	96.07	0.74	0.60	2.45	0.11
2	0.04	95.84	0.77	0.66	2.56	0.13
3	0.01	96.18	0.76	0.60	2.39	0.11
4	0.09	95.96	0.80	0.60	2.44	0.13
5	0.04	96.00	0.77	0.63	2.53	0.05
$\bar{x}$	0.05	96.02	0.77	0.62	2.47	0.11
σ	0.03	0.11	0.02	0.03	0.07	0.03

Table 3. Analysis of eight sub-samples from a pewter spoon handle

	Composition, % *m/m*					
	Sb	Sn	Bi	Pb	Cu	Fe
1B	0.04	95.95	0.80	0.57	2.64	0.01
2B	0.05	97.12	0.57	0.50	1.73	0.07
3B	0.0	96.55	0.60	0.64	2.12	0.12
4B	0.05	96.02	0.77	0.62	2.47	0.11
1T	0.0	96.60	0.61	0.68	2.06	0.07
2T	0.03	96.89	0.65	0.55	1.84	0.07
3T	0.07	96.55	0.57	0.48	1.67	0.68*
4T	0.04	97.00	0.56	0.53	1.83	0.04
$\bar{x}$	0.04	96.89	0.64	0.57	2.05	0.15
σ	0.03	0.43	0.09	0.07	0.35	0.22
					$\bar{x}$	0.07
					σ	0.04

* Excluding 3T.

The sample is then analysed quantitatively by measuring the X-ray intensity at the relevant 2θ values for the element lines and their associated backgrounds, the 2θ values and relevant counting times being permanently stored in a programmer which is linked to the X-ray spectrometer. A blank, consisting of Scotch 810 tape stuck on to Mylar, and the relevant standard are analysed twice with each batch of samples, once at the start of a batch and then again near the end of a batch. The average values of these measurements are then used in the subsequent calculation of quantitative data. This calculation is undertaken on a microcomputer, the variation of sample size being overcome by use of a normalisation calculation.

A Mediaeval pewter spoon was obtained and the handle sampled in 8 places, 4 samples on the top of the handle (1T–4T), 4 from the bottom (1B–4B). One sample (4B) was selected at random and analysed five times, at intermittent intervals during the analysis of the batch of the 8 samples, while each of the other samples was analysed once. The results are given in Table 2 and 3.

The results of Sn, Bi, Pb and Cu show that the precision of the method is several times greater than the variation in composition. With Sb and Fe it is of about the same order of magnitude when sample 3T, which on close examination was seen to contain corrosion products, is discarded. Both of these elements are, however, only present at a low concentration. The results indicate that provided care is taken, particularly with heavily corroded objects, with sampling, the accuracy of the method used is sufficient when the constraint of sample heterogeneity is taken into account. If, as is usually the case, only a single sample is permitted, then the results obtained are usually sufficiently accurate to satisfy "archaeological requirements.".

X-ray Fluorescence Analysis of Non-ferrous Archaeological Metalwork

Part 2. Archaeological Applications

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Consideration is given to the contribution which analytical surveys of relatively large numbers of objects have made to a number of issues of interest to the archaeologist. These discussions are illustrated by reference to examples from analytical work on copper-alloy and pewter objects, mainly from the Mediaeval period.

Establishing Basic Alloy Type

The purpose of this type of work is to put alloy description on a better footing. Terms such as "bronze" and "bell-metal" have been widely used in archaeological reports and articles without analytical support, although more recently "copper-alloy" has been substituted. Designation presents no analytical difficulties, the main problem being one of terminology with copper alloys. Fig. 1 is a useful means of presenting alloy compositional data and some of the terms used are indicated. It is evident from our work that the alloy used in making skillets and mortars was not "bell-metal" but a heavily leaded bronze,[1] and spurs and purse-frames, commonly referred to as made of "bronze," are in fact made of latten.

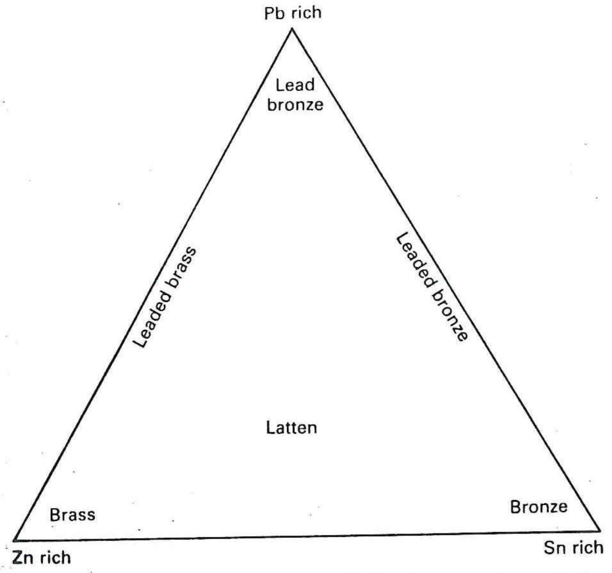

Fig. 1. A scatter diagram for displaying large numbers of alloy compositions of copper alloy in respect of the three main elemental additions zinc, lead and tin. Some alloy terms are indicated

Detection of Repairs, "Marriages" and Reproductions

Repairs can usually be confirmed because they have a significantly different alloy composition from the original. In a similar way "marriages," the occurrence together of parts not originally put together, can be detected. These may not always be innocent attempts to retrieve the situation of a broken object by "cannibalising" a similar object. It is important that "marriages" should be recognised as such, otherwise efforts at classification and stylistic analysis can be thwarted. Reproductions of early objects can be more difficult to detect as they have no internal reference material. However, by comparison with data from a number of similar objects and by taking other indications into account it is often possible to identify reproductions.

Aid to Object Classification and Stylistic Analysis

A confused picture can sometimes be clarified when alloy compositional data on a population becomes available. Classification of 13th century steelyard weights on stylistic grounds had been attempted previously with limited success; a more comprehensive survey of alloy compositions has allowed a more satisfactory classification to be produced.[2]

Mediaeval pewter is rarely found in good condition and flatware (plates, etc.) classification has not previously been attempted. However, a correlation between an angled-bead rim reinforcement and a high copper content for what are believed to be early mediaeval items might form a basis for flatware classification because pewter flatware of the late mediaeval period has a rounded bead and a lower copper content.

Information on Technology of the Period

The additions used to harden pewter were left to the pewterer, subject only to a density constraint to curb excessive additions of lead. Copper, bismuth and antimony are mentioned in historical sources but the amounts to be used are not clearly stated. Analysis has shown that copper was the main hardening addition, with occasional high levels, whereas bismuth and antimony were rarely above trace level in mediaeval pewter flatware[3] and spoons. An interesting example has been found[4] of the use of mercury to harden a pewter spoon, as described by Theophilus.

Analysis of a later plate by Taudin (*c*1700) has shown that small antimony additions may have been responsible, at least in part, for the success of this pewterer in selling his "Hard Metal."

In respect of copper alloys, no attempt has been made to seek detailed correlations between impurities and ore-bodies, as has been carried out in the past, because of the attendant risks. However, the general ore-type can often be deduced from analysis of the alloy. For example, high antimony and arsenic levels are suggestive of a *fahlerz*-type ore, rich in these elements, and high nickel levels are thought to indicate the use of a *kupfershiefe*-type ore from the Mansfeld area.

Analytical data on the main elements copper, zinc, tin and lead indicate the broad approach used in alloy selection. For example, it is clear that highly leaded bronzes were widely used to cast cooking vessels; the alloy was relatively cheap and easy to cast in the thin-walled form required. The use of this alloy was extended to mortars and weights, objects required to be massive and subject to modest stresses. These essentially zinc-free alloys were not used where colour was important; latten, containing zinc, was then used. Cast latten often contains significant lead (whether added deliberately or not is not clear at present) but lead levels are low in objects that have been gilt and in wrought objects.

In the Mediaeval period zinc was introduced into copper to produce latten or brass by a cementation process, using finely divided copper and calamine. The efficiency of this process increased with time and it has been shown[5] for memorial "brasses" that the zinc content increases with time. It was hoped that simulated cementation experiments would establish a maximum achievable zinc content as an aid to the detection of fakes or reproductions but there are some associated problems. From the 16th century onwards (and perhaps also during the mediaeval period) it became possible to produce brass by the modern method of adding zinc metal brought from Asia to molten copper and so achieve higher zinc levels.

It may prove possible to trace the presence of unusually high levels of lead (and perhaps other elements) to the source of calamine used in the cementation process. However, from the 16th century, the use of furnace calamine from the Harz area must be taken into account.

Provenancing and Dating Objects

There are indications that alloy analysis may be successful in these respects for cast copper-alloy objects from north-west Europe from the Mediaeval and immediately Postmediaeval periods. There is no direct dating technique for such materials comparable with the ^{14}C or TL methods. However in broad terms it appears to be possible to suggest provenance and date for some groups of objects.

Past efforts at linking object alloy composition and ore-bodies have been less than fully satisfactory, due in major part to the probable use of scrap. This leads to the blurring of possible links. In the Mediaeval period, however, it is believed that this presents a much less serious problem, as the massive expansion in output of newly extracted metal would ensure that the vast majority of objects would have been made without the use of scrap (apart from "in-house" scrap). The present approach in any case concentrates on the levels of the major elements zinc, tin and lead in the copper alloys.

The development of this approach stemmed from an early realisation that objects, believed from their style to have been made in broadly the same area at broadly the same time, had roughly similar alloy compositions.[6] This led to the concept of an alloy compositional profile, which differed with time and place. The underlying causes of these differences are essentially those of local availability and cost of the metals concerned. A particular benefit to the archaeologist of alloy compositional comparisons is the facility to compare objects of very different form but likely to have been made by the same craftsmen using the same materials and technique. Thus, for example, candlesticks can be compared compositionally with chafing dishes and lavers.[6]

It is recognised that the results of such data comparisons do not constitute proof of any date or provenance, but because the information is additional to any stylistic or other information, the contribution can be important.

In conclusion, it must be said that the degree of certainty associated with comments derived from alloy analysis decreases through the sequence of the foregoing sections and the information must be treated accordingly. However, as work proceeds the levels of confidence will almost certainly increase.

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Archaeological Applications of Atomic-absorption Spectrometry

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Introduction

Atomic absorption is a widely-used analytical technique with features of particular value for analysing archaeological objects. The British Museum Research Laboratory has used AAS for a number of years and made several thousands of elemental analyses; other laboratories also use AAS for archaeological materials. Its applications can be broadly divided into two categories, namely metals and silicates. Among ancient metals the major amount of work has been on copper alloys but other studies have been on gold, silver, lead and tin and their alloys, and on iron. Analysis of silicate-based materials has included ancient pottery, rocks and minerals, glass, enamels and refractories for metalworking.

Analytical Technique

For most applications, the flame mode provides sufficient sensitivity but occasionally electrothermal atomisation is necessary where the elements selected are in low concentrations.

In order to analyse solid objects it is necessary to remove some of the object in a sample form, weigh the sample and dissolve it, usually with acids. The techniques used at the British Museum have been described elsewhere.[1] For copper-alloy objects we normally analyse drillings (20–30 mg) taken with a 1 mm steel twist-drill. After weighing out about 15 mg, dissolving in aqua regia and diluting to 20 ml, the solution obtained is suitable for the analysis of 13 elements (Cu, Pb, Sn, Zn, Ag, Fe, Sb, As, Bi, Ni, Co, Cd, Au) in batches of 50–150 samples at a time.

For sampling ceramics or glass various drills can be used, such as synthetic sapphire, tungsten carbide or diamond-embedded drills (the latter especially for glass or enamels). Dissolution of silicates is carried out either using hydrofluoric acid - perchloric acid or a lithium metaborate fusion (Si can be measured). On the general question of accuracy, for major elements in copper alloys and silicates with 10–20 mg samples the coefficient of variation on repeated analysis is about 1–3%, for minor elements 5–10% and for trace elements it can be 5–20%.

Metals

Copper alloys are numerically the largest group; among the many programmes of bronze analysis[2,3] we have recently been looking at the composition of Early Bronze Age (EBA) axes in southern Britain with regard to changes in alloy types with time and changes in minor elements, especially as they may relate to the use of different metal sources. This work has shown that very low tin and high arsenic (4–6% As) percentages occur in the earliest part of the EBA, followed by a rapid increase in tin and fall in arsenic percentage, the tin stabilised at about 10–11% of tin by mass in the copper alloy. One may note in passing that for such projects one needs to undertake analyses of largish numbers of objects in order to see a pattern emerging and for this AAS is well suited.

One may use the analyses of copper alloys in different ways, the most useful we believe to be that of revealing aspects of ancient technology, *viz.*, how objects were made and the types of alloys being used at different chronological periods.

Other metals present greater analytical difficulties; for gold alloys, the main elements are gold, silver and copper, and high acid concentrations can usually keep all three in solution simultaneously. Some Bronze Age gold torcs (neck rings) from Ipswich were analysed by AAS[4] and contained between 11 and 28% of silver and 0.3–12% of copper, both metals (except copper below about 1%) probably representing deliberate additions to the gold. For silver alloys, most elements including silver can be analysed with a sample dissolved in dilute nitric acid. Gold and tin (the exceptions) can then be measured with a further sample dissolved in aqua regia (silver precipitated). In recent years analyses of silver and gold objects at this Laboratory have mostly been by X-ray fluorescence.[5]

Silicates

The major use of AAS for ceramics has been provenance studies, *i.e.*, indicating the source of the pottery by matching its analysis with a chemical profile of pottery samples taken from a number of known possible sources of manufacture. We have used AAS in a relatively limited way for the provenance of ceramics, having in recent years introduced instrumental neutron activation analysis[6] because of the larger numbers of elements that it is possible to measure in a single sample.

One project involving the use of AAS has been on Anglo-Saxon pottery[7]; the question arose as to whether Anglo-Saxon pots found in Kent were local Kentish products or were imported from the Continent. By analysing pots found definitely associated with Kent and Continental kilns the pottery from these kilns was characterised. The analyses of pots found in Kent but of unknown origin could then be matched against those characteristics using appropriate statistical techniques and many were shown to be Continental imports.

In order to digest the mass of elemental data, multivariate statistical techniques need to be used, *e.g.*, discriminant analysis[8] and cluster analysis.[9] Other laboratories have been engaged in the analysis of ancient ceramics by AAS.[10–12]

Other silicate materials which can be usefully analysed include materials associated with ancient metalworking such as crucibles, furnace linings and slags; the analyses can shed light on the processing techniques.[13] Rocks and minerals present a further application for AAS; a recent large project at the Laboratory,[14] now being continued at Imperial College using ICP spectrometry, has been the analysis of Neolithic and Bronze Age flint axeheads as a means of determining how far the flint was distributed from the flint mines.

Finally, glass and enamels can be analysed for major and