
Analysis of Ancient Metals

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Analysis of ancient metals

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The study of the chemical composition of ancient materials dates back to the work of the pioneer analyst, Martin Heinrich Klaproth, towards the end of the eighteenth century. From that time onwards thousands of specimens of ancient materials have been analysed, and from the beginning the composition of ancient metals attracted particular attention, because of the inherent interest of chemists in metals and their corrosion, and because of the importance that archaeologists attached to metal artefacts as a source of information about technological developments in ancient cultures. The early analytical researches on metals have been reviewed by Caley (1951, 1964). These were, for the most part, of a rather spasmodic nature and somewhat restricted in scope because of the limitations imposed by the analytical methods available at that time which required relatively large samples. The intensive application of analysis first became possible when precise and sensitive microchemical methods were used, and it has undergone further development with the introduction of the modern ultra-microchemical techniques of analysis that have opened up new possibilities. The application of these modern techniques to the analysis of ancient metals has, however, introduced certain problems that must be taken into consideration, if one wishes to obtain analytical results that are both reliable and meaningful. This is because the analysis of ancient metal objects presents problems that are not encountered in the examination of modern metals and alloys in an industrial or conventional research laboratory. It is therefore appropriate to consider in general terms what are the particular requirements of analytical procedures in a museum laboratory. The factors involved may be conveniently discussed as follows:

1. TYPE OF ANALYSIS

Here two main categories may be considered. The first may be referred to as systematic analysis, i.e. the analysis of large numbers of metal antiquities of a similar kind in order to obtain analytical results of statistical significance that can be used to provide information about such archaeological questions as sources of ore materials, possible trade routes, significant changes in composition that might be correlated with different types of objects, e.g. in bronze objects, or with changes in technology. The second category is that of specific analysis, i.e. the analysis of single objects or small groups of objects to obtain information that may help to solve specific problems, including questions of authenticity.

2. NATURE OF ANALYSIS

Here one is concerned with the fact that the method of analysis must be related to the type of problem to be solved. It may, for example, in some cases be sufficient to determine the major elements present, whereas in other cases a knowledge of the relative concentrations of minor or trace elements may be required so as to establish a correlation between a given pattern of

12-2

trace impurities and a particular geographical source of origin of objects. Also the question of the degree of precision of the analysis may be a deciding factor in solving the problem; this means that a number of different analytical techniques must be used and adapted to particular problems. Thus, emission spectrography with an inherent accuracy of only *ca.* 10 to 15 % may be sufficient in some cases, but if an accuracy of *ca.* 1 % is required, then methods such as polarographic and atomic absorption analysis must be employed.

3. SAMPLING

This question of sampling is of such vital importance in the analysis of ancient metal objects that it is necessary to consider it in some detail, because the precautions that must be taken to obtain a truly representative sample of the bulk metal are not always clearly understood by the archaeologist. The factors that must be taken into account are:

- (a) The minimum size of sample necessary to give a reliable analysis (this will be related to the size of the object, and in the case of large objects the need to take multiple samples will arise).
- (b) The method of sampling and the need to avoid risk of contamination by corrosion products.
- (c) The possible inhomogeneity of certain alloys.
- (d) The physical condition of the object, i.e. the need to study the extent of corrosion and the effect of any chemical treatment;
- (e) The need for collaboration between the scientist and the archaeologist in the taking of samples.

The precautions that have to be taken in sampling will, of course, be more stringent, if it is necessary to carry out accurate quantitative analysis (say within $\pm 1\%$) in order to obtain meaningful results.

The effect of sample size on the analysis may be illustrated in connexion with a recent study of the gold coins from the Sutton Hoo ship burial carried out in the British Museum Research Laboratory. The purpose of this study was to determine the composition with an accuracy of about 1 % so as to obtain information that might lead to a more precise dating of the coins. To evaluate the potentiality of polarographic analysis a gold *tremissis* (diameter 15 mm; mass 1.3604 g) was taken as a test piece, and the copper content was determined. Scrapings ranging in mass from 1 to 25 mg were taken in triplicate from fresh areas along the edge of the coin; and each sample was analysed for copper content. The results obtained were as follows:

mass of sample/mg	copper content/%	mean copper content/%
1	0.08; 0.17; 0.07	0.11
3	0.12; 0.08; 0.33	0.18
10	0.19; 0.28; 0.27	0.25
22	0.22; 0.32; 0.30	0.28

This shows that a surface scraping of at least 10 mg is necessary before sufficient body metal in relation to surface layer is removed to compensate for the effects of changes in composition in the surface layers—a phenomenon that is referred to as ‘surface enrichment’. This occurs because during burial in the ground silver and copper are leached out leaving a surface layer richer in gold than the bulk metal. Since the taking of samples as large as 10 mg from gold coins would not normally be permitted, it was clear that polarographic analysis was not a

suitable method of analysis, and an alternative non-destructive method of analysis had to be adopted, which will be discussed later.

This example also shows the inadequacy of scraping as a method of sampling, and the only reason for using this method of sampling, particularly on small objects, such as coins, medals, etc., is because less visible damage is caused if very small samples are taken. A more satisfactory method for the proper sampling of ancient objects is by drilling—using a micro-drill of 0.5 mm in diameter. By this method of sampling it is possible to sample corroded objects, and to obtain a representative sample of the underlying sound metal free from corrosion products as has been described by Organ (1962). The damage to the appearance of objects caused by micro-drilling is slight, and it can be readily concealed by plugging the hole with wax, coloured to match the surface.

It must, however, be realized that drilling may not always be a suitable method for sampling objects made from thin sheets of metal that have corroded on both sides. In such cases a representative sample can best be obtained by cutting out a small fragment of the corroded metal, mounting it in a disk of synthetic resin with the corroded surfaces exposed, and grinding away the mineralization on both sides until metallographic examination shows that the corrosion fronts have been passed. The sample of metal remaining is free from corrosion products and represents the metal that was lying between the two corrosion fronts. Metallographic examination is particularly important in these cases because the mineralization of worked sheet metal is commonly intercrystalline and necessarily microscopic in scale. It must, however, be noted, that if there is extensive internal corrosion, it may be almost impossible to obtain a sample of unaltered metal free from corrosion products.

The next factor of importance is the possible inhomogeneity of ancient metal objects. It has been suggested (Jedrzejewska 1962) that the inhomogeneity of ancient alloys may be caused by the segregation of components on ageing due to diffusion, crystal growth or phase change. This, however, is normally an insignificant cause of inhomogeneity, since, as has been shown by Organ (1962, p. 49) the crystal grain sizes, even in a cast metal, are extremely small relative to the size of a sample normally taken for analysis with a micro-drill. A possible exception in the case of certain silver-lead or silver-copper-lead alloys in which age-precipitation can occur has been mentioned by Thomson & Chatterjee (1954). Of greater significance is the inhomogeneity that may occur at the time of manufacture caused by segregation during cooling. Thus, in the case of bronzes containing a high proportion of lead, it can happen that the lead separates as globules irregularly distributed throughout the mass of the metal; if, therefore, small single random samples are taken from small objects for analysis, unreliable results may be obtained. Also in the case of large cast objects, it was a common practice to make these from several small pourings of molten metal that did not necessarily all have exactly the same composition. The differences in the analysis that may arise from this cause have been cited by Picon, Boucher & Condamin (1966) in the case of a large statue. Three samples from different parts of the drapery gave the following results (%):

Cu	Sn	Pb
71.0	8.1	20.9
60.6	9.4	30.0
60.4	6.8	32.8

Finally we must consider the physical condition of a metal object with particular reference to the influence of any cleaning treatment that may have been carried out. Jedrzejewska (1962,

p. 30), in discussing the sampling precautions to be taken in the analysis of metallic antiquities, says that 'objects already cleaned will never provide safe information on their original composition. The ideal specimen should be obtained directly from excavations, and with a sample of adherent soil. . . .' This point of view is unduly pessimistic; it does not apply when the object has a solid core of unaltered metal, because any method of chemical treatment used either to remove corrosion products or to stabilize corrosion products without removing them will not affect the composition of the object except on the surface. It will thus always be possible to obtain a representative sample by the methods already described.

We may now pass on to consider three methods of analysis to which brief reference has already been made, namely emission spectrography, polarography and atomic absorption. The first of these has been used for many years on a very extensive scale, and many thousands of analyses have been reported in the literature; the other two methods have been employed so far on a rather limited scale, but they would appear to have certain advantages which will be discussed later.

A factor that has led to complications in carrying out emission spectrography is that different analysts have employed different experimental techniques, and since the possible sources of error associated with the different techniques vary, it is not always possible to compare the results obtained by different workers. This is particularly so in cases where the concentrations of the elements present are estimated on a purely subjective basis—a procedure that is prone to large errors. This question has also been discussed by Neuninger (1962) and Neuninger & Pittioni (1962) who have compared the results obtained in the analysis of prehistoric copper and bronze objects by different techniques of spectrographic analysis, and Picon *et al.* (1966, p. 201) have described in some detail the strict precautions that must be taken to ensure reliable results. It is clear that it is highly desirable that the laboratories engaged on emission spectrographic analysis should carry out and publish inter-laboratory comparison analyses on material of known composition so as to assess the relative accuracy of the different methods. Such inter-laboratory comparisons would be facilitated if a series of standard alloys covering the ranges of composition found in ancient metal objects could be made available. In the absence of internationally agreed methods of analysis of proved accuracy and reliability, such inter-laboratory comparisons would enable all analytical results to be reduced to a common level, thus eliminating the possibility of mistakes when interpreting analytical results from different laboratories.

Among metal artefacts that have been analysed by far the greatest amount of work has been done on those of copper and its alloys, and consideration will now be given to some of the results which have been achieved. In this field a clear distinction must be drawn between the analyses of early artefacts, that may be presumed to be made from metal freshly won from ores, and artefacts from later periods, when the production of bronzes involved the remelting of scrap metal that may have come from a number of primary sources. In the former case the analytical results can be used with some confidence to indicate the sources and trade-routes of contemporary metal supply; in the latter case this is hardly possible, since the metal that originally came from many different sources may be incorporated in the final objects and, as Hall (1965, p. 105) has pointed out, attempts to obtain meaningful results relating to provenance, etc., must be regarded largely as a waste of effort. However, it may be possible to discover variations in the metal composition that can be correlated with changes in metal technology and with the fabrication of different types of bronze objects.

As an example of the detection of particular ore sources one may cite the systematic analysis

of prehistoric copper and bronze objects from Central Europe carried out by Otto & Witter (1952); in one case the presence of appreciable proportions (in the range of 0.3 to 2%) of arsenic, antimony, bismuth and silver indicated the use of a particular tetrahedrite ore that contains this pattern of impurities, whereas in another case the presence of zinc as a major constituent in prehistoric bronzes pointed to the use of unusual ores containing both copper and zinc minerals. Also Caley & Easby (1959) in a study of South American copper and bronze objects showed the presence of sulphur, indicating that a particular sulphide ore was used.

The results of analyses can also be used to obtain information as to whether ancient metallurgical operations were carried out in a purely random fashion or under controlled conditions. Thus in the case of Egyptian bronze figurines, dating from *ca.* 1900 to *ca.* 350 B.C., analyses showed wide and erratic variations in composition, thus indicating that no attempt was being made to control the composition, probably because no special physical property was needed in the finished bronzes; it is likely that they were made by melting down scrap metal that happened to be available. On the other hand, analyses of flanged axes of Wessex culture of southern Britain made by Britton (1961) showed a general similarity in composition, indicating that the same type of ore smelted in a controlled manner was used to produce this class of object. Similarly, analyses of Greek and Roman statuary bronzes have shown that control was exercised in their production, and also that there were significant differences in the composition of the metal; the Greek statuary bronze contains moderately high proportions (10 to 15%) of tin and no lead, whereas Roman statuary bronze contains a lower proportion of tin (about 8%) and higher but variable proportions of lead (10 to 25%).

Although the analysis of bronzes in which re-used metal is an important component cannot yield information about primary sources of ores, it may reveal variations in metal composition that can be correlated with changes in technology and with the fabrication of different types of bronze objects. Thus, a study by Brown & Blin-Stoyle (1959) of British Middle and Late Bronze Age material has shown that significant deductions of archaeological interest can be drawn. In this investigation 438 bronze objects of different types were analysed quantitatively by emission spectrography for the elements copper, tin, lead, arsenic, antimony, nickel, bismuth, iron, zinc, silver, gold and magnesium. A statistical study of the analyses made it possible to establish two main groups, which corresponded with bronzes of Middle and Late Bronze Age, and to establish the previously unknown fact that in the Middle Bronze Age lead was only present as a trace element, but was regularly an intentional addition in substantial amounts in the Late Bronze Age. Although the precise reason for adding lead may be in doubt, its presence now serves as a useful indication of the Late Bronze character of an artefact.

In connexion with the systematic analysis of bronzes, reference must be made to the very large-scale investigation undertaken by Junghans, Sangmeister & Schröder (1960), who have published the analyses of no less than 2200 Early Bronze Age objects of West and Middle European provenance. These analyses have been subjected to a statistical study as a result of which a very elaborate system of classification of the objects into twelve distinct analytical groups was evolved based on the proportions in which bismuth, antimony, silver, nickel and arsenic were found to be present as minor constituents, and an attempt was made to draw tentative conclusions about the distribution of these groups in geographical regions and in cultural periods. But the question must still remain open as to whether the information thus obtained can be accepted with confidence. Another factor to which sufficient regard does not seem to have been paid in this investigation is that of the precise provenance of many of the

objects analysed; in many cases they would appear to be of unknown or uncertain provenance. The analysis of such objects must be looked upon as being of dubious value in a systematic analysis of this kind.

In surveys of this kind involving thousands of analyses it may well be that they can only yield information that can be accepted with confidence if all the factors involved in the analysis are subjected to a more elaborate statistical study, which can only be satisfactorily carried out by the use of a computer.

In comparison with the analysis of copper and bronze objects, little analytical work has been done on silver and gold objects other than coins. One recent example of the systematic spectrographic analysis of 500 Irish prehistoric objects has been reported by Hartman (1965), and from the results some interesting deductions have been made about the possible sources of the gold used by the early Irish goldsmiths. It would appear that only a relatively small proportion of these gold objects were made from native Irish gold, and that the majority were made of gold to which a definite amount (*ca.* 6 to 8 %) of copper had been deliberately added; this gold is similar in composition to that used in Central Europe in the Uhrenfelder period.

Although the technique of emission spectrography has been used on a very extensive scale, because it was the generally accepted method applicable to relatively small samples (10 to 100 mg), it suffers from many disadvantages already referred to. For this reason polarographic and atomic absorption analysis are now being studied in the British Museum Research Laboratory as alternative techniques. The important advantages of these methods are that a high degree of accuracy can be achieved (*ca.* $\pm 1\%$) using samples of 5 to 10 mg, that major, minor and trace elements can be determined in the same sample, and that the technique is a standard one so that inter-laboratory comparisons can be made with confidence, as the possible sources of experimental error can be more easily controlled. Furthermore, if greater accuracy (*ca.* $\pm 0.1\%$) should be required, this can be achieved using the modified technique of differential polarographic analysis. So far satisfactory results have been achieved in the following types of analysis:

(i) *Bronzes*—copper, tin, lead, zinc, nickel and iron determined by polarographic analysis, and gold and silver by atomic absorption.

(ii) *Silver*—copper, tin, lead, zinc, iron determined by polarographic analysis and gold and silver by atomic absorption.

(iii) *Gold*—copper, tin, lead, zinc and iron determined by polarographic analysis and gold and silver by atomic absorption.

(iv) *Lead*—lead directly by polarography; tin, copper, iron after solvent extraction determined by polarography; silver by atomic absorption.

The techniques of polarographic and atomic absorption analysis are no more difficult to carry out than quantitative emission spectrography; since they offer certain advantages over the latter and are relatively inexpensive when compared with other sophisticated methods of analysis, it is to be hoped that they will be adopted in museum laboratories on an increasing scale for the analysis of ancient metals.

Reference was made earlier to the fact that polarographic analysis could not be used as a suitable method for the analysis of the gold coins from the Sutton Hoo ship burial, and that an alternative simple non-destructive method of analysis had to be adopted. Measurements of specific gravity have long been used for this purpose, but Caley (1964) and Hawkes, Merrick & Metcalf (1966) have pointed out serious limitations in the accuracy obtainable when the gold

object is very small, as in the case of the coins from Sutton Hoo, which have a mass of only about 1.3 g each. However, Hughes & Oddy (1970) have shown that the accuracy obtainable can be increased by rigorous attention to experimental detail and the adoption of a recently available fluorocarbon as the immersion liquid. Using this technique the gold content could be determined within $\pm 1\%$. The results obtained by this specific gravity method were subsequently confirmed by a special method of neutron activation analysis that was developed at the Atomic Weapons Research Establishment.

The main purpose of this contribution has been to consider some of the more important factors that must be taken into account in order to ensure that significant results are achieved in the analysis of ancient metal. It should be emphasized that close collaboration between the scientist and the archaeologist is essential—they must discuss the nature of the problem, decide upon the best method of sampling and choose the most suitable method of analysis appropriate in the circumstances. Only in this way is it possible to ensure that the impact of the natural sciences on archaeology will be truly meaningful.

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