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The Application of Analytical Chemistry in Archaeology

The following are summaries of five of the papers presented at a Meeting of the South East and Western Regions and the Microchemical Methods Group held on September 10th–11th, 1984, in The Polytechnic, Portsmouth.

X-ray Fluorescence Analysis of Non-ferrous Archaeological Metalwork

Part 1. Analytical Technique

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The basic theory and instrumentation required in wavelength dispersive X-ray fluorescence spectrometry have been described elsewhere. The sampling of "museum objects," which are often unique pieces and of very high value, presents three major problems. Firstly, how representative of the bulk material is the sample taken? In general, the larger the object the greater is the change of heterogeneity being introduced during the manufacture of the object. This is particularly true when complex alloys such as leaded bronze are involved. Secondly, the presence of surface patina, which often differs in composition from the bulk material. While the composition of this surface layer may be of interest it is usually the analysis of the bulk material that is required. Thirdly, sampling must do minimum damage to the object being analysed. This is often the limiting factor; while multiple sampling is desirable this is quite often unacceptable to museum curators.

Two methods of sampling have been used. First, the taking of filings. This method has the advantage of presenting a larger effective volume per unit mass to the primary X-ray source, but has the disadvantage of damaging a larger surface area. More care has also to be taken to make sure that all surface patina has been removed before the sample used in analysis is taken. Secondly, the taking of drillings. This method is favoured by most museum curators as only the minimum of damage is done to the sample. A 1-mm drill is used; the drillings are discarded until bright metal is observed, when approximately 10-mg samples are removed. This usually leaves a hole 1–2 mm deep.

The sample is placed on 6 μm Mylar, spread carefully with a small brush to maximise surface area in the X-ray beam and then sealed under Scotch 810 adhesive tape. The Mylar with the sealed sample is then stretched tightly between two thin cardboard rings (external diameter 50 mm, which is the internal diameter of the sample cup used, internal diameter 35 mm) which are then stapled together, the excess Mylar being cut off. The "810" tape was selected as this gave the lowest blank value for the elements being measured. This method of sample preparation has the advantage of maximising the sample volume "seen" by the primary X-rays. Also, the sample can be labelled on the card rings, thus minimising any chance of sample "mix-up," the method gives a relatively low storage volume for a large "library" of samples, and the samples are available for further study and can be sent "through the post" to other laboratories without the need for extensive packaging.

The elements measured quantitatively are Sb, Sn, Ag, Pb, As, Zn, Cu, Ni and Fe in brasses and bronzes, and Sb, Sn, Pb, Zn, Cu and Fe in pewter. With bronzes, two line-overlap problems are observed, AsK$_{\alpha}$ - PbL$_{\alpha}$ and SnK$_{\alpha}$ (2nd order) - PbL$_{\beta}$. Provided that the tin is in the normal range expected in bronzes it is possible to remove SnK$_{\alpha}$ (2) with PHA (lower level 300 window 400), thus enabling the PbL$_{\beta}$ line to be used to measure Pb. It is not possible, by using pulse height analysis (PHA), to separate AsK$_{\alpha}$ from PbL$_{\alpha}$, hence the weaker AsK$_{\beta}$ line has to be used for the determination of As, the counting time being increased to 100 s. With pewters it is not possible, owing to the very high Sn content, to remove SnK$_{\alpha}$ (2) from PbL$_{\beta}$. Hence, the PbL$_{\alpha}$ has to be used to measure Pb. This is usually satisfactory as the As level in pewter is normally very low. Should a pewter be found that contains a high level of As then a correction of the PbL$_{\alpha}$ line for AsK$_{\alpha}$ has to be used, the AsK$_{\alpha}$ value being obtained by using AsK$_{\beta}$ and the ratio AsK$_{\alpha}$: AsK$_{\beta}$.

One major problem is the provision of meaningful standards. None of the alloy standards commercially available

Table 1. Analysis of standards against drilled subsample "a" of standard 1

	Composition of standard 1, % *m*/*m*				Composition of standard 2, % *m*/*m*			
Element	Actual* value	Subsamp. "b" drilled	Subsamp. "c" drilled	Filed subsamp.	Actual* value	Subsamp. "a" drilled	Subsamp. "b" drilled	Filed subsamp.
Sb	2.09	2.09	2.15	1.84	1.10	1.10	1.08	0.93
Sn	87.7	88.4	87.1	80.1	80.7	81.0	79.5	71.3
Bi	1.95	1.76	1.96	3.29	0.95	0.81	0.91	1.36
Pb	5.36	4.89	5.85	9.15	15.55	15.53	16.84	23.2
Zn	0.82	0.86	0.88	1.41	0.44	0.49	0.51	0.66
Cu	2.00	1.93	1.93	3.59	0.99	1.09	1.13	1.61

* Determined by independent consultant analyst.

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.".

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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.