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Analytical techniques used in archaeometry

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GENERAL

Analysis of archaeological material and museum artefacts has been undertaken since mid-Victorian times, but during most of this period destructive chemical methods have been used. Only during the past 15 years has it been possible to undertake analyses of large quantities of valuable museum material with a minimum of material damage. There are a number of reasons why such analyses will become important to historical and archaeological research.

(a) A study of the composition of objects may give valuable information regarding technical progress of a culture as well as information about how different artefacts were manufactured. Changes of composition with time may be accidental or may be deliberate reflecting increasing knowledge about a technique.

(b) In the production of coinage sudden changes of composition would not be undertaken for technical reasons, but for economic ones and quantitative analysis of coins may give the historian valuable information regarding such topics as devaluation, the relative values of silver and gold and adulteration of coinage at certain times and places.

(c) Studies of trade routes both locally and between different countries can be helped by trace-element analysis. If we can trace a certain type of object by its chemical composition, the fact that from stylistic considerations such objects were made in several places becomes unimportant—we may still be able to say whether different objects were made in the same place or not. Problems concerning the attribution of pottery provides perhaps the most fruitful area of analytical research. In these attribution studies negative answers are much easier to give with certainty than positive ones. The evidence will often be sufficient to tell an archaeologist or art historian that an object *cannot* have a certain attribution rather than to say that it *was* made in a certain place. If the ‘standard’ composition of a certain type of object is well known, and if the unknown falls well outside this, the evidence may be strong enough to give a negative answer. If, on the other hand, the composition of the unknown appears to be similar, there may be no reason why it just happens that the raw material from another site has the same impurity content. In these instances it becomes necessary to evaluate the composition of *all* possible manufacturing sites for that particular object.

(d) An increasingly important role of analysis will be in the detection of deliberate fakes. A considerable number of workshops are operating around the world to produce objects for satisfying an ever increasing demand. Modern T’ang from Hong Kong, Etruscan terracotta from Italy and pottery from the Middle East is being manufactured (and sold) on an ever increasing scale. More detailed knowledge of the pigments used by artists of all periods could also give us criteria for judging the authenticity of paintings.

Under the heading of attribution it might be worth pointing out that chemical analysis should only be considered as another criterion by which to tackle a particular problem; the

scientific evidence should be taken together with such points as stylistic and stratigraphic considerations. The chemist does his best but his evidence may be misleading for obscure reasons or his analyses may be just wrong!

CRITERIA DETERMINING METHOD OF ANALYSIS TO BE ADOPTED

There are certain aspects of archaeometric analysis which are peculiar to this work. The objects are often valuable and as such cannot in many instances be damaged; in certain instances *limited* sampling will be permitted. Museum curators vary in their attitude to this problem. It would seem reasonable that, since the objects are there for study purposes, they should be available for tests using the most up-to-date methods where possible and reasonable. It is a delicate matter for a curator to decide when sampling is reasonable but the position has greatly eased during the past 10 years and many museums have adopted an enlightened attitude. It would be unreasonable to expect numismatists to allow sampling of valuable coins, whereas a small hole in a large bronze object should not in any way detract from its value.

In many research projects involving analysis it is necessary to estimate several elements from perhaps hundreds of objects. The analysis of too small a statistical sample when evaluating attribution problems can give very misleading results. These projects involving many measurements will dictate a *rapid* method of analysis and preferably a method which is capable of estimating several elements simultaneously.

The method chosen either for trace or matrix analysis does not generally need to be very accurate when compared with industrial analysis. Methods capable of giving a result within 10% or even 20% of the correct answer will usually suffice. More accurate results do not enable more conclusions to be drawn—the objects are often not homogeneous and the spread within a group of objects from the same source will generally make accurate analyses pointless.

The question of absolute accuracy is often debated. At one time it was considered sufficient that results should be expressed in comparative terms with little emphasis on converting these to absolute values. No doubt within the confines of one laboratory no extra information would be gained by such conversion, except in so far as publication was concerned. However, with the increasing amount of work being undertaken around the world, it is inconvenient not to have all results as percentages in order that comparisons can be made between laboratories.

The choice of method will also depend on whether we are interested in the main matrix elements or the small trace impurities present. If we are interested in attribution studies we will be using the trace impurities to indicate 'families' of objects having a similar composition. Most work of this nature has so far been concerned with impurities down to the 1 part/10⁶ level; there is room for research in the future in trace element analysis to levels below this figure from 1 part/10⁶ to parts/10⁹.

When we undertake analyses of ancient objects which have been buried for long periods, not only may they have become contaminated with impurities from the soil but also corrosion, diffusion and solution of the object may have occurred. It has long been realized that even the so-called 'noble' metals will have their surface composition changed after long burial. When undertaking an analysis we must, therefore, keep these problems in mind and decide whether a surface analysis is permissible or whether a method which takes into consideration the whole object should be used.

Whatever the ideal method of analysis which we would like to adopt for a particular problem,

assuming a non-destructive technique is called for, we can only use that method if the object's shape and size permit the apparatus in question to be used. Most commercially available apparatus has been designed for specimens of limited size, whereas the objects met in archaeometry vary from large bronzes or small areas of pigment on large ceramic pieces to long swords or small areas of pigment on pictures with dimensions of a few metres.

Before discussion of the various methods available to us some consideration should be given to the types of object which are most likely to give useful information.

Metal artefacts. A great deal of work has been undertaken (particularly in Oxford and Stuttgart) on the analysis of bronzes; by measuring the trace element content it is hoped that their provenance can be deduced. Our experience at Oxford in this field has tended to show that such analyses are a waste of time. In certain specialized instances information can be obtained but due to extensive remelting of old metal it is not surprising that a very confused picture generally emerges from these studies. It is technological improvements in manufacturing technique which can be demonstrated by analysis of the major constituents of bronzes rather than the solution of attribution problems by trace analysis.

There have been attempts to relate the analysis of metals to that of the ore bodies from which they might have originated. These attempts have had little success. The use of scrap and differing smelting conditions will be inclined to thwart such projects; there is also some doubt whether most ore bodies themselves are homogeneous over any considerable depth and area to make such analyses valid.

Coins. Coins can also be remelted and trace impurity analysis could be prone to the same drawbacks which have been mentioned in the preceding paragraph. However it would appear likely that such remelting occurred less often than in the case of bronzes although the possibility must be considered. Studies involving the matrix elements of coins are again more fruitful; the economic consequences of such measurements are often of considerable interest.

Ceramics. Pottery and porcelain are often composite objects consisting of both the body of the pot and an associated glaze. The method of analysis used will depend on which of these parts is of importance. If it is the glaze which we wish to examine it is convenient to analyse this *in situ* by such techniques as X-ray fluorescence. If it is the body of the ceramic which is to be analysed, then we must generally take a sample. In the case of low-fired pottery this is easily accomplished by using a tungsten carbide drill. Even with whole pieces of pottery, museum curators and collectors are in most instances willing to cooperate in allowing a small hole to be drilled; of course sherds present no difficulty. In the case of porcelain there is much more opposition to such attempts to obtain drilled specimens. Moreover, it is extremely difficult to drill porcelain and obtain an uncontaminated specimen—research is required in this direction.

Ceramics are not reused and therefore the trace element composition can give us valuable information from the attribution point of view. In our laboratory we have almost abandoned the analysis of metals by optical emission spectrometry, because of the remelting issue, and have concentrated on the analysis of ceramics with rewarding results.

Some attempts have been made to relate the analysis of original clay beds to the analysis of pottery. Much more success has been achieved in this area than the associated problem of metals and their ores. Again this is probably due to the lack of re-use of the material and also perhaps because the clays tend to be more homogeneous over an area. More work is required on these problems also.

Glass and obsidian. These materials are again difficult to sample. In the case of obsidian the

objects are usually dispensable and destructive methods of sampling are possible, but this is not the case with most glass. X-ray fluorescence may provide one of the few methods of analysis *in situ*. Analysis of obsidian has been undertaken using neutron activation as well as X-ray fluorescence by several workers.

Picture pigments. The vast majority of work on pigments has been undertaken using micro-chemical techniques which entail removal of a very small sample and subsequent wet chemical analyses under the microscope. This is a large subject in its own right and I will have no time to deal with this important area of research. At Oxford we have made two contributions in the instrumentation field in this sphere; the X-ray fluorescent milliprobe was specifically designed for the analysis of pigments *in situ* and the electron probe microanalyser was developed in the laboratory for examining multi-layer cross-sections of pigment in detail. Both these instruments are referred to below.

ANALYTICAL METHODS

In a short paper of this nature it would be impossible to cover all methods of analysis which might be or have been used for archaeometric analysis. Some of these methods have been considered but so far no results have been forthcoming; in fact by far the largest number of results have been obtained using three methods—neutron activation, X-ray fluorescence and optical emission spectrometry. Brief mention will, however, be made to some other techniques.

X-ray diffraction. Although not normally considered as a quantitative method X-ray diffraction can be most useful as a quick method of identification of crystalline substances, for example in ceramics and picture pigments. Very small quantities are required.

Mass spectrometry. The use of this technique for quantitative analysis, using a solid source apparatus, in the less than 1 part/ 10^6 range has not yet been tested although such projects have been suggested. For higher concentrations there would seem little to recommend the method—it is not non-destructive, the apparatus is elaborate and the rapidity of analyses, where many elements and samples are to be examined, would not be great. Of course for isotope analysis no other method exists—another paper in this Symposium describes an aspect of this type of work.

Atomic absorption. This is basically a very powerful method which should be compared to emission spectrometry. Its sensitivity for many elements is greatly superior to the emission spectrometer and can utilize a much smaller sample. However, when many elements from a number of specimens are to be estimated we have to realize that only one element can be measured at a time since a separate source is required for each element. It is true that 'mixed' sources allowing more than one element at a time to be excited at one exposure are now being made, but only certain combinations are possible and most laboratories would only have the single type of sources available. In many problems at least twelve elements have to be estimated and in these instances twelve samples prepared and measured. Some laboratories associated with museum work are investing in this type of equipment although I am not aware of any published results to date.

Optical emission spectrometry. Many analyses using this method of bronzes, ceramics and obsidian have been published. There are a number of factors which make emission spectrometry particularly advantageous when compared with other methods of trace analysis. The apparatus involved need not be elaborate; the sensitivity achievable is generally adequate (a sensitivity of between 1 and 50 parts/ 10^6 can be achieved for most elements); at the same time proportions up to 20% can be estimated by the same process: all elements can be estimated by means

of photographic techniques in one exposure and the resulting plate provides a permanent record which can be referred to at a later date. This technique is not truly non-destructive since it is necessary to obtain a small sample (1 to 20 mg) from the object by drilling, scraping or similar process. There is no doubt that it is the method of qualitative and quantitative analysis which has been used to a far greater extent than any other method. In particular its use has been instrumental in the tracing of the provenance of ceramics in an impressive number of instances.

A new variation in emission spectrometry has been provided by the development of the 'Laser milliprobe spectrometer'. In this instrument a high-power pulse of laser light energy is focused by lenses to a spot of only some 20 μm diameter. This energy is sufficient to 'blast' a crater in the specimen measuring perhaps 30 μm diameter by 20 μm deep. Such a minute spot of damage is scarcely visible to the unaided eye and so may be termed for practical purposes 'non-destructive'. The material from the crater is enveloped in the arc which is struck between two neutral electrodes at the same instant and will be ionized by the arc, providing a spectrum in the usual way. For qualitative work this is an excellent approach but for quantitative results the accuracy is very limited due to the fact that such a small and perhaps unrepresentative sample is vaporized. We can expect to see this apparatus used more in the near future in qualitative and semiquantitative work.

X-ray fluorescence

Whenever atoms are bombarded with X-rays of sufficient energy, secondary or fluorescent X-rays characteristic of the elements being bombarded will be produced. These secondary X-rays can be analysed in wavelength and intensity and can provide a completely non-destructive method of quantitative chemical analysis. For the analysis of such objects as glass, ceramics, ceramic glazes and obsidian it provides a very powerful analytical tool. Unfortunately the depth of penetration of the X-rays (both primary and secondary) is limited and the analytical result is obtained only from perhaps the first 50 μm of the thickness of the specimen—it is therefore a method which can only be used on the surface of objects. Since metal alloys, including those of gold, silver and copper, are subject to surface depletion after many years of burial, a surface analysis may give very different results from that obtained if the whole object was analysed. For this reason published analyses of such objects as coins using this technique should be treated with reserve and the exact procedure of analysis examined. If one had access to a point-source type of spectrometer it is possible to remove the first 50 μm or so of the metal object over a very small area and so obtain an analysis of the underlying metal without effectively damaging the object.

Commercial equipment is often inconvenient for non-destructive X-ray fluorescence analysis. Archaeological objects are in most cases too large to fit the conventional specimen holders and presentation of a particular area to the X-ray path impossible. Moreover, the area of specimen required to obtain a reasonable signal/background ratio is generally comparatively large (at least 1 cm square). Special instruments have been developed at Oxford using a 'target' area of only $\frac{1}{2}$ mm diameter and an infinite specimen volume. The spectrometer uses a linear movement of crystal mount and the Johannsen bent crystal focusing system.

Recent work, particularly at the Lawrence Radiation Laboratory, Berkeley, has demonstrated the feasibility of using radioactive sources for generation of the secondary X-rays in the specimens and the development of a completely mobile spectrometer which can be taken on excavations for the determination of both qualitative and quantitative analyses *in situ*.

The method uses special balanced filters for selection of each spectral line and lithium drifted detectors. Unfortunately these detectors have to be kept at low temperature in a cryostat so liquid air or nitrogen must be available at least once per week. All elements above calcium in the periodic table can be estimated at all concentrations down to 100 parts/10⁶.

Neutron activation

By irradiation of specimens in a high neutron flux (generally in an atomic pile) and subsequent analysis, in terms of wavelength and half-life, of the resulting γ rays, it is possible to find the concentration of both the matrix elements of a specimen as well as the trace elements down to very small concentrations (for certain elements down to parts/10⁹). The technique has been used mainly for trace analysis of small specimens such as coins, ceramic drillings and obsidian. It is basically non-destructive provided that the specimen can be accommodated in the apparatus in such a way that the neutron flux is constant over the whole specimen area.

Neutrons and γ rays have a much greater penetrating power than X-rays; this allows an analysis from a greater thickness of specimen and surface depletion effects can be ignored. The γ ray spectrum from a specimen containing many elements is, however, complicated and it is only with the advent of new semi-conductor detectors, having a greatly increased resolution compared with the old type of sodium iodide detectors, that it is possible to sort out satisfactorily the concentration of these many elements. The use of sophisticated computer programs has made the analysis of large numbers of specimens possible.

There are a few points which are important to remember when considering neutron activation. In the first place certain elements are very insensitive to this method of analysis—lead is an element which cannot be estimated at any concentration. Secondly, if one is looking for low concentrations of trace elements with low cross-sections to neutrons, it may be tempting to irradiate the samples with high integrated flux densities. Although this may be permissible for samples removed from museum specimens, such as drillings from ceramics or metal artefacts, it may not be tolerable if the specimen has to be returned to the museum; the residual radioactivity must decay to a low level in a reasonable time. An obvious example of this hazard is demonstrated by silver coinage; radio-silver has an isotope of 225 days half life and if too high an irradiation dose is given to a silver coin it might not be able to be returned to the museum for hundreds of years!

Electron-probe microanalyser

Finally brief mention should be made of a comparatively new technique which will undoubtedly become increasingly important. Electrons from a hot filament can be accelerated (through perhaps 20 kV) and magnetically focused to a very small spot of 1 μ m diameter. When these high-energy electrons strike a specimen, X-rays will be produced characteristic of the elements in the specimen. By the use of a bent crystal focusing spectrometer these X-rays can be analysed. Since we are dealing with a primary beam of electrons, we can electrostatically scan the specimen in the same way as a television raster over an area of several hundred micrometres square. At the same time we can scan a cathode-ray tube in synchronism with the electron beam. If we modulate the cathode-ray tube with the detector output of the X-ray spectrometer which has been set to register a particular elemental wavelength, we can build up a visual representation of the concentration of that element over the area being scanned. By photographing the resulting display we can obtain a record. The wavelength of the spectrometer can then be changed and then a new display built up in terms of other elements.

Work undertaken in our laboratory recently by Dr E. Sayre of Brookhaven National Laboratory has shown the possibilities of this technique with respect to the analysis of multi-layer picture pigments. After mounting a small flake of paint in an epoxy resin, it is polished as a cross section and has a thin layer of carbon evaporated on to the surface as a conductor for the electrons. The various layers, and even individual particles of pigment, can then be identified by 'tuning into' the various elements which are likely to be present. Some quite unexpected results were obtained which will be published in the near future.

The short length of this paper has only allowed me to mention the major aspects of physical methods of chemical analysis applied to archaeological and art objects. Almost any technique used in chemical analysis could be used for specific problems and have indeed in many instances already been used; polarimetry, vapour phase chromatography and infrared absorption spectrography are a few which rise to mind. What is quite certain is that new methods will be evolved and will be used in this type of work and may even to a large extent supersede the methods which we have developed over the last 20 years.