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Neutron Activation Analysis of Archaeological Artifacts

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Abstract

The elemental compositions of archaeological artefacts, ancient and medieval coins, and metallic art objects have been determined by non-destructive neutron activation analysis. Examples are given of studies of prehistoric trade routes and cultural contacts based on the identification of the geologic origins of obsidian artefacts, of early economic systems based on the determination of debasement patterns in Medieval Islamic and Western gold and silver coinage, the region of manufacture as well as authentication of ancient metallic art objects based on trace element analysis. Special procedures devised for performing these analyses are described.

Introduction

There are a number of reasons why neutron activation analysis is particularly useful in the examination of archaeological artefacts. Because of the high sensitivity of detection of many of the elements, only minute samples are needed; if the object being studied is particularly valuable, reliable analyses can be performed using less than a milligram of material. In other cases, the whole object can be subjected directly to analysis since non-destructive analyses can be

performed. This latter feature is particularly useful in the analysis of coins. Using modern instrumentation, it is possible to automate some of the analysis procedures. Such automation is almost a requirement in cases where it is desirable to analyse hundreds or thousands of samples in order to obtain sufficient data to solve a problem.

A typical analysis procedure is relatively simple. A group of samples and chemical standards of known composition are placed in a nuclear reactor and irradiated with thermal-energy neutrons. Generally, less than one nucleus in every 10^8 is converted into a radioactive nucleus. Some of the radioisotopes so produced have half-lives too short to permit detection unless special rapid-analysis methods are used. A few radioisotopes, upon decay, will either not emit gamma rays or emit gamma rays too weak to detect easily. In some cases another stable isotope of the element will be produced. As a result of these considerations it will be difficult or even impossible to detect certain elements when using thermal neutron activation followed by analysis of the gamma-rays emitted by the irradiated sample. However, this usually is a minor hindrance and may even be desirable to some extent. The elements that are not easily detected tend to be those at the beginning of the periodic table and include the common elements: hydrogen, oxygen, nitrogen, carbon, and silicon. Usually knowledge of the content of these elements in an artifact provides very little information of use in solving problems of

interest to archaeologists. It is the elements present in small, even minor amounts at the parts-per-million levels that are often the most informative. Given in table 1 are typical levels of detection sensitivity for neutron activation analysis. The factors that determine the ordering in this table are nuclear in origin: the probability that a given type of nucleus will absorb neutrons and the half-life for radioactive decay.

Following the irradiation of a set of samples and chemical standards it is only necessary to determine the types of gamma-rays emitted by the sample. Since each radioisotope emits gamma rays having energies characteristic only of that isotope, unambiguous identification of the types of elements present in the sample is possible. From the intensities of the emitted gamma-rays, and from a comparison with the intensities of the same gamma-rays emitted from the chemical standards it is then possible to determine the percentage composition of the samples. Of course, certain precautions must be taken that the samples and standards are irradiated and analysed under reproducible conditions and fairly complex electronic equipment is needed in order to obtain highly accurate data.

It may appear odd that until recently very little use has been made of this method of analysis in working with archaeological artefacts. The reason is that only within the last few years have solid-state lithium-drifted germanium, Ge(Li) , gamma-ray detectors of very high energy resolution become available commercially. Prior to that time, most gamma-ray detection was performed using thallium-activated sodium-iodide, NaI(Tl) , detectors. These low-resolution detectors did not permit analysing for gamma rays from different elements if the gamma-ray energies were similar. In order to obtain reliable quantitative data it was frequently necessary to subject the irradiated samples to complex chemical separation procedures and then analyse each chemical fraction for its individual radioactivity. Non-destructive analyses, therefore, generally were not possible and the amount of time needed to analysis

a single sample was relatively lengthy. The new detectors permit direct simultaneous non-destructive analysis for all gamma-rays in the irradiated sample.

Presented in this paper are two examples of studies being carried out at The University of Michigan. The first is concerned with the determination of the geologic origins of prehistoric obsidian artefacts-- and, thus, establishment of the extent of cultural contact and the direction of trade routes. The second is concerned with the analysis of ancient and medieval coins and the remarkably large amount of information that can be derived from a systematic non-destructive analysis of coins. Special techniques devised for use in these analyses are also briefly discussed.

Obsidian Artefacts

Archaeologists and cultural anthropologists when examining artefacts, whether they be pottery or objects made of flint, chert, obsidian, or other mineral substance, wish to assess the extent of contact a prehistoric group may have had with other cultural groups. On the basis of similarities in design and apparent methods of construction it is frequently possible to suggest the extent of such cultural contact. Elemental analysis of the artefacts, however, could provide direct evidence of contact if it were possible to show that identical clay and mineral sources were used. If, in addition, it is possible to identify the particular geological formation from which the mineral was obtained then the geographical extent of the cultural contact and perhaps also the trade-routes involved in prehistoric times could also be ascertained. We have been successful in identifying the geologic origins of obsidian artefacts and are presently engaged in similar programs of analysis of objects constructed of other minerals.

Most minerals and clays possess similar, but by no means identical compositions. The composition of a typical obsidian sample is given in table 2. In order that the analysis data be of use in archaeological studies it is necessary that the elemental composition of samples from a given geological source be relatively constant but at least

some of the elements should show marked differences in composition between geologic sources. Obsidian perhaps best satisfies these criteria. The glassy mineral is ~~formed~~ upon cooling when certain molten mixtures are ejected from active volcanoes. The trace-level content of a given obsidian flow appears quite uniform but invariably different from other obsidian flows. In addition, the relatively small number of obsidian sources considerably simplifies the problem and, unlike pottery, there is no change in composition of the obsidian artefact due to weathering during the thousands of years it remained buried.

The irradiations and analyses were performed. The first consisted of irradiating 83 samples and 12 standards, each weighing about 30 mg, for 20 seconds in The University of Michigan reactor at a neutron flux of 10^{12} neutrons $\times$ cm^{-2} $\times$ sec^{-1} . About two hours after the end of this irradiation it was found that more than 99 percent of the detected radiation was due to only two isotopes: 14.96 hr. half-life ^{24}Na and 2.56 hr. half-life ^{56}Mn . Analysis for these two isotopes and, by comparison with the irradiated chemical standards, determination of the percent sodium and manganese in each sample was performed automatically followed by computer analysis of the resultant data (Gordus, et. al. 1968a). Since the radioactivity in each sample was almost completely decayed away after about a week, it was possible to re-irradiate the samples and obtain repeat confirmatory analyses. Generally five such replicate analyses were performed for each sample. To date, over 3,500 obsidian samples have been analysed using this method.

These data permit grouping samples in terms of their sodium and manganese contents. Usually, more than one of the geologic sources is found to have similar Na and Mn levels. Hence, final identification of the geologic source of an artefact required analyses of additional elements. The same samples and chemical standards were re-irradiated with neutrons, but this time for 20 hours and at a neutron flux ten times as intense as before. Besides producing large amounts of radioactive sodium and manganese there were also produced detectable amounts

of at least 15 other radioisotopes. The most pronounced gamma radiation emitted by these samples was due to isotopes of lanthanum, iron, rubidium, scandium, and samarium and analysis for these five additional elements was sufficient to permit distinguishing between samples from different geologic sources. Data for four obsidian sources in North America are given in figure 1 where the elemental contents are depicted relative to the content of obsidian from Obsidian Cliff, Yellowstone National Park. These four sources have sodium contents similar to that of Obsidian Cliff samples but differ from it and from each other in the content of many of the other elements.

One example of an identification of the geologic sources of archaeological obsidian artefacts is shown in figure 2. Various obsidian projectile points as well as obsidian flakes have been found in the 2000-year old Hopewell Indian burial mounds located principally in the states of Ohio, Indiana, and Illinois. Although the first obsidian was recovered from these mounds over 120 years ago, and anthropologists had speculated as to the origin of the obsidian, it was not until the present analyses were performed that it was possible to identify the sources. Two types of obsidian were found. The first was matched with the composition of that from Obsidian Cliff and corresponds to the horizontal set of data at 1.0 in figure 2. The second type, whose composition is given by closed circles in figure 2, corresponds in composition to another source of obsidian also located in Yellowstone National Park; data for this second source are given by squares in figure 2. Thus, there had existed in North America, 2000 years ago, contact that extended over 1500 miles.

Similar analyses of prehistoric Near Eastern obsidian artefacts from sites in Syria and Iraq that date to 7500 - 3500 B.C. have been shown to correspond to geologic obsidian sources located principally in the Lake Van region.

As noted earlier, analyses of this type are not limited to obsidian. At The University of Michigan an extensive program is underway involving analyses of flint, chert, chalcedony, jasper,

quartzite, ilmenite, hematite, and magnetite. All of these substances exhibit within single geologic sources much more variability in composition than does obsidian. Hence, it is necessary to determine the composition of many more elements in order to match samples and sources. Preliminary data indicate that such matching will, to some extent, be possible.

Silver Coin Analysis

Although we now progress to objects that belong to the historic period, it should be emphasized that studies of certain cultures, such as those in the Near East and Middle East from about 500 B.C. to 800 A.D., are dependent to a large extent on the examination of coins and metallic art objects found in archaeological excavations. In the past, these examinations have generally been limited to a visual analysis of the objects. For coins especially it is important to know their metallic content for this will provide information of use in suggesting the types of economic pressures which existed.

At The University of Michigan there was developed a rapid, non-destructive neutron activation analysis method for silver in coins (Gordus, 1968b). It involves irradiating a coin and a silver disk taped to the coin, figure 3, for one minute in a low-intensity neutron flux of 10^4 neutrons $\times$ $\text{cm}^{-2} \times \text{sec}^{-1}$. The neutrons are produced in a plutonium-beryllium mixture by a secondary nuclear reaction which occurs when the plutonium decays. Such Pu-Be sources are small and portable. Because of the low neutron intensity only 24 sec. half-life ^{110}Ag and 2.4 min. half-life ^{108}Ag isotopes are produced in sufficient quantity to be detected. The short half-lives of these isotopes result in almost all of the induced activity being completely decayed in 10-15 minutes. The coins are unharmed and there is no residual radioactivity.

It was necessary to modify the usual irradiation procedure by taping a silver disk to the coin being irradiated in order to obtain data to correct for neutron-absorption effects in the coin. These effects are strongly dependent on the coin thickness as seen in figure 4.

where data are given for coins of known silver content. By dividing these same data by the activity produced in the silver disks it was found that thickness-independent values were obtained for most coins as seen in figure 5.

The analysis procedure, therefore, involves irradiating a series of modern coins of known silver content to obtain an average value for the constant: $(\text{counts in coin}) \times (\text{counts in disk})^{-1} \times (\text{gm. coin})^{-1} \times (\text{percent silver in coin})^{-1}$. In analysing a coin of unknown silver content this constant is used and the percent silver calculated from the equation for the constant.

Over 3500 coins have been analysed using this method; generally 8-10 repeat analyses are performed in order to obtain a more statistically reliable silver content, the average of these analyses being valid to about 1.5 percent.

A typical set of data are shown in figure 6 where there are plotted the silver contents for over 350 Sasanian dirhems. Some periods of marked debasement are seen for this pre-Islamic dynasty, the most pronounced being during the reign of Shapur I. This Sasanian king was involved in various wars against Roman armies. A number of possible reasons can be advanced to explain why he would have debased his coinage. Economic pressures due to increased expenses of his military campaigns could have been the cause. Equally possible is that he debased his coinage since his military campaigns carried him into regions where debased Roman coinage was in use.

Other periods where economic pressures were particularly pronounced include the reign of Peroz in the mid-5th century. Yet his coinage is maintained at a high level of fineness. The single coin of Yazdegerd I (ca. 440 A.D.) of 50 percent silver is obvious on this graph in that it is so low compared with all others from his reign; perhaps this single coin was an ancient counterfeit.

Similar studies have been made of the coinage of other dynasties, principally from the Near East, and data such as these are of assistance to historians in that direct unbiased information is obtained concerning monetary policies.

Coin-Streak Analysis

Although the previous method of coin analysis is easy to perform it has the disadvantage of requiring that coins be borrowed for analysis. Another method we are using permits us to obtain samples at the museums where the coins are located and provides us with data suggestive of the intended silver content. But, at the same time, we also obtain data which permits us to postulate silver-ore routes, to determine the minimum number of silver-ore sources used, to suggest the geographical region in which a mint was located, to identify certain types of forgeries, and to correlate coin compositional data with similar data from silver art objects of the same period.

The procedure is exceedingly simple. First a very small portion of the edge of a coin is brightened by stroking with emery paper. A few extra strokes usually ensure that all of the partially oxidized outer layer (generally less than 0.002 in. thick) has been removed. Then this brightened spot on the edge of the coin is rubbed against a small piece of roughened quartz tubing. Less than 10^{-4} gm. of metal is transferred to the quartz. This streaked quartz is later irradiated for two hours in the reactor at a neutron flux of 10^{-13} neutrons $\text{cm}^{-2} \times \text{sec}^{-1}$ and sufficient long half-lived silver, gold, copper, and occasionally antimony and arsenic radioactivity is produced so that gamma-ray spectral analysis can be performed.

Although it would be possible to determine the exact weight of the streak and thus obtain quantitative analytical data, the weight analysis procedure would be too lengthy and in fact probably unnecessary. If coins are debased, invariably this is accomplished by adding copper. Lead is not detected in this analysis and chemical analyses of ancient and medieval coins have shown that the amount of lead and other impurities is generally less than one or two percent. Gold is an impurity associated almost entirely with the silver as is shown by the fact that almost no gold is found in copper coins. The gold contents of ancient silver coins are usually less than one percent and apparently its presence was unknown to the ancient minters. Further, as our data show,

the gold content of the silver provides a means of distinguishing between the silver sources used for the coinage.

Analyses are therefore performed for the relative amounts of gold, copper, and silver in the streaks; streaks of standards of known Au, Cu, and Ag content are irradiated together with those from the coins in order to obtain radioactivity calibrations for each irradiation. It is then assumed that the percent Au plus percent Cu plus percent Ag equals 100. The intended silver content of the coin is assumed equal to 100 minus the percent copper. The percent Au in the silver is calculated as another important quantity. Data of this type for Umayyad coins from two mints are shown in figures 7 and 8.

The data for the coins from the mint at Wasit, which was located at what is now approximately the border between Iran and Iraq, showed a marked improvement in quality commencing with the beginning of the reign of Hisham. Three possible reasons can be given for this improvement. (1) It was the result of a deliberate decision. (2) It was the result of improvements in the refining methods for removing any copper present in the silver ores. (3) It was due to the use of silver ore from a different source that had less copper impurity.

Reason (2) can be rejected since neither data for Damascus, figure 8, nor data from all other Umayyad mints show the same improvement in fineness as found for Wasit. Reason (3) can be rejected because a number of coins minted at Wasit after 720 A.D. were made from silver from the same silver source as was used for many of the coins struck prior to 720 A.D., as is seen in the lower graph of figure 7.

The early data from Wasit suggest the use of silver having about 0.7 percent gold impurity. Around 720 A.D. another silver source having less than one percent gold impurity is mainly used, although occasional coins are struck using silver having 0.7 percent Au. Intermediate gold contents are either mixtures of the two types of silver, mixtures of the new bullion with melted down older coins, and/or an occasional use of silver ore from another source such as the coin having 1.7 percent gold.

Data from other mints show different patterns. For example,

silver with less than one percent gold was being used by mints to the North of Wasit at least 10 years prior to its use in Wasit. Apparently the source of this silver ore lies in that general direction. Damascus, on the other hand, does not use the silver ore with less than one percent gold. The ores its mint uses have about 0.7, 0.9, 1.1, and 1.4-1.6 percent gold. Mints in the Northeast region of Persia use silver usually having more than one percent gold.

In a few cases, historians have been in doubt about the location of a few of the Umayyad mints—and many of the Sasanian mints. These data indicating the type of silver in use have assisted in defining the geographical regions in which these mints were located.

The type of data presented here also has other uses. Historians can determine, from the silver fineness of the coins produced at each mint, the extent of control a monarch exercised over the various regions of his kingdom.

In addition, data of this type assist in the identification of modern coin forgeries. If the forgery was made of modern silver, the gold content would be almost zero since present-day silver is highly refined. This application of the method is particularly suited to the analysis of silver art objects.

Sasanian Art Objects

Many museums possess silver plates, bowls, and figures attributed to the Sasanian period. A number of these objects show a Sasanian king, usually on horseback hunting boar. A few historians have suggested that some, and perhaps many of these objects were manufactured in post-Sasanian periods since the later dynasties have glorified the Sasanian era.

Our streak analyses of over 400 Sasanian coins have shown that virtually all were made from silver having between 0.4 and 0.9 percent gold. Only two of the coins had more than one percent gold and these contents were only 1.1 percent.

Of the 55 Sasanian silver art objects we have analysed by the streak method, over 30 percent have gold impurity levels in excess

of one percent, and on occasion the gold level is as great as 1.5 to 2.0 percent. These objects clearly were not manufactured in the Sasanian kingdom. The only Islamic period during which high gold-content silver is used in coinage is during the Umayyad period from 700 to 750 A.D. These coins, having high gold contents, as noted in the previous section, were minted mainly in the Northeast region of Persia. It is precisely in this region that the art objects are claimed to be found.

Other Studies

Analyses are being performed on the Anglo-Saxon gold coins in the Crondall hoard. The most extensive study, however, is the fineness of coins of the Mediterranean world from 500 B.C. to 1500 A.D. In addition to coins of the classical world, this project includes the coins of the Crusaders, the Islamic dynasties of the Near East, French feudal coinage, Byzantine coins, and coins of the medieval Italian city-states.

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Table 1. Detection sensitivity by neutron activation analysis

10^{-12} gm.	Mn, Re, Ir, In, Sm, Eu, Dy, Ho, Lu
10^{-11} gm.	Na, Al, Sc, V, Cu, Ga, As, Br, Pd, Sb, I, La, Ta, W, Au, Pr, Tb, Tm, Yb
10^{-10} gm.	P, Cl, K, Co, Ni, Zn, Ge, Se, Rb, Y, Cd, Cs, Ba, Hf, Os, Gd, Er, U
10^{-9} gm.	Cr, Sr, Zr, Mo, Ru, Ag, Sn, Te, Pt, Hg, Tl, Ce, Nd
10^{-8} gm.	Ne, Mg, Si, S, Ar, Ca, Ti, Fe, Kr, Nb, Rh, Xe

Table 2. Percentage composition of a typical obsidian sample

O	42	H	0.14	Y	0.003
Si	41	P	0.06	Sc	0.002
Al	7	Zn	0.06	La	0.001
K	3.4	Co	0.04	Hf	0.001
Na	3.0	Mn	0.02	Sm	0.0001
Fe	2.2	C	0.01	Lu	0.0001
Ca	0.9	Sb	0.003	Eu	0.0001
Mg	0.3	Ce	0.003	Ir	0.000004
Ti	0.2				

Figure Captions

- Figure 1. Composition of four obsidian sources relative to that of Obsidian Cliff, Yellowstone National Park. Glass Butte, Ore. ○. Cerro de la Nevejas, Mexico ●. Vias Mountain, New Mexico △. Powder River, Montana ▲.
- Figure 2. Composition of obsidian samples relative to that of Obsidian Cliff, Yellowstone National Park. Archaeological obsidian artifacts from Hopewell Indian burial mounds ○ and ●. Another geologic source in Yellowstone National Park. □.
- Figure 3. Method of neutron irradiation of coins using a Pu-Be Neutron Howitzer source.
- Figure 4. Specific activity of silver in an irradiated coin as a function of the thickness times the silver content of the coin.
- Figure 5. Specific activity of silver in an irradiated coin per unit activity in a silver disk shielded by the coin as a function of the coin thickness. Refer to figure 4 for coin identifications.
- Figure 6. Silver contents of pre-Islamic silver coins of the Sasanian dynasty. Alternating opened and closed circles are used to assist in visually identifying coins associated with each ruler.
- Figure 7. Silver plus gold contents of coins from the Umayyad mint of Wasit and the corresponding percent gold impurity in the silver for each coin. Closed circles are based on chemical analysis data.
- Figure 8. Data similar to that of figure 7 except for the Umayyad mint of Damascus.

CONTENTS RELATIVE TO OBSIDIAN CLIFF SAMPLES

- 5 Glass Butte, Ore.
- 10 Cerro de la Navajas, Mex.
- △ 5 Vias Mtn., New Mex.
- ▲ 4 Powder River, Mont.

CONTENTS RELATIVE TO OBSIDIAN CLIFF SAMPLES

Fig. 4.

Fig. 5.

Wasit Mint

Damascus Mint