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POTTERY ANALYSIS BY NEUTRON ACTIVATION [*]

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I. INTRODUCTION

Archaeologists have long been concerned with the provenance of pottery
and have evolved elaborate systems of classification based largely upon form
and decorative style. In more recent years such deductions have been supple-
mented by examination of the fabric, in particular, the identification of the
minerals which appear in the fired clay.[1] Such studies bear the implicit
assumption that pottery produced in a particular area will carry a specific
geochemical fingerprint. Another form of chemical fingerprinting considers
the elemental composition of the pottery. For reasons which will become clear,
the only feasible techniques for this type of analysis are those which can
determine many elements simultaneously and those which are sensitive to the
minor components. Two such techniques have been exploited: emission spectros-
copy[2] and neutron activation.[3] Of these two, neutron activation is capable
of measuring a considerable number of trace elements down into the parts-per-
million range.

The present study is a detailed evaluation of the accuracy attainable by neutron activation analysis employing a germanium gamma-ray spectrometer.[4] When pottery samples are irradiated with neutrons, many radioactive species are formed and the mixture produces very complex gamma-ray spectra. Analysis of a spectrum gives information which can be converted to the abundances of those elements measured. For a large number of analyses, the data processing becomes so tedious that the use of a computer is virtually mandatory.

Addressed to problems in archaeology, there were no a priori guidelines for the accuracy required nor the number and kinds of elements for which data would be useful. The questions so posed are still not completely answered. However, the initial premise — that the highest possible accuracy on the largest number of elements is desirable — seems born out. Even so, some compromises were necessary in order to economize on time and equipment utilization.

II. METHOD OF ANALYSIS

The method of analysis is given here as concisely as possible but some amplification is provided in the footnotes.

The surface of the sherd or pot is cleaned over an area of ~ 1 cm^2 with a sapphire scraper and the remainder masked with tape to avoid contamination by substances with which the surface may have come in contact. A drill was fashioned from a rod of synthetic sapphire whose base could be placed in the chuck of an ordinary electric hand drill. The first portion of the powder drilled is discarded and then more powder removed to provide a sample of 100 mg. The weighed powder (~ 100 mg) is mixed with 50 mg of cellulose and compacted into

a pill using a hand-operated hydraulic press[a]. The pills (1 cm × 1.5 mm) are

wrapped in pure aluminium foil[b] and packaged in an aluminium capsule[c] for

irradiation.

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[a] A standard pill size is required to obtain the accuracy inherent in the

method because the solid angle from the pill to the detector must be kept

constant. After irradiation, the pills are again compressed to a known thick-

ness. It was shown that inaccuracies as great as 2% could result from swelling

during irradiation if the pills are not flattened again. Correction is made for

pill thickness and this is part of the computer program.

[b] Each batch of aluminium foil must be analyzed for impurities so that

corrections can be made where necessary. Experience has shown that foil can be

obtained which introduces no serious errors except for the element, gold. The

gold contents of pottery so far analyzed lie in the range of several parts in

10^8. Aluminium foil so far used lies in the lower register of this range but,

what is worse, the gold is not distributed uniformly. So far, the ability to

obtain useful values for the gold content of pottery is impeded on this account.

The cellulose binder employed is found to be quite free of disturbing

levels of impurities.

[c] The cylindrical capsule is fitted with a jig which holds the pills on edge

in radial array. Twelve pills fit on one tier and two tiers fit in a capsule.

Two "standard pottery pills" are placed at diametric positions on each tier.

The capsule is suspended by a wire in the central thimble of the Berkeley Triga

Reactor and rotated during irradiation. The rotation of the pills ensures that

Each capsule contains "standard pottery" which will be described in
Section III. The use of this standard material is a central issue in this report
and constitutes the means for obtaining reproducible results and also absolute
values for abundances of the elements.

The recipe for irradiation, cooling, and counting was devised to optimize
the accuracy in determining the maximum number of useful elements. Each batch
of pills is subjected to two irradiations; the first for six minutes at a flux
of about 1.7×10^{12} neutrons/cm^2-sec, the second for eight hours at a flux of
2×10^{13} [d]. Following the short irradiation, the pills are placed on the

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[c] continued - all see the same radial flux pattern and all pills in each tier
have virtually identical vertical positioning. The reproducibility, which
results from this system of irradiation and the standardization of geometry in
gamma-ray counting (footnote a), carries a standard error of about 0.4%.

[d] The neutron exposure in the short irradiation is geared to the gamma ray
intensities of a couple of the shorter-lived radioactivities, Mn^{56} and Na^{24}.
The accuracy of the computer analysis of the spectrum depends upon control of
the gamma-peak widths and these are influenced to a significant degree by the
counting rate. For pottery, counting rates below 10,000/sec permit the use of
corrections (determined empirically) which are not serious. Further comments
on the neutron fluxes will be found in the introductory paragraphs of Appendix B.

analyzer for 15 min each after an initial cooling period of 120 min[e].

Only two elements (Mn and Na) are determined with high precision in the short irradiation. Three others (Eu,Ba,Sr) are measured in terms of short-lived isotopes but other values are obtained from other isotopes in the long irradiation. These are being carried along in the program until such time as it seems definite that they serve no useful purpose. Three other elements (K,Cu, and Ga) can only be measured in the short irradiation but the precision is relatively poor. The analysis for potassium is simply insensitive whereas the other two are sensitive but the element is present only in minute amounts.

Our equipment for gamma-ray analysis consists of a germanium detector ($\sim$5 cm^3 volume) and a 1600-channel analyzer. This assembly gives gamma-ray peak half-widths of about 2.1 keV under ideal operating conditions but about 2.8 keV at 1 MeV energy under the actual conditions employed in pottery analysis. The loss of resolution comes from compressing the spectrum to about 1 keV per channel and operating at counting rates up to 10,000 counts per second. The stored data is placed on magnetic tape for computer analysis and we also print out the actual numbers on paper tape and obtain an automatically printed graph

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[e] The elements aluminim (half-life 2.3 min) and magnesium (half-life 9.5 min) are not determined in this schedule. The cooling time (120 min) is set to permit decay of Mg^{27} one of whose peaks interferes with that used for manganese (Mn^{56}) analysis. To guard further against interference, the computer program determines the amount of residual Mg^{27} under the Mn^{56} peak by analyzing another peak belonging to Mg^{27}.

of the spectrum either from the analyzer storage or from the magnetic tape.
The data processing will be described separately.

The pills, following the short irradiation, are repackaged and irrad-
iated again for eight hours at the highest flux of the reactor, about
2×10^{13} neutrons/cm^2-sec. They are stored for eight days and then counted for
50 min each. As will be explained in more detail the principal obstacle in
obtaining high accuracy for many elements is the Compton background, and eight
days was chosen to permit decay of the sodium activity which is the heaviest
single contributor to the background at earlier times. This analysis is pro-
grammed for radioactive species with half-lives in the range 1-10 days and
gives results for the following elements: uranium, samarium, lutetium, titanium,
calcium, ytterbium, lanthanum, arsenic, bromine, and antimony. The attainable
accuracies differ considerably but discussion of this feature will be deferred
to Appendix B.

The same pills are again set aside for a further cooling period of at
least two weeks. This further lowers the background permitting better analysis
of the longer-lived species. The pills are counted for periods upward of three
hours, depending upon the availability of analyzer time. As a result of these
long counts, data are obtained for iron, cerium, scandium, tantalum, europium,
zinc, cobalt, cesium, antimony, chromium, hafnium, thorium, barium, nickel,

rubidium and ytterbium.   This list includes many of the most accurately

determined elements but also present are a number which have proved of little

use so far. Beyond the initial calibration of standards, the added labor of

carrying along elements not used is insignificant.

III. STANDARDIZATION AND THE ANALYSIS OF ERRORS

Counting Statistics and Other Sources of Error

The statistics of counting radioactive events determines one of the

errors of neutron activation analysis. The contribution to the standard error

of a determination from this source is given by the square root of all of the

counts used in measuring a particular element. For a strongly activated element

such as scandium, this may amount to only a fraction of a percent; for others,

the errors may be so large as to make the analysis of doubtful value. Obvious-

ly, there is advantage in counting the radioactivity with high efficiency and

for as long a period of time as practicable.

Other errors have to do with the reproducibility of all conditions of

the neutron irradiation and the measuring instruments. Errors of this kind are

controllable. A third category, which we shall call the "background error", is

more subtle and will be discussed separately.

Neutron Monitoring

A major concern is the proper monitoring of the neutrons to which the

specimens are exposed. Neutrons within a reactor are not monoenergetic and the

response (cross-section) for absorbing neutrons is an energy-distribution

function which can be quite different for different isotopes. Furthermore, even

within a particular reactor, the energy profile can be different in different

positions and change as the reactor is loaded differently and as fuel burns.

Finally, neutron capture cross-sections are in general poorly known. The only

safe way of handling this problem if accuracy is demanded is to have present

standard amounts of each of the elements for which the specimens are to be

analyzed. For the present problem in which many elements are determined

simultaneously, it is not practicable to have separate monitors for each element

so a composite material is much preferred. This requirement has led to the

preparation and calibration of "Standard Pottery". If the standards and the

specimens are maintained in the same time-averaged neutron environment, the

analytical results become independent of uncertainties in numbers of neutrons

or their energy distribution.

Reproducibility of Gamma-ray Counting

In addition to problems of neutron monitoring, other important diffi-

culties are overcome in using a composite standard. It should be remembered

that each gamma-ray peak in the specimen has its identical counterpart in the

standard. The conversion of raw gamma-ray data to abundances of activated

elements demands implicitly that one determine or know (1) the efficiency of

gamma-ray detection (energy dependent), (2) the absolute gamma-ray intensity

for each decay event, (3) the half-lives of the radioactive species, (4) neutron

flux history throughout irradiation period. All of these are measured quantities

with inherent errors, not always well known. With a calibrated composite

standard, none of these need be determined because they cancel, except for half-

life inaccuracies as they accrue for the relatively short period of time between

the analyses of the standards and the samples. It is now possible even to
change detectors without going through the tedious process of calibrating count-
ing efficiencies and, by the same token, to compare results from different
laboratories using a similar system.

A more subtle issue about which this form of monitoring proves benefi-
cial concerns the computer data processing. In our analyzing equipment, a
spectrum is stored in 1600 channels corresponding with that many small energy
intervals, slightly more than 1 keV per channel. The counts in each peak are
integrated by instructions specifying which channels are to be summed. Even
with stabilized electronics, the peak widths are not strictly the same from day
to day so it is possible that the number of counts summed are not strictly
comparable. Such shifts in resolution will also apply to the standards and
hence are compensated.

Appreciable peak broadening also results when the total number of counts
going into the analyzer becomes large. This effect is corrected separately by
empirically determined factors tabulated according to counting rate.

Standard Pottery

It should be clear that in activation analysis as in others, the
accuracy of analysis for each element cannot be better than that for the parti-
cular element in the standard. This would suggest that in constructing a
composite standard, the typically weak peaks of pottery should be enhanced in
the standard whereas each strong peak should be minimized to a level which still
gives good counting statistics. (The overall gamma-ray intensity should be
kept to a minimum because the Compton distributions from all gamma rays

contribute to the background under the peaks and this is a major source of error for many elements.) In principle, these objectives could be reached by formulating a completely synthetic standard from appropriate compounds. This approach was rejected because of the anticipated difficulty of homogenizing the material and keeping it so. If we consider standards weighing 100 mg with some elements present to less than 1 ppm this means that 0.1 microgram of that element must be dispersed in a statistically satisfactory number of particles, say 10,000 or more. There seemed to be no method of accomplishing this and knowing that it had been accomplished other than by trial and error. Since the calibration of the standard was expected to take at least six months, we were not encouraged to pursue a trial and error approach.

Since fine pottery clay is already a highly dispersed system presumably containing the elements of interest, it was decided to start with this as the basis for the standard. A clay was selected and found (fortunately) to contain a number of the weakly activated elements in amounts more than normal and such strongly activated elements as manganese, sodium, and iron, in low amounts. Its single largest drawback was the presence of scandium in "normal" amount which is more than necessary. As expected of any particular clay, it was undesirably deficient in a few elements, a problem to be handled separately.

The clay was first ground wet in a ball mill for 40 hours. Then the wet mix was put through a 60-mesh screen, and dried. The clay was broken up, ground wet for 10 hours, and then spiked with a water solution containing desired amounts of cobalt, nickel, bromine and arsenic. The original clay was deficient in these substances and it was thought that by adding them in this fashion, they would be uniformly dispersed by coating the large surface area

of the clay particles. The "doped" clay was then ground wet for 26 hours,
strained with a 120-mesh screen, cast into convenient shapes, dried and fired
to 705°C for 1/2 hour. The fired ceramic was ground in the ball mill for 9
hours yielding a final product of about 2 kg of fine powder.

Before undertaking the laborious task of calibration, eight random
samples were pressed into standard pills, irradiated, and analyzed for uniform-
ity. Each of several radioactive species agreed virtually within counting
statistics so the pottery was considered suitable for calibration and use as a
standard.

For calibrating the standard pottery, known quantities of chemicals
representing each of 38 elements were separately pressed into pills and
irradiated with the standard pottery. At least two independent sources of each
compound were employed and where attested primary standards were not available,
conventional chemical analysis was employed to establish the absolute content
of the element. This turned out to be a long process because most compounds
are not stoichiometric with the nominal formula and many preparations and
irradiations were required. Further comments will be found in Appendix A.

During the course of these calibrations there was ample opportunity to
test the reproducibility of the entire analytical process quite aside from the
absolute accuracy. If one chooses gamma-ray peaks which give good counting
statistics, all other factors causing variations in analysis become lumped
together in the scatter of the values. Included, of course, is the lack of
uniformity of the standard pottery. The reproducibility was found to be about
0.4%, a value low enough to permit concentration on the assessment of other
errors and finally the real differences between potteries. For many of the
elements, the apparent reproducibility will not be this good because the

limiting errors are set by the statistics of counting.

Tables 1, 2, and 3 give the composition of the standard pottery in terms of the elements detected by neutron activation analysis as well as constituents determined by other means. It is important to make clear the nature of the errors shown for the absolute abundances because it often appears that agreements between potteries are better than these errors would indicate. The errors shown include those of radioactive counting and calibration but in addition are often dominated by the "background error" to be explained presently. As an example, the value given for cesium in Table 3 is 8.31 ± 0.55 ppm, an error of 6.6%. This is an expression of how well we think we know the cesium content of our standard pottery should one wish to analyze it by any method. Relative to the standard pottery, however, the cesium content of another ceramic can be determined more precisely as will now be explained.

From the data presented in graphical form in figure 1, one can show that the counting error for the cesium peak at 796 keV is 1.2%, and this includes the counting statistics of both the peak and the background. However, the cesium content in the standard pottery was calibrated with pure cesium sources which give essentially no background so the question concerns the absolute reliability of background counts in the pottery. If the background chosen in this case is off by 2%, this would make an error 7.0% in the absolute abundance of cesium in the pottery.

For the central issue of archaeological studies, the comparison of potteries, the errors involved need not be as great as the errors shown for the absolute abundances. Using a pottery standard to analyze pottery, the makeup of the background will not be as different as that between pottery and the

separate pure substances used for calibration. Furthermore, the closer in

composition two pieces of pottery are to each other the more nearly identical

will be the backgrounds, so, for relative comparisons, the errors should

converge on what we term the precision of measurement. Examples will be given

to show that this situation actually occurs. The difficulty which arises is in

comparing abundance profiles of pottery analyzed in different laboratories using

different methods of standardization or different methods of analysis. Where

this applies, it would be prudent to use the more liberal errors.

One element for which analyses are carried out, calcium, has only a limit

in Table 3. Calcium is very insensitive toward neutron activation so that very

large amounts of a calcium compound would have had to be added to the standard

pottery (approximately 20% by weight) in order to obtain an internal standard

which would surpass in accuracy alternative ways of handling this problem.

Addition of such a large amount of material as a separate solid was considered

too risky. The analysis for calcium is accomplished indirectly by using an

iron peak for reference as explained in Appendix B. Indirect comparisons of

this kind can be made for any element provided one is willing to accept the

errors which result from changes in neutron energy distribution as they affect

the two elements differently. For an element such as calcium which is deter-

mined with poor precision, the added error from this effect is not considered

serious. The interest in calcium determination, albeit with large error, is

two-fold: (1) It varies tremendously between different sources of pottery, so

even a rough value is of diagnostic value; (2) in some potteries it is a major

constituent and, if arising from added temper, variations could effectively

produce different dilution factors for all of the elements determined.

It will be recalled that bromine (as KBr solution) was added to our clay before firing. It turned out that most of the bromine was lost during firing. We had already noted in analysis of pottery from a single site that the bromine content was often extremely variable and had suspected that its presence is sensitive to firing conditions. In confirmation, a sample of clay from the Nile Valley was analyzed before and after firing in an electric furnace at 800°C and 90% of the bromine disappeared. The amount as shown in Table 3 is too small to be used as an internal standard. The interest in continuing to analyze bromine in pottery lies not in fingerprinting but conceivably in obtaining information as to firing conditions. Since our standard pottery does not contain useable amounts of bromine, this element, like calcium, must be analyzed in terms of another element.

Finally, in order to characterize our standard pottery more completely, we attempted to obtain a material balance of the major constituents. This information is shown in Tables 1 and 2. All components were determined by neutron activation analysis except for the volatile fraction, SiO_2, CO_2, and Ca. As already mentioned our standard pottery is atypical in its low values for Na, Fe, and Ca.

IV. GROUPING OF ANALYTICAL DATA

Sensitivity of the Method

In a number of instances during the course of our analysis of many sherds and vessels, two independent drillings were taken from the same piece. Thus far the agreement has been better between such duplicates than has been encountered between any two different pots of the same archaeological grouping.

The inferences to be drawn are several: (1) the potter's lump of clay from which the vessel was made had been well homogenized; (2) we have not yet encountered more than one vessel made from the same lump; (3) local clay sources have a certain variation in composition; and of course, (4) the method of analysis is sensitive enough to make these distinctions.

In a few instances pairs of separately marked sherds agreed in composition within the experimental error and upon careful examination proved to have come from the same pot. The results from one such pair is shown in Table 4. Abundances of twenty elements are listed along with errors due only to the statistics of gamma-ray counting. Two-thirds of the elements should agree within one unit of the standard error and in this case 15 of the 20 elements do so.

Also shown in Table 4 are results from two different pots which we classify within a group. These come from the same general area as the other pot. Even a cursory examination shows that they agree better with each other than they do with the "twins" but show internal discrepancy beyond the counting errors.

We should not leave the impression that we have proved that all clays prepared by the potter will be uniform toward this form of chemical analysis. Quite obviously ceramics are not homogeneous, and when small samplings are taken, they must in some degree differ from the body as a whole. It seems, however, that in the limited number of tests we have made, either we have obtained representative amounts of both clay mineral and temper or   the temper did not differ in composition from the clay sufficiently to show up strongly as a "sampling error". We have not yet had the opportunity to follow up on some fragmentary evidence for substantial difficulties of the type just alluded to.

We suspect, but have not proved, that one of our sources of pottery has temper consisting in part of high concentrations of certain elements present in clays to a much lower degree.

Establishment of Pottery Groups

Analyses from about 1000 sherds from many different sites have shown that there is no difficulty in distinguishing these. It has been possible to show in many instances that pieces which are stylistically different are all local in the sense that they have a common origin of source materials. Also pieces have turned up which must clearly be labeled imports both on stylistic and chemical grounds. Nevertheless, difficulties in interpretation do exist and these are both challenging and sobering.

In most instances in which a sizeable number of sherds from one site have been analyzed, the results have been quite complex. Although the whole array may look like nothing yet seen elsewhere, they may divide into two or more distinct groups. Often these groups will not differ grossly in composition and lead one to suspect that they are all local but that somewhat different clay sources were used in a single settlement. In other cases, they may be quite different in composition. These too could well be local because it should not be surprising that in some areas, there can be clay beds with distinctly different geochemical history. The sobering aspect of the situation just outlined is the realization that a large number of analyses must be made to establish which pottery is local to a particular site because there are few apparent independent guidelines. It is always tempting to exploit a technical

method for all it can tell and this now appears to be a formidable task.

With this background, it is obvious that the first task is to establish pottery groups from sherds found at a site whatever might be the archaeological story behind the groupings. It is also clear that some quantitative index of chemical similarity must be devised. A system of statistical analysis will be presented which is not entirely satisfying but perhaps as good as our present state of knowledge permits. It lacks some rigor in statistical formulation and includes some intuitive bias developed in examining large numbers of results.

The basis of the method is to treat the various elements analyzed as independent variables, a supposition which is by no means obviously true. If it should turn out that the proportions of certain elements are always constant, it would be incorrect to attach statistical significance to the behavior of more than one of these. As an example, we determine seven rare earth elements and, although their ratios do change in different potteries, there is still a high level of coherence in their variance. In selecting a group of elements for diagnostic purposes, we have included only lanthanum and lutetium, which do seem to vary with respect to each other as much as most other elements. The examination of large numbers of data has led us to use 20 elements. Aside from an effort to eliminate redundancies, we have not included a number of other elements because they are determined with poor accuracy, and one element, bromine, because its abundance seems to be sensitive to the firing temperature of the pottery. It will be noted that some families of the periodic system are represented by more than one element. In all cases the geochemical pro-cesses leading to clay formation apparently do not see these elements as similar.

The first step in handling the data is to create a <u>trial</u> <u>pottery</u> <u>group</u> by visual determination of chemical similarity. A computer program has been written to calculate the mean value and standard deviation for each of the 20 elements in this pottery group. If we have chosen a statistically valid array, one might expect a normal distribution of values for each element whose spread is characterized by the standard deviation. Now any sherd, within or outside of the trial group, may be tested for agreement with the group on the basis of this single element. If it lies at two standard deviations from the mean, for example, the odds are about 20 to 1 that it does not belong. Now if all of the other elements may be treated as independent variables, the <u>odds</u> become the product of the odds for each element. It may readily be visualized that this treatment is extremely sensitive and that numbers of astronomical magnitude appear when pottery compositions are appreciably different for a large number of elements.

If the 20 elements were to constitute a perfect statistical array, one can now write down a quantitative <u>index</u> <u>of</u> <u>disagreement</u> for any sherd we wish to compare with the group. Comparison is made element by element. The deviation, d, between the element's value in the sherd and the mean value in the group is divided by the standard deviation for the group, σ. We call this ratio X. To each of these values of X, one can assign the odds, found in standard statistical tables, that the sherd does not belong. The odds that the sherd does not belong based on all of the elements is the product of the individual odds.

At this point, we depart from rigorous statistical practice. For a number of reasons we assign odds of 1 for any value of <u>d</u> that lies <u>within</u> 0.675 σ,

the point of equal odds. If now, the other members of the array are given
their statistical odds, the product will be a large number even if the distri-
bution is normal. From the 20 elements, we next throw out the four with great-
est disagreements. If the distribution were normal this would simply involve
the elimination of four members from the tail of the distribution and not
otherwise change the interpretation. The objective, however, is to be sure to
eliminate occasional values which may be wild for reasons having little or
nothing to do with the normal distribution. The remaining 16 elements are then
treated as described above.

The subjective choice to be made is the cut-off value for the index of
disagreement beyond which we say that the pot does not belong to the group.
We have tentatively chosen the number 1000. Examples will be given which are
taken from actual analytical data and then the matter will be discussed further.

As already mentioned, two sherds shown in Table 4 (ACU 6 and ACU 7) are
members of a chemical pottery group. This group, comprising several stylistic
types, is made up of 12 sherds so far. If each of these two sherds is compared
with its group through the statistical analysis just mentioned, the index
numbers found are 4.6 and 30.3 for ACU 6 and ACU 7,respectively. The number
for acceptability in the group, it will be recalled, is 1000. The differences
between these numbers and 1000 are not as dramatic as it may seem because of
the extreme sensitivity which ensues when so many elements are involved.

Examination of the data in Table 4 shows that AYA 1 is perceptibly
different from ACU 6 and ACU 7 but one must compare it with the actual spread
in values for the group to which these sherds belong in order to be convinced
that AYA 1 does not belong to the group. Using the same analysis which gave

index numbers of 4.6 and 30.3 for ACU 6 and ACU 7, AYA 1 gave 6.8×10^{20}. This should give adequate demonstration that there is no problem in distinguishing potteries which differ even less than the example given here.

The larger difficulty is what to do with the inevitable borderline cases which might arise from archaeologically insignificant reasons. Suppose, for example, that quartz temper were used in this pottery and that ACU 6 had additional quartz to the extent of 5% of the pottery weight. Quartz is quite free of elements analyzed by neutron activation, therefore it acts as a simple diluent. The effect can be simulated by revising downward by 5% each value for ACU 6 in Table 4. When the diluted ACU 6 is now compared with the group, the index number has changed from 4.3 to 460. It would still have been retained in the group but not by a large margin.

It is worth re-emphasizing that the criterion adopted for judging whether or not a sherd belongs to a group is rather arbitrary. We strongly suspect that some of the basic assumptions that would make possible rigorous statistical treatment are not strictly valid. For example, the index number 4.6 found in comparing ACU 6 with its group is smaller than would be expected from a normal array. This might mean that there is a small level of coherence in the variation of the elements so that a sherd with a few of its elements near the median of the group will have a larger number of elements brought near the median. Conversely, one might expect to find valid members of the group with rather large index numbers. Despite the obvious shortcomings of this system for data interpretation, it must be emphasized that our uncertainties arise from very fine distinctions. Further experience may dictate that other methods are more realistic and rigorous but in the meantime we feel that the method can yield useful information.

The labor of forming pottery groups and testing agreement is considerable

if handled manually. A computer program has been devised which makes all of

the statistical computations pertinent to the trial group. It then tests

successively each member of the group for agreement with the group by the preset

value for the odds, say 1000. When it comes to a pot which falls outside this

value, it discards the pot, recomputes the statistical parameters for the new

group, and then starts over. Only when the sherds remaining all fit does the

iterative process stop. Needless to say, any pot not in the original test

group may be tested in like manner. The amount of computer time required for

these operations is trivial, but not so the amount of printing generated.

V.   ILLUSTRATIVE RESULTS

It is not possible within the confines of this report to give an

account of the archaeological problems to which the methodology described here

has been directed. The following paragraphs are aimed only at displaying

representative data and to convey some feeling for how archaeological problems

might be attacked.

Pottery Groups from Upper Egypt

A rather large number of analyses have been made on materials from three

early cemeteries within a small area of Upper Egypt: Nag ed Deir, Ballas, El

Ahaiwah[f]. A complex picture of pottery compositions is emerging. For the

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(f) The staff of the Lowie Museum at the University of California have been most

present purposes, we are showing analytical results on two groups simply to
give the reader a view of how an array of compositions appears (see Table 5).
All three cemeteries contained a chemical pottery type which we ascribe to
Nile mud. Stylistically these appear as (1) burnished red-slip ware, (2) black-
top ware, and (3) coarse ware. The first group shown pertains to these wares.
Pottery was also made from calcareous clays brought in from regions away from
the river. A considerable number of distinct groups have been characterized,
one of which is shown as the second group of analyses. Wavy-handled pottery,
decorated ware, and drab wares were made from these clay types. Occasionally,
a red-slip jar is found from these calcareous clays, and these vessels look
superficially like the dominant redware made of Nile mud.

The errors shown for the individual numbers are simply the statistical
errors of counting the radioactivity and are a reflection of how accurate the
analyses could be done if the calibrations were carried out meticulously and
great pain were taken to control background errors. The numbers in parentheses
are the mean values for the group and the standard deviations. The latter
indicate the spread encountered for the various elements in these particular
groups and are used in the statistical analysis to determine if any vessel
belongs to a particular group. It will be noted that the standard deviations
(if expressed as percentages of the mean values) vary considerably from element

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(f) continued - cooperative in giving us access to the extensive Reisner Collec-
tion. Professor Robert Rodden, who is collaborating with us in this study, has
selected the materials and otherwise helped us greatly.

to element.   An element which has a small spread in one pottery group is not

necessarily a well behaved element in another group.

Each of the pottery pieces shown here belongs to its respective group

according to the statistical analysis described in Section IV.   Examination of

the individual numbers reveals that now and again a wild value appears.   The

statistical analysis discards such data as described in Section IV.

Relation of Clay to Finished Pottery

The pottery analysis could, in principle, be related to actual clay beds

establishing provenance in an absolute manner.   Important as this approach may

be, it is unfortunately not one which can be employed generally.   Even if it

were possible to obtain clay samples from each site under consideration, it is

by no means possible to know that these are the sources used by the ancient

potters.   Furthermore, there will usually be uncertainties as to how the potters

treated the clays before fabrication.   At present, the relation between clay

sources and ceramics from an area appears to be a separate and difficult problem,

albeit an important one and susceptible to experimental attack.   Some exploratory

investigations are underway in our laboratory aimed at coming to grips with this

problem.

Under uncomplicated circumstances, the relation between pottery and clay

can be simple as illustrated in Table 6.   Among the jars from Upper Egypt which

we analyzed, a few were sealed with clay plugs and there is every reason to

believe that these were inserted between the time the jars were fabricated and

placed in the burials.   A sample of one of these plugs was fired and analysis

shows that it fits well with the "Nile mud" pottery.   For contrast, analysis is

also shown for the jar in which it was found. This jar was made from one of the

clays which appears in pottery of this area.

Imports — Example of an Unfinished Problem

In the development of the current methodology, there was little to tell

us what to expect from archaeological material, hence, the selection was often

purely exploratory. Experience has indicated that exploratory examination of a

limited number of sherds may often be an efficient prelude to the design of a

more ambitious archaeological problem. The examples presented here aim to

illustrate this point. It will be seen that the sherds are too few in number to

define pottery groups as well as one would like but they do permit one to define

problems and to set up sampling schedules accordingly.

We are concerned here with two sites in Israel; one, Tell Ashdod, is a

large habitation site in the southern coastal region, and the other, Tell Eitun,

represents tomb finds in a region inland from Ashdod. The dominant pottery style

in both places was Philistine (or earlier local types) and a few pieces of

Cypriote and Mycenaean styles were included. (All of these are, of course, not

of the same age.)

The results used for illustration are shown in Table 7. There are five

sherds in each of the two groups of "local" pottery displayed in Columns 1 and 2.

Statistical analysis shows that these two groups are indistinguishable and likely

came from the same place, Ashdod[g]. In order to be certain of this deduction,

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[g]   We are indebted to Dr. Gershon Edelstein of the Department of Antiquities

one would need a larger sampling from Ashdod to establish better its composition as well as sampling from other coastal sites to make certain that these are distinguishable from Ashdod.

Column 3 gives the analysis of a single "Mycenaean Style" vessel from Eitun. It appears to be very much like the two other groups but statistical analysis reveals that it does not belong. This deduction should be viewed with caution because it could turn out that a more adequate sampling from Ashdod would broaden the present group to include this piece. The other possibility, of course, is that this vessel came from another site in the vicinity yet to be revealed. It seems fairly unlikely that it is an import from some distance.

The Cypriote piece (Column 4) is distinctly different. Fifteen of the 20 elements differ from those of the groups by more than two standard deviations; some differ hugely. Note, for example, the high values for La, Sc, Cs, and Cr, and the low value for Hf. Clearly this is an import but at present we have no library of information on Cypriote ware to tell from where.

The next column (Column 5) pertains to a Mycenaean piece from Ashdod. It again is distinctly different. Although it is clearly not from the exact source as the Eitun Cypriote piece, there are some intriguing resemblances. Note for example that they are both very high in Cs and Rb, and low in Hf. We

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(g)continued - and Museums, Jerusalem, for the Tell Eitun samples and for his comments on the interpretation. He stated that these sherds contain quartz inclusions common to pottery of the coastal region (e.g., Ashdod) whereas Eitun lies in Eocene hill country.

have some fragmentary information that compositions of this general type are characteristic of the Greek mainland and islands. Of course, the objective of this work is to pin-point places of origin and not to delineate general areas.

Finally, a Cypriote sherd from Ashdod is shown in Column 6. This is completely different from any of the others but at this point our repertory of local potteries is too limited even to guess at its provenance.

The purpose of displaying these fragmentary results is to illustrate how they might be the basis for a series of archaeological problems. Among the questions which come to mind and the materials necessary for their answers are the following:

1. A better sampling is needed to establish the characteristics of Ashdod Philistine ware and this should be expanded to include other coastal sites.

2. The diffusion of such ware to inland sites such as Eitun can then be tested more meaningfully.

3. The determination of the provenance of the imported Cypriote and Mycenaen wares demands a systematic examination of pottery from suspected sites of origin and a more comprehensive sampling of suspected imported ware at the sites in Israel.

Table 1.   Composition of Major Components in Standard Pottery

	Composition Element (%)	Composition Oxide (%)	
SiO$_2$		60.4±0.3	(SiO$_2$)
Al	15.9±0.2	29.9	(Al$_2$O$_3$)
K	1.45±.04	1.75	(K$_2$O)
Fe	1.02±.01	1.5	(Fe$_2$O$_3$)
Ti	0.79±0.03	1.3	(TiO$_2$)
Mg	0.5 ±0.2	0.8	(MgO)
Na	0.26±0.01	0.3	(Na$_2$O)
Ba	0.072±0.003	0.08	(BaO)
$\sum$ Trace elements		0.1	
Volatile components		3.99±0.10	
Total components		100.1	

Table 2. Composition of Volatile Components in Standard Pottery

	Composition Element (%)	Composition Oxide (%)
C	0.03 ± 0.03	$0.11 \ \{0.13 \pm 0.07\}$[*]
H	$0.54^{+0.00}_{-0.05}$	4.7
Total		4.8

[*]Measured directly.

Table 3. Composition* of standard pottery.

Element	Species studied	— Technique[†]	Composition		Chemical symbol
			Diff. techniques	Best value	
Aluminium	^{28}Al	neut act 1		$(15.9\pm0.2)\times10^{-2}$	Al
Antimony	^{122}Sb	neut act 3	$(1.66\pm0.12)\times10^{-6}$		
	^{124}Sb	neut act 4	$(1.73\pm0.06)\times10^{-6}$	$(1.71\pm0.05)\times10^{-6}$	Sb
Arsenic	^{76}As	neut act 3		$(3.08\pm0.22)\times10^{-5}$	As
Barium	^{139}Ba	neut act 2	$(7.13\pm0.32)\times10^{-4}$		
	^{131}Ba	neut act 4	$(7.0\pm1.1)\times10^{-4}$	$(7.12\pm0.32)\times10^{-4}$	Ba
Bromine	^{82}Br	neut act 3		$(2.3\pm0.9)\times10^{-6}$	Br
Calcium	^{47}Ca	neut act 3	$<1\times10^{-2}$		
		opt spec	$<1\times10^{-3}$		
		wet chem	$<2\times10^{-4}$	$<2\times10^{-4}$	Ca
Carbon	CO_2	C-H anal		$(3\pm3)\times10^{-4}$	C
Cerium	^{141}Ce	neut act 4		$(8.03\pm0.39)\times10^{-5}$	Ce
Cesium	^{134}Cs	neut act 4		$(8.31\pm0.55)\times10^{-6}$	Cs
Chlorine	^{38}Cl	neut act 1		$<1.3\times10^{-4}$	Cl
Chromium	^{51}Cr	neut act 4		$(1.151\pm0.038)\times10^{-4}$	Cr
Cobalt	^{60}Co	neut act 4		$(1.406\pm0.015)\times10^{-5}$	Co
Copper	^{64}Cu	neut act 2	$(6.0\pm0.8)\times10^{-5}$		
	Cu	wet chem	$(5.8\pm0.5)\times10^{-5}$	$(5.9\pm0.5)\times10^{-5}$	Cu
Dysprosium	^{165}Dy	neut act 2		$(4.79\pm0.19)\times10^{-6}$	Dy
Europium	^{152m1}Eu	neut act 2	$(1.418\pm0.048)\times10^{-6}$		
	^{152}Eu	neut act 4	$(1.477\pm0.047)\times10^{-6}$	$(1.448\pm0.034)\times10^{-6}$	Eu

(continued)

Table 3. Continued.

Element	Species studied	Technique[†]	Composition		Chemical symbol
			Diff. techniques	Best value	
Gallium	^{72}Ga	neut act 2		$(4.44\pm0.46)\times10^{-5}$	Ga
Gold	^{198}Au	neut act 3		$\leq1\times10^{-8}$	Au
Hafnium	^{181}Hf	neut act 4		$(6.23\pm0.44)\times10^{-6}$	Hf
Hydrogen	H_2O	C-H anal		$(5.4^{+0.0}_{-0.5})\times10^{-3}$	H
Iron	^{59}Fe	neut act 4		$(1.017\pm0.012)\times10^{-2}$	Fe
Lanthanum	^{140}La	neut act 3		$(4.490\pm0.045)\times10^{-5}$	La
Lutetium	^{177}Lu	neut act 3		$(4.02\pm0.36)\times10^{-7}$	Lu
Magnesium	^{27}Mg	neut act 1	$(5\pm2)\times10^{-3}$		
		opt spec	$(7\pm2)\times10^{-3}$	$(5\pm2)\times10^{-3}$	Mg
Manganese	^{56}Mn	neut act 2		$(4.09\pm0.05)\times10^{-5}$	Mn
Nickel	^{58}Co	neut act 4		$(2.79\pm0.20)\times10^{-4}$	Ni
Potassium	^{42}K	neut act 2		$(1.45\pm0.04)\times10^{-2}$	K
Rubidium	^{86}Rb	neut act 4		$(7.00\pm0.63)\times10^{-5}$	Rb
Samarium	^{153}Sm	neut act 3		$(5.78\pm0.12)\times10^{-6}$	Sm
Scandium	^{46}Sc	neut act 4		$(2.055\pm0.033)\times10^{-5}$	Sc
Silicon dioxide	SiO_2	wet chem		$(6.04\pm0.03)\times10^{-1}$	SiO_2
Sodium	^{24}Na	neut act 2		$(2.61\pm0.04)\times10^{-3}$	Na
Strontium	^{87m}Sr	neut act 2		$(1.45\pm0.22)\times10^{-4}$	Sr
Tantalum	^{182}Ta	neut act 4		$(1.550\pm0.044)\times10^{-6}$	Ta
Thorium	^{233}Pa	neut act 4		$(1.396\pm0.039)\times10^{-5}$	Th
Titanium	^{47}Sc	neut act 3		$(7.82\pm0.34)\times10^{-3}$	Ti

(continued)

Table 3. Continued.

Element	Species studied	Technique[†]	Composition Diff. techniques	Composition Best value	Chemical symbol
Uranium	^{239}Np	neut act 3		$(4.82\pm0.44)\times10^{-6}$	U
Ytterbium	^{175}Yb	neut act 3		$(2.80\pm0.36)\times10^{-6}$	Yb
Zinc	^{65}Zn	neut act 5		$(1.26\pm0.08)\times10^{-4}$	Zn

[*]These compositions and all others in this paper refer to the elements unless otherwise noted.

[†]The entries in this column have the following meanings: neut act 1, neutron activation measurement with special irradiations for very short half lives; neut act 2, usual neutron activation measurement for half lives less than 1 day; neut act 3, usual neutron activation measurement for half lives from 1 to 6 days, neut act 4, usual neutron activation measurement for half lives longer than 6 days; neut act 5, special neutron activation measurement about 8 months after irradiation; opt spec, measurement with optical spectrograph; wet chem, measurement by wet chemical analysis; C-H anal, measurement of carbon and hydrogen by combustion analysis.

Table 4. Analyses on two sherds from same pot and two pots from same group.[*]

	AYA1	AYA3	ACU6	ACU7		AYA1	AYA3	ACU6	ACU7
Mn	597±14	560±12	652±11	738±12	Co	8.79±.13	8.66±.13	7.14±.11	8.68±.11
Na(%)	.952±.015	.958±.015	1.268±.015	1.051±.012	Ta	.868±.031	.846±.031	1.663±.039	1.654±.028
U	5.56±.13	5.67±.13	5.97±.12	5.45±.12	Cs	13.95±.19	13.54±.19	10.96±.17	8.86±.15
Lu	.356±.012	.340±.012	.271±.010	.285±.012	Cr	24.65±.59	24.76±.70	26.76±.70	34.04±.70
La	36.53±.37	35.33±.37	23.59±.30	25.63±.31	Hf	6.52±.12	6.68±.12	4.05±.10	3.84±.10
Ti(%)	.435±.010	.422±.010	.314±.017	.387±.14	Th	18.44±.06	18.37±.06	14.93±.06	14.10±.06
Sb	2.39±.05	2.26±.05	1.33±.03	1.15±.03	Ba	466±22	442±22	564±24	735±27
As	22.63±.65	20.85±.67	8.66±.38	14.55±.43	Rb	157±6	158±6	168±7	156±7
Fe(%)	3.10±.03	3.06±.03	2.34±.03	2.58±.03	Zn	131±5	135±5	105±5	122±5
Sc	11.36±.04	11.34±.04	9.19±.04	10.32±.04	Ca(%)	1.6±.8	1.8±.8	3.7±.8	3.0±.8

[*] We are indebted to Professor John Rowe, Dr. Dorothy Menzel, and Mrs. Betty Holtzman for the Peruvian pottery from whose analyses these illustrative data are taken.

All sherds are from the region of Ayacucho, Peru.

AYA1 and AYA3 are two sherds of the Ocros style which proved to come from the same vessel.

ACU6 and ACU7 belong to a group of chemical composition embracing at least five different styles. These particular two sherds are classed Regular Chakipampa.

Errors shown following each value are the standard errors of radioactive counting. The abundance of elements are in parts-per-million except for those designated (%).

Table 5. Pottery groups from Ballas*

	Mn	U	Lu	La	Fe(%)	Sc	Co	Cs	Hf	Th
BAL 1	1151±18	1.84±.15	.502±.016	32.86±.37	6.51±.06	22.38±.04	33.09±.39	1.00±.22	7.95±.19	6.80±.06
BAL 2	1269±19	2.03±.13	.513±.016	31.33±.34	6.12±.06	21.11±.04	30.25±.38	1.07±.22	11.15±.21	6.65±.06
BAL 3	1209±18	2.52±.15	.555±.016	33.28±.36	6.96±.06	23.59±.04	34.81±.41	1.21±.22	9.22±.19	8.20±.06
BAL 6	1178±18	1.81±.15	.525±.017	30.90±.36	6.60±.06	22.61±.06	33.89±.45	.84±.26	9.53±.23	6.49±.07
BAL 7	1250±18	1.66±.15	.534±.017	32.96±.36	6.81±.06	22.96±.06	35.06±.42	1.44±.22	9.61±.21	6.91±.06
BAL 8	1228±17	1.87±.15	.521±.016	33.52±.36	6.95±.06	23.92±.06	35.44±.42	1.45±.22	8.59±.19	7.60±.07
BAL 9	1059±15	2.32±.13	.489±.016	31.54±.34	6.73±.06	22.85±.06	33.62±.41	1.04±.22	8.76±.19	6.79±.07
BAL 10	1154±16	2.30±.13	.511±.016	35.66±.36	6.34±.06	22.28±.04	30.42±.38	1.71±.22	7.72±.19	7.72±.07
Mean	(1187±77)	(2.04±.37)	(.519±.022)	(32.76±1.67)	(6.63±.35)	(22.71±.92)	(33.32±2.30)	(1.22±.35)	(9.07±1.20)	(7.15±.77)
BAL 12	350±7	5.23±.15	.362±.014	37.69±.37	4.59±.04	16.51±.04	17.03±.25	2.88±.20	5.92±.15	9.90±.05
BAL 17	365±5	4.36±.13	.334±.013	35.33±.33	4.41±.04	16.27±.04	17.30±.28	2.18±.22	4.75±.15	8.86±.06
BAL 18	387±5	4.42±.14	.334±.013	38.32±.36	4.18±.04	15.66±.04	15.75±.25	3.12±.20	5.54±.15	10.08±.06
BAL 20	410±5	4.43±.15	.325±.013	38.95±.37	4.55±.04	17.23±.04	19.31±.27	2.97±.20	5.21±.12	9.70±.06
BAL 21	372±5	4.52±.15	.389±.014	40.27±.39	4.62±.04	18.13±.04	17.61±.24	2.80±.18	5.56±.12	10.18±.05
BAL 22	335±4	4.75±.15	.378±.013	40.61±.39	4.58±.04	17.85±.04	17.07±.25	3.24±.21	5.62±.15	10.04±.06
BAL 24	454±7	4.16±.14	.379±.014	37.48±.36	4.71±.04	17.56±.05	17.49±.31	2.72±.24	6.14±.17	9.32±.07
Mean	(382±45)	(4.55±.37)	(.357±.033)	(38.38±1.99)	(4.52±.19)	(17.03±1.22)	(17.37±.98)	(2.84±.35)	(5.53±.47)	(9.73±.55)

*The upper series is made up of representative pots from a larger group made of a clay which we term "Nile mud." The lower series are taken from another group made of a calcareous clay. This group is one of several distinct groups of the same general type found in this region.

The 36 elements for which analyses are made are reduced to 20 for diagnostic purposes and 10 of these are shown in this table. All abundances are in parts-per-million except for Fe which is in percent.

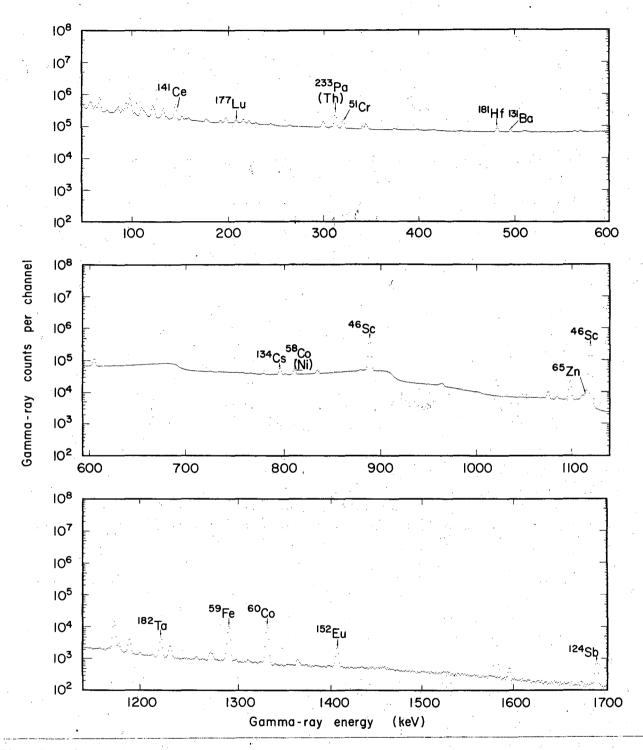Table 6. Comparison of fired clay and pottery of same provenance

	"Nile mud" ware 32 sherds (mean values)	BAL38F	BAL14
Mn	1204±68	1277	421
Na(%)	1.335±.215	1.271	.500
U	2.26±.41	2.05	3.70
Lu	.512±.027	.520	.319
La	32.77±1.20	33.92	32.93
Ti(%)	.996±.049	1.037	.433
Sb	.29±.07	.29	.70
As	.88±1.14	1.42	4.58
Fe(%)	6.82±.24	7.33	4.00
Sc	23.11±.96	25.46	14.78
Co	34.96±1.60	39.64	16.13
Ta	1.445±.106	1.372	.89
Cs	1.39±.21	1.66	2.86
Cr	180.8±15.6	194.5	156.8
Hf	8.67±.75	8.66	5.56
Th	6.94±.49	6.76	8.19
Ba	493±74	475	320
Rb	61±7	51	47

The "Nile mud" group is made up of 32 sherds from three neighboring cemeteries in Upper Egypt. The clay plug after firing at 900°C (BAL38F) fits in this group. Twelve of the 18 elements should lie within one standard deviation and exactly that number do. The jar BAL14 is the vessel in which the clay plug was found. It was made from quite a different type of clay as shown by the analysis.

Table 7. Local ware and imports (Tell Ashdod and Tell Eitun)

	(1) Ashdod Philistine (5 pieces) mean values	(2) Eitun Philistine (5 pieces) mean values	(3) Eitun Mycenaen	(4) Eitun Cypriote	(5) Ashdod Mycenaen	(6) Ashdod Cypriote
Mn	779±76	733±48	795	874	958	776
Na(%)	.668±.026	.707±.088	.873	.687	.587	1.163
U	2.48±.17	2.30±.10	2.54	3.30	2.58	1.34
Lu	.464±.033	.448±.024	.514	.444	.392	.378
La	29.22±1.50	27.92±1.14	31.65	42.93	31.57	9.05
Ti(%)	.665±.078	.628±.027	.655	.504	.444	.342
Sb	.398±.061	.338±.076	.446	.713	.880	.229
As	4.45±.58	4.92±2.27	3.77	8.27	2.31	1.28
Fe(%)	3.86±.07	3.70±.07	3.95	4.79	5.28	6.26
Sc	12.84±.36	12.98±.18	13.69	18.84	21.37	36.68
Co	18.95±.93	17.02±1.15	17.80	22.64	29.33	34.33
Ta	1.198±.040	1.138±.048	1.125	1.311	.817	.356
Cs	1.62±.13	1.56±.28	1.83	7.94	9.17	.68
Cr	126.2±5.8	116.7±1.7	126.5	154.4	251.4	185.7
Hf	13.40±2.38	11.56±.73	10.54	5.21	3.92	2.24
Th	7.98±.83	7.29±.53	7.83	13.75	11.23	2.51
Ba	387±122	557±209	366	383	375	145
Rb	53±5	53±2	51	154	158	31
Zn	142±6	140±5	212	209	292	262
Ca(%)	6.2±2.3	7.0±1.5	10.1	3.6	10.6	4.4

Analytical results are expressed in parts-per-million for the respective
elements except those designated by the % sign. The ± limits denote standard
deviations for the elements within the pottery group for which mean values are
given. The single sherds have the analytical figures without error limits.
The experimental errors on these numbers are almost always smaller than the
spread of values encountered in a group.

Fig. 1. Gamma-ray spectrum of long-lived radioactivities in standard pottery.
Only those peaks used in the analysis are identified. Symbols in paren-
theses indicate the elements for which the isotopic symbols above provide
gamma-rays for analysis. Note the logarithmic ordinate scale. This
particular spectrum was taken on a 101.5 mg sample for a counting period
of 642 min, 25.2 days after an 8 hr irradiation at a flux of
$\sim 2 \times 10^{13}$ n/cm^2 sec.   (XBL-692-1932)

ACKNOWLEDGMENTS

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APPENDIX A

Chemical standards for pottery calibration

Generally we used two different sources (and often two different compounds) of pure chemicals to calibrate our pottery by neutron activation techniques. In many cases it was necessary to analyze the "pure" chemicals because of discrepancies in the results. Normally at least 20 mgm of the desired chemical would be weighed out, and completely dissolved (at least by visual observation), diluted to a known volume, and carefully mixed. One hundred microliters of the solution was pipetted onto a mixture of ~100 mgm of silicon dioxide and ~50 mgm of cellulose in a porcelain crucible. The contents were dried at 110°C, mixed, scraped into the die of the pellet press and made into a pill. The pills were wrapped with aluminium foil which had been precut to a standard size. Thus we would have two pills corresponding to two different sources of a particular element. These two standards would be placed in our aluminium irradiation capsule along with four 100 mgm pills of standard pottery evenly spaced in the same tier. When differences between the two standards were larger than 3%, the solutions of the standards were analyzed by the Analytical Group in the Chemistry Department. In addition, all determinations of rare earth oxides were based on the residual weight after firing to constant weight at 1000°C. Unless otherwise noted, all discrepancies greater than 3% between standards have been resolved. Discrepancies of 3% or less are included in the individual errors.

The rare earth analyses, as well as many others, were made by Mrs. Ursula Abed in the Analytical Group.

APPENDIX B

This account gives the details of the experimental techniques used in the determination of the abundance of each element in our standard pottery and therefore presents useful information for the analysis of any pottery.

It was necessary to evaluate each gamma-ray peak used in the analysis for each element. This included the determination of interfering peaks arising from other elements and the optimum method for evaluating the background under each peak. Part of the description is given in terms which strictly apply only to our equipment. For example, a gamma-ray peak is specified by its energy but the manner in which the total counts are summed is specified in terms of data storage channels of our pulse-height analyzer, as are the positions relative to the peaks where the backgrounds are determined. However, anyone employing a similar system of analysis may readily convert the instructions to the particular amplification of his instrument. The reason for this approach lies in the use of computer data processing which operates on the non-continuous entity of channels rather than the continuous energy scale.

Some of the details presented are not of great importance for pottery analysis but are set down to make this work more general. For example, the analysis of metals, glass and other artifacts can present interferences not encountered in pottery because of higher concentrations of certain elements. Similarly, a recipe is given for copper analysis even though it is present in insufficient quantities for accurate analysis in any pottery yet encountered. The elements we have found most useful in the diagnostic aspects of pottery analysis are marked with an asterisk. Included are some elements which are

determined with relatively poor accuracy (Ca,K,Ba); unmarked are a number
which are accurately measured (certain rare earth elements).

Section B1 deals with radioactivities produced in neutron activation
which have half-lives of less than one day. Usually these activities were
produced by a 6 min irradiation at a reactor flux of ~1.7×10^{12} n/sec/cm^2.
Section B2 is concerned with activites with half-lives from one to six days.
These activities were usually produced by an 8-hour irradiation at a reactor
flux of ~2×10^{13} n/sec/cm^2. The sodium activity (15 hrs half-life) produced
in the long irradiation is very intense and must decay by many orders of
magnitude in order that the longer lived activities may be measured with
precision. An optimum decay time for pottery in general was found to be about
eight days. Significantly longer decay times are not desirable because the
sensitivity for detecting 1.1 day ^{76}As is reduced. Section B3 is concerned
with radioactivities with half-lives longer than six days. These radioactivi-
ties were produced in the same irradiation as those described in Section B2.
Gamma-ray analyses for long half-life components are begun about 23 days after
the end of the long irradiation. This gives a considerable reduction in the
intensity of 1.7 day ^{140}La and 1.9 day ^{153}Sm as well as 2.3 day ^{239}Np made
from the uranium. A significantly longer decay time would make the determina-
tion of 12 day ^{131}Ba less precise. Section B4 describes abundance measurements
made by techniques other than neutron activation.

In Sections B1, B2, and B3 the elements are arranged in alphabetical
order. The heading for each element contains the following: 1) the element
name, 2) the nuclear reaction causing the detected radioactivity, 3) the
half-life of the radioactive species, and 4) the energy of the detected

γ-ray in keV. Under the heading in order of increasing energy are possible
interferences from other radioactivities. In parentheses are given the half-
life and the energy in keV. These interferences include all of the prominent
gamma ray photopeaks for each nuclide expected to appear as the direct product
of (n,γ) reactions on any natural material. In addition, there are included
most of the weaker gamma rays of detectable isotopes in our activated standard
pottery. Those interferences which could cause problems with our analysis
regime in pottery are then discussed in detail. In nearly all cases the gamma
rays were analyzed with a 1600 channel pulse-height analyzer with an energy
dispersion of about 1.023 keV/channel and a threshold of about 51 keV. The
dispersion was somewhat higher in the first 100 channels and increases pro-
gressively after the first 1000 channels. The computer instructions are given
for each gamma ray peak as well as any expected interferences from other gamma
rays. The reader is referred to the "Table of Isotopes"[5] for a compilation of
the properties of all of the radioactive nuclides mentioned in this paper.

B1 (Half lives less than 1 day)

Aluminum $^{27}Al(n,\gamma)^{28}Al$; 2.3m, 1780 keV.

Interferences — None

   We do not normally analyze pottery for Al primarily because it would
necessitate additional reactor irradiations to make measurements with such
a short half-life as 2.3 min. A less significant reason is that substantial
quantities of ^{28}Al are produced in our irradiations by n,p reactions on ^{28}Si.
As the SiO_2 content of our pottery samples is generally not known, this
reaction could introduce several percent uncertainty in the numbers.

For our measurements of Al abundances on standard pottery we used two
unwrapped pills each of standard pottery, Al_2O_3, and SiO_2. These had been
irradiated in a plastic capsule for 3 min at $\sim 2 \times 10^{12}$ n/sec/cm^2. Measurements
were begun about 17 min after the end of irradiation and 2 min counts were
made on each sample. The gamma-ray amplification was reduced by a factor of
2 to about 2 keV/channel in order to observe the 1780-keV gamma ray of ^{28}Al
with our 1600 channel analyzer. Our computer program summed the top 6 channels
of the Al peak. To determine the background, which was about 6 percent of the
gross counts, the computer looked 6 channels above the Al peak and integrated
the lowest 6 consecutive channels containing that channel. As will be dis-
cussed in Section B4, the SiO_2 content of our standard pottery was found to be
60.4%. ^{28}Al made by n,p reactions on this much SiO_2 in our irradiations
contributes about 7.4% to the total ^{28}Al radioactivity. The corrected Al
composition of standard pottery, (15.9±0.2) percent is based on 3 irradiations
which were consistent within the statistical errors.

Barium $^{138}Ba(n,\gamma)^{139}Ba$; 82.9m, 166 keV.

Interferences − ^{136m}Ba (0.32s, 164keV), ^{139}Ce (140d, 165keV), ^{239}Np (2.35d, 166keV),
^{137m}Ce (34.4h, 168keV), ^{233}Th (22m, 171keV), ^{27}Mg (9.5m, 171 keV).

The 170.6-keV gamma ray of ^{27}Mg would interfere with the background
determination of the ^{139}Ba gamma ray. The Mg gamma ray, however, has essen-
tially decayed away ($T_{1/2}$ = 9.5 min) by the time the pottery runs usually
started. The 171-keV gamma ray of 22-min ^{233}Th could cause at most about a 1%
effect in the earliest runs. Its overall effect would be negligible. The computer
sums the 5 top channels of the peak.   For background the computer looks
5 channels above and 5 channels below the ^{139}Ba peak, integrates these

channels plus one channel on both sides of each, and corrects the final 6
channels of background to the 5 channels integrated in the peak. The back-
ground is about 70% of the gross counts in the peak or over twice the net
counts. We have assumed a 2% uncertainty in the background value in addition
to the counting errors leading to a value of $(7.13 \pm 0.32) \times 10^{-4}$ for the Ba
composition. Barium is also determined through a longer-lived isotope, ^{131}Ba,
which is better for analysis only because ^{139}Ba is inconveniently short-lived
for our counting schedule.

Chlorine ^{37}Cl$(n,\gamma)^{38}$Cl; 37.3m, 1642 keV.

Interferences — None

There was no evidence of the ^{38}Cl gamma rays in our activated stan-
dard pottery. A limit of 0.013% can be set on the Cl content. We measured
the energy of one of the ^{38}Cl gamma rays as 1642 keV.

Copper ^{63}Cu$(n,\gamma)^{64}$Cu; 0.533 day, 511 keV.

Interferences — ^{115}Cd (54h, ~490keV), ^{121}Te (17d, 508keV), ^{101}Mo (14.6m, ~510keV),
^{71}Zn (2.4m, 510keV), ^{36}Cl (3×10^{5}y, 511keV), ^{65}Zn (245d, 511keV), ^{80}Br (17.6m, 511keV),
^{80m}Br (4.4h)$\xrightarrow{\text{IT}}$ ^{80}Br (17.6m, 511keV), ^{79}Kr (35h, 511keV), ^{85}Kr (11y, 514keV),
^{108}Ag (2.4m, 511keV), ^{107}Cd (6.5h, 511keV), ^{165m}Dy (1.3m, 514keV), ^{85}Kr (11y, 514keV),
^{85}Sr (64d, 514keV), ^{83}Se (25m, ~520keV), ^{115}Cd (54h, ~530keV).

The copper radiation is due to annihilation of positrons emitted by
^{64}Cu. Annihilation radiation arising from the pair production by the 2754-keV
gamma ray of ^{24}Na is the primary interference of concern in pottery. We
determined empirically in our usual geometric arrangement that the annihilation

radiation due to ^{24}Na is 3.3% of the net counts in the ^{24}Na 1369-keV peak. The computer program removes this amount from the 511-keV peak. We calibrated the Cu content of the standard pottery with 100 mgm SiO_2 pills spiked with a known amount of a Cu solution which had been analyzed in this laboratory. Thus the geometric arrangement for stopping the positrons was the same for both the pottery and the Cu standards. 4.4-hour ^{80m}Br decays to 17.6-min ^{80}Br which causes a contribution of about 10% of the residual annihilation peak in our standard pottery after removing the ^{24}Na contribution. This amount was deduced from the ^{80}Br gamma rays observed in our bromine standards about 6 hours after irradiation.

The computer program integrates the 10 highest channels of the 511-keV peak. For background it looks 12 channels above and below the peak, integrates in each spot the lowest 10 consecutive channels and then divides the value by 2. The background accounts for nearly 90% of the gross counts in the 511-keV peak. In addition to counting errors we have assumed an inherent error of 1-1/2% of the background counts which leads to a 10% error in the Cu value. This together with the other errors result in a total error of 14%. After all the corrections are made the Cu content of the standard pottery was found to be $(6.0\pm0.8) \times 10^{-5}$. An analysis by R. G. Clem of the Analytical Group of this Laboratory gave a Cu content of $(5.8\pm0.5) \times 10^{-5}$.

Dysprosium ^{164}Dy$(n,\gamma)^{165}$Dy; 140.2m, 95 keV.

Interferences — ^{152m2}Eu (96m, 90keV), ^{147}Nd (11.1d, 91keV), ^{180m}Hf (5.5h, 93keV), ^{233}Th (22.1m) $\xrightarrow{\beta-}$ ^{233}Pa (27.0d, UKα_2- 95keV, UKα_1- 98keV), ^{79m}Se (3.9m, 96keV), ^{191}Pt (3.0d, 96keV), ^{75}Se (120d, 97keV), ^{104m}Rh (4.4m, 97keV), ^{183m}W (5.3s, 99keV),

^{153}Gd (242d, 99keV), ^{239}U (23.5m) $\xrightarrow{\beta}$ ^{239}Np (2.35d, PuKα_2 - 100keV),
^{182}Ta (115d, 100keV), ^{185m}W (1.6m, 100keV),

This peak is not obviously affected by other radiations in pottery. The most serious contaminant would be 96-min ^{152m2}Eu which has a 90-keV gamma ray which could influence dysprosium values by ~1-1/2%. At our resolution the interference is negligible. The dysprosium however, is in a region where the background has a considerable and varying slope. In addition the peak density in this region is sufficiently high that there is considerable uncertainty as to the value of the background.

The computer sums the top six channels in the dysprosium peak. It looks 16 and 48 channels above the peak, sums these channels plus one channel on either side for both regions, and then extrapolates the background to the peak. The background is comparable to the net counts in the dysprosium peak. We have assumed an inherent error of 4% in the background determination and this is the major source of error in the measurement. The Dy content is $(4.79\pm0.19) \times 10^{-6}$. The half-life of ^{165}Dy was measured as 0.0973 days to an accuracy of 0.1% (140.17$\pm$0.13 min).

Only dysprosium from a single source, the Michigan Chemical Company, was available for our calibration experiments. Upon firing the oxide to constant weight, it lost 1% of its mass.

Europium ^{151}Eu(n,γ)^{152m1}Eu; 0.387 d,   122 keV.
Interferences — ^{151}Nd (12m, 118keV), ^{71}Zn (2.4m, 120keV), ^{75}Se (120d, 121keV), ^{177}Yb (1.9h, 122keV), ^{152}Eu (12.7y, 122keV), ^{154}Eu (16y, 123keV), ^{131}Ba (12d, 124keV).

Long-lived ^{152}Eu also has the same 122-keV gamma ray but it makes a negligible contribution to the short-lived isomer in our measurements. ^{131}Ba has a gamma ray of 124 keV but its contribution is also negligible for this irradiation. 7.5-hour ^{171}Er has a gamma ray of 124.0 which will contribute ~1-1/2% to the ^{152m}Eu peak and 1.9-hour ^{177}Yb has a gamma ray of 121.6 keV which will do the same not long after the end of bombardment. The ^{171}Er and ^{177}Yb activities could not be positively identified in our spectra because of their low intensity. The given amounts correspond to possible peaks deduced from the spectrum with the best statistics and are in agreement with the expectations from the literature cross-section values and the relative amounts of Eu, Er, and Yb found in the earth's crust. We have decreased the Eu composition by (3±1.5)% because of these impurities. Because of the difficulty in determining the proper background in this low energy region, we have assumed an inherent error of 3% in the background counts, which results in an error of 3% in the net Eu counts. The total error in our value including counting errors and errors in the standards is then 3.49%. The two sources of Eu_2O_3 used for our calibration measurement came from Research Chemicals and Trona. Upon ignition they lost respectively 3.3 and 4.2% in weight. The Eu values were adjusted for the correct weights. Our best Eu composition from the short runs is then (1.418±0.048) × 10^{-6}.

Gallium ^{71}Ga(n,γ)^{72}Ga; 0.588 days, 835 keV.
Interferences — ^{81m}Se (57m, ~830keV), ^{166m}Ho (1.2 × 10^{3}y, 830keV), ^{117}Cd (2.4h, 832keV), ^{83}Se (25m, ~833keV), ^{54}Mn (303d, 835keV), ^{79}Kr (35h, 836keV), ^{87}Kr (76m, ~850keV).

Although ^{54}Mn has a gamma ray of the same energy as ^{72}Ga and can appear in substantial quantities in pottery from the ^{54}Fe(n,p)^{54}Mn reaction, the amount is insignificant in our short irradiations. The computer expects the Ga peak at channel 767 and sums 5 channels from channel 765 to 769 inclusive. For background the computer looks at channels 755 and 746, integrates the lowest 5 consecutive channels around each point and averages the two values. We assumed an inherent error of 2% in the Ga background. This leads to an uncertainty of 8.5% in the Ga value in addition to counting error. Our value for the Ga composition is $(4.44\pm0.46) \times 10^{-5}$.

Magnesium $^{26}Mg(n,\gamma)^{27}Mg$;   9.5m, 1013 keV.

Interferences - ^{83m}Se(70s, ~ 1010 keV), ^{101}Mo(14.6m, ~ 1020 keV).

As with Al we do not normally analyze pottery for Mg because of its

short half-life. With high energy neutrons ^{27}Mg can also be made by the

$^{27}Al(n,p)^{27}Mg$ reaction which complicates the analysis. The major gamma ray

of ^{27}Mg is at 843 keV, and it is difficult to measure in the presence of

the 847-keV gamma ray of ^{56}Mn. In a special neutron irradiation of $MgSO_4$

pills with no aluminum wrapping and with a reduced neutron flux in order to

diminish the proportion of high energy neutrons, we measured the intensity of

the 1013-keV gamma ray in standard pottery. We determined the amount of the

$^{27}Al(n,p)^{27}Mg$ reaction by irradiating Al_2O_3 as well as Mg standards. The

best value for the Mg intensity is (0.5±0.2)%. An optical spectrograph

determination of the Mg content by G. Shalimoff of this Laboratory gave

(0.7±0.2)%.

*Manganese $^{55}Mn(n,\gamma)^{56}Mn$;   0.107 d,   847 keV.

Interferences - ^{81}Se(18.6m, ~ 830 keV), ^{83}Se(25m, ~ 830 keV), ^{27}Mg(9.5m, 843 keV),
$^{152m1}Eu$(9.3h, 842 keV), ^{87}Kr(76m, ~ 850 keV), ^{131m}Te(30h, ~ 850 keV).

The 843-keV peak of 9.46-min ^{27}Mg could interfere with the ^{56}Mn

gamma ray, but 2 hours after the end of irradiation its effect is small. With

usual potteries, we begin the analyses 1 hour after irradiation because of the

higher Mn content. In any event our computer program looks at the 1013-keV

peak of ^{27}Mg and corrects the ^{56}Mn events for this small contribution

($\lesssim 1\%$) due to the ^{27}Mg 843-keV peak. The computer program sums the top six

channels in the Mn peak. Background is chosen 20 channels above the peak

where the lowest six consecutive channels are integrated. The abundance of manganese in standard pottery is $(4.09\pm0.05)\times10^{-5}$. Most pottery will have a manganese content about an order of magnitude higher than this value.

*Potassium $^{41}K(n,\gamma)^{42}K$; 0.515 day, 1524 keV.

Interferences - None

Potassium is almost 200 times less sensitive to analysis than sodium on a weight basis. The peak is free of interference, but sits on the Compton distribution of the 2754-keV ^{24}Na gamma ray. KCL and carefully dried K_2CO_3 were used for calibration. The computer hunts for the K peak around channel 1435 and sums the 10 highest consecutive channels around the peak. For background it looks 12 channels higher than the peak, integrates the 10 lowest consecutive channels, and then uses 98% of this value. The principal sources of error are the counting errors and the uncertainty in the true background. This latter uncertainty we assume is 1.5% of the background or 1.9% of the K value. The K content of the pottery is $(1.45\pm0.04)\%$.

*Sodium $^{23}Na(n,\gamma)^{24}Na$; 0.623 d, 1369 keV.

Interferences - $^{134}Cs(2.0y, 1365 keV)$, $^{124}Sb(60.4d, 1369 keV)$, $^{19}O(29s, \sim 1370 keV)$, $^{101}Mo(14.6m, \sim 1380 keV)$.

No interference has been encountered with the ^{24}Na peak. The ^{24}Na can also arise, however, from the reaction $^{27}Al(n,\alpha)^{24}Na$. The sodium content was determined by irradiations of standard pottery pills wrapped with known weights of Al foil. Al of known weight was irradiated simultaneously. The sodium abundance was $(2.61\pm0.04)\times10^{-3}$ after making a 7.4% correction due

to the Al in the wrapping and a 5.1% correction due to the Al in the
pottery. Pottery as a rule will have a sodium content about 4 times higher
than this value. The computer hunts for the Na peak around channel 1289
and sums the top 10 channels in the peak. For background the computer looks
20 channels above the peak and sums the 10 lowest consecutive channels. The
principal uncertainties in the measurement are the corrections due to the Al.

Strontium $^{86}Sr(n,\gamma)^{87m}Sr$; 0.118 day, 389 keV.

Interferences - ^{71m}Zn(3.9h, 385 keV), ^{193}Os(31.5h, 388 keV), ^{71}Zn(2.4m, ~
390 keV), ^{199m}Pt(14.1s, 393 keV).

There are no interferences with the strontium peak. Three standard
solutions of $SrCO_3$ and one of $SrCl_2$ were prepared to calibrate the standard
pottery. R.G. Clem of this Laboratory analyzed all of these solutions gravi-
metrically and found deviations of from 1 to 5 percent from the assumed
concentrations. The corrected values were used in our determinations. The
computer hunts for the Sr peak around channel 332 and sums the 6 highest consecutive
channels around the Sr peak. For background it looks 7 channels above and
below the peak, sums two channels above and below each of these points, and
multiplies by 0.6 to normalize to the 6 channels summed in the peak. The
major error comes from the uncertainty in the proper background for which we
have assumed an error of 1.5%.   The Sr composition is then
$(1.45\pm0.22)\times10^{-4}$.

B2   (Half-lives from 1 to 6 days)

*Antimony $^{121}Sb(n,\gamma)^{122}Sb$;   2.80 day,   564 keV.

Interferences - $^{76}As(26.4h, 559, 563 keV)$, $^{104m}Rh(4.4m, \sim 560 keV)$, $^{104}Rh(43s, \sim 560 keV)$, $^{86m}Rb(1.0m, \sim 560 keV)$, $^{134}Cs(2.0y, 563 keV, 569 keV)$, $^{117m}Cd(3.4h, 565 keV)$.

Two isotopes of Sb, 2.8-day ^{122}Sb and 60.4-day ^{124}Sb are produced in normally detectable amounts in neutron activation of natural antimony. ^{125}Sb can be produced by $^{124}Sn(n,\gamma)^{125}Sn \xrightarrow{\beta-} {}^{125}Sb$, but there is not enough tin in pottery to detect ^{125}Sb gamma rays. ^{122}Sb is readily detected in our analyses 8 days after irradiation of pottery and ^{124}Sb is best measured in the analysis made two weeks later. ^{124}Sb will be discussed in a later section.

The most troublesome interference with the 564-keV gamma ray of ^{122}Sb comes from the 563-keV gamma ray of 2 year ^{134}Cs. It contributes about 8% to the ^{122}Sb peak at the time of analysis and this is removed by the computer program. The ^{76}As 559- and 563-keV gamma rays contribute 3.5% to the ^{122}Sb peak under the conditions of our measurement. The ^{82}Br gamma ray of 554-keV causes no interference at all with the Sb peak. The Al used in wrapping the pills contains enough Sb to contribute about 2% to the peak. In order to evaluate the Sb, As, and Br peaks in this energy region accurately and still have the method applicable in the range of composition of these elements for pottery, it was necessary to pick the areas of summation with respect to the position of a well-defined gamma ray of another element. The computer assumes the Sb peak is 76 channels above the 487-keV gamma ray of ^{140}La. This normally puts the Sb peak in channel 502. The computer sums this channel plus two below and one above. For background it looks 22 channels below and 20 channels above the peak, sums these channels plus two

on each side in each case, interpolates the value to the peak channel, and

normalizes to the 4 channels of peak integration. The computer looks for the

796-keV peak of ^{134}Cs at about channel 728, integrates the top 5 channels,

looks 6 channels below for background and integrates the 5 lowest consecutive

channels, multiplies the net Cs counts by 15.3% and removes this value

from the antimony value.

The principal source of error is the uncertainty in the true background

which we have assumed to be 2%. This effect leads to an error of 5.4% and

the total error is 6.7%. Our best value for the Sb composition from the

^{122}Sb measurement after removing 3.5% due to As is $(1.66\pm0.12)\times10^{-6}$.

*Arsenic ^{75}As$(n,\gamma)^{76}$As; 1.10 day, 559 keV.

Interferences – ^{82}Br(35.3 h, 554 keV), ^{193}Os(31.5 h, 558 keV), ^{104m}Rh(4.4 m, ~ 560 keV), ^{104}Rh(43 s, ~ 560 keV), ^{86m}Rb(1.0 m, ~ 560 keV), ^{77}Ge(11.3 h, 563 keV), ^{122}Sb(2.8 d, 564 keV), ^{117m}Cd(3.4 h, 565 keV).

The 559-keV peak is the most abundant in ^{76}As by almost an order of magnitude. It could be interfered with by the 554-keV gamma ray of 1.5-day ^{82}Br and the 564-keV gamma ray of 2.8-day ^{122}Sb. The bromine interference is 2.7% of the counts in the bromine peak and the antimony interference is 1.1% of the counts in the antimony peak. These lead to errors of less than 1% in our arsenic composition.

The computer assumes the As peak is 5 channels below the ^{122}Sb peak. It sums the peak channel plus 2 below and one above the peak. For background it looks 25 channels above and 17 channels below the peak, sums these channels plus two on either side in each case, interpolates to the peak position and normalizes to the number of channels summed in the peak.

The major errors are 6% due to discrepancies with different arsenic standards and 4% due to uncertainties in the true background. We have assumed the latter to be 2% of the background. The resulting arsenic composition is $(3.08\pm 0.22) \times 10^{-5}$. As the standard pottery was spiked with arsenic, it was worthwhile investigating how evenly the arsenic was distributed throughout the pottery. The ratio of the flux determined by the arsenic counts to that determined by the samarium counts was measured for 51 standard pottery pills over a period of about four months. The 51 values agreed within a standard deviation of 2.4%. The standard deviation expected from the counting errors was 1.8%. Therefore, the arsenic was certainly dispersed evenly throughout our standard pottery within 1.5% of the composition.

Bromine ^{81}Br(n,γ)^{82}Br; 1.47 day, 554 keV.

Interferences — ^{187}W(23.9 h, 552 keV), ^{153}Sm(46.8 h, 555 keV), ^{193}Os(31.5 h, 558 keV), ^{76}As(1.1 d, 559 keV), ^{81}Se(18.6 m, $\sim$ 560 keV), ^{86m}Rb(1.0 m, $\sim$560 keV), ^{104}Rh(43 s, $\sim$ 560 keV), ^{104m}Rh(4.4 m, $\sim$ 560 keV).

The 559-keV peak of ^{76}As interferes somewhat with this Br peak. The computer program subtracts 3.2% of the net As counts from the bromine before calculating the Br composition.

^{187}W has a gamma ray of 552 keV which could interfere with the ^{82}Br 554-keV peak. We have not observed any gamma rays of ^{187}W in our standard pottery (or any other pottery we have looked at to date), and can place a limit on the interference of 10% of the ^{82}Br 554-keV peak. ^{153}Sm has a gamma ray of 555 keV, but its intensity would be smaller than 1% of our bromine peak.

Bromine has an intense peak of 619 keV, but this is interfered with by the 620-keV peak of ^{131}Ba. ^{82}Br also has an intense peak at 777 keV which is interfered with by the 779-keV gamma ray of ^{152}Eu. There are a number of other Br gamma rays but they are appreciably less intense than the gamma rays just discussed.

The computer assumes the ^{82}Br peak is five channels below the ^{76}As peak and sums the peak channel plus two channels above and two channels below the peak. For background the computer looks 30 channels above and 12 channels below the peak, sums these channels plus two on either side in each case, interpolates the background to the peak channel and normalizes to the number of channels summed in the peak. The major source of error is the uncertainty in the proper background which we have assumed to be 2%, or 35% of our ^{82}Br value. In conjunction with other errors our final bromine composition is $(2.3\pm0.9)\times10^{-6}$. As remarked earlier we spiked our clay with about 10 times

this amount of bromine but it was lost in the firing of the clay. This resulting bromine content is too small to use as a standard. For general pottery analysis we measure bromine with the reactor flux determined from the samarium in standard pottery.

Calcium $^{46}Ca(n,\gamma)^{47}Ca$; 4.535 day, 1297 keV.

Interferences - ^{115m}Cd(43d, ~ 1290 keV), ^{59}Fe(44.9d, 1292 keV), ^{116}In(13.4s, 1293 keV), $^{116ml}In$(54m, 1293 keV,) ^{41}Ar(1.8h, 1293 keV), ^{152}Eu(12.7y,1298 keV), ^{114}In(72 s, 1299 keV).

Although 4.5-day ^{47}Ca and 9-min ^{49}Ca can both be detected by neutron activation techniques, we find the longer-lived isotope more suitable when many samples must be processed. The most prominent gamma ray of ^{47}Ca (at about 1.3 MeV) is 74% abundant. The calcium peak at 1297.1±0.5 keV (value in the literature is in error) is found by the computer in reference to the ^{59}Fe peak at 1291.8 keV. As mentioned below, our standard pottery contains no detectable Ca so there is no internal standard for other potteries being analyzed. The abundance of the Fe peak is also used as a flux monitor for the Ca. Since Ca is not determined with high precision by neutron activation, the error so introduced is not considered serious.

^{152}Eu has a gamma ray at about the same energy, 1298 keV, but its intensity is usually smaller than the errors in the Ca measurement. ^{59}Fe has a 1292-keV gamma ray which, however, can be resolved from the Ca gamma ray. 43-day ^{115m}Cd has a 1.29 MeV gamma ray whose abundance in our standard pottery is negligible.

The computer assumes the Ca peak is five channels above the ^{59}Fe gamma ray at 1292 keV, sums that channel plus two above and two below the peak. For background the computer looks eight channels above the peak and sums the five

lowest consecutive channels. In order to determine the Eu contribution the
six top channels of the ^{152}Eu peak at 1408 keV are first integrated. For the
background in this case the computer looks six channels above and below the
Eu peak, sums those channels plus one on either side in each case, normalizes
to the total number of channels integrated in the peak, multiplies the net Eu
counts by 7.2% and subtracts from the Ca peak.

No Ca was detected in standard pottery and a limit of 1% can be placed
on its abundance. A spectrographic analysis by G. Shalimoff of this Laboratory
showed less than 0.1% Ca and a wet chemical analysis by R. G. Clem of this
Laboratory showed less than 0.02% Ca. Ca in pottery generally varies con-
siderably and has been as high as 30% in some of our measurements.

Gold ^{197}Au$(n,\gamma)^{198}$Au; 2.697 day, 412 keV.
Interferences − ^{109}Pd(13.5 h, $\sim$ 410 keV), ^{191}Pt(3.0 d, 410 keV), ^{166m}Ho(1.2 $\times$ 10^3 y,
412 keV), ^{177m}Lu(155 d, 414 keV), ^{77}Ge(11.3 h, 417 keV),^{116m1}In(54 m, 417 keV),
^{127}Te(9.4 h, 417 keV), ^{152}Eu(12.7y, 411 keV), ^{233}Th(22m) $\xrightarrow{\beta}$ ^{233}Pa(27d, 312 keV).

We only measure an upper limit on the amount of gold in our standard
pottery. Gold could be detected in concentrations as low as 1 $\times$ 10^{-8}. Unfor-
tunately the high-purity Al foil with which we wrap the pottery pills prior
to bombardment has a larger and quite variable gold concentration. Ordinary
Al kitchen foil on the other hand contains a number of elements in sufficiently-
high concentrations to cause problems in our analyses, but the gold concentra-
tion is lower than with high-purity material. The total gold content of our
pottery pills plus aluminium wrapping varied from 1 $\times$ 10^{-8} to 2 $\times$ 10^{-7} of the
pottery weight. Our best estimate of the gold content of the standard pottery

is then $\leq 1 \times 10^{-8}$. We cannot be sure that gold is homogeneously distributed in our pottery as it might be due to scattered metallic inclusions. Therefore, even our limit is only an approximation.

The gamma rays which would interfere with the gold determination would be the 411.2-keV gamma ray of ^{152}Eu and the 415.9-keV gamma ray of ^{233}Pa. The latter is the daughter of ^{233}Th produced by ^{232}Th$(n,\gamma)^{233}$Th. The respective contributions of ^{152}Eu and ^{233}Pa are respectively about 6% and 10% of the limit (1×10^{-8}) we have set for the gold content of our pottery.

The computer finds the Au peak around channel 353 and sums the six highest channels. For background it looks five channels above and five channels below the peak, averages the results, and corrects to the number of channels summed in the peak. The computer sums the ^{233}Pa 312-keV gamma-ray peak at around channel 255. For background it looks 12 channels above and seven channels below the peak, interpolates to the peak channel and corrects to the number of channels summed in the peak. The Pa counts are multiplied by 0.27% and then removed from the Au counts. The computer obtains the net counts in the 1408-keV gamma ray of ^{152}Eu the same way as in the Ca calculation except that this net is multiplied by 77% and then removed from the Au counts.

*<u>Lanthanum</u> $^{139}La(n,\gamma)^{140}La$; 1.676 day, 1596 keV.

Interferences — ^{72}Ga (14.1 h, ~1598 keV)

There are other gamma rays which could be used for lanthanum analysis, especially the one at 487 keV; but these other gamma rays occur in regions of much higher background and would lead to a less accurate measurement. There are no interferences with the 1596-keV gamma ray. ^{140}La in equilibrium with ^{140}Ba can arise as a fission product of ^{238}U, but this contributes only about 0.05% to the ^{140}La in our standard pottery.

The computer hunts for the La peak around channel 1501, sums the ten highest channels in the peak, looks ten channels above the peak for background, sums the ten lowest consecutive channels including the background channel, and then calculates the net counts in the La peak.

Two independent sources of La_2O_3 were used to calibrate our standard pottery. These were analyzed by Mrs. Ursula Abed of the Analytical Group of our Laboratory. About 1 gram of La_2O_3 powder from American Potash and from Heavy Minerals were fired to constant weight at 1000°C for 11 hours and 800°C for 14 hours. Both samples lost 14% of their weight. About 200 milligrams of the La_2O_3 powder from the two companies were dissolved, precipitated as the oxalate, and fired at 1000°C for one hour. Both samples lost about 14.5% of their weight. We have assumed that the chemical analyses made by the Analytical Group are correct and that the powder from American Potash is 85.7% La_2O_3 and that from Heavy Minerals is 85.6% La_2O_3.

Because the 1596-keV gamma ray is intense in our irradiated pottery and has such a small background it can be measured with high precision. The random errors we approximate as about 0.9% from the scattering of the values

from four measurements.   The non-random errors should come principally from

the uncertainty in the chemical composition of the La_2O_3 standards (~0.5%).

Our best value for the lanthanum composition of standard pottery is then

$(4.490 \pm 0.045) \times 10^{-5}$.   If we use the 487-keV gamma ray instead of the 1596-keV

one, the lanthanum composition is 4.489×10^{-5} with about a 1% additional error

due to uncertainties in the background.

*Lutetium $^{176}Lu(n,\gamma)^{177}Lu$; 6.74 day, 208 keV.

Interferences — ^{127}Xe (36.4 d, 204 keV), ^{167m}Er (2.3s, 208 keV), ^{199}Au (3.15 d,

208 keV), ^{127}Te (9.4 h, 203 keV, 214 keV), ^{177m}Lu (155 d, 204 keV, 208 keV,

214 keV), ^{239}Np (2.35 d, 210 keV), ^{149}Nd (1.8 h, 210 keV), ^{77}Ge (11.3 h,

210 keV), ^{82}Br (35.3 h, ~220 keV), ^{83}Se (25 m, ~220 keV).

There is a longer-lived isomer of ^{177}Lu which is made in the irradia-

tions but its neutron capture cross section is so small that it has a

negligible effect on the 6.74-day gamma rays at the time we make our measure-

ments.   The 210-keV gamma ray of ^{239}Np causes a substantial interference.   As

will be discussed later it arises from the neutron activation of uranium.

The ^{239}Np contribution will vary with the amount of uranium in the pottery,

but is of the order of 30% of the 208-keV peak in our 50 min runs (8 days

after the end of irradiation) and about 1% in the long runs about two weeks

later.   Although we determine Lu in both measurements and the results are

quite similar we prefer the value on the 50 min runs because the relative

background under the Lu peak is smaller. ^{177}Lu is also produced by the

$^{176}Yb(n,\gamma)^{177}Yb \xrightarrow{\beta^-} {}^{177}Lu$ reaction.   The amount of the ^{177}Lu 208-keV gamma

ray produced in the irradiation of a pure Yb sample was measured and found to

be $(4.6\pm0.4)\%$ of the 397-keV peak of ^{175}Yb, when the intensities of both were extrapolated to the end of the irradiation. In our standard pottery this led to a correction of 2.9% in the Lu intensity which we made subsequent to the computer calculations. As the ratio of Lu to Yb is not expected to change substantially in natural materials, the effect will cancel out for other natural materials such as clay or pottery which are calibrated with our standard pottery.

The computer finds the ^{177}Lu peak around channel 154 and sums the 5 highest channels. For background the computer looks 4 channels above and 5 channels below the peak, sums in each case the background channel plus the channel below and the one above, interpolates to the peak channel, and corrects to the number of channels summed in the peak. The computer sums the 278-keV ^{239}Np peak as described in the uranium section, multiplies the sum by about 0.47 and subtracts from the net counts in the $(^{177}$Lu$+^{239}$Np$)$ peak. The major error is the uncertainty in the background which we have assumed to be about 2% of the background value or 8% of the net Lu counts. Our best value for the Lu composition is $(4.02\pm0.36)\times10^{-7}$.

One commercial source (Research Chemicals) of Lu_2O_3 was used in the standardizations. Upon firing for 14 hours at 1000°C it lost only 0.2% of its weight.

<u>Samarium</u> $^{152}Sm(n,\gamma)^{153}Sm$; 1.95 days, 103 keV.

Interferences — ^{233}Th (22.1m)$\xrightarrow{\beta-}$ ^{233}Pa(27d, $UK\alpha_1$- 98keV), ^{195m}Pt (4.1d, 99keV),
^{183m}W (5.3s, 99keV, 102keV, 108keV), ^{239}U (23.5m)$\xrightarrow{\beta-}$ ^{239}Np (2.35d, $PuK\alpha_2$- 100keV,
$PuK\alpha_1$- 104keV), ^{153}Gd (242d, 103keV), ^{182}Ta (115d, 100keV), ^{185m}W (1.6m, 100keV),
^{161}Gd (3.6 m, 102keV), ^{131m}Te (30h, 102keV), ^{81m}Se (57m, 103keV), ^{155}Sm (23.5m)
$\xrightarrow{\beta-}$ ^{155}Eu (1.8y, 105 keV) ^{177m}Yb (6.5s, 104keV), ^{155}Sm (23.5m, 104keV),
^{177m}Lu (155d, 105keV), ^{177m}Hf (1.1s, 105keV), ^{188m}Re (18.7m, 106keV),
^{131m}Ba (14.6m, 107keV), $^{165m1}Dy$ (1.26m, 108keV).

The 103-keV gamma ray of ^{153}Sm is the most intense radiation in the
gamma-ray spectra of pottery taken 8 days after the irradiation. There are a
number of radiations which could interfere with the ^{153}Sm measurement but most
of these would be quite small. The most serious interferences come from the
Kα x rays of Pu arising from ^{239}Np beta decay. The neptunium is made by
neutron capture of ^{238}U followed by beta decay to ^{239}Np. In standard pottery
the Np contribution to the ^{153}Sm 103-keV gamma ray is about 10%, and it is
removed in the computer operations. The Kα_1 x rays of U arising from ^{233}Pa
beta decay cause an interference of about 1%. The ^{233}Pa comes from the beta
decay of ^{233}Th made by neutron capture of ^{232}Th. The 100.1 keV gamma ray of
^{182}Ta causes an interference of about 0.5%.

The computer looks for the ^{153}Sm peak at about channel 52 and sums the
5 highest channels around the peak. For background the computer looks 5
channels above the peak, scans for the lowest channel in the immediate region,
multiplies by 5 and subtracts from the counts summed in the peak. It calcu-
lates the net 278-keV ^{239}Np peak as discussed under uranium, multiplies by
11.4, and subtracts from the ^{153}Sm net.

We used Sm_2O_3 from Research Chemicals and Heavy Minerals Company. The Research Chemical material lost 7.9% of its weight upon ignition for 14 hours at 1000°C and the Heavy Materials material lost 4.3% of its weight upon ignition for 17 hours at 1000°C. The ignited weights were used in the calibrations.

The principal error comes from the discrepancy in the standards, the uncertainties in the Np subtraction, and the uncertainties in the background. Our best value is $(5.78\pm0.12) \times 10^{-6}$ for the samarium composition.

*Titanium ^{47}Ti(n,p)^{47}Sc; 3.43 days, 159 keV.

Interferences — ^{188}Re (16.7h, 155keV), ^{149}Nd (1.8h, 156keV), ^{199}Au (3.15d, 158keV), ^{117m}Sn (14d, 158keV), ^{199m}Hg (43m, 158keV), ^{123m}Te (117d, 159keV), ^{77m}Ge (54s, 159keV), ^{123m}Sn (39.5m, 160keV), ^{183m}W (5.3s, 160keV), ^{77m}Se (17.5s, 161keV), ^{131m}Xe (11.8d, 164keV), ^{136m}Ba (0.32s, 164keV), ^{116m2}In (2.16s, 164keV), ^{77m}Ge (54s)$\xrightarrow{\beta-}$ ^{77}As (38.7h)$\xrightarrow{\beta^-}$ ^{77m}Se (17.5s, 161keV).

Neutron activation of titanium does not lead to any titanium isotopes with suitable half-lives for our measurements. ^{47}Sc, however, is made in measurable amounts from the neutron capture of ^{47}Ti to ^{48}Ti followed by the prompt emission of a proton.

The major complication comes from the ^{47}Sc being also produced from ^{47}Ca made by neutron activation of ^{46}Ca. Although there is no detectable Ca in our standard pottery, some other types of pottery may contain in excess of 25% Ca. In potteries such as these the ^{47}Sc due to Ca will be larger than that due to Ti so our computer program makes appropriate corrections. 14-day ^{117m}Sn probably interferes in pottery to a small degree. By comparing the

159-keV peak intensity 8 days and 29 days after irradiation, we deduced that a maximum of 6% of the peak could be due to ^{117m}Sn. We have subtracted 3±3% from the Ti intensity in our standard pottery to account for possible interference by tin. ^{123m}Te could interfere from our experimental measurement to the extent of about 1%. If Te in pottery has about the same composition as the earth's crust, the ^{123m}Te would be over 1000 times smaller than our limit. We have therefore assumed the ^{123m}Te interference to be negligible. 3.15-day ^{199}Au arising from neutron activation of ^{198}Pt followed by beta decay to ^{199}Au could also interfere. If Pt occurs in pottery to about the same extent as in the earth's crust and ^{198}Pt has a neutron capture cross section of about 4 barns in our experiments, then the contribution of ^{199}Au to the ^{47}Sc 159-keV peak should be smaller than 0.1%. Another possible interference is short-lived ^{77m}Se in equilibrium with 38.7 hour ^{77}As which arises as the beta decay daughter of ^{77m}Ge caused by neutron activation of ^{76}Ge. If Ge occurs in pottery in the same composition as in the earth's crust, 7×10^{-6}, then the interference with the ^{47}Sc gamma ray would be smaller than 0.01%. 16.7 hour ^{188}Re could interfere, but the extent would be less than 0.2%. ^{131}Ba has a gamma ray of 157.0 keV which contributes 0.2% to the peak. ^{182}Ta has a gamma ray of 156.4 keV which contributes 1.3% to the peak.

The computer looks for the ^{47}Sc peak around channel 107 and sums the 6 highest channels. For background it looks 10 channels above and 7 channels below the peak, interpolates and normalizes to the number of channels summed. The computer finds the net ^{47}Ca counts as discussed in the Ca analysis, calculates the count rate at the end of irradiation, calculates the number of ^{47}Sc counts in the gamma ray analysis which would correspond to the ^{47}Ca count rate, multiplies by an empirical constant (0.7953) to compensate for relative

efficiency errors, and subtracts from the ^{47}Sc counts.

Two samples from one source of Ti_2O_3 were used for the standardization. The major errors in the Ti value are caused by the uncertainty in the tin content and the uncertainty in the correct background. The best value for the titanium content of standard pottery after correcting for the Ta and Ba contributions, is (0.782±0.034)%.

*Uranium ^{238}U(n,γ)^{239}U$\xrightarrow{\beta^-}$ ^{239}Np; 2.346 days, 278 keV.
Interferences – ^{117m}Cd (3.4h, 273keV), ^{117}Cd (2.4h, 273keV), ^{147}Nd (11.1d, 275keV), ^{129}Te (68.7m, 275keV), ^{133}Ba (7.2y, 276keV), ^{133m}Ba (38.9h, 276keV), ^{197m}Hg (24h, 279keV), ^{203}Hg (46.9d, 279keV), ^{197m}Pt (78m, 279keV), ^{193}Os (31.5h, 278keV, 281keV), ^{81}Se (18.6m, ~280keV), ^{75}Se (120d, 280keV), ^{165}Dy (140m, 280keV), ^{166m}Ho (1.2 × 10^{3}y, 280keV), ^{177m}Hf (1.1s, 281keV), ^{177m}Lu (155d, 281keV), ^{175}Yb (101h, 283keV).

^{239}U has a half-life of 24 min which is rather short for our neutron activation measurements. ^{239}U, however, decays by beta emission to 2.3-day ^{239}Np which is very suitable for analysis. The gamma ray at 278 keV appears to have the least interference by other elements. ^{175}Yb has a gamma ray at 283 keV which causes interference. To minimize the effect, the uranium peak position is determined relative to the ^{153}Sm peak position. The Yb contribution to the 278-keV peak is still about 4.5%. 47-day ^{203}Hg has a 279-keV gamma ray and 120-day^{75}Se has a 280-keV gamma ray which could interfere. These contributions are less than 2% of the U gamma ray. ^{147}Nd has a gamma ray of 275.4 keV which contributes about 2.5% to the peak.

UO_2 and U_3O_8 from the National Bureau of Standards were used to calibrate the pottery.

The computer looked for the ^{239}Np peak 170 channels above the ^{153}Sm peak and summed this channel plus the adjacent 2 on either side. For background it looked 5 channels below and 11 channels above the peak, summed each of these plus one channel on each side in each case, interpolated to the peak channel and corrected to the number of channels summed in the peak.

The principal source of error is the uncertainty in the background which was taken as 2%. This leads to an error of 8.4% in the uranium value. Our best value for the uranium composition is $(4.82\pm0.44) \times 10^{-6}$ after removing the ytterbium and neodynium contributions.

Ytterbium ^{174}Yb$(n,\gamma)^{175}$Yb; 4.21 days, 397 keV.

Interferences – ^{71}Zn (2.4m, ~390keV), ^{160}Tb (72d, 392keV), ^{79}Kr (34.9h, 398keV), ^{75}Se (120d, 401keV), ^{109}Pd (13.5h, ~410keV).

Ytterbium has two isotopes which would be suitable for analysis by neutron activation, 101-hour ^{175}Yb and 31.8-day ^{169}Yb. The most suitable gamma ray with the least interference is the 397-keV gamma ray of 101-hour ^{175}Yb. 120-day ^{75}Se has a gamma ray of 401 keV, but this will contribute less then 0.6% in our pottery. 13.5-hour ^{109}Pd has an 0.41-MeV gamma ray which would contribute less than 0.1% even if its correct energy were 397 keV.

Two sources of ytterbium oxide were used in the calibrations. One from Research Chemicals gave a yield of 99.2% rare earth oxide upon ignition for 14 hours at 1000°C. The other from Professor Spedding of Iowa State University gave 98.9% rare earth oxide upon ignition for 14 hours at 1000°C.

The computer looks for the 397-keV gamma ray of ^{175}Yb around channel 338 and sums the six highest channels. For background it looks six channels above and below the peak, sums each of these channels plus the two adjacent channels above and below each background channel in each case, interpolates to the peak channel and corrects to the number of channels summed in the peak.

The major ytterbium error comes from the uncertainty in the background which we have assumed to be 1-1/2%. This leads to an error of 12.7% in the ytterbium value. Our best value for the ytterbium composition is $(2.80\pm0.36) \times 10^{-6}$.

B3 (Half lives greater than 6 days)

*Antimony $^{123}Sb(n,\gamma)^{124}Sb$; 60.4 day, 1692 keV.

Interferences — ^{72}Ga(14.1 h, 2201 keV).

The escape peak of ^{72}Ga at 1690 keV will not interfere with the antimony measurements because of the short 14-hour half life. As mentioned earlier, the Sb in the Al wrapping of our pills contributes about 2% to the Sb peak.

The computer hunts for the antimony peak around channel 1590 and sums the six highest consecutive channels. For background it looks 15 channels below the peak, sums the six lowest consecutive channels, and multiplies by 0.9.

The principal counting errors are about 2% and the uncertainty in the true background, which we have assumed to be 5%, contributes a like amount. From ^{124}Sb the antimony content of our pottery is $(1.73\pm0.06) \times 10^{-6}$, in good agreement with the value from ^{122}Sb, $(1.66\pm0.12) \times 10^{-6}$.

*Barium $^{130}Ba(n,\gamma)^{131}Ba$; 12.0 day, 496 keV.

Interferences — ^{115}Cd(53.5 h, ~ 490 keV), ^{131}Te(24.8 m, 493 keV), ^{143}Ce(33 h, 493 keV), ^{71m}Zn(3.9 h, 495 keV), ^{103}Ru(39.5 d, 497 keV), ^{103}Pd(17.0 d, 498 keV), ^{180m}Hf(5.5 h, 501 keV), ^{101}Mo(14.6 m, ~ 510 keV).

Besides the 83-min ^{139}Ba previously discussed, 12-day ^{131}Ba is also suitable for neutron activation studies. The only interference of concern in pottery is 39.5-day ^{103}Ru which results predominantly from the neutron-induced fission of the uranium in the pottery. The ^{103}Ru contributes about 4% to the 496-keV peak which we have removed from our barium values.

Barium carbonate was used to calibrate our pottery. The composition of our barium solutions were checked by gravimetric sulphate analysis and were found to be accurate within 1.3 percent.

The computer looked for the 496-keV gamma-ray peak around channel 435 and summed the highest 5 consecutive channels. For background it looks 25 channels below and seven channels above the peak, in each case summed the background channel plus two adjacent channels on each side, interpolated to the peak channel and corrected to the number of channels summed in the peak.

The principal source of error is the uncertainty in the background which we have assumed to be ~ 1.7%. The best value of the barium composition from this measurement is $(7.0 \pm 1.1) \times 10^{-4}$. This is a good agreement but less precise than the value obtained from ^{139}Ba in the short irradiation, $(7.13 \pm 0.32) \times 10^{-4}$.

Cerium ^{140}Ce$(n, \gamma)^{141}$Ce; 32.5 day, 145 keV.

Interferences — ^{46m}Sc(19.5 sec, 142 keV), ^{59}Fe(44.9 day, 143 keV), ^{99}Mo(66.7 h) $\xrightarrow{\beta^-}$ ^{99m}Tc(6.0 h, 140 keV), ^{127}Xe(36.4 d, 145 keV), ^{182m}Ta(16.5 m, 147 keV), ^{131}Te(24.8 m, 150 keV), ^{85m}Sr(70 m, 150 keV), ^{111m}Cd(48.6 m, 150 keV), ^{85m}Kr(4.4h, 150keV).

The only significant interference comes from the 143-keV gamma ray of ^{59}Fe. This interference which is only about 4% in our pottery can be comparable to the cerium contribution for some pottery. The computer calculates the interference from Fe and removes it. In pottery the uranium content is sufficiently small that less than 1% of the ^{141}Ce results from fission products.

In some measurements the ^{59}Fe gamma ray is larger than that of Ce and would confuse the computer if it hunted for the highest channel. The computer

looks for the Ce peak 23 channels above the ^{152}Eu peak at 122 keV and sums

this channel plus the four adjacent channels below and three adjacent channels

above the peak. For background it looks six channels below and four channels

above the peak, interpolates to the peak channel and corrects to the number of

channels summed in the peak. The computer determines the net counts in the

1292 keV gamma ray of ^{59}Fe (as will be described in a later section), multiplies

by 1.104 and subtracts from the Ce counts.

The major source of error is the uncertainty in the background for

the Ce peak which was assumed to be 3%. Our best value for the Ce content is

$(8.03 \pm 0.39) \times 10^{-5}$.

*Cesium ^{133}Cs(n,γ)^{134}Cs; 2.05 y, 796 keV.

Interferences — ^{151}Nd(12 m, 797 keV), ^{77}Ge(11.3 h, $\sim$ 800 keV), ^{111}Pd(22 m,

$\sim$ 810 keV) and ^{111m}Pd(5.5 h, $\sim$ 810 keV).

2.9-hr ^{134m}Cs has a gamma ray of 128 keV which can be observed after

our short irradiation. The background under this peak is very high, however,

and the resulting Cs intensities would have errors of 20 or 30%. The 796-keV

gamma ray of 2.05-y ^{134}Cs has no significant interferences from other elements.

^{134}Cs has another gamma ray at 802 keV but this is clearly resolved from the

796-keV gamma ray and does not interfere with it.

To calibrate our pottery we used CsCl sources dried to constant

weight at 130° C.

The computer looks for the Cs gamma-ray peak around channel 728 and

sums the six highest consecutive channels. For background the computer looks

eight channels below the peak and sums the six lowest consecutive channels.

The principal error is the uncertainty in the background which we have assumed to be 2%. Our best value for the cesium content is $(8.31\pm0.55) \times 10^{-6}$.

Chromium $^{50}Cr(n,\gamma)^{51}Cr$; 27.8 day, 320 keV.

Interferences — ^{42}K(12.4 h, ~ 310 keV), ^{109}Pd(13.5 h, ~ 310 keV), ^{161}Gd(3.6 m, 315 keV), ^{192}Ir(74.2 d, 317 keV), ^{192m}Ir(1.4 m, 317 keV), ^{147}Nd(11.06 d, 319 keV), ^{177m}Lu(155 d, 319 keV), ^{182m}Ta(16.5 m, 319 keV), ^{51}Ti(5.8 m, 320 keV), ^{194m}Ir(47 s, ~ 320 keV), ^{199}Pt(31 m, ~ 320 keV), ^{193}Os(31.5 h, 322 keV), ^{97}Ru(2.88 d, 324 keV), ^{125m}Sn(9.5 m, 325 keV), $^{54}Fe(n,\alpha)^{51}Cr$.

The principal interference with the 320-keV gamma ray of ^{51}Cr comes from the 319-keV gamma ray of 11-day ^{147}Nd. In pottery at the time of our long runs it contributes about 0.9% to the peak. ^{51}Cr also arises from the irradiation of the iron in the pottery. After capturing a neutron, ^{54}Fe can promptly emit an alpha particle as one of its modes of de-excitation, which makes ^{51}Cr. This contributes 0.9% to the peak in our standard pottery, but could be substantially more for materials with a higher iron content.

The computer hunts for the chromium peak around channel 263 and sums the five highest consecutive channels. For background it looks six channels above the peak and sums the five lowest consecutive channels.

The principal source of error is the uncertainty in the true background which we have assumed to 1-1/2 percent, which corresponds to a 3-1/4 percent error in the chromium value. The chromium content of our pottery is $(1.151\pm0.038) \times 10^{-4}$.

*<u>Cobalt</u> $^{59}Co(n,\gamma)^{60}Co$; 5.26 year, 1332 keV.

Interferences — ^{79}Kr(34.9 h, 1336 keV).

There are no significant interferences with the 1332-keV gamma ray of ^{60}Co in pottery. There is a 1173-keV ^{60}Co gamma ray which is quite intense also, but the background under the latter peak is more uncertain because of other gamma rays in the region.

The computer looks for the cobalt peak around channel 1252 and sums the ten highest consecutive channels. For background the computer looks 15 channels above the peak, sums the ten lowest consecutive channels containing the background channel and multiplies by an empirical factor of 1.040 (because of the background slope in the region).

The errors arise in nearly equal amounts ($\sim 0.5\%$) from the counting statistics, uncertainties in the calibration standards, uncertainty in the true background, and ordinary handling and reactor uncertainties. Our best value for the Co intensity is $(1.406\pm0.015) \times 10^{-5}$.

<u>Europium</u> $^{151}Eu(n,\gamma)^{152}Eu$;12.7 y, 1408 keV.

Interferences — ^{111m}Pd(5.5 h) $\xrightarrow{IT}$ ^{111}Pd(22 m, $\sim$ 1400 keV), ^{117m}Cd(3.4 h, 1408 keV), ^{125}Sn(9.4 d, $\sim$ 1410 keV).

There are no interferences with the 1408-keV gamma ray of ^{152}Eu in pottery in our analyses. The ^{125}Sn contributes less than 0.4%.

The europium used in the calibration was the same as discussed for $^{152m1}Eu$ previously.

The computer hunts for the ^{152}Eu 1408-keV peak around channel 1325 and sums the six highest consecutive channels. For background it looks 16

channels above and 15 channels below the peak, in each case sums the background channel plus two on either side, interpolates to the peak channel, corrects to the number of channels summed in the peak and multiplies by 0.97.

The principle source of error is the discrepancy of 3.6% in the values determined with the two standards. The europium content from this measurement is $(1.477\pm0.047) \times 10^{-6}$. This is in adequate agreement with the value obtained from the measurements on ^{152m1}Eu $(1.418\pm0.048) \times 10^{-6}$.

*<u>Iron</u> ^{58}Fe$(n,\gamma)^{59}$Fe; 44.9 day, 1292 keV.

Interferences $- {}^{115m}$Cd(43 d, 1290 keV), ^{182}Ta(115 d, 1290 keV), ^{116}In(13.4 s, 1293 keV), ^{116m1}In(54 m, 1293 keV), ^{41}Ar(1.83 h, 1293 keV), ^{47}Ca(4.535 d, 1297 keV).

The only interference of any consequence, the 1290-keV gamma ray of ^{182}Ta, contributes about 2 percent to the ^{59}Fe peak in our pottery and is removed by the computer. ^{59}Fe has another intense gamma ray at 1099 keV, but the higher background in this energy region makes this peak less useful than the 1292-keV gamma ray.

Iron oxide powder from J. T. Baker Chemical Co. was used to calibrate our pottery. Chemical analysis of the iron oxide showed it to be 99.3$\pm$0.3% pure.

The computer looks for the 1292-keV peak around channel 1214 and sums the ten highest channels containing the peak channel. For background the computer looks 30 channels above the peak and sums the ten lowest consecutive channels containing the background channel. The net counts in the ^{182}Ta peak are determined as discussed under Ta, multiplied by 0.06 and subtracted from the iron counts.

The major errors arise from the uncertainty in the true background, the counting statistics, and handling and reactor problems. The best value for the iron content is $(1.017 \pm 0.012)\%$.

Hafnium ^{180}Hf$(n,\gamma)^{181}$Hf; 42.5 day, 482 keV.

Interferences - ^{188}Re(16.7h, 478 keV), ^{187}W(23.9h, 479 keV) ^{131}Ba(12.0d, 481 keV), ^{137}Ce(9.0h, 481 keV), ^{90m}Y(3.1h, 482 keV), ^{115m}Cd(43d, 485 keV), ^{145}Sm(340d, 485 keV), ^{131}Ba(12.0d, 487 keV), ^{140}La (40.2h, 487 keV), ^{115}Cd(53.5h, ~ 490 keV), ^{129m}Te(34d) $\xrightarrow{IT}$ ^{129}Te(68 min, 482 keV).

^{181}Hf is the only isotope of hafnium suitable for our neutron activation studies. ^{175}Hf has an abundant gamma ray but it has interference from ^{152}Eu and ^{233}Pa. The 482-keV gamma ray of ^{181}Hf has no major interferences. The 487-keV gamma ray of ^{140}La has nearly died out by the time we start our long runs, ~25 days after the end of irradiation. ^{131}Ba has two interfering gamma rays which contribute a total of about 0.4% to the Hf intensity.

The computer hunts for the hafnium peak around channel 421 and sums the 5 highest consecutive channels. For background it looks 9 channels above and 21 channels below the peak, sums each of these channels plus one on each side in each case, interpolates to the peak position and corrects to the number of channels summed in the peak.

The major source of error is the uncertainty in the true background which we have assumed to be 1.5%. The hafnium content of our pottery is $(6.23\pm0.44)\times10^{-6}$.

*Nickel ^{58}Ni$(n,p)^{58}$Co; 71.3 day, 810 keV.

Interferences - ^{77}Ge(11.3h, ~ 800 keV), ^{47}Ca(4.54d, 807 keV), ^{111m}Pd(5.5h) $\xrightarrow{\beta-}$ ^{111}Pd(22m, ~ 810 keV), ^{166m}Ho(1.2$\times$10^{3}y, 810 keV), ^{125}Sn(9.4d, 811 keV), ^{140}La(40.2h, 815 keV).

Nickel has no isotope suitable for neutron activation analysis studies. ^{58}Co, however, is made when ^{58}Ni is irradiated with neutrons and it is an adequate monitor of the nickel content. In pottery there are usually no serious interferences with the 810-keV gamma ray. When there are very high Ca contents in the pottery, such as 25%, the nickel peak could be affected by the 807-keV gamma ray of ^{47}Ca. Under our operating conditions, the effect would be smaller than the counting errors. As our standard pottery has a very small Ca content, the nickel measurement is not influenced. ^{125}Sn affects our nickel value by <1.1%, probably about 0.1%. ^{140}La affects it by <0.1%, and ^{166m}Ho has an effect less than 5%, probably 0.1%.

Reagent grade NiCO$_3$ from Baker and Adamson was used to calibrate our pottery. The nickel content of the NiCO$_3$ was found by R. G. Clem of our Laboratory to be 45.3±0.1%, which value was used in our measurement.

The computer hunts for the ^{58}Co peak around channel 743 and sums the 5 highest consecutive channels. For background it looks 4 channels above and below the peak, averages the values, and corrects to the number of channels summed in the peak.

The principal source of error is the uncertainty in the true background which we have assumed to be 1.5%. The nickel content of our standard pottery is $(2.79±0.20)×10^{-4}$.

*Rubidium ^{85}Rb$(n,\gamma)^{86}$Rb; 18.66 day, 1077 keV.
Interferences - ^{123}Sn(125d, ~ 1080), ^{177}Yb(1.9h, 1080)

Rb has only one suitable isotope for neutron activation studies in pottery. There are no interferences in pottery with the 1077-keV gamma ray although the Compton distributions under the peak cause larger uncertainties

in the background than usual. One sample of RbCl from Fisher Scientific Co.

which had been dried overnight at $110^{o}C$, was used to calibrate the pottery.

The Rb content of the RbCl was analyzed by R. G. Clem of this Laboratory

and found to be 98.5% of the expected value.

The computer expected the Rb peak at channel 1004 and summed channels

1002 to 1006. For background it looked 4 channels above and 5 channels below

the peak, interpolated to the peak position, and corrected to the number of

channels summed in the peak.

The principal error is the uncertainty in the true background which we

have assumed to be 3%. The Rb content of our standard pottery is

$(7.00\pm0.63)\times10^{-5}$.

*<u>Scandium</u> $^{45}Sc(n,\gamma)^{46}Sc$; 83.9 day, 1120 keV.

Interferences - $^{71m}Zn(3.9h, \sim 1110$ keV), $^{160}Tb(72.1d, 1115$ keV), $^{65}Ni(2.6h,$

1115 keV), $^{65}Zn(245d, 1116$ keV), $^{117m}Cd(3.4h, 1117$ keV), $^{79}Kr(35h, 1.119$ keV),

$^{71}Zn(2.4m, \sim 1120$ keV), $^{151}Nd(12m, 1122$ keV), $^{182}Ta(115d, 1122$ keV).

The gamma rays of ^{46}Sc are in high intensity in neutron-irradiated

materials with composition similar to the earth's crust. Hence, scandium can

be determined with considerable precision. The only interference of signifi-

cance usually in pottery is the 1122-keV gamma ray of ^{182}Ta. The computer

makes a correction of about 2% for this effect. The 1115-keV peak of ^{65}Zn

is normally about 2% of the scandium peak and causes no interference as it

is 5 keV away. ^{46}Sc also has an 889-keV gamma ray in high intensity with

no major interferences. It is on top of the Compton distributions from the

1120-keV peak and the 1099-keV peak of ^{59}Fe and would give, we think,

less precise values.

The principal source of error is the disagreement between the abundances calculated with the two ^{46}Sc gamma rays, 1.2%. We have used the value for the 1120-keV gamma ray and included the 1.2% in the error. The scandium content of the pottery is $(2.055\pm0.033)\times10^{-5}$.

Tantalum $^{181}Ta(n,\gamma)^{182}Ta$; 115.1 day, 1222 keV.

Interferences – None

      Tantalum has one isotope suitable for neutron activation analysis. The 1222-keV gamma ray has no major interferences, but it is on a sloping background which contributes additional uncertainties in the composition.

      The two sources used for calibration were tantalum foil and Ta_2O_5, each dissolved in 0.7 M HF.

      The computer hunts for the tantalum peak around channel 1145 and sums the 6 highest consecutive channels. For background it looks 20 channels above and 13 channels below the peak, sums each of these channels with two on either side in each case, interpolates to the peak position and corrects to the number of channels summed in the peak.

      The major errors are the uncertainty in the true background which we have assumed to be 3%. This corresponds to a tantalum error of 2.1% which together with the counting error of 1.9% gives a total error of 2.9%. The tantalum content of our pottery is $(1.550\pm0.044)\times10^{-6}$.

*Thorium $\qquad$ $^{232}Th(n,\gamma)^{233}Th \xrightarrow{\beta^-} ^{233}Pa$; 27.0 day, 312 keV.

Interferences - ^{169}Yb (32 d, 308 keV), ^{171}Er (7.5 h, 308 keV), ^{192}Ir (74 d, 308 keV), ^{160}Tb (72 d, 310 keV), ^{42}K (12 h, ~310 keV), ^{109}Pd (13.5 h, ~310 keV), ^{117}Cd (2.4 h, 314 keV), ^{117m}Cd (3.4 h, 314 keV), ^{161}Gd (3.6 m, 315 keV), ^{192}Ir (74 d, 316 keV), $^{192ml}Ir$ (1.4 m, 317 keV)

^{233}Th with a half life of 22 min is not a useful neutron activation product to determine thorium contents of pottery. The ^{233}Th, however, undergoes beta decay to 27-day ^{233}Pa which is very suitable for gamma ray analysis. In our pottery there are no interferences. The 310-keV gamma ray of ^{160}Tb contributes around 0.3% and the two ^{192}Ir gamma rays less than 0.35%. In materials where the ratio of rare earths (or Ir) to Th might be larger by an order of magnitude or more, these interferences could be substantial.

The computer hunts for the ^{233}Pa peak around channel 255 and sums the 5 highest consecutive channels. For background it looks 23 channels below and 14 channels above the peak, sums in each case the background channel plus two on either side, interpolates to the peak channel and corrects to the number of channels summed in the peak.

The principal source of error is the spread in the values with different Th standards, 2.4 percent. The best value for the Th content of the pottery is $(1.396\pm0.039)\times10^{-5}$.

Zinc $^{64}Zn(n,\gamma)^{65}Zn$; 245 day, 1116 keV.

Interferences - ^{121m}Te (154 day, $\sim$1100 keV), ^{163}Er (75.1 m, $\sim$1100 keV), ^{143}Ce (33 h, $\sim$1100 keV), ^{71m}Zn (3.9 h, $\sim$1110 keV), ^{152}Eu (12.7 y, 1113 keV), ^{160}Tb (72.1 d, 1115 keV), ^{65}Ni (2.6 h, 1115 keV), ^{117m}Cd (3.4 h, 1117 keV), ^{79}Kr (34.9 h, 1119 keV), ^{46}Sc (83.9 d, 1120 keV), ^{71}Zn (2.4 m, $\sim$1120 keV)

The only isotope of Zn made in neutron activation which is suitable for our gamma ray analysis techniques is ^{65}Zn. This isotope has annihilation radiation, which can be interfered with by other sources of annihilation radiation, and a gamma ray of 1116 keV. The gamma ray is influenced by the 1113-keV gamma ray of ^{152}Eu and the 1115-keV gamma ray of ^{160}Tb. Worst of all it is nearly obliterated by the intense 1120-keV gamma ray of ^{46}Sc. The ^{46}Sc peak is nearly two orders of magnitude more intense than the zinc peak, and its contribution to the zinc peak will vary with its resolution. We determined the intensity of the zinc peak by analyzing the spectra over a period of 245 days, in which the scandium decayed by a factor of 8.

In order to measure the zinc content of pottery in general, however, it is desirable to determine the value in one of our regular analyses, i.e., the long runs starting about 25 days after the end of irradiation. We measured the contribution of ^{46}Sc to the zinc peak as a function of the full width at half maximum (FWHM) of the Sc peak. The Sc contribution was roughly comparable to the zinc contribution and could be expressed by an equation with the half-width of the Sc peak as a variable. The equation was checked experimentally over a period of nine months and found to be reliable. About 75 measurements of the zinc content of our standard pottery taken about one month after some 19 irradiations over a period of about 9 months gave values with a

standard deviation of 4.2 percent. The mean value was within 2 percent of the value obtained from the analyses made 245 days after the end of irradiations. Thus we believe we can measure accurately the zinc content of pottery in general in our analyses taken one month after irradiation.

Although we corrected for the ^{152}Eu contribution to the zinc peak in our computer program, the ^{160}Tb contribution was removed subsequent to the computer operations.

The computer expects the zinc peak at channel 1042 and sums channels 1040 to 1043. For background it looks 16 channels above channel 1042, sums the 4 lowest consecutive channels, multiplies by 1.09 and subtracts from the peak sum. It determines the net counts in the 1408-keV ^{152}Eu peak, multiplies by 9.7%, and subtracts from the net zinc peak. The computer determines the net counts in the 1120-keV peak of ^{46}Sc as previously described. It then measures the half-width of the Sc peak, calculates the percentage of the peak which should be removed from the zinc counts from the half width, does the arithmetic and removes the calculated Sc interference.

The principal error is due to the counting error of 5.9%. The zinc content of our pottery is $(1.26\pm0.08)\times10^{-4}$. For measuring zinc contents of other potteries with respect to our standard pottery we use the flux measured for the 889-keV gamma ray of ^{46}Sc.

B4 (Components of standard pottery not determined by neutron activation)

$\underline{SiO_2}$ - This analysis was made by R. G. Clem of this Laboratory. Two samples of pottery were fused with Na_2CO_3. After fusion they were dissolved out of the crucibles with HCl and fumed with perchloric acid. After dilution with water the solutions were carefully filtered with #541 filter paper and flame-fired until the SiO_2 was white. The samples were cooled in a dessicator and then weighed. After weighing they were treated with H_2SO_4 and HF and heated to red heat. The loss in weight gave the SiO_2 content. The two values were 60.2 and 60.7 percent SiO_2 with a best value of 60.4±0.3 percent.

Volatile Components

213 mgms of our pottery were fired by R. G. Clem of this Laboratory at 1000°C for 6.5 hours. The loss in weight was 3.99±0.10 percent. A carbon-hydrogen analysis of our pottery was made by Dr. C. Koch of the University of California at Berkeley. The carbon content was 0.03±0.03 percent and the hydrogen content was $0.54^{+0.00}_{-0.05}$ percent. The carbon content could be low if it were present as carbonate. A carbonate analysis made by D. Okita, a University of California student, showed the CO_2 content of the pottery was 0.13±0.07 percent. The hydrogen content corresponds to $4.7^{+0.0}_{-0.5}$ % water which is not in bad agreement with the total volatile components of 4.0±0.1 percent.

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