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Provenience Studies Using Neutron

Activation Analysis: The

Role of Standardization *

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In several laboratories ceramics of archaeological origin are currently being chemically analyzed -- one can guess at a total yearly production rate running into the thousands. Since the present commercial price for multielement analyses by neutron activation is \$500/sample or more, it is clear that a great deal of money is involved. I do not think it is necessary today to justify the method or expenditure: the steady stream of publications, theses and privately-circulated reports amply reward the archaeologist and his collaborator-analyst for their efforts by giving new answers and insights into ancient ceramic production and trade, insights that would not, in most cases, have been provided by stylistic analysis alone.

The first chemical analysis of an archaeological artifact took place in 1790 (Caley, 1962): I thought at one time that the first analysis of an archaeological ceramic dated to Fouque's investigations at Santorin in the 1860's (Murray, 1900) but this is not so certain if one reads Fouque's report itself (Fouque, 1869). In any case, T. W. Richards at Harvard in 1895 analyzed ancient Athenian pottery "at the request of Mr. Edward Robinson, of the Boston Museum of Fine Arts" and reported the results fully in the J. Am. Chem. Soc. (Richards, 1895). Two significant points emerge: the first being this collaboration between the Humanities and the Sciences. The second was Richard's observation that "the variations in the relative amounts (of the different chemical elements) are singularly small, the range being not nearly so large as that given by Brougniart, in his "Traite' des Arts Ceramiques". Hence it is possible, that all of these specimens, which

were picked up in the city of Athens itself, were the product of a local pottery." This observation carries the germ of what has been called the Provenience Postulate, which will be further mentioned below.

After the Harvard work, although there were analyses of archaeological metals (Caley, 1964) little was done with ceramics for a long time. The reason is simple: anyone who was, like myself, trained in the classic school of wet quantitative analysis, which had in its curriculum the horror of an experiment in rock analysis, with peroxide or carbonate fusion for openers (Swift, 1940), can easily see that the processing of the hundreds of archaeological specimens, which are very much like rocks, in a typical investigation, would be daunting to say the least. Emission spectroscopy has been used to shortcut the work (Richards, 1959) but its precision is strongly concentration, and to some extent matrix-dependent. Although it is still used, it produces results that are, in my opinion, of limited value in the resolution of ceramic groups, especially similar ones.

The history of the first application of neutron activation to archaeological ceramics has been told in detail elsewhere (Harbottle, 1976): suffice it to say that 20 or more elements can be simultaneously measured in a single specimen and, as we shall see, the results are quite precise and may even be, or become, accurate as well.

The distinction between precision and accuracy of chemical analysis is an important one. Although in principle one could calculate the concentrations of elements in a neutron-activated specimen from an exact knowledge of neutron flux, its intensity,

duration and spectral (energy) distribution, plus an exact gamma ray count calibrated for efficiency, corrected for branching ratio, etc. in practice it is far easier to compare one's unknown to a "standard" of hopefully known or assumed composition. Different laboratories have used different standards, but within one laboratory's work with its own archaeological problems, what is important is the precision: the ability to relate the concentrations of elements in one's samples reliably, in terms of ratios, to the assumed concentrations in the standard. Obviously, all the data generated in a given laboratory is intercomparable, provided only that the standard employed is homogeneous, and the level of intralaboratory precision is sufficiently good. Some laboratories and their standards are given in Table 1.

For a long time, probably extending from the beginning up to about the mid 1970's, the archaeological ceramic analysis projects were isolated, "self-contained" usually even within the laboratory concerned. That is, the data generated was useful to the archaeologist concerned, but did not overlap, in the universe of all conceivable data, the spheres of interest of any other archaeologists. But that situation has changed dramatically, and at Brookhaven in current archaeological studies extensive use is being made of our own past work, and of the "data bank." A few recent examples will suffice:

- 1) sherds of a Mycenaean appearance are found in certain levels in the excavation of a cave in Jordan. They are analyzed and the computer search picks out Mycenaean sherds from Mycenae in Greece as

the very closest match (McGovern, 1979).

2) Sherds of a supposed "imitation" Crema ware are found in preclassic levels in a site called La Canada that was thought to have only faint connections with Monte Alban. This great site in Oaxaca, Mexico is the home of Crema ware. Analysis shows that some of the Crema is imitation, but some of the sherds are authentic, intrusive trade pieces (Radmond, 1979): this is shown by reference to authentic Crema analyses in the data bank.

3) Examples of Tell-el-Yahudiyeh ware (small jugs) from along the Nile are thought possibly to have been fabricated in Palestine where the ware is also found. Analyses are compared with an extensive, already-existing data bank of Nile and Palestinian clays of different types. Result: almost all the Tell-el-Yahudiyeh pieces are locally made, and the hypothetical "extensive trade" in these objects (and in whatever valuable commodity they contained) evaporates. This constitutes important information about the Hyksos (Kaplan, 1978).

Numerous other examples of the "overlap" and reuse of data, within our own laboratory and, we are sure, within others, could be cited. It is also becoming increasingly clear that the fields of archaeological interest investigated by different groups are overlapping. For example:

1) Both the Berkeley and Brookhaven groups have carried out extensive analyses of "Nile Mud" wares (Perlman and Asaro, 1969, Kaplan, 1978).

2) At Berkeley an archaeologist analyzed wares from the Postclassic Valley of Mexico that are typologically related to similar

wares analyzed at Brookhaven (Branstetter, 1980).

3) Greek ceramics are being analyzed both at G.A.N.O.S. by Attas from McGill and at Brookhaven (Attas, 1980, Fillieres, 1980).

At a wild guess, there must exist worldwide some 40-50,000 analyses. It is obvious that there would be a great benefit if analyses could be exchanged among all users and/or generators of data. This benefit would increase constantly, with increase in the data. The main thrust of this paper will be: (1) how far are we from interlaboratory comparability of ceramic data (2) what has been proposed in the past to achieve this goal and (3) a new proposal. All of this may be subsumed under the general heading of "Analytical Quality Control" - i.e. how to achieve precise and accurate analysis, in the neutron activation sense. Then, (4) the relationship of Analytical Quality Control to provenience location will be examined.

Some time ago, I attempted to indicate the rough ranges of concentrations of different elements encountered in "homogeneous" "natural" archaeological ceramic groups (Harbottle, 1976). If an archaeological ceramic group -- let us say a particular ware or group of wares made from a particular clay source, disregarding for a moment the possible deliberate addition of temper, is thought of as occupying an ellipsoid of 95% probability in the multivariate space whose n coordinate axes represent the (usually log-transformed) concentrations of the n analyzed elements, then it will be easier to discuss questions related to precision, accuracy, and the probability of group assignments. We may ask, for example,

- (a) How large are the axial extensions of the group, expressed as standard deviation divided by the mean value, in percent? This is the "natural" size of the group, before sampling and measurement error have been folded in, and gives one the feeling of multivariate volume of the group.
- (b) Does the inevitable analytical precision error, within a given laboratory, in the analyses that constitute the group enlarge the "natural" variation, or volume, appreciably?
- (c) Could a second laboratory, using the same standard but a different reactor, counter, etc. place the same samples in the same multivariate volume?
- (d) Could a second laboratory, but using a different standard also do this?

If (d) is possible, then at one stroke we have greatly increased the mass of data available to the archaeometrist.

Before proceeding, let us answer the easy question first, that is, (c), and the answer is yes. If two laboratories use the same standard, they get the same answers (Yellin et al., 1978). What this study says is, that between two laboratories using the same standard, the precision is no worse than within either one of the laboratories alone. Which brings us back to (b), the question of the analytical precision within one laboratory, and the effect of this in enlarging the multivariate volume of the "natural" group. The Berkeley group early on studied and reported their precision: the small numbers which they obtained are a tribute to the care which they have taken in their methodology (Perlman and Asaro, 1969).

I would like to report a new set of data from the BNL group, which will also bear on the question of in-house analytical precision. The data derives from the way in which we standardize: namely, we always bombard weighed samples of all six USGS standard rocks, PCC1, DTS1, GSP1, AGV1, BCRI and G2, together with our unknown ceramic samples. Then, using the "Master Table" of "best value" concentrations which we derived from data in Flanagan's Report (Abascal, et al., 1974, Flanagan, 1976) we calculate for each element, in each standard in which it occurs (for example PCC1 and DTS1 have almost no rare earths, alkalis, alkaline earths, etc.) a constant which is essentially the corrected number of characteristic gamma-counts recorded, per unit weight of the element present, per unit time. The unit weight is calculated from the weight of standard rock taken, times the "Master Table" concentration. If our "Master Table" concentrations were either (a) correct or (b) all different from the correct values by a constant factor, then the constants for a given element would all be the same. Some typical examples, from a neutron bombardment which took place on Sept. 20, 1978 are given in Table 2: for simplicity the exponential factors, which are the same for all the constants reported for a given element, have been eliminated. In some cases, 6 independent values of this constant are reported (Fe, Co), in other cases 4 or fewer (Ba, Rb, Cr, etc.) since, as mentioned above, some of the rocks are so deficient in some of the elements that they cannot be used as standards for those elements (Bieber, Jr. et al., 1976). For these 6 or 4 independent constant values, the geometric mean, the standard deviation and the standard error (standard deviation of the mean) are also listed (Table 2).

Table 1

A Partial List of Laboratories engaged in Archaeological Ceramic
Neutron Activation Analysis, and their standards

| <u>Laboratory</u> | <u>Standard</u> | <u>Reference</u> |
|---|---|--|
| GANOS (Groupe d' Archeologie Nucleaire d'Orsay-Saclay) | Asaro-Perlman | (Attas et al., 1979) |
| Brookhaven National Lab. | 6 USGS Rocks Ohio Red (in-house) | (Bieber Jr., et al., 1976) |
| RISO | Danish Clay (in-house)* | (Hansen et al., 1978) |
| Berkeley | Asaro-Perlman | (Perlman and Asaro, 1969) |
| Jerusalem | Asaro-Perlman | (Yellin et al., 1978) |
| Manchester | Podmore P1033 Red Plastic Clay (in-house) | (Newton and Krywonos, 1974-1975) |
| Smithsonian (Conservation- Analytical) | USGS Rocks and NBS Fly Ash | (De Atley et al., 1980) |
| McGill | Asaro-Perlman | (Attas, et al., 1977) |

*Analyzed by comparison with USGS-BNL 6 rocks,
and Bradford Standard

Table 2

Intensities of Characteristic Gamma Rays, in Counts per unit time, per Unit Weight of Element activated, of the Six USGS Rocks, for a Bombardment on 9/20/78

| | PCC1 | GSP1 | DTS1 | BCR1 | AGV1 | G2 | Geo. Mean | Std. Deviation % | Std. Error % |
|----|------|-------|------|------|------|------|-----------|------------------------|--------------------|
| Eu | | 2.75 | | 2.85 | 3.05 | 2.93 | 2.89 | 4.4 | 2.2 |
| Lu | | 12.56 | | 7.11 | 5.96 | 5.58 | 7.38 | 44. | 22. |
| Hf | | 5.88 | | 5.55 | 4.85 | 5.83 | 5.51 | 8.6 | 4.3 |
| Th | | 6.11 | | 5.84 | 5.91 | 5.95 | 5.95 | 1.9 | 1. |
| Cr | 5.00 | | 4.86 | | | | 4.93 | 9.9 | 7. |
| Fe | 5.00 | 4.86 | 5.14 | 4.90 | 4.93 | 5.01 | 4.97 | 2.0 | 0.8 |
| Co | 3.08 | 2.68 | 3.00 | 2.87 | 2.89 | 2.69 | 2.86 | 5.6 | 2.3 |
| Sc | 5.65 | 4.15 | 5.10 | 5.53 | 5.63 | 4.88 | 5.13 | 11.4 | 4.6 |
| Ba | | 1.55 | | 1.54 | 1.64 | 1.64 | 1.59 | 3.5 | 1.7 |
| Rb | | 8.51 | | 7.85 | 7.86 | 7.89 | 8.03 | 4.0 | 2.0 |
| Cs | | 2.28 | | 1.84 | 2.14 | 2.31 | 2.13 | 10. | 5. |

It will be seen that some elements (Fe, Th) agree "across the board" very well. Others (Eu, Sc, Hf) are less consistent, while Lu is downright terrible, with a group standard deviation of 44%. The inconsistent constant values like Lu and Sc (large standard deviations) could be due to errors in recording the gamma counts (geometry errors, spectrum processing etc.), inhomogeneous standards, weighing errors or simply, incorrect, or, at least, non-internally consistent values of the concentrations of the elements in our "Master Table". To investigate this we standardized the constants in Table 2 by dividing each constant by the corresponding geometric mean. For example, the six values for Fe become 1.006, 0.978, 1.034, 0.986, 0.992 and 1.008 when standardized, while the four values for Lu become 1.70, 0.96, 0.81 and 0.76. Then we similarly standardized all the elementary constants, in tables similar to Table 2, resulting from a whole series of bombardments in each of which the six USGS rocks were included. Altogether, about 50 data sets, one from each bombardment, were processed. We felt that this unique data set probably would furnish the best possible self-consistent sets of elementary concentration ratios in the six USGS rocks that could be obtained.

In the final step, for each element and for each rock the standardized constants were arithmetically averaged, and the standard deviation and standard error in this quantity calculated, across the whole set of ~50 bombardments. The results of this exercise are presented in Table 3, where the "mean ratios" are the means of the 50 or so values of the ratio of the calibration coefficient for each standard to the geometric mean for 6 (or 4) standards, as given for Fe and Lu in the example just above.

Our choices of values for the concentrations of elements in the "Master Table" are very directly reflected in the closeness with which the "mean ratio" entries in Table 3 approach each other, and unity. For example, the six values for Fe are 0.995, 0.995, 1.013, 1.006, 0.998, and 0.995, each with an error of $\text{ca}\pm 0.004$ (Table 3). Obviously we have chosen for our "Master Table" a set of iron concentrations that are internally highly self-consistent. But each of those six concentration choices was made independently, by statistically treating some 30-40 independent iron values reported by Flanagan (1976) from nearly that number of laboratories, using methods as diverse as emission spectroscopy, atomic absorption, titration, neutron activation and XRF to establish their absolute iron concentrations. Is it too much to think that we have here a very close approach to the true concentration values?

Looking through Table 3 we can see that, like iron, there are other "well-behaved" elements. These would include Fe, Th, Cr, Na, K. In this group, the standard deviation taken across the 6, 4 (or 2 for Cr) mean ratios are around 1% - indicating that, for these elements, our "Master Table" values are highly internally consistent. Mn would also belong to this group except for G2, where we have obviously taken too large a standard concentration. Doing almost as well is a group where the ratios agree at a level of 2-4%. This would include Co, Ba, Sm, Mn. Then there is a group in the 7-10% standard deviation range, Eu, Hf, Ta, Sb, Zn, Ca, Yb, Sc, Cs, Ce, La. Finally there is the atrocious Lu, with a standard deviation of 38%: the standard deviation values discussed here correspond in a certain average sense to the values listed, in the case of a particular

bombardment, in the next to last column to the right in Table 2.

Thus far, I have discussed only the mutual consistency of concentration values more or less arbitrarily chosen by us for our "Master Table". But Table 3, based as it is upon the six-way intercomparison of standards repeated 50 or more times with many variables and errors randomized, can equally well, by a slight mathematical manipulation, enable us to test any other table of concentration values, and to compare its consistency with that of our "Master Table". In Table 4 the BNL mean ratios for scandium (Table 3) are recomputed to what they would have been had they been based on the "best literature" values of Katz and Grossman (1976, Table 56), the final least-squares fitted values of the same authors (Table 57), the Flanagan 1972 compilation "Estimates" (Flanagan, 1976, Table 107) and to a synthesis of self-consistent ratio-determined values, taking an arbitrary value for BCRI.

To test the internal consistency of the various choices of concentrations mentioned above, one need only calculate, as before, the standard deviation of the six ratios. These are given in Table 4 below the mean ratios: the results indicate that the Katz-Grossman least-squares fitted values are a substantially better choice of scandium concentrations than our "Master Table", that the Flanagan 1972 values are the least consistent, and that it is possible, by using our average observed ratios of line intensities, to calculate a set of values that are very, very self-consistent. This last set is based on Sc_2O_3 in BCRI arbitrarily equal to 50.28 ppm. Any change in this figure would require a proportionate change in the other five standards.

Table 4

Internal Consistency of Various Choices for Concentrations of
 Sc_2O_3 in Six USGS Rock Standards

| Standard Rock | Concentrations of Sc_2O_3 | | | | | Mean Ratios | | | | |
|------------------|---|----------------------------|-----------|-------------------------------------|---|-----------------|---------------|-----------|----------|--------------------------------|
| | Master Table ^a | Katz-Grossman ^b | | Flanagan ^c | Based on Gamma Intensity ^d | Master Table | Katz-Grossman | | Flanagan | Based on Gamma Intensity |
| | | Best Lit. | Least Sq. | | | | Best Lit. | Least Sq. | | |
| PCG1 | 12.55 | 12.73 | 12.58 | 10.58 | 12.67 | 1.1020 | 1.0508 | 1.0460 | 1.2461 | 1.0063 |
| GSP1 | 12.19 | 10.94 | 10.28 | 10.89 | 9.22 | .8208 | .8845 | .9260 | .8758 | 1.0009 |
| DTS1 | 5.89 | 5.45 | 5.38 | 5.52 | 5.37 | .9829 | 1.0274 | 1.0239 | .9997 | .9939 |
| BCR1 | 49.93 | 51.39 | 50.62 | 50.62 | 50.28 | 1.0983 | 1.0320 | 1.0308 | 1.0326 | 1.0054 |
| AGV1 | 18.19 | 18.87 | 18.71 | 20.55 | 18.44 | 1.1061 | 1.0312 | 1.0232 | 1.1911 | 1.0059 |
| G2 | 6.12 | 5.57 | 5.64 | 5.68 | 5.29 | .9368 | .9954 | .9672 | .8288 | .9992 |
| | | | | Standard Deviation, as % of mean | | 11.6 | 6.1 | 4.6 | 16.6 | 0.5 |

a. Abascal et al., 1974

b. Katz and Grossman, 1976. "Best Literature" is Table 56. "Least Squares" is Table 57.

c. Flanagan, 1976 Table 107

d. A set whose values are calculated from ratios of scandium gamma ray intensities, averaged over 45 intercomparisons, with BCR1 arbitrarily taken to have $\text{Sc}_2\text{O}_3=50.28$ ppm.

e. Table 3

It may be argued that this last set is "good" by circular methods: the same procedures are used to generate and then to test the numbers. This is certainly so, but that is the goal: to find a set that will be consistent with the gamma intensities, as expressed through the mean ratios. However, the data processed in Table 3 can tell us more than a message about mutual consistency of concentrations: it can also provide a measure of precision.

The 50 or so intercomparison runs that form the basis of Table 3 each involved the preparation of samples of each of six different standards by drying and precise weighing (about 40 mg.), bombardment together, but not in any very precisely-defined geometry, counting in a geometry that was made to be the same, as well as possible, for all six, processing the spectra, correction for various periods of decay, and various degrees of dead time in the counting device etc. All these error sources, including the ever-present counting statistics, along with the more subtle possibility of inhomogeneity in the standards themselves, are included in the "standard deviation" values in the Table: this is the square root of the variance in the distribution of ratios sampled by the 50 intercomparison runs, and measures the variance to be expected in a real laboratory (namely, BNL) working day-to-day with routine neutron activation analysis procedures.

As expected, the elements present in large concentration and well-activated (Fe, Cr, Na) show standard deviations that are small, averaging 2.7, 3.3 and 3.6% respectively. A number of other elements, though present at trace concentrations, show small standard deviations: Sc, Ba, Ce, La (Table 3). These relatively small values

reassure us that the elements themselves must be reasonably homogeneously distributed in the samples of standard rock supplied to us by the USGS.

Several elements, though present at large concentrations (K, Ca) show substantial standard deviations. In these cases the lack of precision is surely not due to inhomogeneity but, very simply, to the weak activation of the radioisotope of interest, leading to poor counting statistics. The same is, at first sight surprisingly, true of Mn: although this element is strongly activated, our counting procedures result in some standards being counted when the Mn^{56} has already much decayed: it has a short half-life.

In summary, it would appear that the best routine precision attainable at BNL is around ± 2.5 to 3%: of this standard deviation I would guess that about 1% is due to the spectrum processing and counting statistics, and the (combinatorially speaking) remainder comes from many small errors such as counting geometry and flux gradient.

The discussion of analytical precision and self-consistent standards has perhaps been over-long: what we are concerned with is what effect this may have on application of the analyses to provenience location. Reverting to questions (a)-(d) asked earlier, of which we answered (c) in advance, it would appear that the available intralaboratory precision is adequate at present. (Question (b)). "Natural" groups rarely have a uniformity of under 8-10%: more typically they are 15-20%. Sampling and measurement error inevitably add something to this (see std. deviations in Table 3) but the measured extension of the multivariate group is close enough to the

natural variance to yield, in most cases, a significant resolution from neighboring groups. A more subtle reason for seeking enhanced analytical precision is that many natural ceramic clays have highly correlated element pairs and multiplets. These correlations, operating through factor and discriminant analysis provide a powerful tool for the resolution of closely-similar archaeological groups (Harbottle, 1976): the methods work better, the more nearly the analysis reveals the full extent of correlation.

From the practical standpoint, analytical precision is a trade-off with production. If you wish to analyze many samples, you can only count each one for a certain time, and that determines the statistical error.

Question (d), the placing of samples by a second laboratory, using their own standard, into a multivariate group established by the first laboratory, with their (different) standards, is the crux of this essay. I believe that we are already quite close to valid interlaboratory data exchange. At BNL we have analyzed, as mentioned above, 161 sherds of "Nile Mud" ware (Kaplan, 1978). Perlman and Asaro (1971, Table 13.6) report the analysis of 32 sherds of "Nile Mud" -- and it must be remembered that these are different sherds from ours, coming from different proveniences. Nonetheless, it will be seen in Table 5 that there is a high degree of correspondence, with no attempt made to adjust for differences in the two standardization techniques. If, at our present state of experience we examined the data in Table 5, with no knowledge of the material analyzed, we would have a strong suspicion that we are both dealing with the same pottery paste type.

Table 5

Concentrations of Oxides in "Nile Mud" were
measured in Two Laboratories

| Element Oxide | Berkeley ^a n = 32 | BNL ^b n = 161 | |
|--------------------------------|---------------------------------|-----------------------------|-----|
| MnO | 1555 ± 88 | 1545 ± 540 | ppm |
| La ₂ O ₃ | 38.4 ± 2.0 | 33.8 ± 4.5 | ppm |
| Fe ₂ O ₃ | 9.75 ± .50 | 9.74 ± .94 | % |
| Sc ₂ O ₃ | 35.45 ± 1.47 | 36.2 ± 3.7 | ppm |
| CoO | 44.45 ± 2.0 | 42.9 ± 5.6 | ppm |
| Cs ₂ O | 1.47 ± .22 | 1.54 ± .48 | ppm |
| HfO ₂ | 10.22 ± .88 | 7.46 ± 1.21 | ppm |
| ThO ₂ | 7.90 ± .56 | 7.25 ± .90 | ppm |
| Na ₂ O | 1.80 ± .29 | 1.70 ± .42 | % |
| Cr ₂ O ₃ | 264 ± 23 | 226 ± 46 | ppm |
| BaO | 550 ± 83 | 592 ± 169 | ppm |
| Rb ₂ O | 66.7 ± 7.7 | 53.4 ± 13.1 | ppm |

^aPertlman and Asaro, 1971, Table 13.6

^bKaplan, 1978

Table 6

Concentrations of Oxides in Mycenaean Sherds
Measured in Three Laboratories^a

| Element Oxide | Berkeley ^b | BNL ^c | Mycenae Subgroup | | McGill ^d |
|--------------------------------|-----------------------|------------------|------------------|----------|---------------------|
| | n = 16 | 1 n=13 | 2 n=10 | 3 n=6 | n=45 |
| Rb ₂ O | 159 ± 15 | 164 | 126 | 142 | 139 |
| Cs ₂ O | 9.8 ± .9 | 8.8 | 6.3 | 7.6 | 9.6 |
| Sc ₂ O ₃ | 32.4 ± .9 | 34.8 | 30.3 | 34. | 33.4 |
| La ₂ O ₃ | 40.0 ± 1.4 | 39.8 | 36.1 | 39.1 | 39.9 |
| Lu ₂ O ₃ | .425 ± .018 | .51 | .49 | .50 | .457 |
| ThO ₂ | 12.2 ± .4 | 13.4 | 11.6 | 13.0 | 13.2 |
| HfO ₂ | 3.78 ± .4 | 3.64 | 3.72 | 3.69 | 4.65 |
| Ta ₂ O ₅ | 1.00 ± .05 | 1.22 | 1.20 | 1.27 | 1.11 |
| Cr ₂ O ₃ | 323 ± 20 | 340. | 352. | 324. | 418. |
| Fe ₂ O ₃ | 7.38 ± .26 | 7.51 | 6.70 | 7.63 | 7.89 |
| CoO | 35.9 ± 1.8 | 36.7 | 36.3 | 35.0 | 39.4 |
| BaO | | 427 | 502 | 444 | 1028. |
| CeO ₂ | | 81.9 | 73 | 82.7 | 78.7 |
| Eu ₂ O ₃ | | 1.62 | 1.55 | 1.56 | 1.46 |

^aAll concentrations in ppm, except Fe₂O₃, %

^bKarageorghis et al., 1972 p. 196 (Asaro-Perlman std.)

^cBieber Jr. et al., 1976a, 1976b (6 USGS Rocks)

^dAttas et al., 1977, Table 3 (Asaro-Perlman std.)

Another example, the analysis of three completely different groups of Mycenaean sherds in three laboratories, is given in Table 6. Again, no adjustment for standardization was made, and good similarity is noted.

Still another example concerns analyses of ceramics from Cerro Portezuelo in Mexico, carried out by Branstetter (1979) at Berkeley. She kindly forwarded her data to us, and when it was examined it was found that her main group was readily recognizable as our "Valley of Mexico" composition (Abascal et al. 1974, Harbottle and Sayre, unpub.).

In the past the conversion of one laboratory's analyses to another's standardization has often been discussed, and the proposal has usually been either (a) for everyone to use the same standard or (b) to exchange and mutually analyze each other's standards and thus arrive at a matrix of intercomparisons. I now feel that (a) is impractical in that there is already so much data referenced to existing standards, and that (b) is useful, but only as an interim measure. In fact, at BNL we are at present engaged in a project to provide an intercomparison between the Asaro-Perlman and 6 USGS rocks standards, carried to the highest possible precision. My new proposal is that, given the kind of data seen in Tables 5 and 6, what we should aim for is that anyone wishing to analyze archaeological ceramics should simply use his own standard, but attempt to calibrate that standard as nearly as possible to absolute (i.e. accurate) concentration values. The proposal arises not merely from the fact that we seem to be approaching absolute calibrations anyhow, but also from the accumulation of error that results from procedure (b).

If laboratory A using standard M wants to compare analyses with laboratory B using standard N then we have comparisons of not merely samples to standards but M to N also, with errors adding up all along the line. The same argument applies to the idea of a new, universal standard. If existing standards are calibrated to a higher absolute accuracy, on the other hand, I believe that they will be quite adequate in permitting meaningful intercomparison. Of course, the exchange of reference material should continue, but the goal should be not the overall shifting of all of A's analyses to B's standards but rather the pointing up and elimination of errors or discrepancies in all standardization systems.

The important question is, "will this every-man-for-himself" procedure really provide data adequate for the archaeometrist to establish ceramic provenience?" I believe that it will, after the discrepancies are ironed out. I base this belief on our experiences in studying a large number of archaeological "systems", i.e. geographic areas in which several ceramic groups involving tempered and/or untempered pastes have been analyzed and resolved from one another, and on our recent use of a "search" computer program, UPDPL (Bernstein, unpub.). In this program, with which we are only beginning to gain experience, the analytical data for a specimen for which the archaeologist wishes to establish origin, or to match with other ceramic specimens, is considered element-by-element. The concentration in each element is taken as the center of a plus-minus range which can be specified. For example, if the iron concentration is 5% and the range is set at $\pm 10\%$, then any other specimen is a "match" if its iron concentration falls between 4.5 and 5.5%. The

program then searches the entire data bank, utilizing as many elements as desired, and records those specimens which are "hits" i.e. fall within the specified ranges for all elements, or have one or two "misses" -- i.e. agree on all but one or two elements. These are recorded, as are "hits" and "misses" in which the error ranges are increased by a specified factor -- let us say a factor of two, to $\pm 20\%$.

What we are finding is that, at least in the few examples studied, if the ranges are set at $\pm 5\%$ and the search is carried out through a few thousand Old-World analyses, there are almost no authentic "hits" and certainly no accidental ones, if about 15-20 elements are being considered. At a level of $\pm 10\%$ there are still very few accidentals. At $\pm 20\%$ one begins to see matches, and if the sherd happens to belong to a well-defined group, for example Attic Black Glaze, many hits, with none, one and two misses, are recorded from members of that group. It must be emphasized that the search algorithm in UPDPL is Euclidean, that is, the groups are assumed to be spherical in multidimensional space. The actual ellipsoidal shape would further reduce the chance of accidental "hits", if one were to incorporate that feature.

It is not difficult to see why there are so few accidentals even with rather broad "error" ranges: Sneath and Sokal (1973, pp 124-5) have demonstrated how an increase in the number of dimensions in a multivariate coordinate system decreases the variance in the expected Euclidean distances between points, hence "tightens" the grouping.

This, then, is the bottom line on both the "Provenience Postulate" (Weigand et al., 1977) and the accuracy of analysis

needed. If enough elements are analyzed, the Provenience Postulate, which amounts to a statement about the relative sizes of within-groups and between-groups multivariate variance, is more readily fulfilled. Because the "accidentals" occur so infrequently in a population of ceramic analyses searched at the $\pm 10\%$ level, it would seem that, for intercomparison of data, absolute standardizations may not have to agree down to $\pm 1\%$. It may well be that more modest levels of accuracy -- perhaps, ± 3 to 5% , are perfectly adequate. In any case, we are already in a position to put these questions to the test, given the size of the Old- and New-World data banks on hand.

In closing, and because there are so many archaeologists present, it is worth mentioning tempered ceramics as a separate class. Temper analysis alone is often not adequate for unequivocal provenience assignment. We make use of it however as a preliminary separator of great value -- in other words, if the ware is carbonate-tempered, for example, we try not to insert it into taxonomical procedures involving classes of non-tempered wares. On the other hand, a knowledge of the type and quantity of the temper is enormously helpful in connecting the clay-matrix portion of the ceramic to its proper fine-paste grouping or raw-clay provenience (Bishop, 1980).

Although the limits tend to be somewhat broader, many of the procedures ordinarily used in the formation and testing of ceramic groups will work equally well with tempered wares. Our extensive investigations of Thin Orange and Granular wares from Mexico are in this category. The assignment of tempered wares to clay source is, however a much more difficult problem.

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Table 3. Mean Ratios of Elementary Calibration Constants to Geometric Means

| Element Oxide | Number of Runs | Standard | DTS1 | GSP1 | PCC1 | BCR1 | AGV1 | G2 | Std deviation of mean ratios as % of mean |
|--------------------------------|----------------|---------------|--------|--------|--------|--------|--------|--------|---|
| Eu ₂ O ₃ | 45 | Mean Ratio | | .9143 | | 1.0316 | 1.0961 | .9832 | 7.4 |
| | | Std Deviation | | .0609 | | .0677 | .0616 | .1059 | |
| | | Std Error | | .0090 | | .0101 | .0091 | .0157 | |
| Lu ₂ O ₃ | 39 | Mean Ratio | | 1.5797 | | 1.0781 | .8054 | .7502 | 38. |
| | | Std Deviation | | .1554 | | .1712 | .0902 | .0805 | |
| | | Std Error | | .0248 | | .0274 | .0144 | .0129 | |
| HfO ₂ | 49 | Mean Ratio | | 1.1491 | | 1.0083 | .8948 | .9681 | 10.7 |
| | | Std Deviation | | .0753 | | .0550 | .0318 | .0556 | |
| | | Std Error | | .0107 | | .0078 | .0045 | .0079 | |
| ThO ₂ | 50 | Mean Ratio | | .9912 | | 1.0059 | .9886 | 1.0087 | 1.0 |
| | | Std Deviation | | .0476 | | .1006 | .0414 | .0360 | |
| | | Std Error | | .0067 | | .0142 | .0058 | .0051 | |
| Ta ₂ O ₅ | 41 | Mean Ratio | | .9264 | | 1.0434 | | 1.0532 | 7.1 |
| | | Std Deviation | | .1204 | | .1209 | | .1087 | |
| | | Std Error | | .0188 | | .0188 | | .0169 | |
| Cr ₂ O ₃ | 45 | Mean Ratio | 1.0102 | | .9954 | | | | 1.0 |
| | | Std Deviation | .0303 | | .0359 | | | | |
| | | Std Error | .0045 | | .0052 | | | | |
| Fe ₂ O ₃ | 50 | Mean Ratio | .9954 | .9949 | 1.0130 | 1.0061 | .9979 | .9947 | 0.76 |
| | | Std Deviation | .0251 | .0257 | .0282 | .0330 | .0250 | .0269 | |
| | | Std Error | .0035 | .0036 | .0039 | .0046 | .0033 | .0038 | |
| CoO | 44 | Mean Ratio | 1.0503 | .9691 | 1.0348 | 1.0218 | .9960 | .9401 | 4.2 |
| | | Std Deviation | .0329 | .0852 | .0438 | .0449 | .0377 | .0426 | |
| | | Std Error | .0049 | .0128 | .0066 | .0067 | .0056 | .0064 | |
| Sb ₂ O ₃ | 44 | Mean Ratio | | 1.0600 | | | .9495 | | 7.8 |
| | | Std Deviation | | .0801 | | | .0814 | | |
| | | Std Error | | .0120 | | | .0122 | | |

| | | | | | | | | | |
|--------------------------------|----|---------------|--------|--------|-------|--------|--------|--------|------|
| ZnO | 28 | Mean Ratio | 1.2100 | .9198 | .9962 | 1.1026 | .9804 | .8689 | 12.4 |
| | | Std Deviation | .1066 | .0555 | .0695 | .0986 | .0743 | .0872 | |
| | | Std Error | .0201 | .0105 | .0131 | .0215 | .0140 | .0164 | |
| CaO | 37 | Mean Ratio | | 1.0593 | | 1.1160 | .9596 | .9109 | 8.9 |
| | | Std Deviation | | .1897 | | .1328 | .0696 | .1097 | |
| | | Std Error | | .0311 | | .0228 | .0114 | .0180 | |
| Yb ₂ O ₃ | 52 | Mean Ratio | | | | 1.0337 | 1.0852 | .8994 | 9.6 |
| | | Std Deviation | | | | .0642 | .0642 | .0734 | |
| | | Std Error | | | | .0088 | .0089 | .0101 | |
| Na ₂ O | 62 | Mean Ratio | | .9839 | | 1.0179 | 1.0033 | .9970 | 1.4 |
| | | Std Deviation | | .0326 | | .0460 | .0373 | .0331 | |
| | | Std Error | | .0041 | | .0050 | .0047 | .0042 | |
| K ₂ O | 53 | Mean Ratio | | .9969 | | 1.0289 | .9996 | .9931 | 1.6 |
| | | Std Deviation | | .0716 | | .1025 | .0769 | .0618 | |
| | | Std Error | | .0098 | | .0140 | .0105 | .0084 | |
| Sr ₂ O ₃ | 46 | Mean Ratio | 1.1020 | .8207 | .9829 | 1.0982 | 1.1067 | .9367 | 11.6 |
| | | Std Deviation | .0353 | .0225 | .0265 | .0435 | .0296 | .0273 | |
| | | Std Error | .0052 | .0033 | .0039 | .0064 | .0043 | .0040 | |
| Rb ₂ O | 43 | Mean Ratio | | 1.0026 | | 1.0253 | 1.0208 | .9751 | 2.3 |
| | | Std Deviation | | .0541 | | .1346 | .0785 | .0681 | |
| | | Std Error | | .0082 | | .0205 | .0119 | .0103 | |
| Cs ₂ O | 38 | Mean Ratio | | 1.0042 | | .8876 | 1.0261 | 1.1263 | 9.8 |
| | | Std Deviation | | .1254 | | .1395 | .1077 | .1149 | |
| | | Std Error | | .0203 | | .0226 | .0174 | .0186 | |
| BaO | 45 | Mean Ratio | | 1.0036 | | .9600 | 1.0063 | 1.0359 | 3.1 |
| | | Std Deviation | | .0400 | | .0507 | .0326 | .0455 | |
| | | Std Error | | .0059 | | .0090 | .0057 | .0064 | |
| CeO ₂ | 54 | Mean Ratio | | .9692 | | 1.1700 | .9002 | .0786 | 11.8 |
| | | Std Deviation | | .0382 | | .0877 | .0415 | .0382 | |
| | | Std Error | | .0052 | | .0088 | .0056 | .0052 | |

| | | | | | | | |
|--------------------------------|----|---------------|-------|--------|--------|--------|------|
| Li ₂ O ³ | 51 | Mean Ratio | .8822 | 1.0424 | 1.1124 | .729 | 10.1 |
| | | Std Deviation | .0308 | .0313 | .0606 | .0393 | |
| | | Std Error | .0043 | .0071 | .0084 | .0055 | |
| Sm ₂ O ₃ | 20 | Mean Ratio | .9499 | 1.0057 | 1.0210 | 1.0332 | 3.7 |
| | | Std Deviation | .0832 | .0557 | .0498 | .0647 | |
| | | Std Error | .0186 | .0124 | .0111 | .0144 | |
| MnO | 40 | Mean Ratio | .9842 | 1.0292 | 1.0061 | .9399 | 3.2 |
| | | Std Deviation | .0557 | .0533 | .0585 | .0650 | |
| | | Std Error | .0132 | .0084 | .0092 | .0102 | |

³The Master Table values differ from those published in Abascal et al., 1974. We now use for Li₂O₃ in GSP1 244.4, BCR1 29.6, AGV1 42.5 and G2 108 ppm.