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D. F. Mosier

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Comparison of Neutron Activation Analysis

from the

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and

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Introduction

Among the various spectroscopic techniques employed in provenience studies of ancient pottery, neutron activation analysis (NAA) employing gamma-ray spectroscopy seems to be the most suitable analytical technique. NAA has been extensively applied to provenience studies over the past several years and a growing body of literature testifies to its success. Representative studies will be found in Refs. 1-5. Much of the information for judging pottering provenience lies in the trace elements and NAA has the requisite sensitivity and precision for measuring many of these. The multielement capability, the ease of sample preparation and large volume capability make NAA particularly suitable for pottery analysis.

This method of elemental analysis has another important feature; it is possible, by experiment, to evaluate the various sources of error because the method is comparatively insensitive to the chemical matrix which influences electronic transitions but not nuclear transitions. In NAA one is concerned only with the proper analysis of nuclear transitions and with certain geometrical factors which can be precisely controlled. This is not to say that NAA can give accurate results on a complex mixture of elements without the expenditure of considerable effort in working out the many details involved in gamma ray spectra analysis and data processing.

A question which naturally arises has to do with the accuracy required of the analytical data if it is to be useful in judging pottery provenience. Examination of the grouping of analytical data within a pottery source indicate that, if the measuring error itself is not to be a major source of the

observed dispersion an accuracy of about 5% is needed. In cases where systematic errors exist valuable information may be lost unless the accuracy is much better than 5%. Such considerations dictate an accuracy of about 2% for a major fraction of the elements measured.

Precision of measurement of the order of 2% has been well demonstrated in individual laboratories but, to our knowledge, the ability to reproduce results between different laboratories has not been demonstrated. This point is crucial since otherwise the results of researches performed at different laboratories cannot be directly related. If NAA is to become a universal method of pottery analysis, interlaboratory comparisons are imperative.

We report here some representative data from a study on the inter-comparability of NAA results obtained in the laboratory at the Institute of Archaeology of the Hebrew University (HU) and results obtained at the Lawrence Berkeley Laboratory (LBL). The study centered on a group of six specimens of pottery and rocks analyzed at both laboratories. (A detailed report on the entire study will be published elsewhere). Some of the instruments and modes of operation of the analytical systems differed considerably but the two laboratories employed the same material for the multi-element standard. In the fine comparison of results which follow we are testing the intrinsic reliability of NAA in complicated mixtures of elements. Since both laboratories employed the same standard, any errors in the composition of the standard would cancel. The absolute values reported here need not agree exactly with another laboratory employing a different standard which has not been calibrated against ours. There is an obvious value in intercalibrating

standards and knowing what is to be expected when different standards are used as well.

Among the published and unpublished analysis of pottery in LBL there are several thousand which could be pertinent to problems which are investigated at HU. The immediate consequence of the present study is the determination of how closely the analysis at one laboratory would agree had they been analyzed at the other. This means that HU can utilize directly and build upon the LBL analysis, a saving of literally years of work. Conversely, LBL can utilize a growing body of analytical data on pottery and rocks which is being accumulated in HU.

Results

The six pottery and rock samples encompass diverse compositions, and for present purposes, need not be identified as to type or source. We are here not concerned with provenience but with how closely an LBL compositional analysis agrees with an HU compositional analysis of the same material. Both laboratories followed similar procedures for sample preparation to insure uniform sample size. Standards received equal exposure to neutrons. These procedures have been previously described (1). Two standards were employed by each laboratory for the measurements.

The characteristics of the gamma-ray spectrometers employed at the two laboratories are different and consequently there are important differences in the operating procedures, as well as in the data reductions. A discussion of the operating procedures and instructions for analyzing the spectra as practiced in the two laboratories involves far too many details to deal with briefly, but will appear in the full report.

Presently, we report data on only six elements of which five are trace elements. The elements selected are: europium (Eu), scandium (Sc), cesium (Cs), thorium (Th), tantalum (Ta) and iron (Fe). These elements were selected from a much larger group of elements which are determined routinely as they have a diversity of problems having to do with gamma-ray interferences and background determination. Differences in the two analyzing systems necessitate different data processing instructions and this makes for a more rigorous test.

The analyses in each laboratory have undergone extensive internal consistency tests. For example, Sc was determined from two different gamma-rays, one of which has an interference from Ta. Tantalum too was determined from two gamma-rays employing two different spectrometers in each laboratory. Our concern in conducting this intercomparison was to see how well self-consistent results from each of two quite different analytical systems can agree with each other. The results of the HU and LBL analysis for each of the six specimens are shown in Table 1. The error shown for each number is simply the "counting error" (one standard deviation) given by the statistics of counting nuclear radiations. This error includes the counting error of the standards since counting the standards is an ingredient in the analysis. The counting statistics gives an irreducible dispersion which differs from element to element. In some cases it is less than 1% and in others considerably more.

In addition to the counting errors there are other sources of random errors which are associated with parameters which can be controlled; sample weighing, geometry of sample relative to the gamma-ray detector, and uniformity

of neutron exposure between sample and standards. It has been shown by experiments that in routine operations the sum of these errors is less than 1%. We shall assume, therefore, that agreement is satisfactory if it is less than 1%, or if it lies within counting statistics — whichever is greater.

Any disagreement beyond the above mentioned limits must be attributed to failure by one or both laboratories to determine accurately the net counts in the respective gamma-ray peaks. The failure to determine accurately the net counts in a peak could be due to a multitude of possible errors which are difficult to assess with high accuracy by experiments on a single analyzing system. These errors are likely to be systematic rather than random. One such source of error, and often the most important one, has to do with the method used to determine the background under each gamma-ray peak. Another source of systematic error has to do with corrections for peak broadening which are a function of total count rate, and the distribution of these counts among gamma rays of different energies. Still another systematic error arises from the manner in which interference corrections are handled. The manner in which these various problems are handled is different for each analyzing system and the present comparison is aimed at seeing how well this has been done. To the extent that the results agree between the two laboratories, both have coped successfully with these problems. A great deal of effort is expended in working out these many details but once this has been done, the analysis and data processing proceed routinely. In both the HU and LBL systems the equipment is automated and the data are processed by computer.

Discussion

The first three samples (CIN5, CIN8, KERMI) are pottery specimens while the last three (BISH25, BISH26, BISH27) are the rock samples. At HU all samples were irradiated at the same time and employed the same standards in the measurements. At LBL the pottery and rock samples were irradiated separately and consequently two sets of standards were employed in the measurements. As stated above, all measurements have undergone extensive self consistency tests. For the elements shown these tests consisted of determinations based on different gamma-rays as well as measurements performed on the same gamma-rays but at different times. Moreover, different detectors were employed at each analytical facility for low energy and high energy gamma-rays. For example, Eu was determined both from the 122Kev gamma-ray of Eu^{152} and from the 1408Kev gamma-ray of Eu^{152} . A different detector was employed for each gamma-ray. For each element there is a best determination. The best measurement is usually but not necessarily the measurement with the lowest counting error. Exceptions occur where there is uncertainty due to interferences or some other corrections, or where the background is high. Thus, for example, the preferred measurement of Sc is based on the 1121Kev gamma-ray of Sc^{46} despite the fact that another measurement based on the 890Kev gamma-ray of the same isotope gives a slightly lower counting error. The lower energy gamma-ray peak has a much higher background associated with it and consequently the Sc measurement based on this gamma-ray is more sensitive to how the background is handled.

The elemental abundances shown in Table 1 for the HU measurements are based on the best determinations. The LBL abundances too are based on the

best determinations or in some cases weighted mean values of best determinations. The LBL analytical program is more extensive than the HU program and some elements were determined with comparable precision in more than one measurement so that a weighted mean value could be used. This applied particularly to the rock specimens.

The agreement of the HU and LBL results is rather remarkable when one considers the classic failure of analytical laboratories to agree in their measurements, often by wide margins. Furthermore, this agreement coupled with our accumulated experience in judging provenience of pottery and rocks tells us that no errors would be made in making such judgements if we use each others' data. However, if we consider the limits of accuracy of the analytical method per se, we find that there are still some unresolved problems. In some instances the known errors of measurement are very small and the differences obtained in the two laboratories are outside of the statistical limits. This means that further effort is still required to understand fully all of the details of analyzing such complex spectra.

In mentioning unknown errors, it should be pointed out that the samples used for analysis were not necessarily identical in composition. Each specimen was ground to a powder and single 100mg. samples removed from the vials. There is no guarantee that the powders were uniform in composition for all elements within the limits of the small counting errors.

All of these uncertainties aside, it is worthwhile to state a figure for the agreement between the two sets of measurements on the basis of the present spectral analysis. This can be done by removing the counting errors from the difference between each paired result, and the remaining difference

expressed as a per cent of the measured value. The average of these residual errors for the 36 paired results can then serve as an index of disagreement for reasons not yet known. In some instances the two results agreed (accidentally) better than the counting statistics, in which case the residual error becomes negative. For such cases, the residual error is taken to be zero. When this calculation was made, it was found that the average residual disagreement for the 36 pairs was 1.1%. Although this disagreement is insignificant for provenience studies, it does show that there are small differences which are not yet understood.

Conclusion

The study reported here shows unequivocally that elemental abundances measured by NAA at HU and LBL agree very well. This agreement means in the first instance that HU and LBL can utilize each others data base with great confidence. It means that a great deal of duplication and time can be saved. But beyond that, it means that any other NAA facility can relate its results to HU or LBL if the respective standards are intercalibrated and the gamma-ray spectra handled properly. The different systems and operational modes used in the present study and the many analyses performed could not have agreed unless the NAA technique was inherently reliable.

Table 1

Comparison of Hebrew University and Lawrence Berkeley Laboratory
Abundance Measurements by Neutron Activation¹

Element	CIN5	CIN8	KERM1	BISH25	BISH26	BISH27
²						
Eu	1.468±0.022	1.423±0.021	1.975±0.027	0.045±0.007	0.344±0.009	0.174±0.007
	1.498±0.013	1.432±0.013	2.031±0.018	0.047±0.005	0.350±0.005	0.172±0.004
Sc	20.08 ± 0.04	19.19 ± 0.04	23.56 ± 0.05	3.049±0.012	1.912±0.009	1.863±0.009
	20.10 ± 0.06	19.23 ± 0.06	24.07 ± 0.07	2.954±0.013	1.854±0.009	1.810±0.009
Cs	7.05 ± 0.23	6.81 ± 0.22	1.14 ± 0.17	5.69 ± 0.15	2.05 ± 0.08	2.66 ± 0.08
	7.41 ± 0.26	7.24 ± 0.25	1.59 ± 0.24	5.38 ± 0.09	2.06 ± 0.06	2.71 ± 0.06
Th	14.47 ± 0.08	13.67 ± 0.08	6.44 ± 0.06	19.87 ± 0.08	12.29 ± 0.06	12.82 ± 0.06
	14.58 ± 0.14	13.84 ± 0.13	6.21 ± 0.12	20.34 ± 0.07	12.23 ± 0.05	13.25 ± 0.05
Ta	1.336±0.024	1.207±0.023	1.438±0.026	2.055±0.033	0.811±0.015	1.023±0.018
	1.33 ± 0.01	1.24 ± 0.01	1.42 ± 0.01	2.01 ± 0.01	0.81 ± 0.01	1.02 ± 0.01
Fe%	5.35 ± 0.06	5.15 ± 0.06	7.04 ± 0.08	0.567±0.008	0.845±0.011	0.629±0.008
	5.44 ± 0.07	5.15 ± 0.07	7.17 ± 0.09	0.547±0.007	0.824±0.008	0.594±0.007

¹ The numbers are in ppm except for Fe which is in percent. The best values for the amounts of these elements present in the Standard pottery are: Eu, 1.291; Sc, 20.55; Cs, 8.31; Th, 13.96; Ta, 1.550; Fe, 1.017%.

² The top entries are HU values and the lower values are the LBL values.

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