

7. Comparison of Data Obtained by Neutron Activation and Electron Microprobe Analyses of Ceramics

SUZANNE P. De ATLEY,
M. JAMES BLACKMAN, and
JACQUELINE S. OLIN
Conservation Analytical Laboratory
Smithsonian Institution

1982

Introduction

In general, chemical analyses of ceramic composition have focused on trace elements because, on the whole, they most readily facilitate discrimination among ceramics from different areas. However, there are types of problems which benefit from an understanding of the major and minor element composition of the constituent clays and tempers, since these can affect the various properties of the finished vessel. It is in this respect that the use of the electron microprobe in the analysis of archaeological or art historical samples can provide data which is supplementary to that obtained using other analytical methods. The microprobe is especially useful in conjunction with petrographic studies to obtain compositional data for specific constituents within the ceramic body. In addition, the demonstrated utility of the microprobe for major element whole-rock analysis (Arrhenius et al. 1964; Gulson and Lovering 1968; Rucklidge et al. 1970; Reed 1970; Mori et al. 1971; Nicholls 1974) suggests that such an approach also may be applicable to ceramic materials and may provide a method of analysis that is less time consuming than a method such as atomic absorption spectrometry. This paper describes procedures of sample preparation which may be used to obtain quantitative bulk composition data on ceramic samples and the problems and advantages of each. The data obtained to date are compared to those from samples analyzed by neutron activation analysis for elements which can be determined by both methods. The comparability of results is considered to be important in anticipation of the reporting and use of the results of such analyses in data banks and in combining the results obtained by different methods.

Procedure

Archaeological ceramics from southwestern United States and southwestern Iran and also Mexican and Spanish majolica ceramics were analyzed by instrumental neutron activation analysis and by electron microprobe using several different preparation methods.

Samples for neutron activation analysis were drilled from the edges of sherds using clean tungsten carbide bits. When possible, at least one gram of sample was taken. Each sample was thoroughly mixed and subsampled for analysis. Irradiation and counting of the samples were carried out at Brookhaven National Laboratory and the National Bureau of Standards. Table 1 shows the nuclides sought and the standards used in the analysis.

The analyses of the majolica ceramics for sodium, potassium, and iron were carried out at Brookhaven using the parameters described in Bieber et al. (1976).

Table 1. Standards used in the neutron activation analysis

A. List of nuclides

Oxide	Nuclide	Half-life	Energy (keV)	Standards Used
Al ₂ O ₃	Al-27	2.2405M.	1779	NBS SRM 1633
Na ₂ O	Na-24	14.96 H.	1369	AGV, GSP, BCR, G-2, SRM1633
K ₂ O	K-42	12.40 H.	1524	AGV, GSP, BCR, G-2, SRM1633
CaO	Sc-47	3.40 D.	159	AGV, GSP, BCR, SRM1633
Fe ₂ O ₃	Fe-59	45.6 D.	1099 & 1292	AGV, GSP, BCR, G-2, SRM1633

B. List of standard concentrations

Standard	Concentrations Used	
	SI	Brookhaven
U.S.G.S. AGV-1	Flanagan 1973	Bieber et al. 1976
U.S.G.S. GSP-1	Flanagan 1973	Bieber et al. 1976
U.S.G.S. BCR-1	Flanagan 1973	Bieber et al. 1976
U.S.G.S. DTS-1	Flanagan 1973	Bieber et al. 1976
U.S.G.S. PCC-1	Flanagan 1973	Bieber et al. 1976
U.S.G.S. G-2	not used at SI	Bieber et al. 1976
NBS SRM 1633	Ondov et al. 1975	not used at BNL

The analyses of the southwestern United States and Iranian ceramics for sodium, potassium, iron, and calcium were carried out at the NBS reactor using the parameters described in Blackman (1979). The aluminum analyses for all three ceramic groups were undertaken at the NBSR. Twenty-five milligram subsamples of the ceramics and of the standard, SRM1633 coal fly ash, were used in the aluminum determination. Samples and standards were dried for 24 hours at 110°C, weighed into clean polyethylene

microcentrifuge tubes, and individually packaged in polyethylene rabbits for irradiation. Each rabbit, containing a single sample or standard, was irradiated at a flux of 1.6×10^{11} ncm⁻² sec⁻¹ for 5 minutes. Irradiations took place midway through the reactor fuel cycle with the reactor operating at a constant power of 9.9 MW. Each sample or standard was counted three times for 100 seconds per count at intervals of two, seven, and ten minutes after the end of the irradiation. Decay time was controlled to the nearest second. The counting was done with an Ortec γ -x intrinsic germanium detector (FWHM at 1332 keV of 1.72 keV) interfaced to a Nuclear Data 6620 using 8192 data channels. Data were stored on disk and processed using the ND data reduction programs.

The microprobe analyses were done on the ARL microprobe at the Mineral Science Department, Smithsonian Institution. This probe has nine spectrometers, which were set for silicon, aluminum, iron, magnesium, calcium, potassium, sodium, titanium, and phosphorus. Operating parameters used for all the analyses were 15 kV accelerating potential, 30 microamp beam current, 10 second counting times, and a defocused beam of 50 microns in diameter.

The first microprobe method used standard polished thin sections of ceramics from the American southwest, such as the thin section illustrated in Figure 1. The samples were carbon coated, placed in the sample chamber, and ten 10-second scans were run across the section. The concentrations reported for each element were the means determined from the ten scans. This was done to average the large-scale inhomogeneities that were likely to be present in a ceramic thin section.

There are several advantages to using a polished thin section. It provides a sample of reasonable size and the structure of the ceramic is preserved. If desired, the chemical data can be used in combination with petrographic analysis, and it is then possible to see which particles contribute to the concentrations of each element. It is also feasible to analyze the clay matrix, avoiding inclusions of a size determined appropriate to the particular problem investigated. In this study the entire section was scanned so the data would be comparable to that obtained by neutron activation, where ceramic powders include both the clay matrix and inclusions.

There are also disadvantages associated with the sections. As can be seen in Figure 1, the ceramics are usually extremely heterogeneous, and it is possible that in random scans an important area or mineral will be missed. This can be controlled to some extent by prior petrographic analysis to determine the sam-

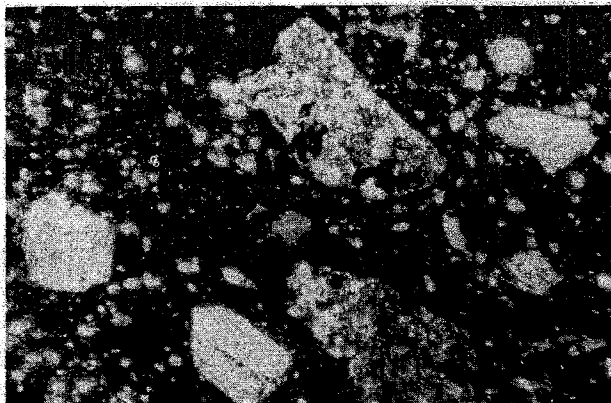


Figure 1. A standard polished thin section of an andesite tempered ceramic from the southwest United States, showing the heterogeneity of the sample.

pling strategy for a particular section and by making a sufficient number of scans. Another problem is that the varying porosity of ceramics results in low sums, even if all elements present are accounted for. This will be discussed in some detail later.

The second probe method employed fused samples. Several edges on each sherd were drilled using a clean tungsten carbide bit and the resulting powder was well mixed. Several milligrams were fused according to the procedure outlined for silicate rocks with compositions ranging between 45 and 65 weight percent SiO_2 (Jezek et al. 1979). The procedure involved the following steps. The powder was placed in a tungsten boat which was then mounted between the two bars in the apparatus shown in Figure 2. After a nitrogen atmosphere was introduced into the bell jar, the powder was rapidly heated for not more than 20 seconds, to prevent sodium volatilization. When the powder fused, it was quenched by shutting off the power and directing a stream of nitrogen onto the bottom of the boat. The resulting glass samples were mounted in a leucite disk and a 50 micron defocused beam was used to analyze ten spots on each sample.

The homogeneity of the glasses was much greater than that of the thin sections, and consequently there was less variation in concentration from analysis to analysis. However, several problems were encountered in using the fusion technique. Many of the ceramic powders were less refractory than the silicate rocks, and adjustments were necessary to prevent the volatilization discussed below. Also, the small sample size was as much a drawback as an asset because chances of sampling error increased markedly.

The third probe method, pressed pellets made from powder samples, was adapted from that used for meteorite samples. Powder drilled from sherds

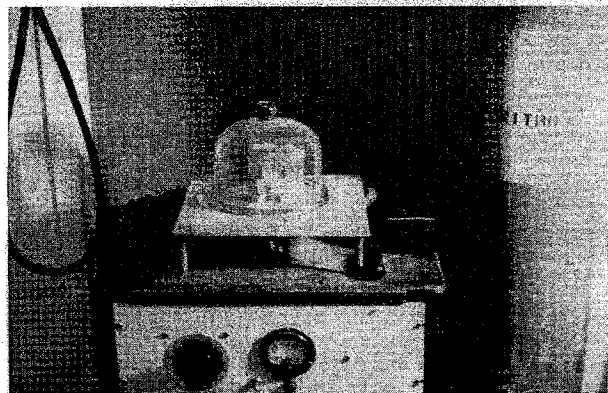


Figure 2. Apparatus used for fusing ceramic powder samples.

was ground to finer than 100 mesh, and one mg or less was mounted on a cylinder and pressed to form a pellet. The pellet had to have a minimum of surface cracks and be of even thickness. Two pellets were made for each sample and they were mounted on a metal washer (shown in Figure 3) with silver paint for conductivity. The pellets were analyzed using a 50 micron defocused beam to scan the surface of the pellets. Ten scans were performed.

The pellets have two advantages. There is no volatilization problem and the porosity problem of the sherd thin sections is reduced. However, the sur-

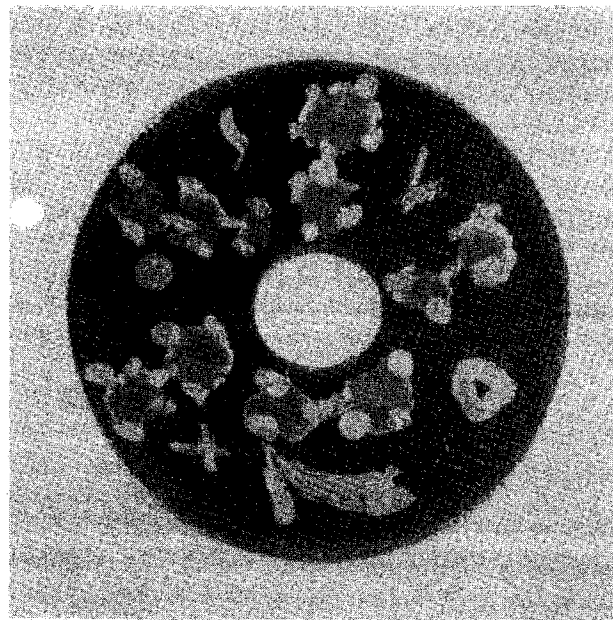


Figure 3. Ceramic powder pellets mounted with silver paint on a metal washer. Washer is 2.5 cm in diameter.

Table 2. Effect of standard selection on electron microprobe concentration values

Standard	SiO ₂	Al ₂ O ₃	FeO	MgO	CaO	K ₂ O	Na ₂ O	TiO ₂	P ₂ O ₅
Kakanui hornblende	46.03	17.18	6.91	5.94	13.72	2.78	0.42	0.84	0.45
BCR-1	45.36	16.03	7.09	6.71	14.69	2.24	0.40	0.79	0.23
G-2	47.14	15.42	6.82	4.98	12.63	2.56	0.40	0.98	0.30
INAA	N.D.	17.43	6.71	N.D.	12.43	2.96	0.45	N.D.	N.D.

Electron microprobe data obtained by analysis of a ceramic pellet using three different standards are compared with data obtained by neutron activation analysis.

face of the pellet is irregular, so the concentration values may be affected because of scattering and absorption properties different from those found with polished thin sections or glass. Once again, the small sample size requires cautious sampling and interpretation of results.

Calculation of Concentrations and Standard Selection for Electron Microprobe Analysis

The data in the form of X-ray intensities were corrected and quantified by an on-line computer. There are several alternative methods of reducing the data, but the shortest method for satisfactory results is calibration by known standards. There is general agreement that the highest accord is obtained by comparing an unknown specimen with a standard whose composition is as close to the unknown as possible, particularly for complex specimens. This is because the required interpolation between the standard and unknown is smaller and introduces less error. When such standards are unavailable, materials which are different in composition must be used, and this may involve additional computations. When similar standards can be used, they generally give results concordant within 5 to 10% of the amount present (Adler 1966; Birks 1971).

The data reduction procedures involve several steps. First, the detector dead time and background corrections are made for the measured counting rates. For extended measurements it may also be necessary to make a drift correction, and therefore during the analysis the standard is remeasured frequently. If the total change in signal intensity for the standard is no more than approximately 5% per hour, then the drift is assumed to be linear, and the data are corrected by recording the time of measurement and correcting for elapsed time (Adler 1966). The resulting intensity values are then converted to concentrations using the Bence and Albee (1968) method to control for matrix effects. The precision and accuracy of these values can be evaluated by running internal standards during analysis of the unknowns. Comparisons between the probe analyses of

these standards and wet chemical analyses permit correction of the unknowns through a method of normalization which brings the internal standard values to values determined by wet chemistry (Melson et al. 1976).

Data

Results for the ceramics analyzed illustrate the ways that preparation methods and standard selection affect the concentration values resulting from electron microprobe analysis. As noted above, the choice of standards is important. Because ceramics can vary widely in concentrations of major and minor elements, they present an initial problem in choosing, a priori, which may be the best set of standards for a particular run. In addition, it can be difficult to find a single standard that matches the ceramics closely in over-all composition. Table 2, shows the concentration values obtained when the same sample, MAP073, was analyzed using three different standards. When compared to neutron activation values, microprobe analyses using Kakanui hornblende as the standard were in good agreement for aluminum, potassium, and sodium, while those using G2 as the standard gave better agreement for iron and calcium. For the subsequent analyses reported here, BCR-1, G2, and Kakanui hornblende were used as standards for silicon, aluminum, iron, magnesium, calcium, sodium, potassium, and titanium. Apatite was used for phosphorous. The weight percent values for these standards are reported in Jarosewich et al. (1979).

Uncertainties in the concentration values of the ceramics may also be introduced by other factors. In the fusion technique of sample preparation for electron microprobe bulk analysis several problems may arise during the heating of the sample. Jezek et al. (1979) were concerned about possible sodium loss during prolonged fusion. They found experimentally that fusion times of 20 seconds or less produced minimal sodium volatilization in several silicate minerals of compositions that approach those of highly fired ceramics. A potentially much more serious problem arises from the breakdown and loss of volatile com-

Table 3. Comparison of carbonate bearing samples analyzed by INAA and by fused sample EM

Constituent	(n)	Mean	Mean	Average	Average	Average Ratio probe/INAA
		Conc. INAA (wt%)	Conc. EM (wt%)	Absolute Difference (wt%)	Relative Difference %	
CaO	(6)	20.55	26.82	6.26	26.4	1.31 ± .05
Fe ₂ O ₃	(7)	4.52	5.83	1.32	25.5	1.30 ± .07
Na ₂ O	(7)	0.57	0.50	0.08	14.8	0.88 ± .14
K ₂ O	(7)	1.85	1.81	0.33	18.0	0.98 ± .23

Table 4. Interpretation of low concentration sums from electron microprobe analyses

Sample	SiO ₂	Al ₂ O ₃	FeO	MgO	CaO	K ₂ O	Na ₂ O	TiO ₂	P ₂ O ₅	Total
<i>SW005</i>										
Random Scan	54.61	19.67	2.94	1.21	1.60	2.04	0.58	0.58	0.04	83.27
Recalculated	65.57	23.62	3.53	1.45	1.92	2.45	0.70	0.70	0.05	99.99
Pressed Pellet	67.32	23.51	3.75	1.21	1.72	2.51	0.86	0.62	0.08	101.58
<i>MAP001</i>										
Pressed Pellet	33.86	11.93	5.39	5.61	21.12	1.88	0.38	0.53	0.12	80.02
Fused	43.24	12.35	5.44	7.26	26.06	1.40	0.41	0.67	0.18	97.02

SW005 shows the effect of porosity on concentration sums while the low total value in the pressed pellet of MAP001 is due to the presence of unmeasured CO₂.

ponents such as structural water in hydrated mineral phases and CO₂ in carbonate minerals. In ceramics fired at high kiln temperatures this process has already occurred in the initial firing. However, a great deal of the ceramics of interest to archaeologists have been fired to temperatures that do not exceed 600°C. Some of these low-fired ceramics contain carbonate minerals either as contaminants in the clays or intentionally added as a tempering agent. The fusion of these ceramics at temperatures in excess of 1600°C results in the loss of CO₂, producing anomalously high yields for other elements in the microprobe analysis. In Table 3, the yields from INAA and fused sample microprobe data are compared for seven low-fired ceramics containing calcite and dolomite. The CaO and Fe₂O₃ concentrations display average relative differences of about 26%, indicating poor agreement between the two analytical techniques. The average ratio of probe data to INAA data for both oxides shows values 1.31 and 1.30 respectively, both with small standard deviations. This indicates a nearly constant analytical discrepancy between the two methods. This discrepancy of about 24% to 26% by weight can be accounted for almost solely by the loss of CO₂ during fusion of the samples. The oxides

of sodium and potassium should behave in the same manner as the oxides of calcium and iron; however, the probe to activation analysis ratios for Na₂O and K₂O are both less than one, and both show much greater variance than CaO or Fe₂O₃. Apparently the evolution of CO₂ during the fusion facilitates the volatilization of the oxides of sodium and potassium.

Another problem involves the significance of low sums obtained in analyses of polished thin sections and pressed pellet samples. The first situation is represented by sample SW005 in Table 4. This is a run on a polished thin section of a southwestern United States ceramic, and it shows a low sum owing to the porosity of the ceramic body. The values obtained from the random scans were normalized to 100%, and were compared with values obtained on a pressed pellet from the same sample, where the porosity would not be a problem. The agreement is good enough to support the contention that the low sum was due to porosity. It suggests that if carbonates or other nonoxides are not present in substantial amounts, the values for thin sections can be normalized to 100% for comparison with other bulk analyses.

The second example in Table 4 illustrates the pres-

Table 5. Comparison of fused sample EM and INAA data

Constituents	(n)	Mean ^a	Range	Mean	Range	Mean C.V.	Mean C.V.	Mean
		Conc. (wt%)	of Analyzed Samples (wt%)	Absolute Diff. (wt%)	of Absolute Diff. (wt%)	INAA %	EM %	Relative Diff. %
Al ₂ O ₃	(10)	18.93	14.28-24.47	1.23	0.41-2.86	1	3.2	6.5
Fe ₂ O ₃	(41)	5.86	2.27-14.71	0.41	0.01-1.52	0.5	7.1	7.0
CaO	(12)	7.97	0.99-13.52	0.56	0.02-1.79	9	5.9	7.0
Na ₂ O	(50)	0.84	0.13- 2.08	0.11	0.00-0.60	2	12.0	13.1
K ₂ O	(41)	2.11	0.75- 3.83	0.21	0.00-1.09	8	9.6	10.0

^aMean concentration is the mean of the value obtained by both methods.

ence of nonmeasured elements in a ceramic. The pressed pellet and fused sample sums for sample MAP001 do not agree, and the assumption is that the components volatilized during fusion were present, but not measured in the pellet sample. In this case, normalization of the values to 100% would be misleading.

Comparison of INAA and Electron Microprobe Data

Because results obtained by electron microprobe analysis might be used as a complement to that obtained by neutron activation, the results of the two methods were compared for those elements that can be measured by both. Table 5 shows the concordance for fused ceramic samples analyzed by microprobe and powders analyzed by INAA. The low-fired, high carbonate samples have been excluded from the group to eliminate the problems discussed above. The mean relative difference was calculated to show the agreement of the two techniques on an average. This is the mean of the absolute differences divided by the mean concentration and expressed as a percent. The mean relative difference is 6.5% for aluminum, 7.0% for iron and calcium, 13.1% for sodium, and 10.0% for potassium. The mean coefficient of variation for the probe samples shows the heterogeneity of the samples analyzed, and it may contribute to the lack of agreement.

Table 6 compares our fusion data with fusions done on silicate rock powders. The rock powders have been ground to finer than 100 mesh to produce more homogeneous glasses. Under ideal conditions this procedure of sample preparation has been shown to give results which have an average accuracy of better than 5% relative for all major components studied, when compared to results obtained by wet chemical methods (Jezek et al. 1979). The mean rela-

Table 6. Comparison of electron microprobe data with chemical data for silicate rocks and with INAA data for ceramics

	Silicate Rocks ^a	Ceramics ^b
	Mean Relative Difference %	Mean Relative Difference %
Al ₂ O ₃	0.9	6.5
Fe ₂ O ₃	2.2	7.0
CaO	1.9	7.0
Na ₂ O	4.5	13.1
K ₂ O	4.5	10.0

^aElectron microprobe and wet chemical data from Jezek et al. 1979.

^bFrom Table 5, this paper.

tive differences for ceramics may be improved in this way and by tailoring the unknowns and the standards more effectively.

To summarize, the electron microprobe can only be employed to get useful bulk chemical composition if the standards are appropriate and if limitations presented by sample preparation techniques are borne in mind. Preliminary sorting of ceramic samples using petrographic analysis, and independent chemical analysis of a member of each group can establish the approximate concentrations of the elements to be included in the analysis group. The most appropriate standard set can then be determined for further microprobe analysis of each group of samples.

While the fusion technique provides the greatest agreement with neutron activation results, the advan-

	Na ₂ O	K ₂ O	TiO ₂	Fe ₂ O ₃	SiO ₂	P ₂ O ₅	Al ₂ O ₃	MgO	CaO
Spanish majolica									
geometric mean	0.82	1.65	0.65	4.7	51	0.30	13.7	3.8	21.3
alog group std. dev.	1.441	1.259	1.292	1.072	1.023	1.179	1.034	1.304	1.108
Mexican majolica									
geometric mean	1.39	0.92	0.65	4.2	50	0.36	16.3	3.9	19.3
alog group std. dev.	1.326	1.147	1.161	1.145	1.089	1.380	1.097	2.192	1.337

Table 7. Concentrations (ppm) for CeO₂, La₂O₃, ThO₂ in majolica

Site	CeO ₂	La ₂ O ₃	ThO ₂
Group I			
<i>Convento de</i>			
<i>San Francisco,</i>			
<i>Dominican</i>			
<i>Republic</i>			
geometric mean	77 ± 18	39 ± 4.0	11.8 ± 0.73
<i>Juandolio,</i>			
<i>Dominican</i>			
<i>Republic</i>			
geometric mean	87 ± 5.4	43 ± 4.0	12.7 ± 1.0
<i>La Vega Vieja,</i>			
<i>Dominican</i>			
<i>Republic</i>			
geometric mean	90 ± 5.5	42 ± 3.0	13.0 ± 1.0
<i>Isabela,</i>			
<i>Dominican</i>			
<i>Republic</i>			
geometric mean	82 ± 4.6	43 ± 2.7	12.6 ± 1.2
<i>Nueva Cadiz,</i>			
<i>Dominican</i>			
<i>Republic</i>			
geometric mean	82 ± 4.8	38 ± 2.7	11.8 ± 0.8
<i>Jerez, Spain</i>			
geometric mean	80 ± 3.3	45 ± 1.9	11.7 ± 0.7
Group II			
<i>Mexico City,</i>			
<i>Mexico</i>			
geometric mean	40 ± 8.6	22 ± 3.9	5.6 ± 0.7

tages of polished thin sections recommends their use in certain cases. They are ideally suited for analysis of inclusions. In addition, they provide the potential for discriminating the extent to which inclusions or clay matrix are responsible for concentrations of particular elements through the use of scanning techniques.

The Combined Use of Neutron Activation and Electron Microprobe Analysis

As noted above, trace element data provide clear differences which enable one to distinguish ceramics from different sources. While major constituents are occasionally useful in this regard, they are also a complement to INAA analysis. They provide an understanding of the kinds of clays (e.g., calcareous and noncalcareous) and inclusions present which make ceramic groups appear similar to or different from one another.

Two hundred and nine majolica sherds from sites of the fifteenth and sixteenth centuries in Spain, the Dominican Republic, Venezuela, Mexico, and from later sites in Central and South America have been analyzed by neutron activation analysis (Olin et al. 1978). Two distinctive groups of pottery could be identified on the basis of neutron activation analysis and petrographic examination. Three oxides in particular distinguish the groups very definitely: CeO₂, La₂O₃ and ThO₂. The average composition of these oxides for the samples of the first group for sherds from six different sites and for samples from the second group which are from Mexico are listed in Table 7.

Fourteen sherds from the "Spanish" group and ten sherds from the "Mexican" group were analyzed by electron microprobe analysis. The average compositions (as geometric means) and the anti-logs of the group standard deviations for the oxides analyzed listed in tabular form at the top of this page.

The concentrations of the elements analyzed by microprobe analysis — see Figure 4 — do not differ in such an obvious way. Although there are slight differences for the elements sodium and potassium, which were analyzed by both neutron activation and electron microprobe analysis, they do not provide a clear-cut a distinction between the two groups as do cerium, lanthanum, and thorium.

By more careful study of the petrographic data, the differences in the concentrations of Na₂O and K₂O might be explained. The close similarity of the CaO concentrations and the relatively high levels in both Spanish and Mexican majolica are important in

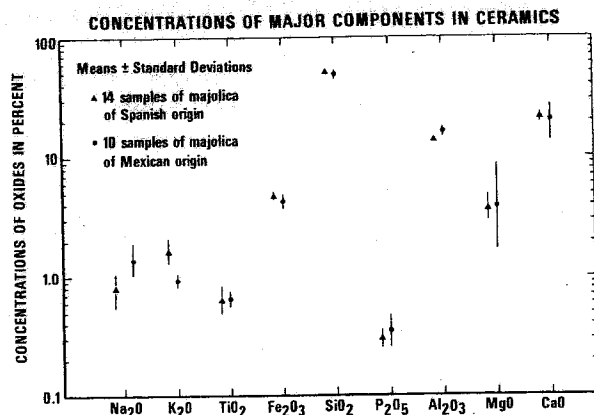


Figure 4. Concentrations of major components in Spanish-Colonial majolica obtained by electron microprobe analysis.

that they show that the presence of a high calcium concentration in the Mexican majolica could be a consequence of purposeful selection or preparation of a calcareous clay rather than the deposition of secondary calcite after burial as postulated earlier (Olin et al. 1978). The decomposition of gehlenite could be suggested as the source of secondary calcite in these ceramics (Kupfer and Maggetti 1978).

Conclusions

We have discussed some of the possible sources of error in electron microprobe analysis of ceramics and pointed out the problem of standard selection in such analyses.

As a consequence of the possible use of electron microprobe data for quantitative purposes, even in papers where it is reported but not used in that manner, it is important to report the sample preparation procedures and the standards used. Without this information it is difficult to evaluate the precision or accuracy of the concentration data, and therefore how it should be "weighted" when combined or compared with results from other methods.

Acknowledgments: We would like to thank the Staff of the Reactor Radiation Division, National Bureau of Standards. We are also grateful to the following people from the Mineral Sciences Department at the Smithsonian Institution for their advice and assistance in sample preparation and standard selection for the microprobe analyses: W. G. Melson, K. Fredriksson, E. Jarosewich, P. Brenner, J. Nelen, F. Walkup, R. Johnson, and C. Obermeyer.

References

- Adler, Isidore. 1966. *X-ray emission spectrography in geology*. Methods in Geochemistry and Geophysics, no. 4. Amsterdam: Elsevier Publishing Co.
- Arrhenius, G.; Fitzgerald, R.; Fredriksson, K.; Holm, B.; Sinkankas, J.; Bonatti, E.; Bostrom, K.; Lynn, D.; Mathias, B.; Ceballe, T.; and Korkisch, J. 1964. Valence band structure and other La Jolla problems in microprobe analysis. (Abstr.). *Electrochem. Soc. Meeting. Wash.* 214:100-103.
- Bence, A. E., and Albee, A. L. 1968. Empirical correction factors for the electron microanalysis of silicates and oxides. *Journal of Geology* 76:382-403.
- Bieber, A. M., Jr.; Brooks, D. W.; Harbottle, G.; and Sayre, E. V. 1976. Application of multivariate techniques to analytical data on Aegean ceramics. *Archaeometry* 18 (1):59-74.
- Birks, L. S. 1971. *Electron probe microanalysis*. 2d ed. New York: Wiley-Interscience.
- Blackman, M. J. 1979. The mineralogical and chemical analysis of Banesh Period ceramics from Tal-i Malyan, Iran. A paper read at the 19th International Symposium on Archaeometry and Archaeological Prospection, March 1979, London, U.K.
- Brown, Roy W. 1977. A sample fusion technique for whole rock analysis with the electron microprobe. *Geochimica et Cosmochimica Acta* 41:435-38.
- Flanagan, F. J. 1973. 1972 values for international geochemical samples. *Geochimica et Cosmochimica Acta* 37:1189-200.
- Gulson, B. L., and Lovering, J. F. 1968. Rock analysis using the electron probe. *Geochimica et Cosmochimica Acta* 32:119-22.
- Jarosewich, E.; Nelen, J. A.; and Norberg, J. A. 1979. Electron microprobe reference samples for mineral analyses. In Fudali, R. F., ed., *Smithsonian Contributions to the Earth Sciences*, no. 22.
- Jezeck, Peter A.; Sinton, John M.; Jarosewich, Eugene; and Obermeyer, Charles R. 1979. Fusion of rock and mineral powders for electron microprobe analysis. In Fudali, R. F., ed., *Smithsonian Contributions to the Earth Sciences*, no. 22.
- Kupfer, T., and Maggetti, M. 1978. Die Terra Sigillata von La Peniche (Vidy) Lausanne. *Schweiz. mineral. petrogr., Mitt.* 58:189-212.
- Melson, W. G.; Vallier, T. L.; Wright, T. L.; Byerly, G.; and Nelen, J. 1976. Chemical diversity of abyssal volcanic glass erupted along Pacific, Atlantic, and Indian Ocean sea-floor spreading centers. In *The geophysics of the Pacific Ocean Basin and its margin*. Geophysical Monograph, no. 19. American Geophysical Union.
- Mori, T.; Jakes, P.; and Nagaoka, M. 1971. Major element analysis of silicate rocks using electron probe microanalyzer. *Sci. Rep. Kanazawa Univ.* 16:113-20.

Nicholls, I. A. 1974. A direct fusion method of preparing silicate rock glasses for energy-dispersive electron microprobe analysis. *Chem. Geol.* 14:151-57.

Olin, J.; Harbottle, G.; and Sayre, E. 1978. Elemental compositions of Spanish and Spanish-Colonial majolica ceramics in the identification of provenience. In *Archaeological chemistry II*, chap. 13. Advances in Chemistry Series. American Chemical Society.

Ondov, J. M., et al. 1975. Elemental concentrations in the National Bureau of Standards environmental coal and fly ash standard reference materials. *Analytical Chemistry* 47 (7): 1102-109.

Reed, S. J. B. 1970. The analysis of rocks in the electron probe. *Geochimica et Cosmochimica Acta* 34:416-21.

Rucklidge, J. C.; Gibb, G. F.; Fawcett, J. J.; and Gasparrini, E. L. 1970. Rapid rock analysis by electron probe. *Geochimica et Cosmochimica Acta* 34:243-47.