CHEMICAL HOMOGENEITY OF NATIONAL BUREAU OF STANDARDS COAL FLYASH (SRM 1633a)

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The chemical homogeneity of 10 mg samples of the (U. S.) National Bureau of Standards standard reference material 1633a (coal flyash) was determined for several elements by instrumental neutron activation analysis. The homogeneity was tested for the purpose of using small samples of the flyash as a multielement comparator standard. For small sample masses the flyash may be unacceptably heterogeneous for Fe, Co, Ba, and perhaps As and Sb. Homogeneity is improved by grinding the flyash. For comparison, homogeneity data for USGS GSP-1 is also presented.

Introduction

This paper and a companion paper detail an effort to characterize and standardize the National Bureau of Standards (NBS) standard reference material (SRM) 1633a (coal flyash) for use as a multielement comparator standard for instrumental neutron activation analysis (INAA). KOROTEV has shown that compared to many rock-powder SRMs, 1633a is particularly advantageous with respect to relative elemental abundances for use as a multielement INAA standard. We anticipated that because of its mode of formation it would also be reasonably homogeneous.

To demonstrate that an SRM is heterogeneous for a given element is not a simple task. In order to prove heterogeneity conclusively, it must be shown that the precision of replicate analysis of the SRM is significantly worse than the analytical precision. In a recent paper, FILBY et al. report relative standard deviations (RSDs) of > 20% for Ni, Tb, Ba, and Se in samples of 1633a ranging in mass from 0.83 to 4.94 mg and imply that this indicates heterogeneity of the flyash. No information is given regarding the analytical precision, so although 1633a may be heterogeneous for these elements, their experiment offers no proof. In our experience, "counting statistics" are not necessarily a good measure of the true analytical precision, particularly for low relative values (< 5%), because systematic effects in peak area integration and instrumental factors become more important. To test for...
heterogeneity, a large number of samples must be analyzed under identical conditions. This is difficult using INAA because significant decay of some isotopes will occur during the course of the experiment. In order to evaluate the chemical homogeneity of small samples of 1633a, the following experiment was devised.

Experimental

General experimental conditions were similar to those described in KOROTEV\textsuperscript{1}. Ten samples of 1633a each weighing 9-11 mg in mass were prepared. The samples were designated A,B,C,\ldots,J. They were irradiated for 24 hours and radioassayed for 3.5 hours each between 7 and 12 days following irradiation and again between 27 and 33 days. Each sample was radioassayed once during each period except sample A, which was radioassayed ten times. These ten analyses of A were designated A\textsubscript{1},A\textsubscript{2},A\textsubscript{3},\ldots,A\textsubscript{10}. All spectra were taken with a single detector and the samples were analyzed in the sequence A\textsubscript{1},B,A\textsubscript{2},C,\ldots,A\textsubscript{10},J in order to minimize any systematic effects resulting from different decay times for the various spectra. For each sample, data from the 7-12 and 28-35 day radioassays were combined. Finally, for each element, means and standard deviations were calculated for the single analysis each of ten samples (A\textsubscript{1},B,C,\ldots,J) and for the ten analyses each of a one sample (A\textsubscript{1},A\textsubscript{2},\ldots,A\textsubscript{10}). The latter are used to determine a very accurate estimate of the analytical precision (i.e., the precision of radioassay) by which to judge the former. All effects resulting from radioassay of the standards are systematic effects for both data sets and do not affect the precision of either.

This experiment was originally done in a manner very similar to that described above in 1982 and briefly reported by KOROTEV and LINDSTROM\textsuperscript{3}. On the basis of that experiment, we concluded that the standard deviation for Fe, Co, Ba, and Sr in the ten different samples significantly exceeded the analytical precision at the 97.5\% confidence level as based on the F-test. Our experience with using 1633a as an INAA standard since then has frequently indicated considerable heterogeneity of Fe. For example, in the standardization experiment described by KOROTEV\textsuperscript{1}, two of the six 80 mg samples differed from each other in Fe concentration by 3.4\% (relative) and we have observed at least one case where the two 80 mg samples included in a routine analysis differed by 6\%. (For comparison, two of the four 50 mg BCR-1 samples analyzed by KOROTEV\textsuperscript{1} differed in Fe concentration by 1.6\%, relative, and in a