Development of the First Natural-Matrix SRM for Solid-Sampling Analytical Instruments

The analysis of materials by introducing solid test samples directly into the graphite furnace or the plasma of an atomic absorption, emission, or mass spectrometer is regarded as a powerful analytical approach. After three decades of development, the instrumentation and the methodology are available to apply solid sampling successfully for the analysis of almost every material in the form of about 0.1 mg to 1 mg solid test portions. A significant problem in the use of these emerging solid sample techniques is a general lack in suitable certified reference materials (CRMs) for calibration and quality assurance purposes. No CRMs have been certified for the small sample sizes typically used for these techniques. Direct utilization of most existing CRMs in solid-sampling analysis procedures is often unreliable because trace components may not be sufficiently homogeneously distributed in the sample, and their homogeneous distribution has not been validated for sample sizes below 100 mg to 250 mg. NIST is addressing this issue with the production of a new Standard Reference Material (SRM).

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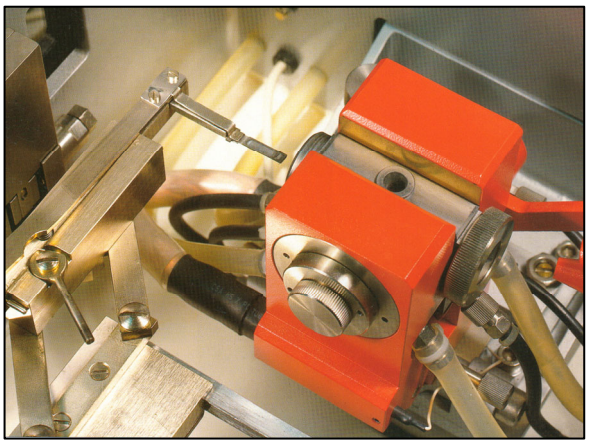
NIST has developed specialized instrumental neutron activation analysis (INAA) procedures to study the homogeneity of SRMs. Homogeneity studies must be conducted on small sample sizes, and these procedures permit the analysis of 1 mg and smaller-size samples with essentially no degradation of analytical uncertainty. The use of an analytical procedure with known small random uncertainties allows for a direct evaluation of the sampling error of a test sample from the experimentally observed standard deviation (assuming a sufficiently large number of test samples have been measured). As a consequence, Kurfürst has postulated an elemental homogeneity factor (H_E) as a measurable property of a sample. Small-sample INAA procedures provided survey data for H_E on a broad variety of natural-matrix materials and SRMs. Materials with narrow size distributions of small (<20 µm) particles were identified as best candidates. In addition, the developing solid-sampling community identified "higher" density materials such as soils and sediments as the technically most challenging materials as well as an important application domain leading to the SRM 2702 Organics in Marine Sediment parent material as the best candidate for this development. This material was further processed by jet-milling to exclude large particles as sources for heterogeneity and, after processing, contained no particles larger than 20 µm. The material was then tested by INAA for acceptance, and subsequently during the certification campaign further characterized for its small-sample homogeneity by micro-x-ray fluorescence spectrometry (micro-XRF), micro-proton-induced x-ray emission (micro-PIXE), and laser ablation inductively coupled plasma mass spectrometry (ICP-MS). These techniques confirmed reproducibility of results at microgram sample sizes. The jet-milled sediment material is designated SRM 2703.

The certification effort for SRM 2703 involved ten expert laboratories with active research programs in solid sampling techniques. In combination with the analytical capabilities at NIST, and including the extensive characterization of the parent material, SRM 2702, it was possible to provide certified and reference mass fractions for 29 elements for a sample size of 0.7 mg. H_E was determined for twelve elements between 0.28 and 1.6 (the value representing the expected relative (%) standard deviation of the results if the element would be determined in 1 mg test portions with no other analytical uncertainty). This will serve as a first standard against which future SRMs for solid sampling can be tested, and it will help to broaden the foundation of solid sample analysis.

This material provides a new benchmark for homogeneity in a natural-matrix SRM. It will help to fill a critical gap in the availability of SRMs to the growing use of solid-sampling techniques in industrial, environmental, clinical, and other applications.



Future Plans: The capability to quantify heterogeneity by INAA for a large number of elements will be utilized to expand the NIST SRM inventory for solid sampling techniques; the renewal materials SRM 1648a Urban Particulate Matter and SRM 1577c Bovine Liver will be investigated next.