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MASS-SPECTROMETRIC MEASUREMENTS FOR NUCLEAR SAFEGUARDS*

J. A. Carter, D. H. Smith, and R. L. Walker
Analytical Chemistry Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

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The requirements of nuclear safeguards place great stress on obtaining results of the highest possible precision for uranium and plutonium isotopic abundance measurements from all phases of the nuclear fuel cycle. Because some phases of the cycle necessitate sampling radioactive solutions, it is necessary to analyze small (1-3 ng) samples. The resin bead sampling technique[1,2] provides a convenient means to acquire uranium and plutonium samples while simultaneously separating them from other actinides and fission products. By proper adjustment of acid strength and uranium concentration, only the two elements of interest will adsorb on the beads. For isotope dilution work, Marsh et al.[3] have investigated various plutonium equilibration procedures. The preferred method for fresh dissolver solutions is reduction with Fe(II)-sulfamic acid and oxidation with $NaNO_2$. After 10 minutes agitation of beads and solution on a vortex mixer, each bead will contain 1-3 ng of each element. One bead comprises one sample for mass analysis, where sequential analysis of plutonium and then uranium is performed on a single bead. These quantities are low enough in radioactivity to eliminate the need for heavy and costly shielding during shipment.

To analyze samples of this size, mass spectrometers especially designed for the purpose are required. Instruments built by the various laboratories concerned have been in operation for many years,[4-6] and the newest generation of commercial mass spectrometers approaches the sensitivity requirements.[7] A round robin to evaluate results obtained from resin bead samples has recently been completed,[8] and excellent agreement between laboratories was reported.

Efforts to improve precision beyond what is routinely available through meticulous sample preparation and mass spectrometric analytical procedures are bearing fruit. Two basic approaches are being pursued. The first involves trying to achieve more rigorous control of the evaporation process. The resin bead technique contributes significantly in this area,[9] but overcoating the sample with rhenium seems to be even more helpful.[10] Both electrolytic deposition[11] and addition of rhenium powder in a slurry with a sucrose solution[12] greatly enhance ion emission and reduce evaporation of the sample as oxide species.

The second approach to improving precision is even more promising. This is to use an "internal standard,"[13-16] which is a spike of two isotopes whose ratio is well known (e.g., ^{233}U and ^{236}U). The bias correction necessary to apply for a given filament is calculated on a run-by-run basis and yields far better results than the previous method of applying an average bias correction, determined by analyzing isotopic standards, to all data. Recent work[17,18] has shown that improvements in precision of isotopic ratio measurements of about a factor of five can be attained. The technique is particularly useful in isotope dilution analyses to calculate concentration; its application to improving $^{235}U/^{238}U$ is limited because a truly high purity ^{236}U spike (>99.9% ^{236}U) is not available.

The need of an on-site inspection device to provide isotopic ratio measurements led to the development of a quadrupole mass spectrometer mounted in a van.[19] This mobile laboratory has the ability, through the use of the resin bead technique, to acquire, prepare, and analyze samples of interest to nuclear safeguards. Precision of the measurements is about 1-2%.

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