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Total Evaporation in Thermal Ionization Mass Spectrometry

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Introduction

The total evaporation method, in which the entire sample is evaporated while integrating the signal from each isotope using a multicollector system, has now been in routine use at our laboratory for uranium and plutonium analyses for several years [1,2]. By integrating out the effects of isotope fractionation, high precision, typically <0.02% relative standard deviation (RSD), is obtained with a minimum of rigor in sample loading and treatment schemes. In fact, the advantages of total evaporation become more apparent in real-world analysis situations in which the precise quantity of sample loaded may not be known and sample purity may be questionable. Recently, we have performed tests to demonstrate the effectiveness of the method on actual and impure test samples.

Experimental

In a study conducted with the International Atomic Energy Agency (IAEA) Safeguards Analytical Laboratory (SAL) in Seibersdorf, Austria, uranium and plutonium samples were prepared and analyzed by SAL using conventional techniques, and a portion was shipped to Los Alamos for analysis using the total evaporation technique. Average precisions (% RSD) obtained on four replicate runs on each of 12 uranium and 12 plutonium samples, ranged from <0.01% for 240/239 Pu ratios to <0.02% for 233/238 U and 244/239 Pu ratios. These results demonstrated that standard chemical purification methods used at SAL were more than adequate for analyses by the total evaporation method, and that significant improvements in precision and accuracy were provided by the total evaporation method. These techniques have since been implemented at SAL with good results; see [3] and R. Fiedler's paper in these proceedings.

Recently, in a continuation of this work, experiments were conducted to assess the effects of certain impurities on the total evaporation method for uranium. Solutions of NIST U-500 isotopic standard were spiked with Na, Ca, K, Fe, Zr and Ba (individually) at levels of 1%, 10%, and 100% (by weight) relative to the uranium concentration of 1 mg/ml. Four analyses of each of these 18 solutions were performed, interspersed with analyses of unspiked U-500.

Results and Discussion

The results of these analyses are shown in Table 1. It appears that only Fe, and possibly Na display any discernible effect, and then only at the highest concentration level. Hopefully, this situation is not encountered often in most laboratories! In addition, the effect is small, about 0.02%. This is certainly good news for laboratories working with impure materials. Of course, many other impurity elements should be studied, but it would be surprising if the effects were large.

Table 1: Percentage Deviations of the Average Observed 235/238 U Ratios from the Observed Pure U-500 Value and the Precision Observed on 4 Filament Loadings

Concentration	Impurity Added					
	Na	Ca	K	Fe	Zr	Ba
1%	-0.013	+0.004	+0.010	+0.016	+0.016	-0.002
	±0.014	± 0.010	±0.010	±0.028	±0.033	±0.009
10%	-0.000	-0.008	+0.010	-0.004	+0.002	+0.011
	±0.24	±0.017	±0.010	±0.011	±0.011	±0.006
100%	-0.015	-0.002	+0.010	-0.022	-0.007	+0.004
	±0.009	±0.021	±0.010	±0.008	±0.006	±0.008

Note: The observed value for unspiked U-500 was 0.99991 ± 0.000126 (1s) for N=29. The certified value is 0.9997 ± 0.001 .

In spite of the success of this technique, there are nagging problems which currently limit the ultimate precision and accuracy of the method. One of these, of course, is the determination of the relative efficiencies of the collectors. It appears that a versatile, reliable, and accurate method has not yet been developed. At the present time, calibration methods appear to be good to about 0.01%. A method previously discussed by this author [2], applicable to adjustable collector systems, requires special isotope mixtures and is rather time consuming. The method of "peak-jumping" a single stable ion beam to each collector in turn by stepping the magnet, often seems to give strange results. The efficiencies vary with element and filament loading, well outside the apparent precision of the data. An explanation for these variations is not readily apparent, and the calibration problem certainly should be investigated further.

Another problem is that of the occasional "odd" result. For uranium, this usually appears as a high 235/238 ratio (0.03 to 0.07%) and is accompanied by a high-temperature "tail" on the intensity vs. filament current profile. This may be due to the production on the filament of chemical species, perhaps carbides, that are less volatile and hence prevent total evaporation. Further work is planned to try to resolve some of these questions.

References

- [1] E.L. Callis and R. M. Abernathy, Proceedings of the 36th ASMS Conference on Mass Spectrometry and Allied Topics, June 5-10, 1988, San Francisco.
- [2] E.L. Callis and R. M. Abernathy, Int. J. Mass Spectrom. Ion Proc. 103, 93 (1991).
- [3] R. Fiedler, D. Donohue, G. Grabmueller, A. Kurosawa, Int. J. Mass Spectrom. Ion Proc. 132, 207 (1994).

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