ISOTOPIC MEASUREMENTS OF URANIUM AND PLUTONIUM BY RESONANCE-IONIZATION MASS SPECTROMETRY*

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ABSTRACT

Isotopic measurements of the elements uranium and plutonium have been carried out using laser-excited resonance ionization mass spectrometry (RIMS). This technique makes use of the high elemental selectivity inherent in the resonance-ionization process which results in complete removal of isobaric (same-mass) interferences. The requirements of the laser system and atomization source will be discussed with emphasis on maximizing the efficiency of temporal overlap, thus increasing the sensitivity of the technique. Results will be shown for resin-bead loaded samples containing a mixture of NBS standard reference materials of U and Pu at the nanogram level. Data will be presented which demonstrate the selectivity, accuracy, and precision of RIMS compared to the conventional thermal ionization technique.

INTRODUCTION

The technique of resonance ionization mass spectrometry (RIMS) has been extensively studied in recent years (refs. 1-9). Work in our laboratory has centered on understanding the physical processes involved in ionizing rare earth (refs. 2,3) and actinide (ref. 4) elements using thermal filament vaporization and pulsed dye lasers. This paper will describe the most recent results for the elements uranium and plutonium, demonstrating the precision, accuracy, and sensitivity achieved to date. The goal has been to make isotope ratio measurements on these elements comparable to those obtained by the thermal ionization method, incorporating the unique advantage of RIMS, namely its high elemental selectivity which can reduce or eliminate isobaric interferences.

Resonance ionization techniques are based on the photo-excitation of electrons in free (gas-phase) atoms. Various schemes or excitation ladders, leading to ionization have been reported for nearly all the elements proceeding through one or more intermediate state and involving one or more wavelengths of excitation energy (ref. 10). The simplest scheme (Scheme 1) involves absorbing a photon of one wavelength, raising the electron from a low-lying energy level (usually the ground state) to an allowed intermediate state. From this excited state the atom can then be ionized by absorption of a second photon of the same wavelength. This scheme can be applied to most of the lanthanide and actinide elements.

In classical resonance ionization spectroscopy (RIS), the free electron which is produced in the photo-excitation process can be multiplied and detected in a gas proportional counter. However, more information can be obtained by accelerating and mass analyzing the positive ion produced. The hybrid technique of RIMS was developed to take advantage of the elemental selectivity inherent in the resonance ionization process. This results in less interference between elements having overlapping isotopes or isobars. An additional advantage is in the reduction of molecular ion interferences.

The isotopic analysis of U and Pu is important for fissile materials accountancy and safeguards. These two elements have an isobaric overlap at mass 238 which degrades the accuracy of thermal ionization measurements. In addition, ^{241}Pu suffers from overlap with its decay product ^{241}Am, which grows in rapidly ($t_{1/2}$ = 14.3 years). These two interferences occur when using the "resin-bead method" (refs. 11,12) of sample preparation, in which both U and Pu are adsorbed onto anion resin beads which are then used for the sequential mass spectrometric analysis of both elements. Americium is produced in situ and retained by the resin bead matrix. Delays of only a few weeks between resin bead preparation and mass spectrometric analysis can result in a significant bias in the ^{241}Pu assay.

Our experimental set-up for RIMS consists of a flashlamp-pumped dye laser (Chromatix Model CMX-4, LCD/Milton Roy Co., Sunnyvale, CA) interfaced to a 2-stage magnetic mass spectrometer of ORNL design (ref. 13). The laser produces 5-10 mJ pulses of tunable radiation, 1 μsec in duration, with a 0.1 nm (3 cm^{-1}) bandwidth. The pulses are directed into the ion source region of the mass spectrometer by mirrors and a silica lens. The focused laser beam interacts with a cloud of sample atoms produced by a heated metal filament in a manner similar to triple filament thermal ionization mass spectrometry. The laser generated ions are accelerated and passed through two 90° magnetic sectors in

tandem (for abundance sensitivity of 1 x 10^6) and are collected by an electron multiplier detector operated in the current integration mode. Each bundle of ions at a given mass produced by a single laser pulse is digitized and accumulated in our computer (MINC-11, Digital Equipment Corp., Maynard, MA). Typically, 7,000-10,000 pulses are accumulated during an analysis for a major ion species, with up to 30,000 pulses collected for a minor isotope. The total number of ions collected for each isotope is approximately 5 x 10^5, giving a theoretical precision of ±0.14%.

One problem associated with pulsed laser ionization is the poor temporal efficiency. The laser is "on" for only 30 μsec/sec, for an efficiency of 3 x 10^{-5}. If the sample atoms are being produced continuously, there will be a significant loss of sample during the "off" time of the laser. Therefore, we have implemented a pulser circuit to heat the sample filament briefly before each laser pulse (ref. 14). It has also been found that the efficiency of this pulser depends on the conduction of heat away from the filament between pulses. Using heavy gauge Pt filament legs, it was found that sample utilization efficiency was improved by a factor of 10 compared to continuous heating.

This pulser, along with optimization of the laser beam optics, has allowed us to make high quality isotope ratio measurements with samples as small as 10 ng of U or Pu. The ratios shown in Tables 1 and 2 were obtained with samples containing 10 ng of each element adsorbed on anion resin beads. The Pu and U were analyzed sequentially from the same resin bead, with each analysis requiring 15 minutes. The precision obtained for $^{240}Pu/^{239}Pu$ is excellent, ±0.24%, and compares favorably with thermal ionization results for the same size sample. Precision for the minor isotope ^{241}Pu is not as good, reflecting the smaller number of ions collected in the analysis. Results for $^{235}U/^{238}U$ from the NBS-500 standard are also quite good and compare well with the ±0.3-0.5% precision obtained by conventional single filament mass spectrometry.

The analytical bias for these measurements appears to be a characteristic of RIMS, at least at the wavelengths used in this study. The U wavelength, 591.5 nm, is known to be a three-photon scheme 1 process. This means that two transitions must match in energy closely enough to allow ionization with photons of a single color (within the bandwidth of the laser). These three-photon transitions seem to occur for many actinide elements due to their densely packed upper energy levels. Since these processes originate at or near the ground state, they are usually the most intense features in the ionization spectrum in the wavelength range we used (R6G dye at 580-605 nm). The Pu wavelength used was 588.1 nm and is also believed to be a three-photon transition.

TABLE 1				TABLE 2	
RIMS – plutonium measurements				RIMS – uranium measurements	
Analysis	$^{240}Pu/^{239}Pu$	$^{241}Pu/^{239}Pu$		Analysis	$^{235}U/^{238}U$
1	0.2456	0.0353		1	1.025
2	0.2471	0.0362		2	1.034
3	0.2467	0.0361		3	1.036
4	0.2460	0.0351		4	1.022
5	0.2464	0.0354		5	1.024
Avg.	0.2464	0.0356		Avg.	1.028
SD	0.0006	0.0005		SD	0.0067
RSD	0.24%	1.4%		RSD	0.65%
NBS Cert.	0.2414	0.0341		NBS Cert.	0.9997

Apart from the expected hyperfine splittings and isotope shifts of the transitions involved, the three-photon excitation mechanism requires an exact match of two transitions. The degree to which they match and the fine structure of each transition will result in more or less bias as a function of wavelength for a given isotope ratio. The important consideration is, therefore, how well can the wavelength (and thus the bias) be controlled from one analysis to another. We have used a computer routine to locate the centroid of the U line at 591.54 nm and that of a Ne line at 591.38 nm using the optogalvanic effect in a U hollow cathode lamp. The computer automatically scans the Ne line at the beginning of each analysis and sets the laser wavelength to the same position on the U line with a precision which is better than the short-term drift of the laser itself. The resulting precision in the isotope ratio measurements can be seen in Table 2.

The selectivity obtained for mixed U-Pu samples was determined from the $^{239}Pu/^{235}U$ ratio at both RIMS wavelengths and using thermal ionization. At the Pu wavelength, 588.1 nm, a selectivity ratio of 200 was obtained for Pu with respect to U, normalized to equal thermal ion signals. The selectivity for U compared to Pu at 591.5 nm was found to be 3400. These values are not as high as those reported elsewhere (refs. 5,7) for classical scheme 1 RIMS transitions, but can be explained by non-resonant ionization processes, especially for U, producing a "background" which is independent of wavelength.

Recent studies have sought to measure the ionization spectra of the actinide elements Th, U, Np, Pu, Am, and Cm. Such studies provide information about ionization routes (three- vs two-photon schemes) as well as help in the selection of analytical wavelengths for highest sensitivity and selectivity. It has been found, for instance, that most actinide elements can be ionized via three-photon processes originating near the ground state, and that these lines can be the most intense in the spectrum. Other lines have been attributed to a two-photon (scheme 1) mechanism originating from high-lying excited levels. These excited states are probably populated by hybrid resonances occurring when small molecular species such as dimers are photo-dissociated.

It was found that the analytical line of Pu, 588.1 nm, was close to a relatively strong line of Am at 588.2 nm, thus potentially eliminating any selectivity for Pu with respect to Am. However, in measurements of samples containing equal amounts of Pu and Am (verified by thermal ion signals), a selectivity ratio for Pu of 15,000 was obtained at 588.1 nm. It appears that the Pu line is a three-photon excitation process originating from the ground state, while the Am line originates from a highly excited level and proceeds to ionization via a two-photon process. The slight mismatch in wavelength between the Pu and Am lines was responsible for the high selectivity observed.

SUMMARY

Laser-induced resonance ionization has been found to be a powerful tool when coupled with isotope ratio mass spectrometry. Our studies have shown that the ionization process is frequently more complex than originally predicted. This, however, provides the analyst with many possible routes, expanding the wavelength range over which ionization can be accomplished. In addition, RIMS represents a unique tool for studying the processes of thermal atomization and excitation of neutral atoms. In the future, we will continue to develop RIMS into a viable analytical method, and to use it to probe physical and chemical systems of interest.

REFERENCES

1. D. W. Beekman, T. A. Callcott, S. D. Kramer, E. G. Arakawa, G. S. Hurst, and E. Nussbaum, Int. J. Mass Spectrom. Ion Phys., 34 (1980) 89.

2. D. L. Donohue, J. P. Young and D. H. Smith, Int. J. Mass Spectrom. Ion Phys., 43 (1982) 293-307.

3. J. P. Young and D. L. Donohue, Anal. Chem., 55 (1983) 88-91.

4. D. L. Donohue and J. P. Young, Anal. Chem., 55 (1983) 378-379.

5. C. M. Miller, N. S. Nogar, A. J. Gancarz, and W. R. Shields, Anal. Chem., 54 (1982) 2377-2378.

6. C. M. Miller, J. B. Cross, and N. S. Nogar, Optics Communications, 40 (1982) 271-276.

7. C. M. Miller and N. S. Nogar, Anal. Chem., 55 (1983) 1606-1608.

8. J. D. Fassett, J. C. Travis, L. J. Moore, and F. E. Lytle, Anal. Chem., 55 (1983) 765-770.

9. J. D. Fassett, L. J. Moore, J. C. Travis, and F. E. Lytle, Int. J. Mass Spectrom. Ion Phys., 1983, in press.

10. G. S. Hurst, M. G. Payne, S. D. Kramer, and J. P. Young, Rev. Mod. Phys., 51 (1979) 767.

11. R. L. Walker, R. E. Eby, C. A. Pritchard, and J. A. Carter, Anal. Lett., 7 (1974) 563.

12. D. H. Smith, R. L. Walker, and J. A. Carter, Anal. Chem., 54 (1982) 827A.

13. D. H. Smith, W. H. Christie, H. S. McKown, R. L. Walker, and G. Hertel, Int. J. Mass. Spectrom. Ion Phys., 10 (1972/73) 343.

14. J. D. Fassett, NBS, personal communication, May, 1983.

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