tageous in any detector and are important considerations to the potential user of this thermal lens detector.

The system should also be suitable for use with short, high efficiency columns (5–15 cm length, 4.6 mm internal diameter, 3 μm diameter packing material). These columns require the same small flow cells and detector sensitivity as microbore HPLC.

## ACKNOWLEDGMENT

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# Detection of Plutonium by Resonance Ionization Mass Spectrometry

*Sir:* The development of resonance ionization spectroscopy (RIS) and related methods (1, 2) has provided analytical chemists with a tool of unique usefulness. This technique of photoionization through quantum-allowed intermediate states provides complete elemental specificity in most cases. This capability is well suited to solving the problem of isobaric (same-mass) interferences in isotope ratio mass spectrometry. We have, therefore, pursued the development of resonance ionization mass spectrometry (RIMS) for a number of elements of interest, including Nd and Sm (3). Other workers in the field have studied the elements K (4) and Lu (5).

RIS schemes necessary to produce ionization of most elements in the periodic table have been predicted (1, 2). These schemes vary from the simplest, single wavelength process to those involving more than one wavelength of excitation. Among the most easily ionized elements by RIS are the lanthanide and actinide series, including Pu. Because of its importance in safeguards and the nuclear fuel cycle, Pu has been extensively studied in our laboratory by high sensitivity thermal ionization mass spectrometry (6, 7). However, such measurements have suffered in the past from isobaric interference due to U (at mass 238) and Am (at mass 241). The former is found in samples of spent reactor fuel at a concentration $10^2$ to $10^3$ times higher than the Pu, while the latter isotope is a decay product of $^{241}$Pu. The goal of this study, therefore, has been to demonstrate that RIMS would be applicable to Pu isotopic measurements and also to define the analytical parameters of such measurements.

## EXPERIMENTAL SECTION

The experimental setup was essentially identical with that previously described (3). Pulses of monochromatic light radiation in the range of 430–450 nm were produced by a nitrogen-pumped dye laser system (Lumonics Model TE-262-2 N$_2$ laser, Lumonics, Inc., Ontario, Canada, with NRG Model DL-0.03 dye laser head, National Research Group, Inc., Madison, WI). The dye used was C-440 (Exciton Chemical Co., Dayton, OH) at a concentration of $5 \times 10^{-3}$ M in ethanol. The pulses were focused into the ion source of a single-stage magnetic sector mass spectrometer of ORNL design (8). Atoms produced by a heated Re filament (at 1600–1700 °C) were ionized by the laser radiation and were extracted and focused by the mass spectrometer ion optics.

Detection of ions was accomplished by a 14-stage electron multiplier operated in the current integration (analog) mode. This was followed by preamplification and amplification (Model 575,

EG&G, ORTEC, Oak Ridge, TN) of the signal before being digitized by an analog-to-digital converter (Model 800, EG&G, ORTEC). During the experiments, a computer was used to control the firing of the N$_2$ laser, the selection of mass position monitored, and/or wavelength of laser radiation. The optical spectrum of Pu as tabulated in Table I was obtained by scanning the wavelength range 431–451 nm in 0.04-nm steps, taking one laser pulse per step. The range was scanned six times and compressed in the final output so that each data point represented the average of 12 laser pulses with an optical resolution of 0.08 nm. The optical power of each laser pulse was approximately 300 μJ, with a pulse-to-pulse variability of ±5% (vendor's specification). The bandwidth of the dye laser was 0.03 nm, with a usable spot size of <0.01 cm$^2$ when focused.

The sample consisted of a mixture of Pu isotopes containing 1 μg of $^{242}$Pu (99% pure) and 30–50 ng of NBS SRM 947e containing the isotopes of Pu from mass 238 to 242. In addition, 100 μg of Sm was present on the filament to aid in the initialization and focusing of the mass spectrometer and optical system. The Sm and $^{242}$Pu were added to the filament as solutions in dilute HNO$_3$, while the NBS 947e was adsorbed onto anion resin beads (6, 7) following our established procedures. After drying of the solutions, a coating of colloidal graphite in water (Aquadag) was added to provide a reducing matrix under operating conditions in the ion source, thus preventing loss of sample as oxide species.

## RESULTS AND DISCUSSION

To verify that the signals obtained under laser excitation were, in fact, due to resonance ionization of Pu, it was necessary to demonstrate the following things. Firstly, was the signal at a given wavelength of excitation observed at the mass positions of the Pu isotopes present and in the approximate ratios expected (as determined by thermal ionization)? Secondly, did the signal for a given mass (i.e., $^{242}$Pu) appear only at discreet wavelengths, and were these wavelengths characteristic of allowed Pu electronic transitions?

The first question was answered satisfactorily by using an excitation wavelength of 431.1 nm (an expected RIS transition for Pu) and sweeping through the mass spectrum in the range of 238–250 mass units. Mass peaks for $^{239}$Pu, $^{240}$Pu, and $^{242}$Pu appeared at approximately the same abundance as the thermal ionization spectrum obtained from the sample. The signal-to-noise ratio for the $^{242}$Pu was estimated to be ≥20. This indicated that the ionization process was effective for Pu and that no unexpected chemical or isotopic discrimination factors were at work. No quantitative data were obtained because

Table I. Observed and Predicted Resonance Ionization Wavelengths for Plutonium

| obsd wave-length, nm | intens | lit. wave-length (10), nm | initial sublevel of $^7F$ state | error, nm |
|---|---|---|---|---|
| 431.1 | s | 431.0 | 1 | +0.1 |
|  |  | 431.1 | 2 | 0 |
| 431.4 | m | 431.4 | 3 | 0 |
| 431.5 | w | 431.4 | 3 | +0.1 |
| 431.9 | m | 431.8 | 3 | +0.1 |
| 432.4 | w | 432.3 | 4 | +0.1 |
| 432.6 | w | 432.3 | 4 | +0.3 |
|  |  | 432.9 | 3 | −0.3 |
| 433.2 | w | 433.1 | 5 | +0.1 |
| 433.5 | m | 433.1 | 5 | +0.4 |
| 435.7 | s | 435.5 | 2 | +0.2 |
| 436.1 | m | 436.2 | 1 | −0.1 |
| 436.2 | m | 436.2 | 1 | 0 |
| 436.6 | s | 436.6 | 2 | 0 |
|  |  | 436.7 | 3 | −0.1 |
| 437.0 | m | 436.7 | 3 | +0.3 |
| 438.8 | w | 438.9 | 4 | −0.1 |
| 439.1 | m | 439.2 | 3 | −0.1 |
| 439.3 | w | 439.2 | 3 | +0.1 |
| 439.6 | m | 439.9 | 4 | −0.3 |
| 440.0 | w | 439.9 | 4 | +0.1 |
| 440.2 | m | 440.3 | 0 | −0.1 |
| 440.7 | s | 440.4 | 1 | +0.3 |
| 442.2 | w |  |  |  |
| 442.5 | w |  |  |  |
| 442.8 | w | 442.8 | 3 | 0 |
| 443.1 | w | 443.4 | 1 | −0.3 |
| 443.5 | s | 443.4 | 1 | +0.1 |
| 443.7 | m |  |  |  |
| 443.9 | m |  |  |  |
| 444.5 | m |  |  |  |
| 445.5 | m | 445.6 | 2 | −0.1 |
| 445.7 | w | 445.6 | 2 | +0.1 |
| 446.0 | m | 445.9 | 3 | +0.1 |
| 446.2 | m |  |  |  |
| 446.9 | w |  |  |  |
| 447.2 | w | 447.2 | 4 | 0 |
| 447.7 | m | 447.6 | 2 | +0.1 |
|  |  | 447.8 | 3 | −0.1 |
|  |  | 447.8 | 5 | −0.1 |
| 448.0 | m | 447.8 | 3 | +0.2 |
|  |  | 447.8 | 5 | +0.2 |
| 448.5 | m | 448.8 | 2 | −0.3 |
| 448.9 | w | 448.8 | 2 | +0.1 |
| 449.5 | w | 449.8 | 3 | −0.3 |
| 450.3 | w | 450.7 | 5 | −0.4 |
| 450.8 | s | 450.7 | 5 | +0.1 |
|  |  | 450.8 | 0 | 0 |

of the signal levels involved (estimated 1–5 Pu$^+$ ions detected per laser pulse).

The second problem, that of verifying that resonance ionization was the source of the signals, was addressed by setting the mass spectrometer to monitor $^{242}$Pu ions while scanning the laser wavelength. Our experience with Sm, which lies directly above Pu in the periodic table, suggested that certain transitions would be expected in the wavelength range of 430–450 nm resulting from ionization of ground state and low-lying excited state atoms. The low-lying levels of Sm were found to be more highly populated than the ground state due to the temperature of the atomizing filament (1500 °C) (9).

The resulting spectrum, tabulated in Table I, shows the wavelengths at which ionization of $^{242}$Pu was observed. The peaks were characterized as either strong (signal-to-noise ratio (SNR) of greater than 10), medium (SNR between 5 and 10), or weak (SNR between 2 and 5). The predicted spectral lines are also shown (10), along with the starting level notation. The average deviation obtained for those lines which have been tentatively assigned was ±0.012 nm, indicating a high degree of correlation.

Due to the small numbers of ions collected in each spectral peak, the intensity data are only approximate. However, it is possible to obtain useful information from the wavelengths observed, along with the tentative assignments of the transitions involved. The case of Pu appears similar to that of Sm, which has been more extensively studied (9). A distribution of starting states is seen, with few transitions arising from the ground state, $^7F_0$. The initial levels most populated were $^7F_2$ and $^7F_1$. Most of the RIMS peaks can be identified with previously reported transitions (10). Some 15% were not identified; it seems likely that these are associated with Pu but are, as yet, not characterized. The processess involved in desorption of atoms from a heated metal filament are complex, and a satisfactory theory which predicts the population of electronic excited levels is not available. RIMS offers a method of unique usefulness in studying these phenomena.

The limitation on analytically useful RIMS measurements of Pu isotope ratios with our present equipment is that not enough ions can be collected in a reasonable time period (30 min to 1 h) to obtain useful precision (less than ±1% relative standard deviation). To obtain an isotope ratio in this time period using a laser pulse repetition rate of 1 Hz would involve the accumulation of only 1000–2000 pulses per isotope. A more efficient laser system having a larger pulse duty cycle would eliminate this deficiency.

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