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Trace analysis of plutonium in environmental samples by resonance ionization mass spectroscopy (RIMS)

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Abstract

Resonance ionization mass spectroscopy (RIMS) is well suited for trace analysis of long-lived radioisotopes in environmental, biological and technical samples. By multiple resonant laser excitation and ionization of the elemental atoms under investigation, an extremely high element selectivity can be achieved. In addition, isotope selectivity is obtained by subsequent mass analysis. The excellent sensitivity results from the large atomic cross-sections in the excitation–ionization process and the good detection efficiency for ions. The element selectivity of RIMS allows a simplified procedure for the chemical preparation of the samples compared to the requirements of thin sources for α-spectroscopy. Various samples have been determined by RIMS with respect to their content and the isotopic composition of plutonium in the ultra-trace regime. A detection limit of 10^6 to 10^7 plutonium atoms has been achieved for all isotopes, independent of their half-life and decay mode. For ^{239}Pu, this value is distinctly below the radiometric detection limit. © 1998 Elsevier Science S.A.

Keywords: Trace Detection; Plutonium; Resonance ionization mass spectroscopy

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1. Introduction

Trace amounts of plutonium are present in the environment mainly as a result of global fallout from nuclear weapons tests, nuclear accidents and releases from nuclear facilities. A sensitive and fast detection method is required for risk assessment, low-level surveillance of the environment, studies of the migration behavior and personnel dose monitoring. The origin of a plutonium contamination, e.g. its method of production, is directly related to its isotopic composition. The standard method for plutonium determination, α-spectroscopy, cannot distinguish between ^{239}Pu and ^{240}Pu due to their very similar α-energies and ^{241}Pu cannot be measured since it is a β-emitter. The measuring time for each sample containing ~10^8 atoms of ^{239}Pu requires at least 1 day.

Non-radiative detection methods, like mass spectroscopy, are independent of the half-life and decay type of the isotope. They allow a determination of the isotopic composition within a measuring time of 1–2 h. However, these methods often suffer from interferences from isobars.

2. Resonance ionization mass spectroscopy

RIMS of vaporized atomic samples provides an excellent element selectivity, and thus minimizes isobaric interferences, as the relevant atomic transitions are characteristic for each element. The multiple resonant excitation and ionization is selective for one element and with appropriate resolution even for a single isotope of this element. An additional isotope selectivity is achieved by subsequent mass analysis of the ions via a time-of-flight (TOF) measurement, which serves for efficient background reduction as well. The measuring time is, as in mass spectroscopy, 1–2 h.

RIMS meets the following requirements for ultra-trace analysis of plutonium: (a) high element and isotope selectivity, (b) good detection limit, due to high sensitivity and low background, (c) short measuring time.

3. Sample preparation

Prior to the sample preparation, calibrated amounts of tracer isotopes are added to determine the yield of the chemical separation and of the RIMS measurement. For

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plutonium samples, a combination of the shorter-lived ^{236}Pu and the longer-lived ^{244}Pu is best suited as tracer. The available ^{236}Pu contains other isotopes (up to 10%), and therefore only 10^7 atoms ^{236}Pu (77 mBq) are added to the sample to check the chemical yield via α-spectroscopy, and 10^9 atoms ^{244}Pu (98% enriched, NBS reference material SRM966) are used for monitoring the efficiency of the RIMS detection.

After adding the tracers to the sample, it is ashed, fused with $Na_2O_2/NaOH$ and dissolved in water. The remaining residue is dissolved in 8 N HCl, and the plutonium is coprecipitated with $Fe(OH)_3$. After dissolution of the precipitate in 4 N HNO_3 this solution is passed through a column filled with TEVA·Spec SPS resin (Aliquat 336N). The column is washed with 4 N HNO_3 and the plutonium is eluted from the column with 0.5 N HCl. The eluate is evaporated to dryness and fumed with concentrated H_2SO_4 to destroy polymeric and colloidal species. Subsequently, plutonium hydroxide is electrolytically deposited on a tantalum backing from a 20% $(NH_4)_2SO_4$ solution. Finally, the sample is covered with a thin titanium layer by sputtering [1]. When heating such a 'sandwich-type' filament in the vacuum of the measuring setup, the plutonium hydroxide is converted to the oxide. During diffusion through the titanium layer, plutonium oxide is reduced to the metallic state, and an atomic beam is evaporated from the filament [2].

4. Experimental setup

The experimental setup for RIMS, consisting of the laser system and the time-of-flight (TOF) mass spectrometer, is shown in Fig. 1, and described in detail in Ref. [3]. Three tunable dye lasers are simultaneously pumped by two copper vapor lasers at a pulse repetition rate of 6.5 kHz. In order to obtain optimum spatial overlap, the three dye laser beams are guided to the vacuum chamber by a single quartz fiber and focused into the interaction region, where they cross the atomic beam evaporated from the filament. The filament is heated by a continuous current and the plutonium atoms are evaporated in the direction of the TOF mass spectrometer. The atomic beam is intercepted by a pulsed poly-chromatic laser beam ($\lambda_1 = 586.49$ nm, $\lambda_2 = 665.57$ nm, $\lambda_3 = 577.28$ nm, for ^{239}Pu) and excited to an autoionizing state via a three-step resonance. The ions are accelerated to 3 keV and detected after mass selection in a reflectron-type TOF mass spectrometer by a channel plate device. A mass resolution of $m/\Delta m \approx 600$ is achieved (Δm is the FWHM). A detailed description of the mass spectrometer is given in Ref. [4].

With this technique, a reproducible detection efficiency, defined as the ratio of the number of ions detected with RIMS to the number of atoms deposited on the filament, of $\epsilon = 4 \times 10^{-5}$ has been determined. Taking into account the background count rate, a detection limit of 1×10^6 atoms for a single isotope is derived, which is by more than two orders of magnitude better than that for α-spectroscopy of ^{239}Pu. Fig. 2 shows the α spectrum and the RIMS spectrum of a sample containing 10^9 atoms of ^{239}Pu covered with a titanium layer. With the standard method (α-spectroscopy) only 20 counts were registered within 23.5 h, whereas with RIMS 14 700 counts could be measured in 1.5 h.

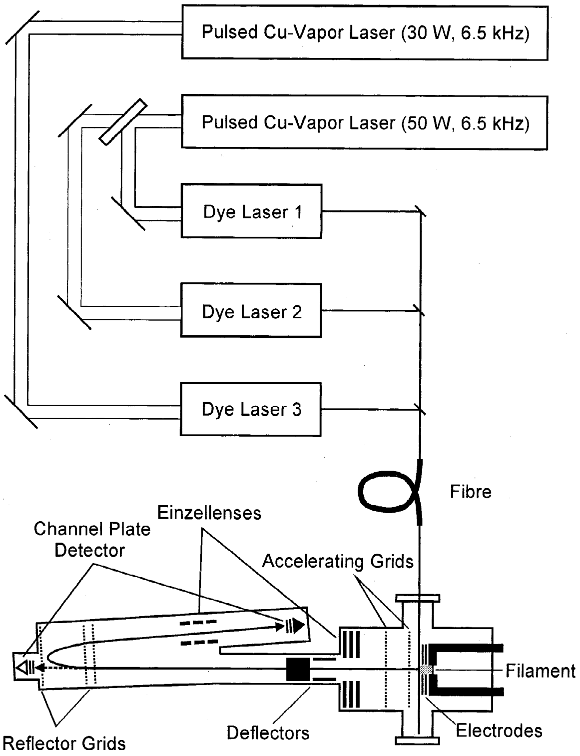

Fig. 1. Experimental setup for RIMS measurements with a reflectron type time-of-flight mass spectrometer.

The first and third laser resonances of plutonium show a substantial isotope shift in the atomic line, and need an appropriate tuning [5]. To determine the isotopic composition of plutonium, the first and third laser are scanned over the region of resonance. This leads to small losses in the ionization efficiency [6], so that 10^7 atoms of the least abundant isotope are necessary to obtain an statistical accuracy of ≈10%.

5. Results

The RIMS method has been applied for trace analysis of different environmental samples with respect to the total amount and isotopic composition of plutonium.

5.1. Soil samples from the Chernobyl area

Several soil samples from the Chernobyl area were investigated. Typical RIMS spectra for such samples are shown in Fig. 3. The upper part shows the spectrum of a

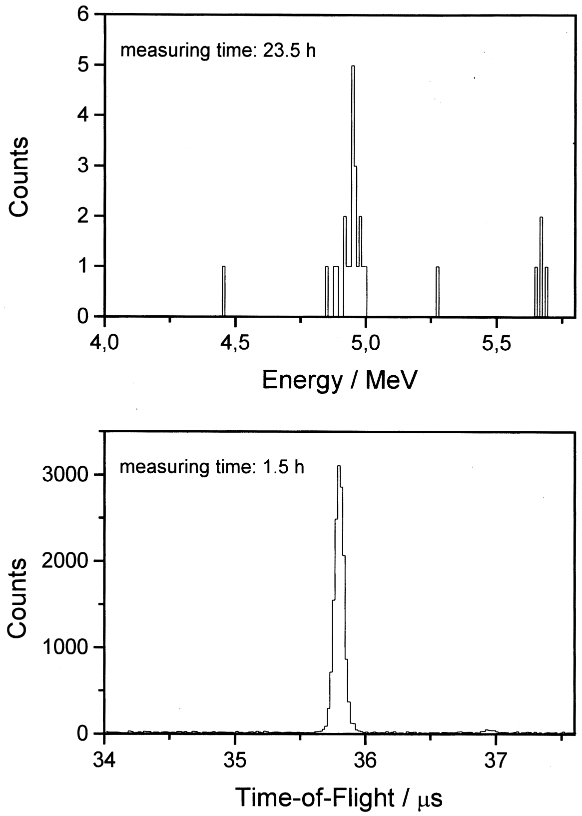

Fig. 2. Comparison between an α spectrum (upper part) and RIMS spectrum (lower part) of a sample containing 10^9 atoms of ^{239}Pu. Note the differences in count rate and measuring time.

hot particle which was collected in Masany some kilometers northwest of Chernobyl. The spectrum of a soil sample from Shpilevskaja (some kilometers south of Chernobyl) is shown in the lower part. The measured isotopic composition is typical for ‘reactor plutonium’, and in good agreement with values calculated from reactor parameters given by the management of the Chernobyl nuclear power plant [7] (see Table 1).

5.2. Pacific Ocean sediment

Fig. 4 shows a RIMS spectrum from 1 g of sea sediment collected at the Mururoa Atoll in the Pacific Ocean (reference material IAEA-368). The isotopic composition was determined to be 97% ^{239}Pu and 3% ^{240}Pu which is typical for weapons plutonium. The specified content of 31 mBq g^{-1} (^{239}Pu+^{240}Pu) could be confirmed.

5.3. Urine samples

The National Radiological Protection Board (NRPB) in Great Britain is interested in determining the uptake and urinary excretion of plutonium in human volunteers [8]. These were injected with ^{244}Pu (NBS reference material SRM966); the chemical separation of plutonium from the

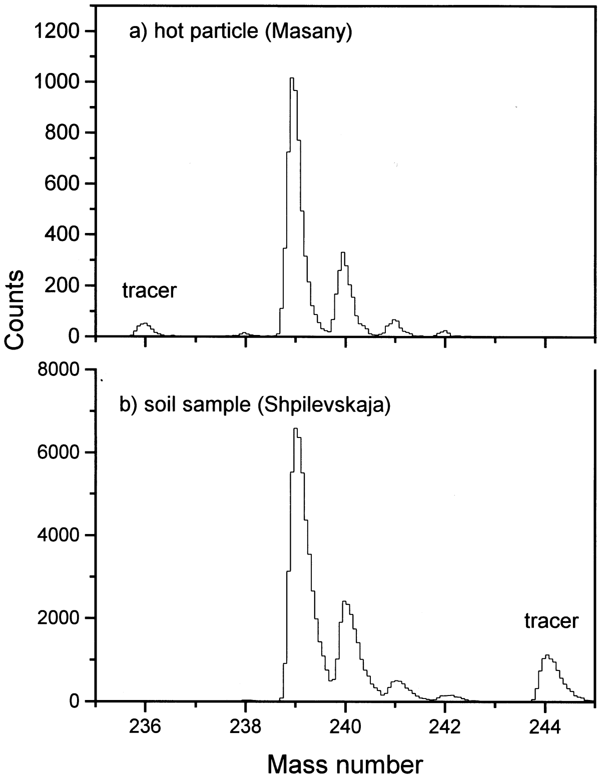

Fig. 3. Isotopic abundances of plutonium in samples from the Chernobyl area observed by RIMS (see text for details). The tracers used are seen at $A=236$ and $A=244$.

Table 1
Relative isotopic abundances of plutonium samples from the Chernobyl area in comparison with calculated values from published reactor parameters [7]

Isotope	Masany (%)	Shpilevskaja (%)	Calculated data (%)
^{238}Pu	0.25(2)	0.31(2)	0.22
^{239}Pu	66.9(4)	66.2(4)	64.6
^{240}Pu	25.3(2)	26.1(2)	27.6
^{241}Pu	5.9(1)	5.5(1)	5.5
^{242}Pu	1.6(1)	1.8(1)	2.2

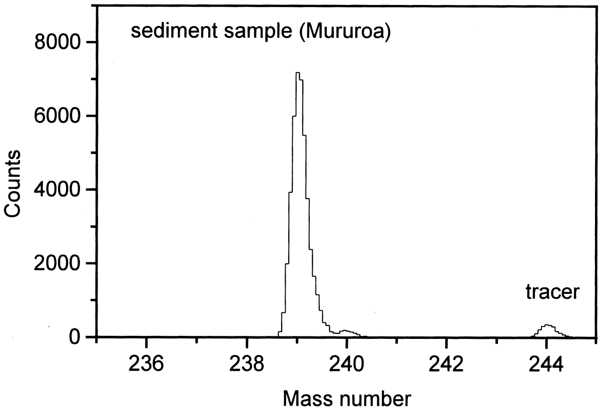

Fig. 4. Isotopic composition of the plutonium contamination in a sea sediment sample from the Mururoa Atoll in the Pacific Ocean.

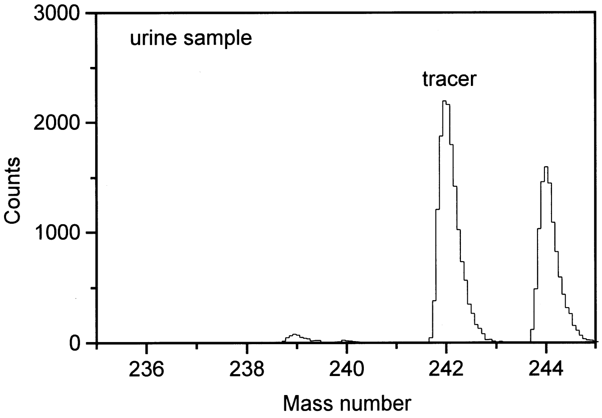

Fig. 5. ^{244}Pu in a urine sample measured with RIMS (see text for details). The ^{242}Pu tracer also contains a small amount of ^{239}Pu.

urine samples after spiking with ^{242}Pu tracer was done at the NRPB. A series of 30 urine samples was measured with RIMS. Fig. 5 shows the RIMS spectrum of a 1-day pooled urine sample taken 3 days after injection; a content of 3×10^9 atoms of ^{244}Pu was determined. The results are in excellent agreement with mass spectrometric data for other volunteer samples.

6. Conclusion

RIMS is a powerful tool for ultra-trace analysis of plutonium in environmental samples due to its excellent detection limit, which gives access to the sub-femtogram regime, and because of its extreme elemental and isotopic selectivity. The detection limit of this technique is by more than two orders of magnitude better than that of conventional α-spectroscopy for ^{239}Pu. The practicability and reliability of RIMS has been proven for a variety of samples.

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