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Determination of Plutonium in Urine: Evaluation of Electrothermal Vaporization Inductively Coupled Plasma Mass Spectroscopy*

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ABSTRACT

Mass spectroscopy has the distinct advantage of detecting atoms rather than radioactive decay products for nuclides of low specific activity. Electrothermal vaporization (ETV) is an efficient means of introducing small volumes of prepared samples (<100 uL) into an inductively coupled mass spectrometer (ICP/MS) to achieve the lowest absolute detection limits. The operational characteristics and capabilities of ETV/ICP/MS were evaluated. We describe its application as a detection method for determining Pu in urine, in conjunction with a preliminary separation technique to avoid matrix suppression of the signal.

Introduction

Urine and water samples have been analyzed for isotopic plutonium by alpha spectroscopy (1-3) and later by Moorthy et al., by fission track analysis (4). Detection limits of 170 μBq and 4 μBq were reported, respectively. In the less familiar fission track procedure, Pu-239 is detected by subjecting the sample, prepared on a quartz slide, to thermal neutron-induced fission. Fission fragments are observed by optical microscopy as tracks on the quartz slide. The fission track method requires a two-step anion-exchange separation with highly purified reagent acids in a dust-free environment and is specific for detecting any fissionable isotope. Recent improvements to the fission track methodology appear to have lowered its detection limit below about 1 μBq (5).

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Mass spectroscopy as a detection method offers the possibility of multi-element determination and simplified chemical preparation, with a sensitivity between that of alpha spectroscopy and fission track analysis. Several types of commercial mass spectrometers are available. Thermal ionization mass spectroscopy has been used extensively but preparation of the sample is difficult; ICP/MS is much more convenient for rapid analysis. Wyse and Fisher (6) reported detecting plutonium by mass spectroscopy, using an ultrasonic nebulizer system for introducing the sample in a peak jumping mode for multi-element determination. A detection limit (3σ) of 50 fg (110 μBq) for Pu-239 was observed. Hall and others (7) earlier reported a detection limit of 2 fg Pu-244 and 0.8 fg U-235 by ETV/ICP/MS using the single ion monitoring (SIM) mode to demonstrate the capability of the technique, using acidified standards. The ETV/ICP/MS technique was reviewed recently by Carey and Caruso (8).

Experimental

An ICP/MS[b] was used in conjunction with an ETV unit for introducing the sample. Plutonium was initially co-precipitated with calcium rhodizonate from urine (3). The dried precipitate was wet-ashed in an open-vessel automated microwave digester[c] with nitric acid and hydrogen peroxide to remove organic residues and solubilize the inorganic materials (1-4). The sample's matrix elements were removed by an anion-exchange separation based on the methods described for alpha spectroscopy and fission track analysis (4,5). The use of ETV to introduce the sample and the SIM mode maximized the sensitivity of detection by minimizing the volume of the final sample, eliminating the introduction of solvent into the plasma, and focusing on a single isotope.

A standard solution containing 50 ppb uranium was used initially to tune the mass spectrometer and maximize the detection signal. The heating profile and the carrier gas-flow in the ETV unit was then adjusted to obtain a signal for Pu-239.

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[b] Plasmaquad II+ and Microtherm III, Fison Instrument Company, Merrimac, MA 01860

[c] Prolabo A301, Questron Corp., Mercerville, NJ 08619

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Results and Discussion

Pu-239, prepared from the National Institute of Standards and Technology (NIST) traceable standard solutions in nitric acid, was used to calibrate the ETV/ICP/MS detection system. Current results give a detection limit of 2 fg, (4 μBq) based on 3σ of the background for Pu-239 with artificial urine blanks. Artificial urine samples containing known amounts of Pu-239 were used to determine the chemical recovery during the separation process.

Future analyses will be performed on synthetic urine used in fission track detection of Pu-239, with a long-term goal of using ICP/MS/ETV for routine bioassays of activities in humans and the environment.

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