Simultaneous determination of uranium and plutonium at trace levels in process streams using Arsenazo III by derivative spectrophotometry

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A derivative spectrophotometric method has been developed for the simultaneous determination of uranium and plutonium at trace levels in various process streams in 3M HNO₃ medium using Arsenazo III. The method was developed with the objective of measuring both uranium and plutonium in the same aliquot in fairly high burn-up fuels. The first derivative absorbances of the uranium and plutonium Arsenazo III complexes at 632 nm and 606.5 nm, respectively, were used for their quantification. Mixed aliquots of uranium (20-28 μg/ml) and plutonium (0.5-1.5 μg/ml) with U/Pu ratio varying from 25 to 40 were analysed using this technique. A relative error of about 5% was obtained for uranium and plutonium. The method is simple, fast and does not require separation of uranium and plutonium. The effect of presence of many fission products, corrosion products and complexing anions on determination of uranium and plutonium was also studied.

Introduction

Determination of uranium and plutonium in all the process streams is a necessary part of an efficient nuclear materials accounting system in a fuel reprocessing plant. The radiometric method is normally used for the determination of plutonium in process solutions.¹ This, however, needs separation from other α-emitters and a knowledge of the isotopic composition. For the determination of uranium at trace concentrations in process streams, many methods are reported. Fluorimetry² and isotope-dilution mass spectrometry³ (IDMS) are generally used but they require specialized and expensive instrumentation and necessitate prior separation. An alternate method that involves simple instrumentation was therefore, sought for the determination of uranium and plutonium, preferably in the same aliquot.

Arsenazo III (3,6-bis[(2-arsonophenyl)-azo]-4,5-dihydroxy-2,7-naphthalene disulphonic acid) is known to form coloured complexes with uranium, plutonium and other actinide elements in strongly acidic medium⁴,⁵ and their complexes have high molar extinction coefficients. Although the method has high sensitivity, it is not selective because of the mutual interferences with each other. Tedious separations are required before their determination is possible.

Derivative spectrophotometry is normally used to resolve overlapping bands as well as to eliminate background interferences.⁶,⁷ Potential application of this technique has been recently demonstrated in certain areas of the nuclear fuel cycle.⁸ The present paper describes the development of a derivative spectrophotometric method for the determination of uranium and plutonium at ppm levels in some of the reprocessing streams of the nuclear fuel cycle. The effect of the presence of many corrosion and fission products which are present in significant amounts in high burn-up fuels was also investigated to the accuracy of the measurements of uranium and plutonium. The effect of complexing anions like sulphate, oxalate and fluoride ions was also studied with a view to finding direct application of this method in waste streams generated during fabrication of plutonium fuels.

Experimental

Apparatus

A SHIMADZU UV-2100 double beam spectrophotometer was used with 10 mm path-length disposable polystyrene cuvettes.

Reagents

A U(VI) stock solution (0.660 mg/g) was prepared from well characterized U₂O₈ powder and Pu(IV) stock solution (0.303 mg/g) was prepared from a solution of Pu(NO₃)₄ of known concentration. Mixed aliquots of U and Pu (U/Pu ratio varying from 25 to 40) were prepared using these solutions. Arsenazo III (S.D. Fine Chemicals) was dissolved in 0.01 M NaOH to obtain a stock solution of concentration 2 mg/ml.

Procedure

Colour development: Evaporate a mixture of uranium and plutonium to dryness. Take up the residue in 5 ml of 3M HNO₃. Add 0.5 ml of 1.5M sulphuric acid to destroy nitrous acid present in HNO₃ acid. Transfer the solution to a 10 ml standard flask, add 0.5 ml of Arsenazo III solution and dilute to the mark with 3M HNO₃.
Spectral measurements: Place reagent blank solution in the sample and reference cells and scan from 750 to 600 nm to set up the base line at a scan speed of 100 nm/min with 2 nm slit width. Replace the blank solution in the sample cell with the sample solution and repeat the spectral scan. The whole spectrum was stored on a 3½-inch floppy disk and then the first derivative spectrum was obtained at a wavelength interval (Δλ) of 5 nm. The derivative amplitudes was read at 632 nm (zero-point wavelength for plutonium complex) and 606.5 nm (zero-point wavelength for uranium complex) for the determination of uranium and plutonium, respectively. In this way derivative amplitudes for uranium and plutonium were measured and a calibration curve for uranium (20–28 μg/ml) and plutonium (0.5–1.5 μg/ml) was constructed by plotting the derivative amplitudes (measured at appropriate concentration) vs. the metal ion concentration (Figs 1 and 2).

Results and discussion

The spectrophotometric methods for uranium and plutonium with Arsenazo III are highly sensitive and are widely used for trace determination of these elements. The absorbance of the Arsenazo III complexes of uranium and plutonium increases with increasing HNO₃ conc. Though U(VI)-Arsenazo III and Pu(IV)-Arsenazo III complexes are known to have maximum absorbance between 5–7M HNO₃, measurements were carried out at 3M HNO₃ which is the acidity encountered under plant conditions.

Absorption spectra of Arsenazo III complexes of uranium and plutonium (Fig. 3) are too similar to allow the direct spectrophotometric determination of one element in presence of the other. Therefore, first derivative spectra were taken to resolve the overlapping spectra of U(VI)-Arsenazo III and Pu(IV)-Arsenazo III complexes. The first derivative spectra of the complexes of plutonium and uranium at different concentrations are shown in Figs 4 and 5, respectively, showing three zero-point each. The zero-point at 632 nm for plutonium and at 606.5 nm for uranium were found suitable for U and Pu estimation, respectively.