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DETERMINATION OF TRACE URANIUM IN PUREX AQUEOUS WASTE WITH ARSENAZO III

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ABSTRACT

A method was developed for determining trace uranium in aqueous wastes from processing nuclear reactor fuels. Uranium(VI) is determined colorimetrically with the metal indicator Arsenazo III, after removing fission product interferences by solvent extraction of ammonium nitrate solutions with tributyl phosphate in xylene. The range of the method is 0 to 5 μg uranium/ml in the final extraction, with a standard deviation of ±0.1 μg uranium/ml.

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DETERMINATION OF TRACE URANIUM IN PUREX AQUEOUS WASTE WITH ARSENAZO III

INTRODUCTION

Determination of uranium losses is a necessary part of the Savannah River Laboratory study of reprocessing nuclear fuels from light water reactors (LWR).[1] Analysis of aqueous waste (1AW) from the solvent extraction step of the Purex process[2] poses a special analytical problem because the solutions contain only traces of uranium in the presence of major amounts of fission products. The high burnup of these LWR fuels has resulted in higher levels of fission products than are ordinarily encountered in this type of analysis. Because of the high radioactivity of the solutions, the volume of sample must be kept to a minimum.

Many methods have been developed for determination of traces of uranium. Fluorophotometry and isotope dilution-mass spectrometry (IDMS) are commonly used,[3] but they require specialized instrumentation. A sensitive method that involves simple manipulations and a common laboratory instrument was sought for routine analyses. A colorimetric determination that consists of uranium separation by solvent extraction, followed by color development with Arsenazo III,[3] is described in this report.

DEVELOPMENT OF METHOD

Background

The LWR waste solutions to be analyzed for uranium consisted of 2M HNO_3, $<10^{-4}$M uranium(VI), and $>10^{-2}$M fission products and other cations. Because the solutions were highly radioactive, a sample volume smaller than 500 µl was desirable. Because of the limited volume and low uranium content, a sensitive method was required.

The metal indicators Arsenazo I* and Arsenazo III** were investigated for colorimetric determination because they form intensely colored complexes with uranium. The molar extinction coefficients for the uranyl complexes are 22,900 at pH 7.5 for Arsenazo I,[4] and 53,000 at pH 2 for Arsenazo III.[5]

The Arsenazo indicators form colored compounds with many other polyvalent cations, including the actinides, lanthanides, and other fission products, all of which are anticipated in the sample solutions. Therefore, the uranium must be isolated prior to the determination. The uranium was simply and effectively separated by solvent extraction with tributyl phosphate (TBP).

Metal-Arsenazo Absorption Spectra

Arsenazo I at pH 7.6 was used for developing the solvent extraction procedure to eliminate interferences. With this reagent, the absorption maxima for uranium and the interferences (e.g., lanthanum) occurred at different wavelengths (Figure 1). The spectrum of the final solution (Figure 2) thus immediately indicated the success or failure of the separation scheme. With Arsenazo III, absorption maxima for uranium and the interferences were indistinguishable.

Arsenazo III at pH 2.5 was used for color development in the final procedure because of its greater sensitivity and because the lower pH was more compatible with the acidic nature of the sample and the extraction solutions. Absorption spectra of several concentrations of uranyl nitrate with Arsenazo III are given in Figure 3.

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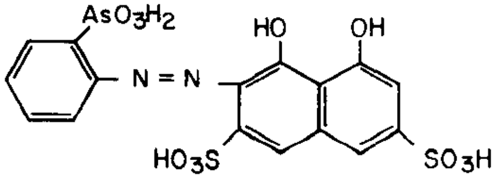
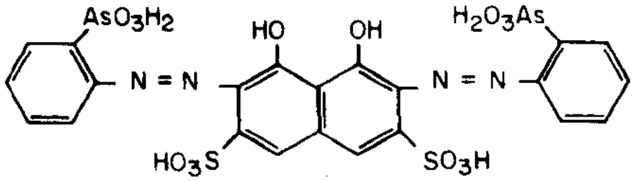
* Arsenazo I is o-[(1,8-dihydroxy-3,6-disulfo-2-naphthyl)azo]-benzenearsonic acid:



** Arsenazo III is 2,2'-[(1,8-dihydroxy-3,6-disulfo-2,7-naphthalene)bis(azo)]di-benzenearsonic acid:



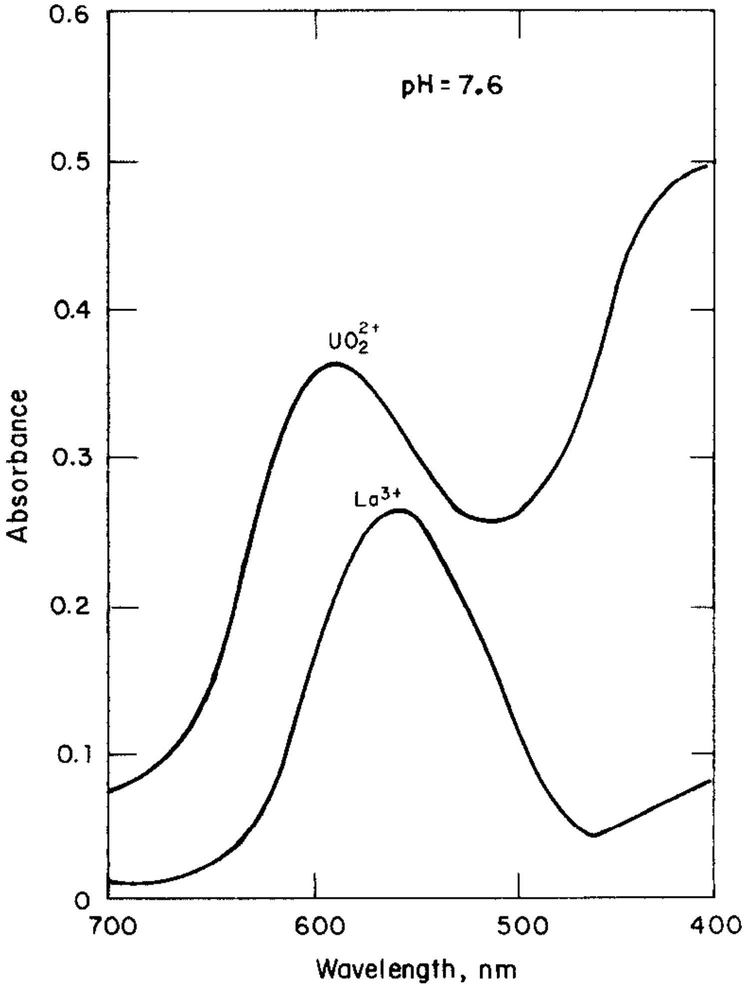


FIGURE 1. Absorption Spectra of the Arsenazo I Complexes with UO_2^{2+} and La^{3+}

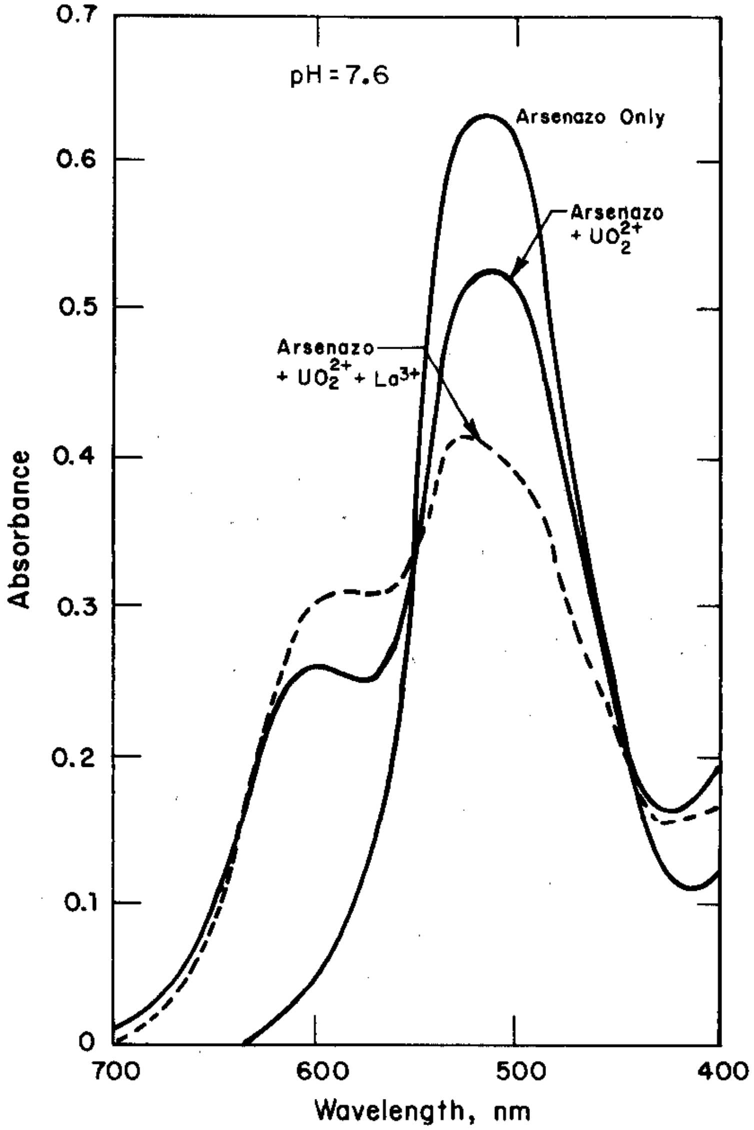


FIGURE 2. Effect of La^{3+} on the Absorption Spectrum of the UO_2^{2+} Complex with Excess Arsenazo I

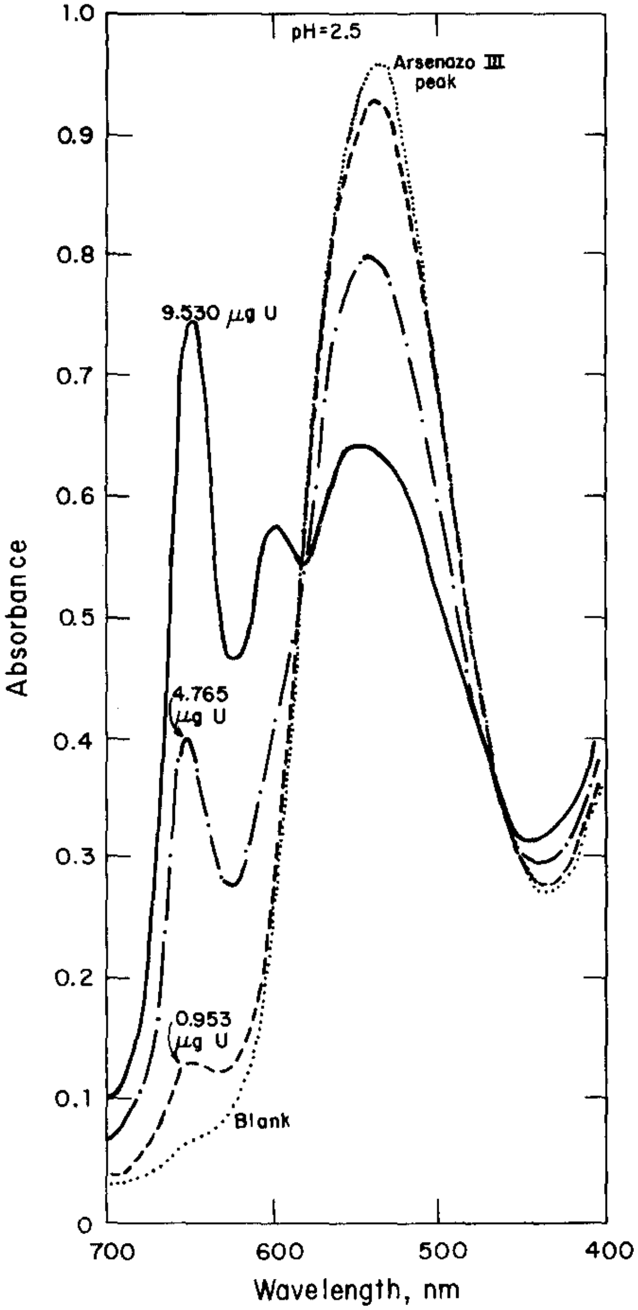


FIGURE 3. Absorption Spectra of the Arsenazo III Complex of UO_2^{2+} at Different Concentrations

Interferences

The interference of lanthanum, zirconium, nitrosylruthenium, molybdenum, palladium, and rhodium at 0.01M concentrations was investigated. Although the actinides, such as neptunium and plutonium, also form colored complexes with the Arsenazo indicators, their concentrations were expected to be insignificant in the samples of interest. Of the other elements, only lanthanum, zirconium, and palladium formed colors with Arsenazo I and III.

Extraction

Extraction of uranium from ammonium nitrate solutions with TBP was adapted from a published procedure.[3] This procedure was modified by using 5% TBP in xylene as the organic extractant. With xylene, the aqueous and organic phases separated rapidly after mixing.

The scheme for extraction and purification (Table 1) evolved as a procedure that successfully separated uranium from the fission product interferences; the procedure was not further optimized. Oxalate in Extraction I prevented the extraction of zirconium into the organic phase. The interim wash, Extraction II with ammonium nitrate, removed entrained acid from the TBP, which otherwise affected the optimum pH of Extraction III. Without Extraction III, which contained ethylenediaminetetraacetic acid (EDTA), traces of lanthanum remained in the organic phase and formed a color with the Arsenazo solution. The walls of the vials were rinsed with water after each extraction step to maintain the requisite conditions for the succeeding extraction and to avoid carryover of interferences.

Decontamination

The solvent extraction separation also decontaminated the LWR sample solutions. The effectiveness of the decontamination is shown in Table 2, where decontamination factors are given for selected radionuclides in a typical LWR aqueous waste solution. Extractions I and II required remote handling in a shielded facility. However, with the radioactivity reduced, Extractions III and IV could be performed with minimum shielding in a radiobench. The final solution for the colorimetric determination contained low-level radioactivity.

TABLE 1

Summary of Experimental Procedure

Extraction Number	*Aqueous Phase*[a]	*Organic Phase*[a]	*Function*
I	Sample in 2M HNO_3, 0.1M $K_2C_2O_4$, and 60% NH_4NO_3	5% TBP in xylene	Separates uranium from bulk of fission products
II	60% NH_4NO_3	Organic from I	Removes entrained acid
III	60% NH_4NO_3, 0.25% EDTA,[b] pH 2.7	Organic from II	Removes fission products as EDTA complex
IV	Arsenazo III in phthalate buffer, pH 2.5	Organic from III	Back-extracts uranium into aqueous phase as colored complex; 2-ml total volume; absorbance read at 652 nm in 1-cm cell

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[a] 2-ml volumes throughout.

[b] Ethylenediaminetetraacetic acid.

TABLE 2

Decontamination of LWR Waste Sample by Extraction Procedure

	Activity in Original Sample, dis/(min ml)	*Cumulative Decontamination Factor for Uranium-Containing Phase After Extraction Step*[a]			
		I (Org)	*II (Org)*	*III (Org)*	*IV (Aq)*
Gross Alpha	1.5×10^9	14	3.2×10^3	8.0×10^3	5.6×10^5
^{106}Ru	4.3×10^{10}	14	4.9×10^3	6.2×10^4	6.2×10^4
^{137}Cs	4.6×10^{10}	14	7.6×10^3	7.2×10^5	7.2×10^5
^{144}Ce	4.4×10^{10}	14	6.0×10^3	3.4×10^5	3.4×10^5
^{154}Eu	2.3×10^{10}	130	$>10^5$	$>10^5$	$>10^6$

---

[a] See Table 1.

Recovery

All the uranium was not recovered in the solvent extraction scheme. The greatest loss occurred with Extraction III, perhaps because of excess EDTA, which has been reported to cause low uranium recovery.[4] A series of tests with known amounts of ^{233}U showed that the recovery in this instance, as determined by alpha counting, was consistent at 66 to 67% for 0.97, 3.88, and 9.70 µg uranium. Because the recovery from different sample environments could not be predicted, the mode of analysis for LWR samples required determination of the uranium content of a sample followed by that of a sample containing a known uranium spike. This technique was expected to correct for possible different extraction behavior in different samples.

RESULTS AND CONCLUSIONS

The detailed experimental procedure of the colorimetric method (Appendix) was applied to standard uranium solutions in the presence and absence of interferences and to LWR aqueous waste samples. In the latter case, results were compared with results obtained by the isotope dilution-mass spectrometry (IDMS) method.

The range of the colorimetric method and the success in separating uranium from miscellaneous fission products is illustrated in the calibration curves (Figure 4). Uranium standards were analyzed in the presence and in the absence of a simulated "fission product mixture," which consisted of 0.01 mmol each of lanthanum nitrate, sodium molybdate, zirconyl perchlorate, and nitrosylruthenium nitrate. Beer's law was obeyed for a concentration of at least 10 µg of uranium in the 2-ml volume of solution measured (5 µg/ml). The standard deviation was ±0.2 µg uranium.

In these determinations, absorbances were measured versus distilled water to establish the magnitude of the reagent blank: 0.04 to 0.05 absorbance units. In practice, the use of the reagent blank in the reference cell is recommended.

The results of uranium determinations on two LWR aqueous waste samples are given in Table 3. The uranium spike in each case consisted of pure ^{233}U, enabling a supplemental independent uranium determination to be obtained by determining the uranium isotope distribution in the spiked sample by mass spectrometry.

The agreement between the uranium determined by colorimetry and that by mass spectrometry indicates that the technique of analyzing a spiked and unspiked sample of LWR waste produces accurate results. The agreement further demonstrates that the solvent extraction procedure adequately decontaminates these samples for IDMS analysis. This procedure is a suitable replacement for the more time-consuming ion exchange procedure currently used for decontaminating and preparing the sample for IDMS.

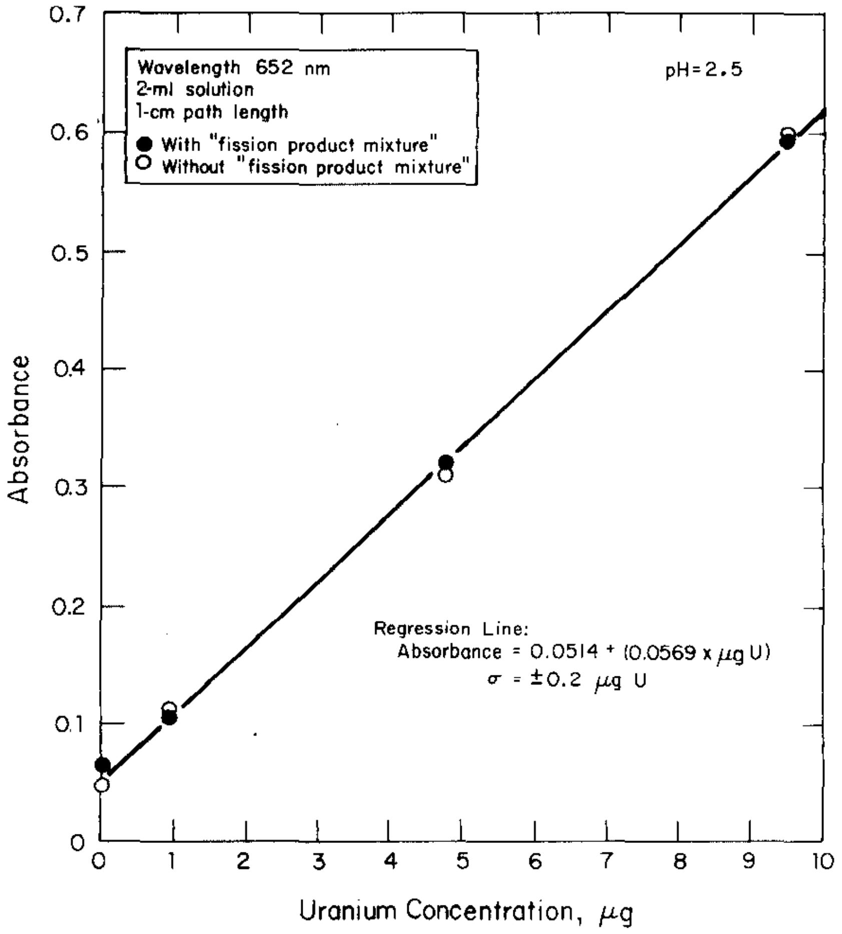

FIGURE 4. Calibration Curve of Uranium(VI) with Arsenazo III

TABLE 3

Determination of Uranium in Typical Samples of LWR Waste from Solvent Extraction Studies

		µg Uranium/ml Sample	
Sample	*Sample Size*	*Arsenazo III*[a]	*IDMS*[b]
1	100 µl 100 µl + 3.88 µg ^{233}U	detected; too low to determine	3.4
	250 µl 250 µl + 3.88 µg ^{233}U	3	3.1
2	100 µl 100 µl + 3.88 µg ^{233}U	23	26.6
	100 µl 100 µl + 3.88 µg ^{233}U	26	26.4

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a. Colorimetric method.

b. Isotope dilution mass spectrometry method.

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APPENDIX: EXPERIMENTAL PROCEDURE

Apparatus

Vortex mixer
Spectrophotometer
One-centimeter light path cells
Four-dram vials with polyethylene-lined caps
Centrifuge
Assorted pipets as required

Reagents

Reagent I	Dissolve 60 g ammonium nitrate and 1.7 g potassium oxalate in distilled water, add 13 ml of concentrated nitric acid and dilute to 100 ml with distilled water.
Reagent II	Dissolve 60 g ammonium nitrate in distilled water and dilute to 100 ml.
Reagent III	Dissolve 60 g ammonium nitrate, 0.25 g Na_2H_2EDTA in distilled water and dilute to 100 ml; then adjust pH to 2.7. Add concentrated nitric acid for initial adjustment, then add dilute nitric acid for final adjustment.
Reagent IV	6 ml 0.05% Arsenazo III and 94 ml phthalate buffer solution. (Dissolve 2 g acid potassium phthalate in distilled water, add 80 ml 0.1M hydrochloric acid and dilute to 200 ml with distilled water. Adjust pH to 2.5.)

5% tributylphosphate (TBP): Dilute 5 ml TBP to 100 ml with xylene.

Uranium standard: 10 µg U(VI)/ml. Use ^{233}U if determination of uranium by isotope dilution mass spectrometry is desired.

Procedure

Note: The procedure must be performed with:

(a) a reagent blank,
(b) a sample solution [4 to 5 µg U(VI)], and
(c) a sample solution plus 4 to 5 µg U(VI) standard spike.

1. Place 2 ml of Reagent I in vial.
2. Add solution appropriate to (a), (b), or (c) in the Note above.

3. Add 2 ml of 5% TBP in xylene to vial.
4. Cap vial and mix on Vortex mixer for 1.5 minutes.
5. Allow phases to separate; discard aqueous phase.
6. Transfer organic phase to clean vial (or rinse with water as described in Step 9 below).
7. Add 2 ml of Reagent II.
8. Repeat Steps 4 and 5.
9. Rinse sides of vial with 2 ml of water; do not mix solution. Discard rinse water.
10. Add 2 ml Reagent III to organic phase in vial.
11. Repeat Steps 8 and 9.
12. Add 2 ml Reagent IV, measured by pipet.
13. Mix in capped vial on Vortex mixer for 1.5 minutes.
14. Centrifuge to obtain complete phase separation suitable for spectrophotometric determination.
15. Transfer the 2-ml colored aqueous phase to a 1-cm spectrophotometer cell.
16. Determine absorbance for (b) and (c) at 652 nm, with reagent blank (a) in reference cell.

Calculation

A = absorbance of sample solution (b)

A_s = absorbance of sample solution plus standard spike (c)

S = uranium in standard spike, μg

V = volume of sample, ml

$$\mu\text{g U/ml sample} = \frac{A \times S}{V \times (A_s - A)}$$