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THE USE OF SELECTIVE EXTRACTION CHROMATOGRAPHIC COLUMNS AS
AN ALTERNATIVE TO SOLVENT EXTRACTION FOR THE SEPARATION OF
URANIUM FOLLOWED BY THE USE OF ARSENAZO III AS A COLORIMETRIC
REAGENT FOR URANIUM DETERMINATION

Lockheed
Idaho Technologies Company

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**The Use Of Selective Extraction Chromatographic Columns as an
Alternative to Solvent Extraction for the Separation of
Uranium Followed by the Use of Arsenazo III as a
Colorimetric Reagent for Uranium Determination**

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INTRODUCTION

The Idaho Chemical Processing Plant (ICPP) is part of the nuclear fuel reprocessing cycle. As of 1992, the mission of the ICPP was changed from fuel reprocessing to waste management. The ICPP as a production facility, operates 24 hours a day when fuel is being processed. The uranium bearing fuel rods are dissolved and the uranium is separated from the fuel cladding and fission products through a series of solvent extraction cycles and recovered as a uranium oxide product. Highly radioactive samples are sent to the analytical laboratories for analysis. One of the analytes which is frequently determined in process samples is uranium. Uranium analyses are currently performed for process control, nuclear materials accountability, and waste management. A rapid sample turnaround while providing accurate analysis results is important to keep the facility operational. For process control, nuclear materials accountability and waste management, it is beneficial to have available a variety of uranium analysis methods which will give the accuracy and precision required with minimum exposure of personnel to ionizing radiation. It is also advantageous to have analytical techniques which may be performed rapidly and easily in a shielded facility or hot cell.

Although a wide variety of techniques have been used to determine uranium, the techniques most commonly used at the ICPP for this purpose are colorimetry, phosphorescence of U(VI) after excitation with a light source, x-ray fluorescence, and mass spectrometry. Uranium is difficult to analyze directly by colorimetry due to the low concentrations in most solutions and the presence of interfering ions from corrosion and fission products which absorb in the same spectral region. All of these techniques, except x-ray fluorescence, require a separation of uranium from the sample matrix prior to its determination. In the past, the separation of uranium in the analytical laboratories at the ICPP has been performed primarily by liquid-liquid extraction or ion-exchange chromatography. In this work, a new commercially-available highly selective extraction chromatographic material, U/TEVA[®] Spec is evaluated and used in combination with several uranium analysis methods. A kinetic phosphorescence analyzer was used to evaluate the performance of the U/TEVA[®] column material. A replacement for the currently used spectrophotometric method was sought and identified. An analytical method was developed which is applicable to a wide variety of ICPP process streams.

The direct spectrophotometric determination of uranium from the spectrum of the uranyl ion is limited to relatively pure, highly concentrated solutions and must be made in the presence of a fixed nitric acid concentration. Prior to its spectrophotometric determination, a solvent extraction from acid-deficient aluminum nitrate salting solution into 4-methyl-2-pentanone (commonly known as hexone) is performed to separate the uranium from fission products, cladding material, fluoride, and other ions which would interfere with the spectrophotometric analysis. The salting solution provides a sufficiently high nitrate concentration to improve the efficiency of the uranium extraction into the organic phase. The acid-deficient salting solution minimizes the amount of acid and unhydrolyzed metal ions that extract into the hexone phase. Hydroxylamine is used with the salting solution as a reducing agent for chromium (VI) and manganese (VII). EDTA is added as a complexer for the plutonium (IV) which was reduced by the hydroxylamine and also as a complexer for thorium (IV). If tetrapropylammonium hydroxide is added to the salting solution, uranium may be determined in the hexone phase from the spectrum of the tetrapropyl-ammonium uranyl nitrate ion pair. However, the lower limit of uranium detection with this procedure is insufficient to be used routinely for process control. Most spectrophotometric determinations of uranium performed in the ICPP analytical laboratories are based upon the absorbance of uranium with bromo-PADAP [2-(5-bromo-2-pyridylazo)-5-diethylaminophenol]. Since Br-PADAP is a pH sensitive metal indicator, and acid is extracted in the hexone phase, pyridine is added to control the pH of the solution. The uranium concentration is determined by comparing the color of the solution to that of standard solutions.

A diode array spectrophotometer equipped with optical fibers is used to run remote determinations. Interferences may occur from the salting solution carry over into the extracted hexone, unclean containers, or co-extraction of metals such as Fe(III) which form anionic chloride complexes. Coprecipitation of uranium with antimony, sulfate and arsenic III and IV ions in the salting solution causes a negative interference. The reduction of uranium from U(VI) to U(IV) by reducing agents in the sample or the depletion of the acid-deficiency of the salting solution by high acid concentrations may also result in low uranium results. Highly oxidizing samples must be mixed immediately (within 5 s) to avoid oxidation of hexone which produces a colored species. Such rapid mixing is nearly impossible to perform during remote operations in a hot cell¹. Remote systems are designed to use the minimum number of sample transfers or use small scale extractions. Although this method performed well and was applicable to the analysis of a wide variety of process sample types, the generation of a pyridine-containing waste became unacceptable. After a brief unsuccessful search for a suitable buffer to replace pyridine, an alternate spectrophotometric reagent and procedure was sought.

Alternatives to Solvent Extraction for Separation of Uranium

U/TEVA[®] Spec extraction chromatography resin is a commercially available material which is specific for uranium and tetravalent actinides. The columns are available prepacked in dilute nitric acid from EichroM Industries. The extraction chromatography resin consists of a dipentyl pentylphosphonate and a nonionic polymeric acrylic ester adsorbent formed into hard opaque beads. The uranium (as uranyl ion) and tetravalent actinides are strongly absorbed onto the column from strong (2M) nitric acid solutions. Uranium is readily eluted from the resin with dilute (0.02M) nitric acid. Plutonium is more strongly absorbed than uranium. Therefore, it is possible to load the uranium and tetravalent actinides on the column in 2M nitric acid, wash the other ions from the column with 2M nitric acid, and then elute the uranium from the column while retaining the plutonium. Plutonium can be removed upon further elution with dilute nitric acid. Oxalic acid can be used to reduce the retention of plutonium and neptunium and at the same time increase the solubility of zirconium and molybdenum. It has little effect on the retention of the uranium.

Search for a Suitable Color Reagent to Replace Br-PADAP

Many different color reagents have been suggested for determining uranium concentrations spectrophotometrically. However, most of them are non-selective for uranium and insensitive². Most of these reagents are organic-soluble and are added directly to the organic phase after performing a solvent extraction step. A reagent was sought which was compatible with the nitric acid, uranium-containing fraction from separations performed with the U/TEVA[®] Spec columns.

Published Studies of Arsenazo III as a Colorimetric Reagent

In 1959, Savvin prepared a compound, Arsenazo III, (1,8-dihydroxynaphthalene-3,6-disulfonic acid-2,7-bis [--azo--]-phenylarsonic acid)), which has been used to determine uranium spectrophotometrically. Arsenazo III is available in the disodium salt form. Both the solid and

¹S. D. Hartenstein, "Spectrophotometric Procedure for the Determination of Uranium with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol at a Nuclear Reprocessing Facility", *Analytica Chimica Acta*, Vol. 228, 1990, pp. 279-285.

²M. Pinta, "Detection and Determination of Trace Elements", Ann Arbor Science Publishers, 1971, pp. 101-109.

solution form are stable but decomposition will occur in oxidizing or strongly reducing environments. The azo group gives the color to a solution while the hydroxy group helps to form a second 6-membered ring with the cations of the complexed element. This makes the complex more stable and the color deeper^{3,4}.

Arsenazo III is a bis-azo derivative and has two functional groups. The functional group that results in the formation of complexes between metals and Arsenazo III is:

Arsenazo III can form very stable chelate complexes with U(VI) and U(IV). Therefore, it is possible to determine uranium in the presence of large amounts of interfering anions such as sulfates, fluorides, phosphates, oxalates, and other uranium complex-forming anions. The determination of uranium can be performed in strongly acidic solutions thereby eliminating partial hydrolysis of uranium and the need for pH control with buffers. In addition, the selectivity is usually increased in highly acidic media.^{5,6} It appears that only elements which form tetravalent cations will react with Arsenazo III under acidic conditions.

Studies done by Luk'yanov, et al., 1960⁷ show that the effects of anions are very small. Most cations were also found to have a minimal effect on uranium determinations. However, zirconium, thorium, iron (II), vanadium, chromium, and actinides interfere quite strongly under acidic conditions^{8,9}. Titanium appears to give high uranium results because it is a strong reducing agent when in the trivalent state and therefore is capable of destroying the reagent. The interference by zirconium can be decreased by the use of oxalic acid as a masking agent.

The absorption spectra of complexes of Arsenazo III with elements have two maxima in the visible region (665 mμ and 610 mμ)¹⁰. The double maxima holds true over wide ranges of pH and ratios of metal concentrations to reagent. The two maxima are associated with the

³S. B. Savvin, "Analytical Use of Arsenazo III-Determination of Thorium, Zirconium, Uranium, and Rare Earth Elements", *Talanta*, Vol. 8, 1961, pp. 673-685.

⁴E. B. Sandell and Haroshi Onishi, "The Photometric Determination of Trace Metals, Vol. 3, Part 1, Fourth Edition", John Wiley and Sons, New York, 1978, pp. 459-466.

⁵P. N. Palei, "Analytical Chemistry of the Elements-Uranium", Humphrey Science Publishers, Ann Arbor, 1970, pp. 116-125.

⁶Ref. 3

⁷V. F. Luk'yanov, S. B. Savvin, and I. V. Nikol'skaya, "Photometric Determination of Microamounts of Uranium By Means of Arsenazo III", *Zhurnal Analiticheskoi Khimii*, Vol. 15, No. 3, 1960, pp. 311-314.

⁸Ref. 3

⁹James S. Fritz and Marlene Johnson-Richard, "Colorimetric Uranium Determination with Arsenazo", *Analytica Chimica Acta*, Vol. 20, 1959, pp. 164-171.

¹⁰Ref. 4

presence of two dissociated chromophoric systems in a single molecule differing in magnitude or ionic states. Arsenazo III, not bound in a complex, gives a single maxima because the molecule is symmetrical and the chromophoric systems are identical. Complex formation at one group disturbs the symmetry of the molecule so the chromophoric systems are no longer equal; then two maxima occur. The maxima at 665 $m\mu$ is related to the metal. The other maxima is related to the chromophoric center not connected with the element but influenced by the first functional group passing into a different ionic state^{11,12}.

The uranium (VI) reaction with Arsenazo III in acid solutions can form two different complexes of

Figure 1: Complex-formation of Arsenazo III with U(VI)

the type ML (metal-ligand). Which complex is formed depends on the hydrogen-ion concentrations. Metals that react in highly acidic solutions appear to replace a hydrogen in the AsO_3H_2 group. The octahedral structure corresponds to the metal:ligand composition of 1:1 with a coordination number of six. The cubic structure corresponds to the metal:ligand composition of 1:2 and coordination number eight. The complex-formation of Arsenazo III with that of U(VI) as shown in Figure 1 was determined by S. B. Savvin (1961)¹³.

¹¹S. B. Savvin, "Analytical Applications of Arsenazo III-III The Mechanism of Complex Formation Between Arsenazo III and Certain Elements", *Talanta*, Vol. 11, 1964, pp. 7-19.

¹²Ref. 4

¹³Ref. 3, pp. 678

EXPERIMENTAL METHODS

General Use of U/TEVA® Columns

Prepacked columns (manufactured by Eichrom Industries, Darien, IL) consisting of a 2 mL resin bed were used in this study. The suggested working capacity of the resin is 20% of the total capacity of the resin material. For a 2 mL prepacked column, the suggested loading is 8 mg uranium. This loading was not exceeded in these studies. The columns were washed with 20 mL of 0.02M HNO_3 followed by 4 mL of 2M HNO_3 . The wash of 20 mL of 0.02M HNO_3 was to rinse off any residual organic from manufacturing of the resin beads. It also was used to remove any residual uranium in cases where the columns were being reused. The 4 mL of 2M HNO_3 were added to adjust the column to the same acid concentration as the load solution to maximize performance. Unless specified otherwise, the preceding wash procedure was used for all new columns, and henceforth this procedure will be referred to as precleaning. The sample was loaded on the column and 1 mL of 4M HNO_3 was added to the column reservoir to ensure that the acid concentration was $\geq 2\text{M}$ nitric acid. The loaded column was then washed with 12 mL of 2M nitric acid to strip out any unbound matrix constituents. The columns were washed with 2 mL of 0.02M nitric acid. Elution tests in this study show that the uranium does not tend to elute off the column within the first 2 mL of 0.02M nitric acid rinse. Both the 2M nitric acid and the 0.02M nitric acid washes in this study were saved for analysis to determine the effectiveness of the column in separating uranium from complex matrices. The uranium was eluted off the column with 4 mL of 0.02M nitric acid. This eluate should contain the separated uranium so it was retained for uranium analysis. A kinetic phosphorescence analyzer (Model KPA-10, ChemChek Instruments, Richland, WA) was used to determine the uranium concentration in various sub-fractions of the eluate to define the elution curve for various loadings of U(VI).

General Sample Preparation for KPA Analysis

The kinetic phosphorescence analyzer (KPA) requires that a sample aliquot be mixed with phosphoric acid or Uraplex before analysis to enhance the uranium solution phosphorescence. All the samples analyzed by KPA in this study used 10% H_3PO_4 in water as a uranium phosphorescence enhancer. The samples for KPA analysis were prepared by taking a 500 μL sample aliquot and adding to 2 mL 10% H_3PO_4 unless noted otherwise in the experimental procedures. All future reference to samples analyzed by KPA will simply state that a sample was taken and analyzed. Unless stated otherwise, the KPA was used to determine the uranium concentration.

Determination of Column Pretreatment Requirements

Several different experiments were performed to identify effective techniques for column pretreatment. Since the columns contain acrylic polymers with organic coatings, it is necessary to wash off any residual organics that may interfere with uranium extraction or sample analysis. Eichrom Industries personnel suggest using a 2M nitric acid wash. The first experiment was to continue washing the column with 2M HNO_3 until the phosphorescence lifetime obtained by KPA analysis was greater than 200 $\mu\text{seconds}$. A lifetime measurement of at least 200 $\mu\text{seconds}$ is expected during analysis if uranium is present. The assumption was made that if the lifetime measurement was $> 200 \mu\text{seconds}$, no residual organic or uranium (in the case of column reuse) remained on the columns. The wash was collected in 2 mL fractions. After 20 mL of 2M HNO_3 were passed through the column, it was filled with 2M HNO_3 and left overnight to see if any residual organics leached off the resin beads over an extended period of time. A 2 mL fraction

was taken off the column. A sample was taken and the lifetime was measured. Next, 8 mL of 0.02M HNO_3 were passed through the column and collected in 2 mL fractions. A sample from each fraction was taken and the lifetime was measured. The column was then washed with another 10 mL of 2M HNO_3 , which were discarded. A sample from the next 2 mL fraction was measured for lifetime. The column was stored in 1 mL of 2M HNO_3 . Forty-eight hours later, the 1 mL fraction of 2M HNO_3 was eluted from the column. A 100 μL aliquot was added to 400 μL deionized water and 2 mL of 10% H_3PO_4 , then a lifetime measurement was taken to determine the elution of column impurities over time. Next a 1.5 mL aliquot of 0.02M HNO_3 was passed through the column. A 100 μL aliquot of this fraction was added to 400 μL deionized water and 2 mL of 10% H_3PO_4 and analyzed. Next 4 mL of 0.02M HNO_3 were passed through the column. Lifetime measurements of three different sample aliquots were taken from this fraction to ensure that the measurements were accurate. The first lifetime measurement was of 100 μL sample, 400 μL H_2O , 2000 μL 10% H_3PO_4 ; the second was 200 μL sample, 300 μL H_2O , 2000 μL 10% H_3PO_4 ; and the third was 500 μL sample and 2000 μL 10% H_3PO_4 . A 10 mL aliquot of 2M HNO_3 was then passed through the column to ensure the column was clean. One milliliter 2M HNO_3 was then added to the reservoir and the column was capped and stored for future use.

The second experiment was to determine if water could be used as a wash solution to remove any residual organics instead of dilute nitric acid. First the column was washed with 50 mL water. The fifty-first mL fraction was saved for lifetime measurements. A sample was taken from this 1 mL fraction and then analyzed. This process was repeated three more times saving the 101st, 151st, and 201st mL aliquots. Each fraction had a sample removed and lifetime measurements were made. Next 10 mL of 2M HNO_3 were passed through the column and discarded to see if changing to acid would change the lifetime measurement readings. Another 1 mL aliquot of 2M HNO_3 was passed through the column and saved. A sample was taken from this fraction and lifetime measurements were taken. Next the column was loaded with 500 nanograms uranium and 500 μL of 4M HNO_3 . Ten milliliters 2M HNO_3 were passed through the column to rinse unwanted sample constituents from the column and discarded. Next a 1.5 mL aliquot of 0.02M HNO_3 was passed through the column and saved. A sample was analyzed for uranium concentration. Next, another 4 mL of 0.02M HNO_3 were passed through the column and saved. A sample of this fraction was analyzed for uranium concentration. Another 4 mL of 0.02M HNO_3 were passed through the column to elute off any residual uranium and discarded. Then 10 mL of 2M HNO_3 were passed through the column to clean up the column for storage and discarded. The column was then stored in 2M HNO_3 . After twenty-four hours, a 1 mL aliquot of 2M HNO_3 and 50 nanograms of uranium were loaded on the column. The column was washed with 10 mL of 2M HNO_3 to remove any unwanted sample constituents. The tenth milliliter eluting off the column was saved for uranium analysis to make sure the uranium was being bound on the column. A sample aliquot from this fraction was analyzed for uranium concentration. Then the column was washed with 1.5 mL of 0.02M HNO_3 . A sample was analyzed for uranium concentration. Then the uranium was eluted with 4 mL of 0.02M HNO_3 . A sample was analyzed for uranium concentration. The residual uranium was eluted with 4 mL of 0.02M HNO_3 . A sample was analyzed for uranium concentration.

The third experiment was performed to determine the minimum volume of wash solution required to clean a new column. A new column was washed with 10 mL of 2M HNO_3 . The last milliliter coming off the column was saved. A sample from this fraction was analyzed for lifetime measurements as well as uranium concentration to ensure that the column was adequately cleaned. Next the column was loaded with 50 nanograms uranium. The column was then washed with another 10 mL of 2M HNO_3 to remove any unwanted constituents. The tenth milliliter was saved. A sample from this fraction was analyzed for uranium concentration. The column was washed with 1.5 mL of 0.02M HNO_3 . A sample from this fraction was analyzed for uranium concentration. The uranium was then eluted from the column with 4 mL of 0.02M

HNO₃. A sample was analyzed for uranium concentration. Five successive 4 mL aliquots of 0.02M HNO₃ were passed through the column and each 4 mL fraction was saved. A sample was taken from each 4 mL fraction and analyzed for uranium concentration (five samples total). The column was then washed with an additional 8 mL of 0.02M HNO₃ to elute off any residual uranium. This fraction was discarded. Next 10 mL of 0.02M HNO₃ were passed through the column to ensure the column was clean and to equilibrate the column for the next uranium load. A 1 mL aliquot of 0.02M HNO₃ was passed through the column and saved. A sample taken from this fraction was analyzed for uranium concentration. The column was then loaded with 100 nanograms uranium. Next 1.5 mL of 0.02M HNO₃ were passed through the column. A sample of this fraction was analyzed for uranium concentration. Four milliliters of 0.02M HNO₃ were used to elute the uranium from the column. A sample of this fraction was analyzed for uranium concentration. Another 4 mL of 0.02M HNO₃ were passed through the column and a sample was analyzed for uranium concentration. Then the column was washed with 10 mL of 2M HNO₃ to ensure the column was clean. This fraction was discarded. The column was stored in 2M HNO₃ for future use.

Column Reusability Study

Many of the tests performed in the determination of column pretreatment requirements involved the reuse of the columns. Combined with the following test, the feasibility of reusing the columns was determined. The 0.02M HNO₃ that was left on a previously used column was eluted off. A sample was analyzed for uranium concentration to make sure no residual uranium was left on the column. The column was washed with 10 mL of 2M HNO₃ to equilibrate the column for the loading of the uranium. It was then loaded with 500 µL of 4M HNO₃ and 500 nanograms uranium. The column was washed with 10 mL of 2M HNO₃ to remove any unwanted sample constituents. A sample taken from this fraction was analyzed for uranium concentration. A 1.5 mL aliquot of 0.02M HNO₃ was passed through the column. A sample taken from this fraction was analyzed for uranium concentration. Next the uranium was eluted off the column with 4 mL of 0.02M HNO₃. A sample of this fraction was analyzed for uranium concentration. The residual uranium left on the column was eluted off with three 2-mL fractions of 0.02M HNO₃. From each fraction, a sample was analyzed for uranium concentration (3 samples total). Then another 10 mL 0.02M HNO₃ were passed through the column to determine the residual uranium that was eluting off of the column after the first 10 mL elution. A sample was analyzed for uranium concentration.

Uranium Elution Studies

A 1 mL aliquot of 4M HNO₃ and 500 nanograms uranium were loaded onto a prewashed U/TEVA® Spec column. The column was washed with 10 mL of 2M HNO₃ to remove any unwanted sample constituents. Twenty-five milliliters 0.02M HNO₃ were passed through the column in 500 µL aliquots. Each fraction was saved and analyzed for uranium concentration. This procedure was repeated for uranium loadings of 50 ng, 200 ng, 250 ng, 500 ng, 750 ng, and 1000 ng. Data for these studies appear in Figure 2.

Low Level Uranium Extraction Procedure

Several different ICPP process samples were used for this study including; evaporator condensate samples, tank farm waste samples, and Second and Third Cycle Raffinate samples. The uranium concentrations were low in all of the samples. By using a variety of ICPP process samples, different matrices could be evaluated.

Prewashed U/TEVA® Spec columns used with Second and Third Cycle Raffinate samples were

loaded with a 1 mL aliquot of sample and 1 mL of 4M HNO_3 . Each column was washed with 20 mL of 2M HNO_3 to remove any unwanted sample constituents. The wash solution was saved to analyze for various metals and fission products. Next 2 mL of 0.02M HNO_3 were passed through the column and discarded, since elution experiments in this study showed that there is an insignificant amount of uranium in this fraction. The uranium was eluted with 4 mL of 0.02M HNO_3 . For the experiments in this study, the wash solution (12 mL, 2M HNO_3) was analyzed for various metals including Al, B, Cd, Ca, Cr, Fe, Mn, Mo, Ni, Zr, and U. Various fission products were also determined in this solution. Since plutonium co-extracts with uranium, the wash solution was analyzed for plutonium to see if the column could be used to separate the uranium from plutonium. The uranium bearing eluate (4 mL, 0.02M HNO_3) was analyzed for all these constituents to determine if there were any interferences, such as residual metals or fission products, left on the resin that came off during the elution process. This process was repeated for three different process samples. A repeat of the third sample was done, spiking it with 30 μg uranium to check for interferences. Metal and fission product concentrations and recoveries appear in Table 1.

A prewashed U/TEVA® Spec column was used for the evaporator condensate sample. It was loaded with 10 mL of condensate sample along with 5 mL of 4M HNO_3 to ensure that the acid concentration of the sample load was >2M. The column was washed with 12 mL of 2M HNO_3 to remove any unwanted sample constituents. A 2 mL wash of 0.02M HNO_3 followed. This fraction was discarded. Four milliliters 0.02M HNO_3 were passed through the column to elute the uranium. This sample eluate was saved for metal, uranium, and fission product analysis.

Prewashed U/TEVA® Spec columns used for the tank farm samples were loaded with 1 mL of sample and 1 mL of 4M HNO_3 . The column was then washed with 12 mL of 2M HNO_3 to remove any unwanted sample constituents. This wash solution was saved and analyzed for various metal and fission product concentrations. Next the uranium fraction was eluted with 10 mL of 0.02M HNO_3 . This eluate was saved and analyzed for metals, common anions, uranium, and fission product concentrations. A larger sample fraction containing the uranium was saved in this experiment because the work was done remotely and chances for sample loss were greater. The entire process was repeated with a different batch of tank farm samples.

The uranium was determined by taking a 500 μL aliquot from each wash and eluate sample saved and analyzed using solid-state uranium phosphorescence techniques. The aqueous uranium-bearing eluate and wash solutions were pipetted directly onto a sodium fluoride pellet and fused prior to analysis. The metal concentrations were determined by inductively coupled plasma emission spectroscopy analysis.

Plutonium Behavior Studies

A precleaned U/TEVA® Spec column was loaded with 1 mL of ^{238}Pu having a concentration of 133.61 dps/mL and 2 mL of 4M HNO_3 . The column was then washed with 12 mL of 2M HNO_3 . The eleventh and twelfth mL fractions were each saved and analyzed for plutonium using scintillation counting. Next the column was eluted with 5 mL of 0.02M HNO_3 . Each 1-mL fraction was saved and analyzed for plutonium using scintillation counting. The plutonium was then eluted off the column using 6 mL of 2M HNO_3 /0.09M oxalate solution. Each 1-mL fraction was analyzed for plutonium once it passed through the column. Data for this experiment appears in Table 2.

A similar experiment was done after adding Fe(II) to ensure that plutonium was reduced to the tetravalent state. A 3 mL aliquot of a 133.61 dps/mL plutonium standard was added to 1 mL of $\text{Fe}(\text{ClO}_4)_2$ solution and heated in a water bath. One milliliter of this solution was added to a

precleaned U/TEVA® Spec column with 2 mL of 4M HNO₃. Four milliliters of 2M HNO₃ were added to the column in 1-mL fractions to remove any unwanted constituents. Each fraction was saved and analyzed for plutonium using scintillation counting. Five milliliters of 0.02M HNO₃ were added to the column in 1-mL fractions. Each fraction was saved for plutonium analysis to determine if the plutonium was retained on the column. Four milliliters of 4M HNO₃/0.1M oxalate were added to the column in 1-mL fractions to elute the plutonium. Each fraction was saved and analyzed for plutonium using scintillation counting.

Evaluation of Arsenazo III

The reagent was prepared by dissolving 34 mg Arsenazo III in 25 mL of 0.02M HNO₃. Not all of the reagent dissolved, so the solution was filtered before use. A calibration curve using the Arsenazo III reagent was created using the Hewlett Packard diode array spectrometer. The standards used were as follows: Blank, 1 µg, 5 µg, 10 µg, 20 µg, and 50 µg. Each standard contained 4 mL 0.02M HNO₃, 0.2 mL Arsenazo III reagent, and an appropriate volume of 100 µg U/mL standard.

Arsenazo III Stability Tests

An experiment was performed to see how long it took for color formation of the Arsenazo III-Uranium(VI) complex to appear and become stable. One milliliter of the Arsenazo III reagent was added to 50 µg U/4.7 mL solution in 0.02M HNO₃. The solutions were measured on a Hewlett Packard Diode Array against a standard calibration curve. The color development was immediate and appeared to remain stable over at least one hour.

Additional studies were performed by measuring Arsenazo III-Uranium(VI) complexes prepared at a 3:1 mole ratio and a 4:1 mole ratio against various calibration curves. The calibration curves were of both 3:1 and 4:1 mole ratios using Arsenazo III prepared in both water and in 0.02M HNO₃. The reagent was prepared by dissolving 34 mg Arsenazo III in 100 mL 0.02M HNO₃ unless a specific mole ratio is stated. The mole ratios used were 1:1, 2:1, 3:1, 4:1, and 5:1.

In all studies, the standards were prepared as follows:

3 mL 0.02M HNO₃, 1 mL Arsenazo III reagent, and 1 mL U standards in 0.02M HNO₃

The blank is 4 mL 0.02M HNO₃ and 1 mL Arsenazo III reagent. The uranium standards used were:

1 µg U/mL, 20 µg U/mL, 25 µg U/mL, and 50 µg U/mL

Solutions used for calibrating the instrument were also analyzed as samples at various times to see if they remained stable.

Compatibility Study of the U/TEVA® Columns Effluent with Arsenazo III

The pH of the 4-mL fraction where uranium is normally eluted from the U/TEVA® columns must be compatible with that required for Arsenazo III color development (pH 1.2-2.0). The pH of this 4-mL fraction was determined using a U/TEVA® column on which a uranium standard had been loaded. One milliliter of 4M HNO₃ and 10 µg U were loaded onto a precleaned U/TEVA® Spec column. The column was washed with 8 mL of 2M HNO₃ then and eluted with 1.5 mL 0.02M HNO₃. Both of these fractions were discarded. The next 4-mL fraction of 0.02M HNO₃ eluate was saved. A 0.4 mL aliquot of Arsenazo III reagent was added to the fraction and the pH was

measured. The measured pH 1.7 was within the pH range of 1.2-2.0 for Arsenazo III, the use of a buffer added during the color development stage would minimize variations in the acidity of the uranium-containing fraction if it included some of the earlier 0.02M HNO_3 wash fraction. However the buffer capacity of buffers such as dichloroacetic acid (pKa 1.3) is very low in these acidic solutions so no buffer was added to the uranium-bearing fraction prior to color development.

RESULTS AND DISCUSSION

Results of the column washing studies show that the organic coming off the column resin was not completely removed by washing the column with 20 mL of 2.0M HNO_3 . Organic in the samples result in an interference during measurements with the KPA. Allowing the columns to set overnight in 2M HNO_3 leaches more organic from the columns. Conversations with EIChrom Industries representatives have revealed that kinetic problems occur with U/TEVA[®] Spec resin beads. The uranium will diffuse deep into the resin beads causing stagnant pools. This problem can be overcome by allowing the column to stand overnight in 2M HNO_3 or by heating the resin to 25-50°C. The kinetic problems with the U/TEVA[®] Spec resin may explain what appears to be an interference by the organic on the KPA measurement. Studies have shown that 6% of the organic (phosphorous) will be lost in 100 free column volumes¹⁴. Therefore, a 20-mL wash solution should be sufficient for prewashing. The additional 8 mL of 0.02M HNO_3 wash did not return the effluent to the expected lifetime reading of more than 200 μ seconds. The sample lifetimes determined using 100- μ L aliquots agree with the sample lifetimes determined using 50- μ L aliquots. From this data we cannot tell if the additional washings beyond the first 10 mL removed more organic. It cannot be ascertained from data obtained from washing the column with water instead of using nitric acid if washing the column with water successfully removes the organic from the resin. Although the lifetime obtained from fraction 4 was >200 μ seconds, it decreased to 150 μ seconds with additional water washing. After washing with 0.02M HNO_3 , the lifetime increased to >200 μ seconds. Although the column pretreatment appears to be adequate, it cannot be ascertained from this data if it is a result of the nitric acid or water washes.

It was then necessary to find the minimum amount of acid that was necessary to wash the columns before use. It was also necessary to determine the acid concentration (2M HNO_3 or 0.02M HNO_3) that gave the best results. Each aliquot analyzed is 500 μ L. The results show that for fractions 4-9, the uranium recovery was low. It appears that the uranium came off the column more slowly than from columns which were prewashed with 0.02M HNO_3 . The tailing appeared to be extensive. The uranium elutes off the column within the first 6 mL after loading onto columns that were prewashed with 0.02M HNO_3 . A dilute nitric acid wash was not used prior to loading the uranium, which may explain why the recovery was low. To test this theory, the columns were reloaded with uranium after using 10 mL of 0.02M HNO_3 to wash the column. Fractions 11-15 show that the uranium recovery improved significantly. Based on these findings, it appears that a dilute nitric acid wash should be performed before the column is loaded with uranium to improve the recovery during elution.

Various studies were performed to see if the columns could be used more than once. Columns from the prewashing experiments as well as some of the elution experiments were reused. It appears that there are no problems with reusing the column as long as it is thoroughly washed

¹⁴E. P. Horowitz, M. L. Dietz, R. Chiarizia, H. Diamond, A. M. Essling, and D. Graczyk, "Separation and Preconcentration of Uranium from Acidic Media By Extraction Chromatography", *Analytica Chimica Acta*, Vol 266, 1992, pp. 25-37.

Uranium Elution Curve Studies

Figure 2: Recovery of Uranium Samples through U/TEVA® Spec Columns

between uses. The uranium appears to elute off at a normal rate, with good recoveries. It seems the problems which might arise when reusing columns will occur when a high uranium concentration sample is eluted and then the column is loaded with low uranium concentration samples. Uranium carry-over and cross-contamination may result from this loading sequence. Without sufficient cleaning any residual uranium from prior samples may come off the column, resulting in high results.

Uranium elution curves for column loadings of 50 to 1000 ng U were determined. The results for the study are presented in Figure 2. Tailing at the end may be the result of several factors. The main factor is the uranium from prior samples may not completely elute off the column and therefore traces will contaminate later fractions. The $>100\%$ recoveries are probably a result of the calibration curve used. Recalibration of the KPA was not performed before these measurements were made. In addition, the calibration curve which was stored was prepared with Uraplex as the diluent while the samples analyzed were diluted with $10\% \text{H}_3\text{PO}_4$. Other sources of error in these elution studies should be mentioned. Different sample cuvettes used in the analysis may have different backgrounds, increasing the error in measuring low uranium concentrations. Pipetting with Eppendorf pipets may give slightly varying aliquots. Cleaning of the cuvettes may be inconsistent. Because of these sources of error, it is essential to run a blank, calibration curve, and standards before sample analysis. Although the percent recoveries in Figure 2 are greater than 100% , they verify that uranium elutes off the columns consistently regardless of sample load. The data shows that the amount of uranium in the first 2-mL fraction

is negligible. Nearly all of the uranium elutes off the column in the next 3 to 4 mL and then decreases rapidly to a trace amount (essentially background levels). Figure 2 shows that the uranium elutes off the column within fraction 5 through fraction 12, (2.5-6 mL). By graphing the elution curves for various uranium concentrations together it can be seen that the elution pattern is consistent regardless of the sample load.

Table 1 contains results from low level uranium analyses on process samples. The results are from the analysis of Second/Third Cycle Raffinate samples. The sample matrix is highly acidic aqueous waste containing fission products and trace amounts of uranium. The sample matrix is similar to non-treated water, except it is very acidic. It is also low in fission products. The flow rate for Second/Third Cycle Raffinate samples through the U/TEVA® columns was very slow (three to four hours for 20 mL). When the samples are shaken, silica particles become suspended in the supernate. The samples are yellow in color and the columns also became yellow. After the columns set overnight in contact with the sample aliquot and 1 mL of 4M HNO₃, the yellow color disappeared and the flow rate increased. It appears that samples from Second/Third Cycle need to be filtered to remove solids and any silica before separation of the analytes through the U/TEVA® Spec extraction chromatographic resin to ensure that the analysis can be performed in a timely manner for process control. The procedure was repeated using tank farm samples. This sample matrix varies from tank to tank but generally is quite acidic, and may be high in sulfate, nitrate and some metals. It is low in uranium and generally low in chloride and fluoride, and high in fission products.

The metal results on very low level samples do not give a clear indication of how the column is affected by matrices containing metals. A >100% recovery of the metals in the uranium fraction is probably not an accurate measurement. The concentrations are so low that the measurements (determined by ICP-OES method) are probably the same as background. Where the metal concentrations are large enough to make more accurate measurements, the metal concentrations in the wash solutions are consistent with data presented by Eichrom Industries. Uranium concentrations determined by ICP-OES are too low for recoveries to be determined. Uranium results by uranium phosphorescence techniques (listed as U-Fluor on Table 3) are more accurate. The 30 µg uranium standard was not passed through a U/TEVA® column. The U-Fluor results were not corrected for the high recovery results of the 30 µg uranium standard. These results still present many uncertainties due to spattering of the aqueous samples during heating and drying times which may be insufficient. Due to direct pipetting of aqueous solutions onto the sodium fluoride pellets drying times had to be increased by a factor of 4X to prevent spattering during fusion of pellets. Problems with using the U/TEVA® Spec columns in conjunction with the uranium phosphorescence method were identified on the 2/3 Cycle Raffinate samples. Corrections for these errors were incorporated into the uranium phosphorescence method prior to analyzing the Tank Farm samples. The 2/3 Cycle Raffinate samples could not be repeated due to lack of sample availability (plant process was not in operation). Figure 3 presents a comparison of metal concentrations and fission products from wash solutions vs. 2/3 Cycle Raffinate eluate.

Data for plutonium behavior studies are shown in Table 2. Since plutonium and uranium co-extract, it was necessary to determine the retention time on the column for the plutonium to make sure it would not coelute with the uranium. From this study, it appears that if the plutonium is reduced, it should not interfere with uranium determinations. From the data, it cannot be determined if the plutonium is in the 2M HNO₃ wash or if it remains on the column. Whether or not the plutonium is reduced, it does not elute from the column at the same time or acid concentration that is used to elute uranium. Based on these studies, it does not appear that plutonium will cause a significant change in the uranium results. Conversations with Eichrom Industries revealed that to reduce any plutonium hangup on the columns, oxalic acid should be

added to the nitric acid wash. This will not work if fluoride is present because the oxalate could not break the fluoride-plutonium bond to elute the plutonium.

It appears that the U-Arsenazo III complex color fades ~1% in 1/2 hour and that it is necessary to read the sample within 1/2 to 2 1/2 hours after color development. The color development was done by adding 1 mL Arsenazo III reagent to 3 mL 0.02M HNO_3 and 1 mL 20 μg U/mL standard. Stability tests performed by Perez-Bustamante, et al. (1971)¹⁵ show that in aqueous systems, the Arsenazo III-uranium (VI) complex remains stable and the absorbance remains constant after 1 to 1 1/2 hours.

Studies done by Ivan K. Kressin (1984) found that the Arsenazo III-Uranium(VI) complex forms immediately and increases in absorbance approximately 1% per hour. It appears from the color formation experiment, that the color formation is immediate and the complex remains stable for at least 1 hour¹⁶. A long term stability study was also performed. New standards of Arsenazo III:Uranium were prepared on 1-21-92, 1-24-92 and 2-23-92. These same standard solutions were run as samples using the new calibration curves prepared with new standard solutions on the three dates. Reanalyzing the solutions that were used to create a calibration curve as samples on the same day, indicates that the data fits a linear calibration curve. Reanalyzing solutions that were prepared at an earlier date, using a new calibration curve shows that the samples remain stable and the results are reproducible. The time stability results show that there is less deviation in the high range over a period of time than the low range. It appears that the Arsenazo III-Uranium(VI) complex remains stable over extended periods of time.

¹⁵Ref. 9

¹⁶Ivan K. Kressin, "Spectrophotometric Method for the Determination for Uranium in Urine", Anal. Chem., Vol. 56, 1984, pp. 2269-2271.

**Table 1: Low Level Uranium Studies
2/3 Cycle Raffinate**

Fraction Element	Original Spl (g/L)	20-mL 2M HNO ₃ Wash (g/L)	% in wash	4-mL 0.02M HNO ₃ Eluate (g/L)	% in U-
Al	69.2	65.5	94.65	.11	.16
B	.01	0	0	0	0
Cd	.01	.04	>100	.01	>100
Cr	.01	.08	>100	.01	57.69
Fe	3.88	4.7	121.13	.04	.98
Mn	.04	.10	>100	.01	34.15
Mo	.01	.10	>100	.02	>100
Ni	.01	0	0	0	0
U	.04	.72	>100	.19	>100
Zr	.01	.14	>100	.03	>100
Ca	.09	.25	>100	.04	41.59
Trans-UA	5460 d/s/mL	1199.73 d/s/mL	21.97	1.43 d/s/mL	.03
Ru-106	29800 d/s/mL	26250 d/s/mL	88.09	None Detected	0
Sb-125	7480 d/s/mL	5943 d/s/mL	79.45	15.44 d/s/mL	.21
Cs-134	3070 d/s/mL	2940 d/s/mL	95.77	None Detected	0
Cs-137	68200 d/s/mL	73600 d/s/mL	107.12	14.6 d/s/mL	.02
Ce-144	None Detected	None Detected	--	None Detected	--
Eu-154	589 d/s/mL	327.6 d/s/mL	55.62	None Detected	0
U-Fluor	.50 µg/mL	.08 µg/mL	15	.39 µg/mL	78.08
30 µg U-Std	33.4 µg	--	111.33	--	--

$$\text{metal conc} = \frac{(\text{conc g/L from instrument})(\text{dilution})}{(\text{aliquot})(1000)}$$

$$\text{d/s/mL} = \text{disintegrations per second per mL}$$

NOTE: The metal concentrations were determined using ICP-OES. The precision for these analyses is $\pm 10\%$. The uranium concentration labelled U-FLUOR was determined by uranium fluorescence. The precision for these analyses is $\pm 5\%$. The radioisotope concentrations were determined by gamma spectroscopy. The precision for these analyses is $\pm 5\%$. Plutonium, tritium, and strontium concentrations were determined by radiometric methods. The precision for these analyses is $\pm 10\%$.

Figure 3: Comparison of Selected components for the Wash Solutions vs. Eluate of 2/3 Cycle Raffinate Samples

Solutions of 3:1 mole ratios and 4:1 mole ratios (Reagent:Uranium) were prepared in water on 2/23/92 and 2/24/92 and stored in a dark cabinet. The solutions were examined periodically over a two month time frame. As of 4/21/92, the reagent appeared to be precipitating out of solution leaving flakes in the bottom of the sample. The color of the solutions changed from a deep shade of purple to brownish-black. Both the 3:1 and 4:1 mole ratio solutions became lighter in color. The 3:1 mole ratio 25 μg U standard turned deep blue and the 50 μg U standard turned blue-green. The 4:1 mole ratio 50 μg U standard turned deep blue. The original solutions were varying shades of purple. The Arsenazo III reagents made up in 0.02M HNO_3 at different mole ratios did not appear to have any precipitate or color change.

Mole ratio studies show that both the 3:1 and 4:1 mole ratios yielded acceptable linear calibration curves and analysis results. The 1:1 and 2:1 mole ratios do not appear to produce results which are as accurate at the upper end of the calibration curve as those obtained using higher mole ratios. The first derivative function is used for the spectrophotometric determinations made in the laboratory due to increased accuracy because it corrects for baseline shifts. This is necessary because ordinary glass test tubes are used instead of optical grade cuvettes for remote measurements. All variations in the baseline due to light scattering by non-optical surfaces or smudges on the outside of the test tubes are eliminated by using the first derivative of the absorbance to construct the linear calibration curve and in calculating analysis results.

CONCLUSIONS

The major part of the uranium loaded onto U/TEVA® Spec extraction chromatography columns will elute off within the first 6-mL fraction of 0.02M HNO_3 . The first 2-mL of eluate may be discarded without losing a significant amount of the uranium. However, for remote operations, it would probably be beneficial to save the entire 6 mL. For determination of uranium by the Arsenazo III color method, the pH would have to be adjusted if the first 2 mL were not discarded because of the acid content in this fraction. Adjusting the pH would be difficult to perform in a hot cell. Therefore, if larger sample aliquots are required for ease of handling and transfer, the first 2-mL eluate should be discarded and then a >4 mL fraction should be collected. Tailing of the uranium appears to occur regardless of the quantity of uranium loaded on the U/TEVA® columns. Therefore, reuse of the columns is questionable. One can safely assume that the reuse of a column is unacceptable in going from a high concentration sample (such as process sample loads) to a significantly lower uranium concentration sample (such as environmental samples). In cases where low concentrations are being analyzed and columns are being reused, it is recommended that the washings be analyzed by kinetic phosphorescence analysis to ensure that residual uranium is removed prior to reusing the columns.

It is recommended that reuse of U/TEVA® Spec columns for methods such as Isotopic Dilution for Mass Spectroscopy, which is used for both isotopic and concentration accountability, not be considered. The accuracy of this analysis is crucial and cross contamination cannot be tolerated. Since quantitative recovery is not required for this analysis, the first 2 mL of eluate should be discarded and only 1 to 1.5 mL of the next 4 mL be saved. This small fraction should contain >90% of the uranium and the small sample size will reduce the time required to evaporate the solution to dryness for the mass spectrometric measurement.

Pretreatment of the U/TEVA Spec columns could be done in batches outside of the hot cell. Once the columns have been prewashed with 0.02M HNO_3 , they can be left stored indefinitely in 2M HNO_3 . This would decrease the preparation time necessary when a sample arrives and ensure a sufficient number of columns would be available during plant processing when quick sample