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ACTINIDE ANALYTICAL PROGRAM FOR
CHARACTERIZATION OF HANFORD WASTE

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ABSTRACT

The objective of this program has been to develop faster, more accurate methods for the concentration and determination of actinides at their maximum permissible concentration (MPC) levels in a controlled zone. These analyses are needed to characterize various forms of Hanford high rad waste and to support characterization of products and effluents from new waste management processes.

The most acceptable methods developed for the determination of ^{239}Pu , ^{238}Pu , ^{237}Np , ^{241}Am , and ^{243}Cm employ solvent extraction with the addition of tracer isotopes. Plutonium and neptunium are extracted from acidified waste solutions into Aliquat-336. Americium and curium are then extracted from the waste solution at the same acidity into dihexyl-N,N-diethylcarbonylmethylenephosphonate (DHDECMP). After back extraction into an aqueous matrix, these actinides are electrodeposited on steel disks for alpha energy analysis. Total uranium and total thorium are also isolated by solvent extraction and determined spectrophotometrically.

INTRODUCTION

The concentration of actinides in defense-generated wastes at the Hanford site is an important criteria in the development of long-term waste management programs because of their very long half-lives and toxic characteristics. The origins of the actinides contained in the large quantities of Hanford waste were the effluents from the bismuth phosphate, Redox, Purex and plutonium reclamation chemical separation plants. Since these effluents were neutralized with NaOH, the majority of the actinides can be expected to be found with other insoluble metals as solids at the bottom of the tanks. However, soluble actinide species

could result from the various organic and inorganic complexants frequently used in the chemical separation plants or from carbonates formed from CO₂ absorption in the NaOH matrix.

The purpose of the actinide analytical program has been to test and evaluate potential analytical procedures and, at the same time, provide development groups with actinide concentration data for their programs. The analytical procedures developed in these studies will be utilized in the characterization of waste tank supernates, salt cake, waste sludge, terminal liquors from the vacuum evaporators, volume reduction effluents, and solids from soils and equipment. These analyses are also needed to support characterization of products and effluents from new processes such as silicate melt, aqueous silicate, and radionuclide removal. From this data, the hazard potentials of actinides can be more accurately evaluated. Future separation and immobilization processes can then be developed to reduce and contain any of these potential hazards.

The basis for the actinide analytical procedures is the separation of the actinides by solvent extraction followed by alpha counting and alpha energy analyses for plutonium-239, -238, americium-241, and neptunium-237. Because of the complex and varying matrices found in Hanford waste, ²³⁶Pu and ²⁴³Am are used as tracers to determine chemical yields through the procedure. Neptunium-239 which is present in equilibrium with the ²⁴³Am tracer and separated from it by solvent extraction provides a convenient and usable neptunium tracer. Neptunium-239 recoveries are determined within eight hours of separation from ²⁴³Am by gamma energy analyses. Because of salts and residual organics carried through the solvent extraction procedures, electrodeposited mounts are necessary for high resolution alpha energy analyses.

Thorium and uranium are also analyzed by using solvent extraction to separate them from the waste solutions. After isolation, their concentrations are determined spectrophotometrically.

EXPERIMENTAL

Reagents and StandardsSample Preparation

Plutonium-236 and americium-243 (10^3 - 10^4 d/m/ml).-- Stock solutions of each are obtained from Oak Ridge National Laboratory.

Thorium (Th-0.1 g/l).--Prepare an 0.1M Th stock solution by dissolving 4.8 g of analytical grade thorium nitrate in 100 ml of 1M HCl.

Aliquat-336 Extraction

Aliquat-336 in xylene (30 v/v%).--Dissolve 300 ml of Aliquat-336 (Cl) [General Mills, Inc., Kankakee, Illinois] in 700 ml of reagent grade xylene in a 2 liter separatory funnel. Shake for five minutes with two successive 500 ml portions of 4M HNO_3 . Wash the organic three successive times with 500 ml deionized H_2O . Allow the phases to thoroughly separate and collect the organic in a dark liter bottle.

DHDECMP Extraction

Diethyl-N,N-diethylcarbonylmethylenephosphonate in trichlorobenzene (DHDECMP/TCB-30%).--Dilute 150 ml of DHDECMP [Wateree Chemical Company, Lugoff, South Carolina] with 350 ml of reagent grade TCB in a 1500 ml beaker. Add 500 ml ethylene glycol. Emulsify for 30 minutes. If a good emulsion cannot be attained, stir for one hour. Separate the phases in a separatory funnel and discard the glycol. Run the 30% DHDECMP through an ion exchange column packed with Amberlist-A 26.¹ Emulsify the DHDECMP twice with 500 ml 4M HNO_3 for 15 minutes. Allow the phases to separate in a separatory funnel. Discard the acid. The residual aqueous can be removed by passing the organic through Whatman phase separating paper. Store in a dark glass bottle.

Electrodeposition

Electrolyte.--Dissolve 132 g of ammonium sulfate in one liter of deionized H_2O . Adjust pH to 3.5 with 15M NH_4OH and 18M H_2SO_4 .

Thorium - Arsenazo III Determination

Arsenazo III (0.05%).--Dissolve 0.05 g of Arsenazo III in 100 ml of deionized H₂O. Use glassware that is free of any residual HNO₃, as it will destroy the purple arsenazo color. Since this reagent dissolves slowly, allow at least one hour of stirring for the dissolution. The solution is stable and will not deteriorate with time if kept in a closed bottle.

Uranium Determination

Tri-n-octylphosphine Oxide (0.1M TOPO).--Dissolve 2.868 g of TOPO in 100 ml of cyclohexane.

Complexing Solution.--Add 25.0 g of (1,2-cyclohexylene-dinitrilo) tetraacetic acid (CDTA), 5.0 g of sodium fluoride (NaF), and 65 g of sulfosalicylic acid to 500 ml of deionized H₂O. Neutralize to a pH of 8.5 with NaOH and dilute to 1.0 liter with deionized H₂O. Dilute 500 ml of this reagent with 500 ml of deionized H₂O and store in a dark bottle for use in the procedure. Final pH is 8.35.

Triethanolamine Buffer (TEA).--Add 149 g (132.5 ml) of TEA to 800 ml of deionized H₂O. Neutralize to a pH of 8.5 with HCl and dilute to 1.0 liter with deionized H₂O. Store in a dark bottle.

Bromo-PADAP [G. Frederick Smith Chemical Company No. 587].--Dissolve 0.05 g of bromo-PADAP in 100 ml of ethanol and store in a dark bottle.

Aliquat-336 [General Mills, Inc., -15%].--Dissolve 75 ml of Aliquat-336 (chloride form) into 425 ml of xylene. Wash the organic twice in a separatory funnel with an equal volume of 2.5M NaOH, twice with 3M HCl, and twice with deionized water.

Uranium Standard (1.0089 g/l U).--Prepare by dissolving NBS U₃O₈ in HNO₃. Final HNO₃ concentration is 1.8M.

Equipment and Apparatus

Electrodeposition

Electrodeposition cell constructed according to Idaho Nuclear Corp. (Idaho Falls, Idaho) drawing no. 340594.²

Glass, O-ring joint chimney - 15 mm i.d. x 15 cm height.

Teflon O-rings constructed to fit glass chimney.

Polished 22 mm diameter, 24 mils thickness, steel disks. Clean disks by rinsing completely with acetone, heating in conc. HNO_3 for 30 minutes and rinsing completely with H_2O . Store cleaned disks in deionized H_2O until ready to use.

Rotating platinum electrode - 45 mesh cylinder of pure platinum supported by wire and stem of 95 percent platinum, 5 percent rhodium [Englehard Industries, Carteret, New Jersey].

Dimensions - Cylinder diameter	-	1.27 cm
Cylinder height	-	5.08 cm
Overall height	-	19.05 cm
Stem diameter	-	0.15 cm

Overhead stirrer with removable chuck capable of operating at 50 rpm.

DC - Power supply capable of operating in constant current or constant voltage mode having a single output, 0-10 volts DC, 5 amps.

Constant temperature water circulator to cool the cell base.

Spectrophotometric Methods

Spectrophotometer capable of scanning from 750 nm to 500 nm using an absorbance range of 1.

Procedures

Sample Preparation For the Analysis of Pu, Np, Am, Cm, and Th

Method.--If solids are present in the sample, it is heated, diluted with a known amount of deionized water, and filtered through an 0.25 μm Solvinert [Millipore Corporation] filter. The filtered insolubles are dissolved and analyzed separately. A sample aliquot ranging from 2 ml to 5 ml is spiked with an appropriate concentration of ^{236}Pu and ^{243}Am . If also analyzing for total thorium, samples are run in duplicate with one being spiked with additional Th of a

known amount. The sample and spikes are allowed to equilibrate for about 24 hours. They are then acidified with conc. HNO_3 to 4M H^+ . Any HNO_2 or NO_x present is destroyed with heat and urea. Plutonium and neptunium are reduced using hydroxylaminehydrochloride and ferrous sulfamate. After cooling, Pu(III) is oxidized to Pu(IV) with sodium nitrite.

Aliquat-336 Extraction of Pu, Np, and Th

This procedure is patterned after a procedure developed by C. W. Sill³ at the ERDA Idaho Falls site for actinide analyses of soils.

Method.--After sample preparation, Pu, Np, and Th are extracted into 30% Aliquat-336 in xylene. At this point ^{239}Np is separated from ^{243}Am and begins decaying without an equilibrium source. Due to the short half life of ^{239}Np , the final mounts and gamma energy analysis (GEA) are made within 8 hours of the separation time.

Residual Am is removed from the Aliquat-336 with an 8M HNO_3 wash. Thorium is quantitatively stripped from the organic into 10M HCl and saved for spectrophotometric analysis. Plutonium and neptunium are then stripped into 0.25M sodium oxalate and prepared for electrodeposition.

DHDECMP Extraction of Am and Cm

Bidentate organophosphorus extractants were first found to be favorable extractants of trivalent actinides by Siddall.⁴⁻⁶ Schulz and McIsaac¹ have done further work using some of these bidentates, such as dihexyl-N,N-diethyl-carbonylmethylene phosphonate, for the removal of actinides from the acidic wastes generated at the Hanford and Idaho Falls sites.

Method.--After sample preparation and the removal of Pu and Np with Aliquat-336, Am and Cm are extracted into 30% DHDECMP in trichlorobenzene (TCB). Americium and curium are then stripped from the organic into 0.1M HNO_3 and prepared for electrodeposition.

Electrodeposition of Pu, Np, Am, and Cm

Due to excessive salts and residual or dissolved organics carried through the Aliquat-336 and DHDECMP procedures, mounts for radiochemical counting could not be made

by evaporation. To produce undegraded alpha energy spectra it was necessary to set up an electrodeposition system. A system similar to one described by Puphal² at the Idaho Falls site, with minor modifications, was found to be compatible with our laboratory. However, a deposition method modified from one used at the Mound Laboratories⁷ produced higher recoveries and was less corrosive to our steel disks than the Idaho method.

Method.--An aliquot of the aqueous strip is evaporated to near dryness with conc. HNO_3 . It is then redissolved in conc. HNO_3 and 5% sodium bisulfate in 9M H_2SO_4 and evaporated to dryness. This melt is dissolved in 5 ml of electrolyte and transferred to the deposition cell with an additional 10 ml of electrolyte. The pH is adjusted with 1.8M H_2SO_4 or 1.5M NH_2OH to a thymol blue indicator color of salmon pink. The actinides are deposited for two hours with a constant current of 1.2 amps requiring about 8 volts. Deposition is terminated with the addition of 15M NH_4OH . After drying with ethanol and heat the mounts are sent for alpha total counting, alpha energy analyses and gamma energy analyses. All results are corrected for spike recovery.

Spectrophotometric Determination of Thorium

The analytical utilization of Arsenazo III, first exploited in 1959, has been extensively reviewed by Savoin^{8,9}, who pointed out its high sensitivity and selectivity for thorium, zirconium, and uranium.

Method.--After sample preparation and extraction into Aliquat-336, thorium is stripped into 10M HCl . An aliquot of HCl is evaporated to near dryness and redissolved in fresh 10M HCl . Sulfamic acid is added to destroy any residual nitrite which would interfere with the stability of the Arsenazo III color. Before diluting with water, 0.05% Arsenazo III in water is added to the HCl . This is scanned spectrophotometrically against a reagent blank from 750 nm to 580 nm. The Arsenazo III-thorium complex has maximum absorbance at 660 nm. Concentrations are determined using a least squares calculation.

Spectrophotometric Determination of Uranium

The total uranium content of the samples is determined by a spectrophotometric method using Br-PADAP [2-(5-bromo-

2-pyridalazo)-5-diethylaminophenol]. This method has been used extensively for the determination of U in ores and natural waters.¹⁰⁻¹³ It was expanded further by extracting the colored uranium complex into Aliquat-336 and thereby increasing sensitivity by a factor of 5.¹⁴

Method.--When applied to waste tank solutions the samples are acidified to 3M HNO₃. Fluoride and ascorbic acid are added to complex other extractable ions and to reduce Ce, V, and Fe. Hydroxylamine hydrochloride is also added to reduce Pu(IV) to Pu(III). The U is then extracted into TOPO. An aliquot of the TOPO is placed in a mixed complexing solution of tri-ethanolamine buffer and Br-PADAP to develop a colored U complex. The uranium complex is then extracted into 15% Aliquat-336 and its absorbance measured against a reagent blank. Maximum absorption is at 578 nm.

RESULTS AND DISCUSSION

These methods of analyses have been applied to both synthetic wastes containing known concentrations of actinides and to actual waste tank sample. Satisfactory and usable data have been obtained in all cases.

Since the lower permissible limits in a controlled zone for Pu, Am, and Np are about 10³ disintegrations per minute per milliliter, our studies have concentrated on sample aliquots containing from 10³ to 10⁴ d/m. In this concentration range, spike recoveries for Pu and Np have ranged from 90 to 100% and Am and Cm from 80 to 90%. Thorium being analyzed at the 1 to 10 µg level has produced recoveries of 90 to 100%. Uranium analyses are run on sample aliquots containing from 1 to 20 µg. Recoveries range from 117.7±19.4% at lower concentrations of U to 97.5±2.6% at the higher levels.

These methods have four major advantages over other methods investigated: (1) larger sample sizes can be used if needed (up to 5 ml); (2) caustic, high salt waste samples are analyzed at a higher, more easily controlled acidity (3-5M H⁺); (3) high resolution alpha energy analysis are attained from electrodeposited mounts; and (4) the use of the ²³⁹Np daughter present in equilibrium in the ²⁴³Am tracer makes a very convenient and usable neptunium tracer.

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