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QUALITY ENGINEERING AND CONTROL
SEMIANNUAL PROGRESS REPORT
MAY THROUGH OCTOBER 1978

Robert L. Carpenter

ANALYTICAL LABORATORIES GROUP

MASTER

Rockwell International

Energy Systems Group
Rocky Flats Plant
P.O. Box 464
Golden, Colorado 80401

U. S. DEPARTMENT OF ENERGY
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ROCKWELL INTERNATIONAL
ENERGY SYSTEMS GROUP
ROCKY FLATS PLANT
P.O. BOX 464
GOLDEN, COLORADO 80401

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for the
Albuquerque Operations Office
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SUBJECT DESCRIPTORS

Absorption Spectroscopy
Alpha Spectroscopy
Americium
Cleaning
Differential Thermal Analysis
Dissolution
Gas Chromatography
Ion Exchange Materials
Liquid Chromatography
Mass Spectroscopy
Materials Compatibility
Metals
Neptunium

Organic Chlorine Compounds
Organic Phosphorous Compounds
Plutonium
Quantitative Chemical Analysis
Radiometric Analysis
Reactivity
Sample Preparation
Separation Processes
Stainless Steels
Thermal Analysis
Thorium
Titrimetry
Uranium
Water

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ABSORPTION SPECTROSCOPY

**THORIUM IN THORIA-TUNGSTEN
WELDING RODS**

Amelia M. Miller

SUMMARY

Analysis of welding rods containing 2 weight percent thorium (ThO_2) in tungsten involves a lanthanum (La) carrier precipitation of thorium fluoride, conversion to sulfate, and colorimetric measurement with thoron. The accuracy of the method is ± 0.1 percent ThO_2 , acceptable for the specification of 1.8 to 2.3 weight percent ThO_2 . This procedure represents an improvement over the standard method which involved treatment by perchloric acid fuming, ammonium hydroxide separation, followed by titration of the thorium (Th).

EXPERIMENTAL

Aliquots of 0.2 gram are placed in 50-milliliter (ml) plastic centrifuge tubes. One ml of a carrier solution containing 15 milligrams La per ml is added. The sample is dissolved with 5 ml nitric acid (HNO_3) and 2.5 ml hydrofluoric acid (HF). A precipitate of fluorides of La and Th results. After dilution to 50 ml with water, the aliquot is centrifuged, and the precipitate of fluorides of La and Th is washed twice with an aqueous solution of 2N HNO_3 containing 5 percent HF. The precipitate is transferred to a platinum crucible, 1 ml sulfuric acid is added, and the treated precipitate is fumed to dryness on a hot plate. The salts are dissolved in 10 ml of 50 percent hydrochloric acid and transferred to a 50 ml-volumetric flask with water. The

thoron-Th color complex is developed in a 3 ml aliquot, diluted to volume in a 25 ml-volumetric flask, and its absorption recorded at a wavelength of 545 nanometers. A standard Beer-Lambert plot derived from the same reagents is used to determine ThO_2 concentrations.

RADIOMETRIC METHODS

**SEPARATION AND DETERMINATION OF
NEPTUNIUM IN PLUTONIUM METAL**

*Richard A. Nixon, Ralph C. Nelson,
and James D. Navratil**

SUMMARY

Four types of anion-exchange resins were evaluated for the separation of neptunium (Np) from plutonium (Pu) metal samples using the following criteria: breakthrough capacity, elution volume, and the ratio of Np and Pu in both the wash solution and ion-column eluate. Of the resins tested, 100 to 200 mesh Dowex® 1X4 had the most favorable separation characteristics.

EXPERIMENTAL

The breakthrough capacity, a measure of the Pu capacity of the resin, is defined as the amount of Pu in milligrams passed per milliliter of resin when the ratio of Pu concentrations in the effluent to

*Division of Research and Laboratories, International Atomic Energy Agency, P. O. Box 645, A-1011 Vienna, Austria.

TABLE 1. Characteristics of Anion Exchange Resins in the Separation of Neptunium From Plutonium

Resin	Mesh Size	Breakthrough Capacity ^a	Elution Volume ^b	Actinide Concentrations ^c		Pu/Np Ratio In Eluate
				Plutonium	Neptunium	
Dowex® 1X4	20 to 50	8	72	---	---	---
Dowex® 1X4	100 to 200	41	3	99	0.7	0.035
Amberlite® IRA-93	20 to 50	4	5	100	0.1	0.37
Amberlite® IRA-938	20 to 50	20	4	85	1.2	37.0

a. Milligrams of plutonium passed per milliliter of resin.

b. Milliliters of 0.35 molar nitric acid necessary to remove 90 weight percent of plutonium.

c. Percent actinides in the ion-column effluents and wash solutions after resin treatment.

FIGURE 1. Elution of Neptunium From Anion Exchange Resins

feed solution is equal to 0.1. Elution is defined as the volume of 0.35M nitric acid necessary to remove 90 weight percent of the Pu on the resin.

Breakthrough capacity and elution volume data for Pu containing about 0.5 weight percent Np with the four resins tested are given in Table 1. Amberlite® IRA-938 and 100 to 200 mesh Dowex 1X4 resins, have a high Pu capacity and small elution volume. However, Amberlite IRA-938 resin has poor Np-elution behavior compared to Amberlite IRA-93 and Dowex 1X4 resins, which allow nearly all Pu but no Np to pass through the columns. Separation data are summarized in Table 1.

The Np-elution plots for these three resins are shown in Figure 1. Dowex 1X4 resin has the smallest elution volume and provides a good separation of Np from Pu. Because it displayed the best all-around performance, 100 to 200 mesh Dowex 1X4 resin was chosen for laboratory use in radiometric analyses requiring Np-Pu separations. Recovery of ²³⁹Np tracer is typically 70 to 90 percent. Typical mean analysis of solutions containing 35 micrograms Np per gram of Pu is 35 ± 7.5 at the 95 percent confidence level (± 2 standard deviations). Accuracy of analyses of solutions containing 10^{-3} gram Np per liter is ± 15 percent at the 95 percent confidence level. The estimated accuracy of Pu determinations is ± 10 percent.

TRACE RADIONUCLIDES IN STAINLESS STEEL

David R. Guhlow and Keith J. Grossaint

SUMMARY

A technique was developed to permit removal of the major interfering elements of the stainless-steel matrix from samples submitted for trace uranium analysis. Iron, chromium, and nickel were preferentially complexed by EDTA (ethylenedinitrilote-tracetate) ion in aqueous chloride solutions. This prevented saturation of anion-resin exchange sites, resulting in good recovery of uranium as the chloride anion complex. Recovery of added tracer isotope was between 80 and 90 percent, compared with less than 10 percent tracer recovery for other attempted methods of alpha spectrometric analysis of stainless steels.

EXPERIMENTAL

The overwhelming amounts of iron, chromium, and nickel in stainless steels interfere with the ion-exchange separation of radionuclides prior to pulse-height alpha spectrometric analysis. The chloride ion complexes of these elements tend to saturate exchange sites of the anion resin, resulting in low recovery of actinides from the resin column strip. The usual practice has been to reduce iron to the relatively-noncomplexed ferrous ion with ammonium iodide prior to passing the sample through the resin. This procedure has not been feasible for analysis of stainless steels and is ineffectual for reducing interference from the chromium and nickel.

A combination of iodide reduction and EDTA-complex formation permitted good recovery of uranium tracer from stainless steel samples. The procedure required dissolving a weighed sample of 1.0 gram in 50 percent aqua regia and diluting with water to a volume of 20 milliliters (ml). A 1-ml aliquot was transferred to a glass beaker and an appropriate amount of tracer isotope added. About 3 grams of potassium pyrosulfate powder was then added, and the resulting slurry was heated slowly to dryness. The sample was then fused at 550 °C for several minutes and allowed to cool.

One-half ml of 12N hydrochloric acid (HCl) was added to the cooled mass, followed by 20 ml of 8N HCl. The sample was then heated until the salt cake was dissolved. The volume of the solution was brought to 40 ml with 8N HCl. One gram of ammonium iodide and 1 gram of the disodium salt of EDTA were added, followed by filtration through Whatman® 40 filter paper. The filtrate was passed through a column containing anion-exchange resin. The characteristic color of chromium and nickel ions was observed to pass through the column, while uranium was held on the resin as the chloride anion complex. The procedure resulted in 80 to 90 percent recoveries of added tracer, compared with less than 10 percent tracer recovery for other attempted analyses of stainless steel by alpha spectrometry.

POTASSIUM PYROSULFATE FUSION METHOD FOR RADIONUCLIDES IN ORGANIC MATERIALS

John R. Stevens and Keith J. Grossaint

SUMMARY

A method was developed which permits dissolution of organic materials for radionuclide analysis. Acceptable reproducibility and recovery were observed for analyses of vegetation and fish flesh samples, which had been *spiked* by the Rocky Flats Chemical Standards Laboratory.

EXPERIMENTAL

Because it is desirable for complete extraction to occur in the analysis of organic materials for radionuclides, chemical digestion is required. The hazards of chemical digestion with such agents as perchloric acid result in requirements of special equipment and procedure controls. A technique for safe digestion of such organic materials as vegetation and fish flesh was developed in support of the environmental monitoring program at Rocky Flats. Sample amounts ranged from 0.2 grams to 8.0 grams, depending on the expected levels of activity and the requirement for a sample to be representative of the bulk material.

TABLE 2. Analysis Results of Samples of Organic Material Containing Standard Additions of Plutonium and Americium

Sample Number	Plutonium (in picocuries per gram)		Recovery (Percent)	Americium (in picocuries per gram)		Recovery (Percent)
	Added	Found		Added	Found	
Veg-40006	0.89	0.74 ± 0.04*	83.1	0.91	0.38	41.8
Veg-40008	8.3	7.3 ± 0.55	88.0	8.7	11.7	134.0
Fish-40018	0.90	0.94 ± 0.30	104.0	0.90	1.68 ± 0.67	187.0
Fish-40019	9.01	9.73 ± 1.5	108.0	9.01	10.7	119.0

* The ± results represent the standard deviation of duplicate analyses.

The procedure involves adding 3 times the sample weight of potassium pyrosulfate powder to the organic material in a glass beaker. An appropriate amount of tracer isotope is then added, and the mixture is fused at 550 °C for about 12 hours. After cooling, the sample is taken up in 0.5*N* nitric acid (HNO₃). Small amounts of barium in vegetation may result in a suspension of fine, white, barium sulfate precipitate in the beaker. The solution may be filtered through Whatman® 540 filter paper to remove this residue without affecting the analytical results.

The filtrate in 0.5*N* HNO₃ can be passed directly through a column containing cation-exchange resin, as the first step in chemical separation of the isotopes. The analysis is then performed in the normal manner, with no interference from the pyrosulfate.

Samples of fish flesh and plant materials such as stems and leaves were spiked with known levels of plutonium and americium by the Chemical Standards Laboratory. These standards were submitted for analysis, concurrent with similar materials for environmental monitoring of radionuclides. The analysis results are given in Table 2. The mean plutonium recovery for the four samples represented was 95.8 percent of the standard addition value; mean americium recovery was 120 percent of the standard addition value.

TRACE RADIONUCLIDES IN ELECTROPOLISH BATHS

John R. Stevens and Keith J. Grossaint

SUMMARY

A technique was developed for the rapid removal of interfering phosphate ion from electropolish solutions by adsorbing radionuclides on a column containing cation-exchange resin and discarding the phosphate-ion eluate. The radionuclides were then stripped from the resin, collected, and analyzed by the normal radiometric procedure. The method worked well for plutonium and americium, and is expected to give good results for uranium determinations as well.

EXPERIMENTAL

The phosphate ion present in some electropolish baths interferes with the normal extraction procedures in preparing samples for pulse-height alpha spectrometric analysis. Some previous analyses were performed in this laboratory on a nonroutine basis by slowly evaporating the phosphoric acid at elevated temperatures and heating in a muffle furnace overnight. The sample was then taken up in nitric acid (HNO₃) and analyzed by the normal procedure. The time required for this treatment was too lengthy for the large number of samples expected during a series of electropolish

TABLE 3. Plutonium Alpha Contamination Removed Versus Increase in Alpha Activity for Electropolish Solutions

Trial	Surface Activity Decrease (disintegrations per minute)	Solution Activity Increase (disintegrations per minute)
1	3,220	2,800
2	11,164	11,400
3	124,600	174,200
4	54,078	70,000
5	25,580	40,000

decontamination experiments. The electropolish-bath solutions were typically concentrated phosphoric acid, containing minor concentrations of iron, chromium, nickel, cadmium, zinc, and varying amounts of the radionuclides plutonium, americium, and uranium.

An aliquot of the viscous solution was transferred to a glass beaker, and an appropriate amount of tracer isotope was added. The solution was then diluted with distilled water by a factor of 20, warmed, and passed through a column of hydrogen-form cation-exchange resin (Dowex® AG 50W-X8, 50-100 mesh). The resin was washed with one column volume of 0.5N HNO₃, and the eluate containing phosphate ion was discarded.

The cations were stripped from the resin with one column volume of 8N hydrochloric acid (HCl), followed by one column volume of 12N HCl. The strip solution was collected and taken to dryness. The chloride was driven off by heating the sample to dryness from concentrated HNO₃. The dried sample was taken up in 8N HNO₃ and analyzed for plutonium and americium by the normal procedure.

The data from successive analyses of an electropolish bath correlated with concentrations anticipated from the removal of surface contamination on stainless steel samples. The decrease in surface contamination was monitored by gas-proportional alpha determination. Representative data are given in Table 3.

SAMPLE PREPARATION

CLEANING METHODS FOR URANIUM SAMPLES

Karl N. Kirchner and Max D. Dixon

SUMMARY

Several methods for cleaning uranium samples prior to carbon analysis using a LECO Carbon Analyzer were evaluated. Use of Oakite® NST Aluminum Cleaner, followed by water and acetone rinses, was superior to the other techniques.

EXPERIMENTAL

The Rocky Flats Plant Analytical Laboratories have been concerned with sometimes erratic carbon results in low carbon (< 100 ppm by weight) uranium metal and uranium alloys. As the instrument appeared to be functioning properly, variability in carbon values was attributed to improperly-cleaned samples. The cleaning method used prior to the present study consisted of ultrasonically rinsing the samples for 30 minutes each in methanol and 1,1,1-trichloroethane, followed by air drying. The carbon results from these samples varied considerably, depending on their shape and surface area.

In this study, three cleaning methods were evaluated: the method discussed above; a method involving an ultrasonic cleaning in aqueous 2 volume percent Oakite NST for 30 minutes followed by washing in acetone and air drying; and a method in which the samples were pickled in aqueous 8M nitric acid containing 2 volume percent of 30 percent hydrogen peroxide, rinsed with water, then washed in acetone.

Machined pellets and drillings were obtained from the same ingot. Some of the drillings were air dried and analyzed without cleaning as a control. The remainder of the drillings were divided into three groups and cleaned by the three cleaning methods. The pellets were ultrasonically cleaned in Oakite NST, rinsed in acetone, and air dried. It was assumed that the carbon results from the pellets represented their actual carbon content because of their machined surface and small surface area.

TABLE 4. Carbon Results for Uranium Samples

Sample Treatment	Number of Samples	Mean Carbon Concentration (ppm by wt)
Control Sample (dried under heat lamp)	10	362 ± 78*
Ultrasonically cleaned for 30 minutes each with methanol, then 1,1,1-trichloroethane	10	41 ± 8
Ultrasonically cleaned for 30 minutes with Oakite® NST, then washed in acetone	10	23 ± 8
Pickled for 2 minutes in 8M nitric acid containing 2 volume percent (30%) hydrogen peroxide	6	51 ± 6
Machined pellets	10	17 ± 6

* The ± results represent the 95 percent confidence levels (±2 standard deviations).

Table 4 summarizes the results of the cleaning study. Carbon concentrations of the machined pellets were slightly lower than for the Oakite NST-cleaned drillings. The acid-pickled and ultrasonic-solvent-cleaned drillings were significantly higher than either the machined pellets or the Oakite NST-cleaned samples. As a result of this study, the laboratory has adopted ultrasonic cleaning uranium samples with Oakite NST as a routine procedure preliminary to carbon analysis.

IMPROVED DISSOLUTION OF PLUTONIUM DIOXIDE SAMPLES

Donald P. Anderson

The substitution of sodium bisulfate for potassium pyrosulfate in the fusion of plutonium dioxide

samples has led to a more efficient dissolution process. This improvement was suggested in a procedure employed at the Rockwell Hanford Operations Analytical Laboratories for amperometric plutonium assay¹ and adopted at the Rocky Flats Plant for samples undergoing plutonium assay and the determination of uranium impurities.

Sodium bisulfate enables the flux to be fused at a lower temperature (625 °C) than in the case of potassium pyrosulfate. Additionally, the resultant melt can be dissolved with stirring only; no heat is required. The melt is water soluble but can be dissolved with dilute aqueous hydrochloric acid or nitric acid. These solutions are sufficiently stable so that precipitation will not occur on prolonged standing. The fused form of sodium bisulfate, ground finely with a mortar and pestle just prior to use, works best. The hydrated form of sodium bisulfate may also be used. However, the reaction (loss of water) occurring during the furnace heating step can result in the spattering of the sample and flux.

This fusion process prepares oxide samples for assay by titration with standard ceric sulfate. Exchange oxide samples of known plutonium contents are assayed bimonthly as a laboratory control measure. Since the introduction of sodium bisulfate as the flux, no significant changes have been observed for the accuracy and precision of the titrimetric method applied to these control samples.

THERMAL ANALYSIS

METAL-SOLVENT MIXTURES

Roger S. Cichorz and Patricia A. Hyman

SUMMARY

Sealed-capillary differential thermal analysis (DTA) experiments were performed on a series of

¹T. G. Ibsen. Private Communication. Rockwell Hanford Operations, Richland, Washington 99352. September 1978.

TABLE 5. Differential Thermal Analysis Results for Metal-Solvent Mixtures

Metal	Onset Temperature (°C) of Exothermic Reactions				
	Chlorothene VG®	Chlorothene NU®	Alk-Tri®	Inhibitor-Free Trichloroethylene	Freon® TF
Iron	none ^a	none ^a	389 ± 1	384 ± 10	none ^b
Stainless Steel	none ^a	none ^a	388 ± 7	366 ± 1	none ^b
Copper	197 ± 10	231 ± 6	391 ± 13	358 ± 11	400 ± 30
Beryllium	>420 ^c	435	363 ± 17	404 ± 1	none ^b
Aluminum	347 ± 132	445 ± 14	305 ± 14	298 ± 11	none ^b
Plutonium	311 ± 3	311 ± 21	283 ± 28	270 ± 42	none ^b

NOTE: The ± results for onset exotherm temperatures represent the 95 percent confidence limits (±2 standard deviations) of the mean results of a series of replicate analyses.

- a. A series of endothermic reactions were observed between 230 and 330 °C and attributed to the iron-catalyzed decomposition of proprietary inhibitors. No exothermic reactions were observed to 450 °C.
b. No exothermic reactions were observed to 450 °C.
c. No exothermic reactions were observed to 420 ± 14 °C.

metal-trichloroethylene mixtures, metal-1,1,1-trichloroethane mixtures, and metal-1,1,2-trichloro-1,2,2-trifluoroethane (Freon® TF) mixtures to assess the reactivities of a particular metal with these solvents. In general, the metals tested (iron, stainless steel, copper, beryllium, aluminum, and plutonium) displayed the lowest reaction temperatures with trichloroethylene and the highest with Freon TF. In most cases, the presence or absence of proprietary inhibitor additives in the chlorinated hydrocarbon solvents did not significantly affect the reaction onset temperatures.

EXPERIMENTAL

This investigation employed the DTA procedure which involves the metal to be in intimate contact with the solvent at all times during the experiment.

The experimental conditions and capillary-loading arrangements for this procedure have been previously detailed by Patricia A. Hyman and Roger S. Cichorz (refer to earlier Progress Report, RFP-2699, March 27, 1978, pages 17-18). All metals used in the experiments were in the form of freshly-filed fines to prevent the testing of partially-oxidized metals. Replicate DTA runs were made to 450 °C at a heating rate of 20 °C per minute on a DuPont® 900 Thermal Analyzer. Results of the DTA tests are summarized in Table 5.

Two proprietary formulations of commercially-available inhibited 1,1,1-trichloroethane manufactured by the Dow Chemical Company, Midland, Michigan, Chlorothene VG® and Chlorothene NU®, were compared. Chlorothene VG appeared more reactive with copper and aluminum, but less reactive with beryllium.

Alk-Tri®, Dow Chemical Company's industrial grade trichloroethylene containing a proprietary inhibitor, was compared with trichloroethylene without an inhibitor, and similar DTA results were obtained. Alk-Tri was slightly more reactive with beryllium but less so with copper when compared to inhibitor-free trichloroethylene. In general, trichloroethylene had a lower onset reaction exotherm temperature than did 1,1,1-trichloroethane for most of the metals tested. The two exceptions were copper, in which a substantially higher reaction temperature was recorded, and plutonium, which reacted exothermically at about the same temperature. Iron and stainless steel, which did not react with 1,1,1-trichloroethane to 450 °C, experienced exothermic reactions with trichloroethylene when heated above 365 °C. Freon TF was the least reactive of the solvents tested, in that it did not react exothermically at temperatures below 450 °C with any of the metals tested except copper.

TITRIMETRY

PLUTONIUM ASSAY BY POTENTIOMETRIC TITRATION

Edward A. Brovsky and Donald P. Anderson

SUMMARY

A potentiometric titration method² has been adapted to determine the plutonium concentration in Hanford feed nitrate solutions. The plutonium (Pu) species are converted to Pu(III), using titanium (III) chloride as a reducing agent, and then titrated to Pu(IV) with standard cerium(IV) sulfate $[\text{Ce}(\text{SO}_4)_2]$ solution. The results of this method are comparable to results obtained by the amperometric-titration method used by Hanford. In general, agreement in the plutonium concentration between the two methods is within the range of 0.4 to 4.2 percent.

²J. Corpel and F. Regnaud. "Cerimetry in Nitric Acid Media. Application to the Determination of Iron, Uranium, and Plutonium." *Analytica Chimica Acta* 27:36. January, 1962.

TABLE 6. Plutonium Assay of Standard Nitrate Solutions Prepared for the Potentiometric Titration Method

Standard Number	Theoretical (grams/liter)	Found (grams/liter)	Recovery (percent)
1	116.88	117.01 ± 0.15*	100.11
2	93.63	93.57 ± 0.24	99.95
3	150.29	150.52 ± 0.22	100.15
4	74.36	74.41 ± 0.32	100.07

* Analysis results of four replicate determinations; the ± values are the 95 percent confidence levels (± 2 standard deviations).

EXPERIMENTAL

Approximately 2 milliliters (ml) of the nitrate solutions are weighed by difference into a 150-ml beaker and diluted to a volume of 60 ml with a mixture of 1N sulfuric acid and 1N nitric acid. One gram of sulfamic acid is added to avoid the presence of nitrite ion which is capable of oxidizing the reduced form of Pu or of reacting with the titrant solution. About 2 ml 20 weight percent aqueous TiCl_3 are added to reduce all of the Pu present to Pu(III). The solution is then titrated with 0.02N $\text{Ce}(\text{SO}_4)_2$ to a potentiometric endpoint, which indicates that the Pu has been converted from Pu(III) to Pu(IV). The Pu concentration is then calculated from the amount of standard $\text{Ce}(\text{SO}_4)_2$ solution needed to reach the endpoint and from a density measurement taken with a 25-ml pycnometer.

The $\text{Ce}(\text{SO}_4)_2$ solution was standardized with National Bureau of Standards plutonium metal standard number 949d. In addition, control samples prepared by the Standards Laboratory were used to assess the accuracy and precision of the method. The mean plutonium recovery of replicate analyses of four different standards was 100.07 percent. The method relative standard deviation on these standards ranged from 0.065 to 0.22 percent. Analysis results of the standards are summarized in Table 6.

MISCELLANEOUS PROJECTS

IMPURITIES IN ORGANOPHOSPHOROUS COMPOUNDS

Keith J. Grossaint and Mary L. Grooms

SUMMARY

Gas chromatography (GC), mass spectrometry (MS), and high-performance liquid chromatography (HPLC) analyses are used to identify and determine relative amounts of impurities in commercial dihexyl-N,N-diethylcarbamoylmethylene phosphonate (DHDECMP). Determination of chromatographic response factors is not complete because reference standards are not available for some of the impurities. Concentrations based on relative areas of chromatographic peaks are used for correlations with extraction distribution ratios of americium and efficiency of purification techniques.

EXPERIMENTAL

Research and development efforts are currently underway at the Rocky Flats Plant to evaluate bidentate organophosphorous extractants for use in the recovery, separation, and purification of actinides. One of the more promising compounds for this purpose is DHDECMP. A serious problem with the use of commercially-synthesized DHDECMP is the presence of impurities which significantly interfere with back extraction for recovery of actinides into a dilute acid medium (e.g., aqueous 0.3 to 0.5 normal nitric acid solutions).

Laboratory identification of the impurities and determination of DHDECMP concentration were requested in support of the research effort. Identification of the components was accomplished by separation on a gas chromatographic column, followed by mass spectral characterization. Separation of early eluting components was efficient, but some components were poorly resolved from DHDECMP (see Figure 2). Severe tailing of the major component occurred with the analysis conditions presented in Table 7. It is presently unclear whether the tailing results from poor chromatographic conditions or from partial thermal decomposition during transfer from the gas chromatograph to the mass spectrometer via

a 3-foot length of heated glass tubing. The unique mass peaks of the components permitted identification of the impurities, including a trace component which eluted concurrent with the DHDECMP.

The components observed in the typical commercial product and their relative GC peak areas are listed in Table 8. At present, relative peak area is taken as representative of component concentration. This is necessary because of the lack of pure reference standards for some of the major components in the mixture.

Good separations of components were achieved by HPLC using a reverse-phase column and an acetonitrile-water gradient system (see Table 9 for conditions of separation). Several components were collected by timing the solvent from detector to outlet. After solvent evaporation, four components were identified by MS solid-probe injection techniques (see Figure 3). This collection technique on multiple injections is currently being used to produce pure compounds for the calibration of instruments and calculation of response factors.

Liquid chromatograms indicated impurities were present in all commercial products and in DHDECMP after attempts at purification. Some resin purification techniques resulted in additional impurities, and, in general, attempts at purification seemed to increase concentration of DHDECMP only slightly.

Acid hydrolysis, solvent extraction, vacuum distillation, sodium hydroxide treatment, and resin-column exchange were some techniques used in the attempt to purify DHDECMP. The analytical data indicated that DHDECMP, which had been purified sufficiently to eliminate back-extraction interferences, still contained several of the impurities present in the commercial product. It has been proposed that the impurity responsible for poor back extraction is actually a protonated (acidic) form of DHDECMP.³ This component has not

³C. T. Bahnek, R. R. Shoun, and W. J. McDowell. *Impurities that Cause Difficulty in Stripping Actinides from Commercial Tetraalkylcarbamoylmethylphosphonates*. ORNL/TM-5878. September 1977. Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830.

FIGURE 2. Chromatogram of Commercial Dihexyl-N,N-diethylcarbamoylmethylene Phosphonate by Combined Gas Chromatography-Mass Spectroscopy

TABLE 7. Conditions for Gas Chromatography-Mass Spectroscopy Analysis of Commercial Dihexyl-N,N-diethylcarbamoylmethylene Phosphonate

Equipment/Parameters	Description
Chromatograph	Varian Model 2700, dual column, modified to permit transfer of column effluent to a mass spectrometer.
Column	Glass, 5-foot, 0.25-inch O.D. by 2.0-millimeter I.D.; 2 percent OV-101 Liquid phase, acid-washed and silanized solid support (Supelcoport®).
Injector	200 °C, silicone septum.
Oven Temperature	Held at 100 °C for 2 minutes, program heated at 8 °C per minute to 260 °C, and held at 260 °C until elution of DHDECMP completed.
Eluent Gas	Helium, nominal flow rate of 25 cubic centimeters per minute.
Separator	All glass, single stage, jet-fabricated by R. H. Allen Glass Co., Boulder, Colorado, and mounted directly to mass spectrometer source housing.
Transfer	Approximately 3-foot, 2-millimeter I.D. glass tube, heated to 200 °C from all-glass-column effluent-switching valve to jet separator.
Mass Spectrometer	Dupont 21-490, magnetic scan, 70 E.V. ionizing energy, 200 °C source temperature.
Mass Range	4 to 600 a.m.u., data acquired low to high mass.
Scan Rate	2.5 seconds up, 2 seconds return, 1.5 second hold, computer-controlled repetitive scan.
Data Acquisition and Reduction	Finnigan-Incos 2100 disk-operated computer system, 32 K memory, operator-interactive, data display during acquisition.
Data Display	Mass spectra, total ion current versus scan number (gas chromatogram), single or multiple ion current versus scan number (mass chromatogram), mass spectra versus scan (ion map).
Data Manipulation	Area of GC peaks, library search, spectrum matching, subtract or add mass spectra, ion current versus scan number maxima.

TABLE 8. Components Separated From Commercial
Dihexyl-N,N-diethylcarbamoylmethylene Phosphonate

Component	Elution Time ^a	Relative Area ^b (percent)
Diethylamine	1:36	0.14
Hexyl Chloride	1:54	2.5
Decane	2:24	0.33
Undecane	3:06	0.33
Chloro-N,N-diethylacetamide	4:42	3.0
Dichloro-N,N-diethylacetamide	5:12	0.71
Unidentified	5:52	0.38
α -diethylamino-N,N-diethylacetamide	6:36	2.4
Unidentified	7:54	0.23
Dihexyl Phosphite	11:18	4.1
Dihexyl Methyl Phosphite	11:36	7.8
Unidentified	13:12	1.1
Unidentified	14:12	0.78
Trihexyl Phosphate	17:00	28.0
α -dihexylphosphonatohexyl Acetate	19:58	trace
Dihexyl-N,N-diethylcarbamoylmethylene Phosphonate	20:06	47.0

a. Elution time in minutes and seconds from point of injection
of sample into the gas chromatograph.

b. Area of unresolved peaks taken from the left or right of
a vertical line at the trough minimum.

TABLE 9. Conditions for High-Performance Liquid Chromatography Analysis of Dihexyl-N,N-diethylcarbamoylmethylene Phosphonate

Equipment/Parameter	Description
Liquid Chromatograph	Waters Associates M-6000A equipped with Model 440 Absorbance Detector and Waters U6K Injector.
Column	1-foot μ -Bondapak® C18.
Ultraviolet Wavelength	254 nanometers.
Solvent	Water-acetonitrile, gradient produced by adding acetonitrile at a constant rate of 2 milliliters per minute to the solvent reservoir containing 100 milliliters water.
Sample Size	10 microliters.
Flow Rate	2 milliliters per minute

FIGURE 3. High-Performance Liquid Chromatogram of Commercial Dihexyl-N,N-diethylcarbamoylmethylene Phosphonate (DHDECMP) Using Acetonitrile-Water Gradient System

been identified in the material analyzed at Rocky Flats. It is assumed this acidic component, if actually present, was sorbed on the GC column.

Future work will involve capillary-column GC coupled with MS, and thin-layer chromatographic separations. The latter should help determine if the proposed acidic component is actually present. The capillary GC method has provided good separations in preliminary work performed elsewhere.⁴ After sufficient collection of pure DHDECMP and other impurity components, response factors and actual concentration of DHDECMP will be determined by HPLC and combined GC-MS techniques.

SOLAR-EVAPORATION-POND WATER PARAMETERS

Jack L. Long and Robert D. Koelmel

SUMMARY

Water from a typical solar-evaporation pond at the Rocky Flats Plant was analyzed in order to assess physical parameters needed to efficiently separate the water by evaporation from its dissolved solids. In this investigation, the following parameters were examined: (1) boiling point versus pressure at varying concentrations of dissolved solids, (2) specific gravity versus temperature at varying concentrations of dissolved solids, and (3) freezing point versus varying concentrations of dissolved solids. Statistical data are presented demonstrating the interrelationships of these parameters.

EXPERIMENTAL

Water from a typical solar evaporation pond has a pH of approximately 10, contains approximately 350 grams of total solids per liter, and has an alpha activity of about 4×10^4 picocuries per liter. As these ponds will be emptied in the near future and water separated from dissolved solids by evaporation, the Analytical Laboratory was requested to

determine the boiling points at varying pressures as a function of dissolved solids content. These data are needed to properly operate the process.

The boiling point of water from one of the ponds was determined in the pressure range of 100 to 300 millimeters of mercury (mm Hg = torr) [For SI (metric) use: 1.0 torr = 133.322 pascals]. The dissolved solids content was varied over the typical ranges of salts encountered, 9 to 46 weight percent (%), either by boiling to concentrate or by adding distilled water to dilute. Plots of the experimental data are given in Figure 4. The lowest curve corresponds to the lowest amount of dissolved solids, while the uppermost curve corresponds to the highest amount of dissolved solids. The curves were transformed into linear relationships by using a form of the Clapeyron-Clausius equation, $\log_{10} P = c - (a/T)$, where P is the pressure, T is the absolute temperature, and c and a are constants. The resulting straight lines are shown in Figure 5. Line number 1 corresponds to the highest dissolved solids content and line number 8 the lowest. The statistical correlation coefficients for the individual lines are given in Table 10. Either +1.00000 or -1.00000 would be perfect correlation.

The final step in this parameter study was the derivation of a single equation which relates the boiling point, the pressure, and the dissolved solids content. First, it was necessary to relate the solids content to the boiling point temperature. This information, shown in Table 11, resulted in the following expression:

$$1/^{\circ}\text{K} = [1.8134 \times 10^{-6} \times (\% \text{ D.S.})] + (3.1145 \times 10^{-3}),$$

where K is the absolute temperature (in $^{\circ}\text{K}$) and % D.S. is amount of dissolved solids (in weight percent). This equation was combined with the Clapeyron-Clausius equation through one form of the equation for a straight line, resulting in the expression:

$$1/^{\circ}\text{K} = [(\log_{10} P - 2) \div (-2109) + (3.1145 \times 10^{-3})] - [(1.8134 \times 10^{-6}) \times (\% \text{ D.S.})]$$

⁴S. J. Johnson. Private Communication. Rockwell Hanford Operations, Richland, Washington 99532. August 1978.

FIGURE 4.—Boiling Points of Solar-Evaporation-Pond Water Versus Pressure as a Function of Varying Concentrations of Dissolved Solids

FIGURE 5. Linear Relationships of Pressure and Temperature Derived From the Clapeyron-Clausius Equation

TABLE 10. Statistical Data of Temperature-Pressure Relationships Derived From the Clapeyron-Clausius Equation

<u>Dissolved Solids (Weight Percent)</u>	<u>Correlation Coefficient (1/°K vs log P)</u>	<u>Slope</u>	<u>$\bar{y}$ Intercept*</u>	<u>$\bar{x}$</u>
9.04	-0.99986	-2044	8.343	0.002820
11.84	-0.99917	-2062	8.374	0.002811
18.08	-0.99968	-2147	8.583	0.002800
24.77	-0.99939	-2093	8.418	0.002791
31.86	-0.99950	-2080	8.359	0.002780
32.42	-0.99968	-2167	8.613	0.002790
38.87	-0.99852	-2182	8.646	0.002781
46.00	-0.99929	-2099	8.370	0.002760

* $\bar{y}$'s for all dissolved solids contents equal 2.576.

TABLE 11. Dissolved Solids Content of Solar-Evaporation-Pond Water Versus Observed Boiling Point

<u>Dissolved Solids (Weight Percent)</u>	<u>Absolute Temperature (1/°K)</u>
9.04	0.003102
11.84	0.003090
24.77	0.003066
31.86	0.003062
32.42	0.003056
38.87	0.003045
46.00	0.003030

Correlation Coefficient = -0.99104

$\bar{y} = 3.064 \times 10^{-3}$, $\bar{x} = 27.829$

$\bar{y}$ Intercept = 3.1145×10^{-3}

Slope = 1.8134×10^{-6}

FIGURE 6. Specific Gravity–Temperature Relationships for Solar-Evaporation-Pond Waters Containing Varying Concentrations of Dissolved Solids

A program was written for a pocket calculator and recorded on a magnetic card, thus simplifying the calculational requirements to that of entering the pressure and the concentrations of dissolved solids to obtain the theoretical boiling point.

The specific gravity of the water, over a temperature range of 10 to 80 °C, varied from 1.01 to 1.25 as

the dissolved salts content varied from 5.93 to 32.42%. The specific gravities, measured at 10 °C temperature intervals for each of the eight dissolved-solids concentrations tested, are given in Figure 6. The spacing of a series of nearly-parallel straight lines, is proportional to the concentration of dissolved solids. The statistical correlation coefficients for all the lines are -0.997 or better.

FIGURE 7. Linear Relationships Between the Concentration of Dissolved Solids and the Freezing Point and Thawing Temperature of Water

The freezing points and thawing temperatures were recorded for waters at each of six dissolved-solids concentrations. The freezing points decreased from -2 to -20 °C as the solids content increased from 5 to 49%. Linear relationships exist between the total solids content and both freezing point and thawing

temperatures (see Figure 7). The lines do not coincide because dissolved solids came out of solution during freezing and did not redissolve upon thawing. The correlation coefficients for the freezing point line and thawing point line, respectively, are -0.9994 and -0.993 .

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