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CURIUM PROCESS DEVELOPMENT

III-1. ANALYTICAL TECHNIQUES FOR CHARACTERIZING SOLVENT

by

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ABSTRACT

Gas and thin-layer chromatographic techniques were developed to use with infrared spectrometry for analyzing virgin or degraded solvent for the curium purification process. A separation scheme was developed to facilitate analysis of highly degraded solvent.

FOREWORD

This report is one in a series that describes the development of separations processes for purifying ^{244}Cm produced in Savannah River reactors. The series is being issued under the general title Curium Process Development. Following the general title, a roman numeral designates the subject area of the report, and an arabic numeral designates the series report number in that subject area. A subtitle describes the content of each report. Subject areas foreseen for this series are:

- I. General Process Description
- II. Chemical Processing Steps
- III. Analytical Chemistry Support

Reports issued in this series include:

- I. General Process Description by I. D. Eubanks and G. A. Burney (USAEC Report DP-1009).

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INTRODUCTION

Extensive studies of large-scale solvent extraction processes for the separation of radionuclides have shown that both initial purity and radiation stability of extractant and diluent are required for optimum process performance.⁽¹⁾ The curium purification process⁽²⁾ for the separation of curium and americium from lanthanides and other fission products includes three cycles of solvent extraction that employ a mixture of tertiary amines (as extractant) and diethylbenzene (as diluent).⁽³⁾

In initial studies of the purity of the curium process solvent, secondary amine impurities in the extractant were shown to lead to the formation of interfacial solids. Tentative purchase specifications were established to limit the amount of this deleterious impurity.⁽⁴⁾ Sensitive analytical techniques were needed for complete characterization of other potentially deleterious impurities in commercial lots of extractant and diluent and for assessment of chemical and radiation stability of both virgin and degraded process solvent. Gas and thin-layer chromatography, complemented by infrared absorption measurements, offered promise of the high sensitivity and specificity needed for analysis of this complex system.

SUMMARY

Gas and thin-layer chromatographic techniques, complemented by infrared spectrometry, were developed to determine the composition and purity of virgin and degraded extractant (long-chain tertiary amine mixtures), diluent (diethylbenzene), and solvents (30 vol % tertiary ammonium nitrate or chloride in diethylbenzene) for the curium purification process.

In the gas chromatographic technique, components of the samples are separated on a column of 5% silicone gum rubber on diatomaceous earth (with a programmed temperature). In the thin-layer chromatographic technique, the components are separated on silica gel; the solvent is benzene (for aromatic components) or a mixture of chloroform, methanol, and ammonia (for amines).

Functional groups can be determined by infrared measurements of discrete thin-layer chromatographic fractions. Attempts to collect gas chromatographic fractions for characterization by infrared spectrometry were unsuccessful.

A sequential separation scheme was developed to facilitate analysis of highly degraded solvent. In a key step, the amine components are separated from aromatic components by extracting the aromatic fraction into dimethylsulfoxide. The resulting fractions were suitable for characterization by gas chromatography, thin-layer chromatography, and infrared spectrometry.

DISCUSSION

GAS CHROMATOGRAPHY

Gas chromatography is useful for separating and identifying the components of curium process solvent. An F & M Model 609 gas chromatograph was arranged for the analysis of highly radioactive solvent samples by isolating the sample injection port, column, and detector in a containment hood. Electronic and control portions of the instrument were left outside the hood to simplify operation and maintenance of the equipment.

Experimental Techniques

Factors considered for the gas chromatographic separation of components of curium process solvent were the selection of column packing material, operating temperatures, and detector. A column of silicone gum rubber on finely divided diatomaceous earth* was chosen because of its high thermal stability and low vapor pressure. Programmed temperature operation from 100 to 330°C at 9°C per minute gives satisfactory resolution of the diluent and extractant components of curium process solvent. Isothermal operation is inadequate for this mixture, but at 100°C is preferable for the diethylbenzene diluent alone. The flame ionization detector is used because it is sensitive to carbon-containing compounds and very insensitive to the common contaminants, air and water.⁽⁵⁾ The sensitivity of this detector, especially for hydrocarbons, is roughly proportional to the carbon content of component molecules.** With oxygenated and halogenated compounds, sensitivity varies with molecular structure and decreases with increasing hetero-atom content.⁽⁵⁾

* 6 ft, 1/4-inch-diameter column packed with 5% silicone gum rubber (General Electric SE-30) on diatomaceous earth (120- to 140-mesh "Gas Chrom" Z from Applied Science Laboratories, Inc., State College, Pa.).

** The sensitivity (minimum detectable amount) for a typical impurity, such as di-n-octyl amine, was 0.1 vol % with an aliquot of one microliter.

Relative retention times are reproducible and qualitatively useful. For example, the relative standard deviation ($n = 6$) for the relative retention time of diethylbenzene (tri-*n*-octylamine = 1.0) is only 1.5%. A list of relative retention times for the common components and impurities found in curium process solvent is given in Appendix A. The observed peaks can be qualitatively identified by introducing standards under similar conditions.

For analysis by gas chromatography, tertiary amines (both isolated and in diethylbenzene solutions) must be neutral or present as HCl salts. When in the form of HNO_3 salts, degradative reactions occur in the sample injection port and complicate the resulting chromatogram. Therefore, tertiary amine and solvent samples containing nitric acid are neutralized with dilute sodium carbonate or hydroxide before chromatographic analysis.

Chromatograms

Tertiary Amine Mixtures. Chromatograms of typical extractant mixtures (from the same manufacturer) are shown in Figure 1. Sample B contains more of the higher boiling components (C_{32} and C_{34}) and less of the more volatile components (C_{22} and an unknown impurity) than does Sample A.

Diethylbenzene. An isothermal chromatogram of a typical commercial sample of diethylbenzene is shown in Figure 2. Commercial diethylbenzene from three manufacturers contained low concentrations of impurities, which were resolved under isothermal conditions (100°C). Unusual functional groups were not detected by infrared spectroscopy. Molecules containing atoms of high electron affinity (halides, oxygen) were not detected by gas chromatographic analysis with an electron capture detector especially sensitive to molecules of this type. The impurities are probably $\text{C}_{10}\text{H}_{14}$ alkylbenzenes, such as isobutylbenzene or methylpropylbenzene, with boiling points similar to that of diethylbenzene ($181\text{--}184^\circ\text{C}$).

Process Solvent. A typical chromatogram of a 30 vol % tertiary amine mixture in diethylbenzene is shown in Figure 3. The portion of the chromatogram immediately following the peak for diethylbenzene is normally a peak-free region in which many solvent impurities, such as primary and secondary amines, fatty alcohols, amides, and some aromatic compounds, may be detected.

FIG. 1 GAS CHROMATOGRAMS OF TWO SAMPLES OF A COMMERCIAL MIXTURE OF TERTIARY AMINES

FIG. 2 GAS CHROMATOGRAM OF DIETHYLBENZENE

FIG. 3 GAS CHROMATOGRAM OF 30 VOL % TERTIARY AMINE MIXTURE IN DIETHYLBENZENE

Isolation of Components

Unsuccessful attempts were made to trap individual components eluted from the gas chromatographic column for further analysis. One such attempt was the condensation of effluent tertiary amine components onto a moving surface of silica gel.^(e) Unfortunately, subsequent chromatographic separation by thin-layer chromatography (described in the following section) revealed that all tertiary amines had degraded on the silica gel surface, which was heated by the hot carrier gas.

THIN-LAYER CHROMATOGRAPHY

Thin-layer chromatography is another technique for the separation and identification of many components in curium process solvent. Reviews of the principles and uses of this relatively new chromatographic technique are now available.⁽⁷⁻⁹⁾

Procedure

In this technique, a sample is placed a short distance (about 2 cm) from one edge of a smooth, thin, adsorbent surface coated on a rigid support, such as a glass plate. The plate is then immersed to about 1 cm, with the sample edge downward, in a jar containing a solvent. The solvent works its way up the adsorbent surface by capillary action simultaneously interacting and separating sample components according to their relative affinities for the adsorbent surface and the mobile solvent.

Silica gel, used for the adsorbent surface, is applicable to the separation of a variety of compounds. A small amount of a binder (such as plaster of paris or starch) is mixed with the adsorbent causing the finely divided adsorbent particles to adhere to each other and to the rigid support. Some surfaces (Adsorbosil P-1*) were prepared containing, in addition, inorganic compounds, which fluoresced intensely when illuminated with 2537Å radiation.

In the early portions of this study, plates were prepared using chemicals, equipment, and a procedure obtained from Research Specialties Corp., Richmond, Calif. Later, commercially prepared plates became available from Analtech, Inc., Uniplate Division, Wilmington, Del., and were used.

Sample components present in micro- to milligram quantities were usually invisible and therefore required detection by non-visual means. Iodine vapor, which darkened amines, was an excellent visualizing agent. After sample separation, plates were placed in a jar containing iodine crystals for 15 minutes to several hours depending on the sensitivity desired. After removal of the plates from the jar, iodine gradually vaporized, and the components became less visible. The plates were therefore photographed immediately after removal from the jar. Alternatively, a spray of 2,7-dichlorofluorescein was sometimes used for amine detection, but it offered no particular advantage over iodine other than stability.

* Adsorbosil P-1 obtained from Applied Science Laboratories, Inc., State College, Pa.

Aromatic compounds such as diethylbenzene and some of its degradation products were poorly detected by iodine and 2,7-dichlorofluorescein. However, aromatic compounds were easily detected and photographed as shadows against a fluorescing background that was excited by 2537Å radiation.

The choice of chromatographic solvent, or mobile phase, is most important in achieving a desired separation. The separation of components weakly or moderately adsorbed on the adsorbent surface, such as diethylbenzene and aromatic alcohols, requires a nonpolar solvent, such as hexane or benzene. The separation of more strongly adsorbed components, such as tri-dodecyl amine and tri-hexyl amine, requires a solvent of intermediate polarity, such as chloroform. Very strongly adsorbed components, such as aromatic acids and primary and secondary amines, require a polar solvent or solvent mixture, such as NH_3 -methanol. When samples contain many components with widely different adsorption properties, a single chromatographic solvent will give incomplete separation.

The solvent systems adopted for the separation of curium process solvent components were benzene for separation of aromatic compounds, and a mixture of chloroform, methanol, and concentrated ammonium hydroxide (95:5:0.25 by volume) for the separation of the three classes of amine (this mixture was suggested by T. H. Lentz of Archer Daniels Midland Co.). The mixture should not be used more than several days after preparation because it gradually loses ammonia to the atmosphere.

Temperature affects the rate and degree of component mobility. In these studies, temperature control was not a problem because all separations were made in a laboratory whose temperature was controlled to within $\pm 2^\circ\text{C}$.

Degree of silica gel hydration also affects component mobility. The initial plates were dried one-half hour at 110°C , and then stored in a desiccator until ready for use. Later, it was found that the drying step could be omitted without appreciably altering component mobility.

Semiquantitative estimates of component concentration in samples were made by comparison with standards run simultaneously on the same plate. Figure 4 illustrates an example of such a determination for three process samples of 30 vol % tertiary amine in diethylbenzene.

FIG. 4 THIN-LAYER CHROMATOGRAMS OF CURIUM PROCESS SOLVENT

Workers analyzing a variety of materials by thin-layer chromatography have reported precisions of 5-10% by methods that involve densitometric measurements of the spots or of their photographs, area measurements of the spots, or elution of each component from the plate followed by a spectrometric measurement.⁽⁸⁾

Advantages of Thin-Layer Chromatography

The unique separative capabilities of thin-layer chromatography offer several advantages in the analysis of curium process solvent:

- Speed. In general, samples can be applied, chromatographed, visualized, and recorded in one to two hours.

- Qualitative Identifications. First, the mobility exhibited by an unknown component can give some idea of its functional groups. Available experimental data relate relative mobility to substituent groups on certain classes of compounds.⁽⁸⁾ For example, mobility of a substituted aromatic hydrocarbon decreases in the following order: -Cl, -H, -OCH₃, -NO₂, -N(CH₃)₂, -COCH₃, -OCOCH₃, -NH₂, -NHCOCH₃, -OH, -CONH₂, and -COOH. Second, comparison of separated mixtures before and after reaction with a highly specific functional group reagent can be made and easily interpreted on thin-layer chromatographic plates.

- Identification of Radioactive Components by Radioautography. Radioautographs made by placing sensitive photographic plates* over separated solvent components relate position of radioactive species to that of solvent components.

- Recoverable Fractions. Small quantities of adsorbent powder are removable by scraping into a counting dish for radioactivity analysis. Alternatively, portions of the adsorbent surface can be removed by vacuum into a small collecting tube for subsequent component elution.⁽⁸⁾ The eluted components can then be characterized by gas chromatography and infrared and ultraviolet spectrometry.

* Kodak SA-3 plates were used in these studies because they were already available and were found to be adequate. Special radioautographic emulsions, although not used here, are commercially available permitting more detailed studies.

INFRARED SPECTROMETRY

Infrared spectrometry can be used to characterize impurities or degradation products in curium process solvent. However, the strong absorption of normal solvent components interferes with the detection of low concentrations of impurities in virgin materials or degradation products in process solvents. Methods described in the following section were devised to simplify the matrix and to facilitate the analysis of impurities. Differential photometric techniques were not investigated.

Portions of curium process solvent fractions were examined (by infrared spectrometry) as thin films on CsBr discs or in microcells of NaCl. On some thin film preparations, diethylbenzene was evaporated leaving only the less-volatile impurities. Functional group assignments of absorption peaks were based on absorption data reported by Bellamy.⁽¹⁰⁾ Isomeric distribution of virgin diethylbenzene was calculated from absorption data of the various molecules in the region 825 to 695 cm^{-1} .

A specially designed transfer cell with NaCl windows was built to hold a standard infrared cell for containment of samples with alpha radioactivity. The transfer cell could be placed in a Perkin-Elmer Model 521 spectrophotometer for analysis.

ANALYTICAL SEPARATION SCHEME

Because degraded solvent is an extremely complex mixture, a method for separating the components was developed to simplify the analysis of the solvent. The separation scheme significantly facilitated the initial studies of degradation product formation. The scheme separates the components of degraded solvent, as follows:

- Acids are removed with dilute sodium hydroxide, which also saponifies some esters to alcohols and acids and removes these.
- Polar and aromatic compounds (diethylbenzene and its degradation products) are extracted with dimethylsulfoxide. Addition of water to the resulting dimethylsulfoxide solution releases the aromatic and most of the polar compounds.
- The amines are retained on a column of strong-acid cation exchange resin ("Dowex" 50W-X4)*, while non-basic impurities are eluted with isopropanol.⁽¹¹⁾ The amines are subsequently eluted with 3M HCl in isopropanol.⁽¹²⁾

The separation scheme is summarized in Figure 5; details are given in Appendix B.

The recovered fractions are analyzed by the chromatographic and infrared spectrometric methods described. Minimum detectability of degradation products in a one-ml sample was estimated to be 0.1% with a precision of about $\pm 50\%$ at this level.

FIG. 5 ANALYTICAL SEPARATION SCHEME FOR CURIUM PROCESS SOLVENT

* "Dowex" is a trademark of Dow Chemical Co.

APPENDIX A

GAS CHROMATOGRAPHIC RETENTION TIMES OF CURIUM PROCESS SOLVENT

Relative retention times for the common components and impurities in curium process solvent are given for the following specific conditions:

Instrument: F & M Model 609 gas chromatograph with
flame ionization detector

Carrier Gas and Flow: He at 33 ml/min.

Temperature Program: 9°C/min. from 100 to 330°C

Initial injection port temperature: 200°C

Initial detector block temperature: 300°C

	<u>Relative Retention Time</u>
Diethylbenzene	0.26
Primary amines	
C ₆	0.19
C ₈	0.34
C ₁₀	0.42
Secondary amines	
C ₁₄	0.59
C ₁₆	0.71
C ₁₈	0.82
C ₂₀	0.90
Tertiary amines	
C ₁₈	0.68
C ₂₀	0.78
C ₂₂	0.89
C ₂₄ (reference)	1.00
C ₂₆	1.10
C ₂₈	1.18
C ₃₀	1.26
C ₃₂	1.34

APPENDIX B

ANALYTICAL SEPARATION SCHEME FOR CURIUM PROCESS SOLVENT

I. Neutralization

- A. Pipet 1 ml of curium process solvent into a 10-ml centrifuge tube (Tube 1). Add 1 ml of 3M NaOH. Stir five minutes. Let phases separate. Centrifuge five minutes. Transfer the lower phase (aqueous) to a second 10-ml centrifuge tube (Tube 2).
- B. Add 1 ml of distilled water to the organic phase remaining in Tube 1. Stir, let phases separate, centrifuge, and transfer the aqueous phase as in Step A.
- C. Repeat Step B. Save a portion (about 200 μ l) of neutralized solvent to analyze for amines, aromatic compounds, and degradation products by gas and thin-layer chromatography.
- D. Pipet 1 ml of chloroform into Tube 2, which contains 3 ml of aqueous solution. Stir and centrifuge. Remove and discard the chloroform (lower phase).
- E. Place Tube 2 containing the aqueous phase in a heated oil bath and evaporate to near dryness (~0.1 ml remaining).
- F. Cool Tube 2. Then carefully add about 200 μ l of 16N H₂SO₄ while stirring.
- G. Pipet 1.0 ml of chloroform to Tube 2 and vigorously stir the phases together. Allow the phases to separate. Transfer the chloroform (lower phase) to a clean vial for analysis for acids and alcohols by infrared spectrometry and thin-layer chromatography.
- H. Repeat Step G.

II. Aromatic Extraction

- A. Add 5 ml of dimethylsulfoxide to Tube 1 from Step I-C. Stir five minutes. Let settle and then centrifuge five minutes. Transfer the dimethylsulfoxide extract (lower phase) to a 50-ml volumetric flask.
- B. Repeat Step A four times. Wash the organic phase remaining in Tube 1 three times with water to

remove the remaining dimethylsulfoxide. Add the washes to the 50-ml volumetric flask.

- C. Reserve a small portion (~75 μ l) of the amine phase (upper phase) to analyze for amine and nonpolar degradation products. The remainder (in Tube 1) is treated according to Step III-A.
- D. Fill the 50-ml volumetric flask (Step II-B) to volume with distilled water. Thoroughly stir the contents for five minutes.
- E. Divide the 50 ml of solution among four 12- to 15-ml centrifuge tubes and centrifuge for ten minutes. Combine all upper phases (containing diethylbenzene) into a clean test tube.
- F. To this test tube add 1 ml each of chloroform and water. Stir one minute and then let settle. Analyze the resulting bottom organic layer for aromatic and polar degradation products by thin-layer and gas chromatography and infrared spectrometry.

III. Ion Exchange Separation

- A. Transfer the amine phase from Tube 1 (Step II-C) to the top of a conditioned column of "Dowex" 50W-X4.* Rinse Tube 1 with 10 ml of isopropanol, and add the rinsings to the column. Collect the effluent in a 100-ml boiling flask having a $\frac{24}{40}$ joint. When the liquid level falls to top of the resin, add 60 ml of isopropanol. After the liquid level again falls to top of the resin, transfer the boiling flask to an evaporation assembly. Amines retained on the column are eluted in Step C.
- B. Evaporate the effluent under reduced pressure and at 70°C. After one hour, remove the boiling flask from the evaporation assembly, and rinse the residue into a clean 10-ml centrifuge tube with chloroform. Adjust the volume to 3 ml with chloroform. Analyze this solution for nonpolar degradation products by infrared spectrometry, gas chromatography, and thin-layer chromatography.
- C. Add 60 ml of 3M HCl in isopropanol to the column to elute the amines. Collect the effluent in a 100-ml bottle. Wash the residual acid from the column with 30 ml of isopropanol.

*The column is always conditioned just before use by washing with 30 ml of isopropanol. A column that has not been washed within three days must be washed with an additional 70 ml of isopropanol.

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