LA-5876-MS

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UC-4
Reporting Date: January 1975
Issued: March 1975

Coprecipitation of Uranium and Plutonium Oxalates Using Sodium Formaldehyde Sulfoxylate Reduction and Diethyl Oxalate Hydrolysis Precipitation

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UNITED STATES
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
CONTRACT W-7405-ENG. 36

This work was supported by the US Energy Research and Development Administration, Division of Safeguards and Security.

Printed in the United States of America. Available from
National Technical Information Service
U S Department of Commerce
5285 Port Royal Road
Springfield, VA 22151
Price: Printed Copy $4.00 Microfiche $2.25

COPRECIPITATION OF URANIUM AND PLUTONIUM OXALATES USING SODIUM FORMALDEHYDE SULFOXYLATE REDUCTION AND DIETHYL OXALATE HYDROLYSIS PRECIPITATION

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ABSTRACT

A procedure was developed for preparing a crystalline coprecipitate of uranium and plutonium. From nitric acid media, uranium and plutonium are reduced to U^{4+} and Pu^{3+}, then coprecipitated as oxalates by hydrolysis of diethyl oxalate.

I. SUMMARY

A series of coprecipitates of uranium and plutonium was needed for reference materials. For this purpose, controlled quantitative coprecipitation in a dense crystalline form from solutions containing exact amounts of uranium and plutonium seemed the most promising method of preparation. A suitable precipitant for hexavalent uranium (and plutonium) was not known, and few reductants were capable of reducing uranium to U^{4+} without themselves coprecipitating. Our investigations showed that sodium formaldehyde sulfoxylate, $NaHSO_2 \cdot CH_2O \cdot 2H_2O$, reduced uranium-plutonium mixtures in $2\underline{M}$ HNO_3 to U^{4+} and Pu^{3+}. Dense crystalline oxalates of these actinides were formed by room temperature hydrolysis of diethyl oxalate. Uniform distribution of uranium and plutonium in the mixed oxalate salts was verified by alpha autoradiography.

II. INTRODUCTION

A series of reference sources of uniformly distributed uranium and plutonium was needed to evaluate certain gamma-assay techniques and equipment. After reviewing the literature, several techniques were experimentally evaluated. None gave a suitable crystalline precipitate. The new technique reported here produces coprecipitated uranium and plutonium oxalates that are highly suitable for reference sources for gamma-assay measurements. Although the technique was not evaluated extensively from the standpoint of chemical reactions and stoichiometry, this preparatory method is reported in brief because it appears to apply not only to the preparation of sources, but also to various nuclear industry processes.

III. EXPERIMENT AND DISCUSSION

Required characteristics of the series of reference sources were (1) exact quantities of uranium and plutonium ranging from 10 to 90 mg, (2) a wide variety of isotopic compositions of both uranium and plutonium, and (3) a uniform distribution of uranium and plutonium. Because we needed many sources, we selected a preparation using standardized solutions of uranium and plutonium, rather than physical blending of powders.

This preparation involved (1) preparing the various enrichment uranium and plutonium solutions on a weight basis from accurately characterized starting materials, (2) combining weight aliquots of these solutions to obtain the desired U/Pu ratio, (3) distributing weight aliquots of these combined uranium-plutonium solutions to beakers, (4) coprecipitating the uranium and plutonium as crystalline salts, and (5) quantitatively collecting the salts on a membrane filter which was mounted as the reference source. The fourth operation, coprecipitation as crystalline salts, was the most difficult.

An evaluation of various techniques for coprecipitating uranium and plutonium led us to conclude that uranium must first be reduced to U^{4+} and plutonium to Pu^{3+}, and that oxalate precipitates are the most quantitative and crystalline. The usual reductants capable of reducing uranium to U^{4+} are highly electronegative metals whose ions also form insoluble oxalates. An unusual reductant without this disadvantage is sodium formaldehyde sulfoxylate, $NaHSO_2 \cdot CH_2O \cdot 2H_2O$. This compound, also known as rongalite, has been used in the textile industry to reduce dyes to their soluble leucocompounds, which are then reoxidized on the fiber.[1] Grinberg et al.[2] reported that the overall reduction of hexavalent uranium by sodium formaldehyde sulfoxylate, which proceeds at room temperature, was:

$$UO_2^{2+} + HSO_2^- \rightarrow UO^{2+} + HSO_3^-.$$

The reaction rate was greatly accelerated, however, by increasing the H^+ concentration. They also reported that SO_2 and H_2S were produced by the reaction in neutral solution. The amount of H_2S produced decreased with increased acidity and was practically undetectable when $1\underline{M}$ HNO_3 was the medium. The rate of uranium reduction can be observed based on the green color of U^{4+}.

If only uranium is to be reduced and precipitated, oxalic acid may be added initially to the reaction vessel to slowly form dense crystals of uranium oxalate. With uranium-plutonium mixtures, however, the reduction of plutonium to Pu^{3+} by sodium formaldehyde sulfoxylate is very rapid. When this reaction is initiated, the blue color of Pu^{3+} is seen immediately and then changes slowly to blue-green as the uranium is reduced. The complete reduction of plutonium and uranium requires 1 to 2 h in $2\underline{M}$ HNO_3, the medium used in our preparation. To prevent the selective precipitation of plutonium oxalate, the addition of oxalate had to be delayed until the uranium also had reduced completely.

A conventional technique for increasing the particle size and purity of a precipitate is slow addition of a dilute solution of the precipitating reagent using heated solutions and vigorous stirring. Even so, high concentrations in the locality of the added drops of reagent solution cause significant amounts of small crystals to form. A disadvantage of using dilute solutions of the precipitating reagent is an increased solubility of the product, particularly at milligram levels. Precipitation from homogeneous solution[3] allows the precipitate to form at a slow and controlled rate by a uniform change of conditions in an initially homogeneous solution. An example is the slow, uniform formation of U^{4+} in a solution containing oxalate ion (described earlier). When dealing with a mixture of uranium and plutonium, however, the oxalate ion must be slowly and uniformly produced in solution to produce a dense crystalline precipitate.

One of the most successful techniques for obtaining slow, uniform release of anions in solution involves the hydrolysis of esters.[3] For our application diethyl oxalate was hydrolyzed at room temperature to produce a very dense, easily filtered precipitate of uranium and plutonium oxalates. A series of 64 reference sources was prepared to contain known amounts of uranium and plutonium, incorporating 4 isotopic levels of ^{239}Pu and 6 isotopic levels of ^{235}U. The uniform distribution of the uranium and plutonium in the precipitate was verified by alpha radiography. The completeness of precipitation, determined by analyzing the supernatant solution, was > 99% for uranium and plutonium. Although this technique has been used only to satisfy our particular needs, it appears to be applicable to various nuclear industry processes.

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