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Chemistry - General

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PRECISE DETERMINATION OF URANIUM IN URANYL NITRATE - ALUMINUM NITRATE SOLUTIONS

by

C. M. MacDonald
Analytical Chemistry Division

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Constance M. MacDonald

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ABSTRACT

A precise method was developed for the analysis of uranium in aqueous solutions that contain aluminum. Uranium was separated from aluminum by an ion exchange technique and was then determined gravimetrically by the 8-hydroxyquinoline method. The coefficient of variation was 0.3%.

CONTENTS

PRECISE DETERMINATION OF URANIUM IN URANYL NITRATE - ALUMINUM NITRATE SOLUTIONS

INTRODUCTION

The determination of distribution coefficients in the study of a solvent extraction process required a precise and accurate analysis of the uranium solute in aqueous and organic solutions. The concentrations ranged from 0.005 to 0.2 mol of uranium and up to 1 mol of aluminum per liter. A precision of at least 1% at 95% confidence limits was required for the uranium results throughout this concentration range.

A number of methods that are usually satisfactory for the determination of uranium in the presence of aluminum were not sufficiently precise for this problem. Solvent extraction methods(1,2) for separating the uranium from aluminum were inadequate. Also, various methods for complexing one component(3-6) while the other is precipitated were unsuccessful. The method of Horton and Thomason(7) for separating elements such as uranium from aluminum by ion exchange showed promise and was chosen for development.

SUMMARY

A precise method was developed for the determination of uranium in tributyl phosphate (TBP) and in aqueous solutions that contain aluminum. In TBP samples the uranium was transferred to an aqueous phase and then was determined by the same analytical procedure that applies to aqueous samples. The uranium was separated from the aluminum with an anion exchange resin and was determined gravimetrically by the 8-hydroxyquinoline method(6). The solutions contained 0.005 to 0.2 mol of uranium per liter and up to 1 mol of aluminum per liter.

The coefficient of variation for the analysis of these solutions was 0.3%.

DISCUSSION

Washing with aqueous ammonium carbonate is known to extract greater than 99% of the uranium that is dissolved in tributyl phosphate (TBP). Therefore a quantitative transfer to an aqueous phase is achievable in three such analytical extractions and the organic samples can be analyzed by the procedure that is outlined below.

The spectrophotometric determination of aluminum by Horton and Thomason(7) was designed to avoid interferences that were present in aluminum alloys. In the present work appropriate modifications were made to the ion exchange portion of their procedure so that the uranium eluate could be analyzed by a gravimetric method that gave the required precision and accuracy.

EXPERIMENTAL PROCEDURE

Samples of TBP that contained 100-200 mg of uranium were extracted with three successive, equal volumes of 0.5M $(NH_4)_2CO_3$. The aqueous phases were combined and analyzed by the procedure described below for aqueous samples.

Aqueous samples of uranyl and aluminum nitrate were made 9M in hydrochloric acid and were passed through a column of "Dowex" 1 (10% DVB) anion exchange resin. The flow rate was less than 1 ml per minute. The uranium was absorbed on the resin as an anion of uranium chloride, while the aluminum cation was not absorbed. After the column was rinsed with 70 ml of 9M hydrochloric acid to ensure complete removal of the aluminum, the uranium was eluted from the column with 100 ml of 0.2M hydrochloric acid(7,8). The resulting solution was then analyzed gravimetrically for uranium by the 8-hydroxyquinoline method(6).

The sample aliquot was chosen to contain 100 to 200 mg of uranium. New columns were filled with resin for each determination because nitrate in the samples caused some decomposition of the resin. The decomposition was evidenced by the presence of a yellow color in the 9M hydrochloric acid eluate. If samples were boiled with hydrochloric acid to remove nitrate, the resin could be used again after proper reconditioning with 9M hydrochloric acid. However, removal of nitrate required an excessive amount of time and this step was not applied.

RESULTS

The precision and accuracy of the method were determined by analyzing five standard aqueous uranium solutions that contained about 27 grams per liter of aluminum, as shown in the following table.

Precision of the Method for Aqueous Solutions

mg of U/ml	Coefficient of Variation	No. Determ.
4.976	0.06	4
4.980	0.2	4
4.991	0.2	4
4.993	0.2	4
5.088	0.3	3

The coefficient of variation of these 19 determinations was 0.2%. The average recovery of uranium was 99.86%.

The standardized solutions of uranium and aluminum were equilibrated under different conditions with TBP - kerosene solutions to obtain organic and aqueous phases for a study of precision. After each equilibration, aliquots of both the organic and the aqueous phases were analyzed for uranium. The results are given in the following table.

Extraction Data

Uranium in Organic			Uranium in Aqueous		
mg/ml	Coefficient of Variation, %	Number of Determinations	mg/ml	Coefficient of Variation, %	Number of Determinations
4.824	0.8	4	46.46	0.3	4
5.206	0.1	4	49.00	0.0	2
14.01	0.4	6	4.000	0.4	6
15.22	0.07	4	3.740	0.2	3
10.87	0.3	3	1.320	0.2	3
11.32	0.2	4	1.170	0.5	4

The coefficient of variation for the 25 organic determinations and 41 aqueous determinations was 0.3%.

This analytical method is attractive because it can be used in the presence of a large number of other ions. Information may be found in the literature about ions that will interfere and ions that will not interfere in the method.(7,9,10)

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