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By

J. M. Schreyer
C. F. Baes, Jr.

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THE VOLUMETRIC DETERMINATION OF URANIUM(VI) IN PHOSPHATE SOLUTIONS

J. M. Schreyer and C. F. Baes, Jr.

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URANIUM CHEMISTRY OF RAW MATERIALS SECTION
K. B. Brown, Supervisor

MATERIALS CHEMISTRY DIVISION
G. H. Clewett, Division Head

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ABSTRACT

The dichromate method of Kolthoff and Lingane for the determination of uranium has been applied to phosphate solutions. The recommended procedure involves the use of 4.5 M sulfuric acid solution in the Jones reductor to avoid uranium(IV) phosphate precipitation. The reduction of uranium(VI) to uranium(IV) in phosphate solution is shown to be quantitative, thus eliminating the need for aeration of the reduced solution.

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INTRODUCTION

Current events in the field of uranium raw materials suggest that extensive treatments may be given to uranium-bearing phosphatic materials. It is believed that additional knowledge of uranium phosphate chemistry could be of considerable value to this work, and, accordingly, a program for research has been set up.

At the present time, investigations are being made which may lead to the identification of the complex ionic species that exist in the uranyl phosphate solutions. Solubility measurements and spectrophotometric techniques are being used in these studies, and the results of these investigations will appear in a later report.

An accurate and preferably rapid method for the analysis of uranium in the presence of phosphate must be available before any reliable investigation of its properties can be made. Such a method has been developed and is described in this report.

The use of dichromate in the analysis of uranium(VI) solutions was first recommended by Kolthoff and Lingane.[1] The method consists in reducing uranium(VI) in sulfuric acid solution to a mixture of uranium(III) and uranium(IV) by means of the Jones reductor. The uranium(III) is then oxidized to uranium(IV) by aeration and after addition of excess ferric ion, phosphoric acid, and an indicator of either diphenylamine, diphenylbenzidrine, or diphenylamine sulfonate, the solution is titrated to a purple end point with a standard dichromate solution.

APPLICATION OF THE DICHROMATE METHOD TO URANIUM(VI) PHOSPHATE SOLUTIONS

It has been reported[2] that the reduction of uranium phosphate solutions in the Jones reductor results in the precipitation of uranium(IV) phosphate. In the present investigation it has been found that precipitation can be

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avoided by adjusting the acidity of the solution to 4.5 M in sulfuric acid.

The present procedure includes one other modification of Kolthoff and Lingane's method; namely the omission of the aeration step. From the experimental results described in the following section it is apparent that uranium(VI) in phosphate solution is reduced quantitatively to uranium(IV) by the Jones reductor.

EXTENT OF REDUCTION OF URANIUM(VI) PHOSPHATE SOLUTIONS IN THE JONES REDUCTOR

A 0.1074 M uranyl perchlorate standard solution was prepared from Bureau of Standards U_3O_8 (99.95% U_3O_8) by dissolving the solid in hot nitric acid, adding perchloric acid, and subsequently evaporating down three times to fuming perchloric acid.

Stock solutions of uranyl sulfate and uranyl chloride were prepared by dissolving repurified uranium trioxide in the equivalent amount of the appropriate acid.

Analyses of these stock solutions, performed by the recommended procedure of Kolthoff and Lingane,[1] are shown in the first column of Table 1.

Analysis by Present Procedure. Aliquots of the three stock solutions were analyzed by the analytical procedure reported in this paper, in which phosphoric acid is added and the aeration step is omitted. The results are listed in the second column of Table 1.

Reoxidation Experiments. Aliquots of the stock solutions, containing 2 millimoles of uranium, were adjusted to 1 M in perchloric, sulfuric, or hydrochloric acid, diluted to 80 ml, and passed through the Jones reductor under nitrogen. The reductor had previously been flushed with nitrogen. Analysis of similarly reduced solutions indicated approximately 45% of the total uranium to be present as uranium(III) in the case of perchlorate solutions, approximately 30% uranium(III) in the case of sulfate solutions, and approximately 97% uranium(III) in the case of chloride solutions. Each of the reduced, dark olive-green solutions (300 ml) were made 3 M in the appropriate acid and 20 ml of 85% phosphoric acid was added. These solutions were again passed through the Jones reductor under nitrogen. The solutions in

Table 1

COMPARISON OF METHODS OF ANALYSIS FOR

URANIUM IN VARIOUS ACID SOLUTIONS

Concentration Expressed in Gram-ions UO_2^{++} Per Liter

Type of Solution	Kolthoff and Lingane Method	Present Procedure	Reoxidation Experiments
Uranyl Perchlorate	0.1076 0.1077	0.1076 0.1075	0.1076 0.1077
Uranyl Sulfate	0.2442 0.2441	0.2440 0.2437	0.2439 0.2441
Uranyl Chloride	0.0942 0.0942	0.0942 0.0942	0.0944 ------

the receiving flasks had a light bluish-green color which indicated that the uranium(III) had been oxidized to uranium(IV) in the reductor. The ferric chloride solution (30 ml) was added to these solutions without aeration and the titration completed with dichromate after adding 15 ml of phosphoric acid and 8 drops of indicator. The results are shown in column 3 of Table 1.

These data demonstrate the quantitative oxidation of uranium(III) to uranium(IV) in the Jones reductor under the conditions of the experiment.

DETERMINATION OF MAXIMUM RATE OF FLOW THROUGH REDUCTOR TO OBTAIN QUANTITATIVE REDUCTION

Five aliquots of a uranium(VI) perchlorate solution were analyzed by the analytical procedure reported in this paper except for each solution being passed through the reductor at a different rate. The results are listed in Table 2 and depicted in Figure 1.

SOLUTIONS REQUIRED

Sodium diphenylamine sulfonate solution. Dissolve 0.32g of barium diphenylamine sulfonate in 100 ml of water and add 0.5g of sodium sulfate. Filter off the barium sulfate.

Ferric chloride solution. Dissolve 100g of ferric chloride hexahydrate in water and dilute to one liter.

Sulfuric acid solution, 7.5%.

Sulfuric acid, concentrated.

Phosphoric acid, 85%.

Amalgamated zinc. Add 300g of pure 20 mesh zinc to 300 ml of 2% mercuric nitrate (or chloride) containing 2 ml of concentrated nitric acid. Wash the amalgam thoroughly with water and 7.5% sulfuric acid solution to remove the nitrate.

Standard dichromate solution, approximately 0.1N.

Table 2

ANALYSIS OF A URANIUM(VI) PERCHLORATE SOLUTION AT DIFFERENT RATES OF FLOW THROUGH THE REDUCTOR

Rate of Flow ml/min	Analysis gram-ions/l
120	0.7724
96	0.8074
40	0.8742
32	0.8765
4	0.8742

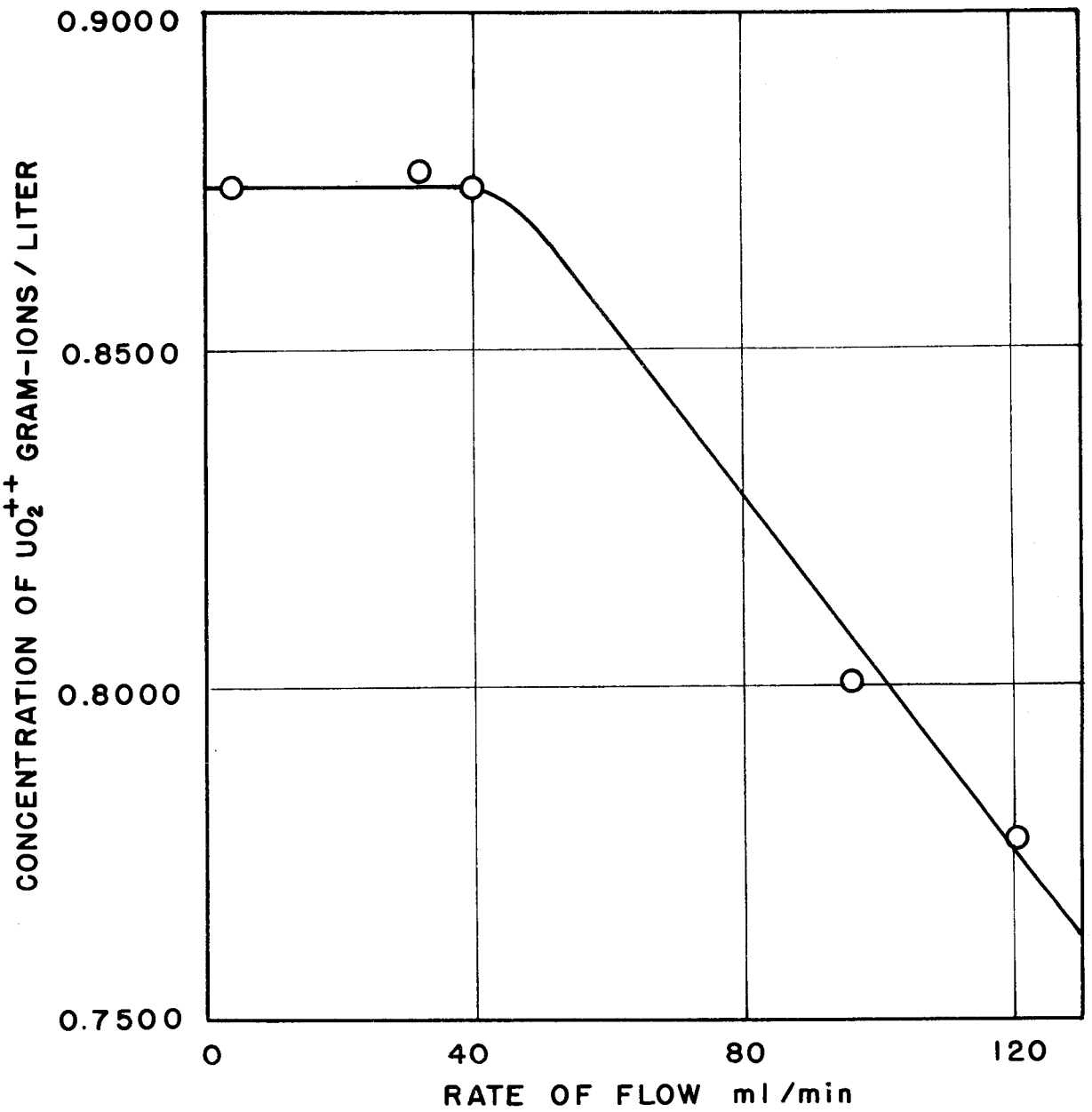

FIGURE I ANALYSIS OF A URANIUM (VI) PERCHLORATE SOLUTION AT DIFFERENT RATES OF FLOW THROUGH THE REDUCTOR

ANALYTICAL PROCEDURE

Introduce a sample containing approximately 2 millimoles of uranium into a 150 ml beaker. (If the sample contains nitrate it must be fumed down with sulfuric acid since reduction of nitrates to hydroxylamine and other compounds takes place in the Jones reductor.[3]) Add 20 ml of concentrated sulfuric acid and 20 ml of 85% phosphoric acid. Dilute with water to 75-80 ml and cool. Using gentle suction, pass the cold uranium(VI) solution through the reductor at a rate of about 30 ml per minute. Wash the reductor with four 40 ml portions of 7.5% sulfuric acid and one 40 ml portion of water, adding the washings to the reduced solution. The reduced solution should have a light bluish-green color characteristic of uranium(IV) in phosphoric acid solutions. Add 30 ml of ferric chloride solution (100g/l), swirl, and let stand for 5 to 10 minutes or until the solution becomes distinctly yellow. Add 15 ml of 85% phosphoric acid and 8 drops of diphenylamine sulfonate indicator. Titrate immediately with standard 0.1N dichromate solution to a sharp purple end point. The indicator blank is negligible.

DISCUSSION OF RESULTS

The results of analysis of uranium(VI) phosphate solutions by the recommended procedure are in satisfactory agreement with those analyses by the method of Kolthoff and Lingane.

Solutions initially 5.6 M in sulfuric acid required careful reduction in order to avoid excessive hydrogen evolution in the column, resulting in local heating and possible reduction of the sulfuric acid. An initial sulfuric acid concentration of 3 M, while sufficient to prevent precipitation of uranium(IV) phosphate in the column, was not sufficient to prevent precipitation in the receiver when the solution was diluted with the 7.5% sulfuric acid wash solution. This could be overcome by using a more concentrated wash solution, but it was found more desirable to increase the initial concentration to 4.5 M in sulfuric acid.

The recommended flow rate through the reductor (30 ml/min) was found to be the approximate maximum rate which permitted quantitative reduction of the uranium (Figure 1), while appreciably slower flow rates caused greater hydrogen evolution and pulsating in the column.

The effects of strong hydrogen evolution, such as "pulsating" and "breaking" of the column may be greatly reduced by tamping down and packing the column from time to time with a stirring rod.

The rather surprising oxidation of uranium(III) to uranium(IV) in acidic phosphate solution in the Jones reductor may be accompanied by either the reduction of hydrogen ion or the reduction of zinc ion at the amalgam surface.

$$2e + Zn^{++} = Zn \text{ (Saturated Amalgam)}$$

Because of the uncertain overvoltage of hydrogen under these conditions, it is not possible to decide which reduction reaction requires the least potential. It can be concluded, however, that the uranium(III)/(IV) couple must be sufficiently more positive than the zinc-zinc ion couple, so that no appreciable fraction of the uranium(IV) is re-reduced. Heal's[4] values for the uranium(III)/(IV) couple in 1 M chloride and 1 M sulfate, +0.69 and 0.85v, respectively, along with the percent reduction of uranium to the trivalent state in hydrochloric and sulfuric acid reported above, 97% and 30%, respectively, suggest a value at least as high as 1.0v for the uranium(III)/uranium(IV) couple in phosphoric acid media. The additional stability of the uranium(IV) oxidation state in phosphate solution may be attributed to complex formation.

Kolthoff and Linganel[1] report that ferric ion reacts very quickly with uranium(IV). In the present investigation, it was found that this reaction in high phosphate solutions is not rapid. It appears that in order to prevent a fading end point the ferric ion-uranous solution should stand until distinctly yellow before titration. Periods of from 5 to 10 minutes were adequate.

Wide application of the recommended procedure to uranium(VI) solutions containing sulfate, chloride and perchlorate has been made with excellent success.

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