Determination of Uranium by Reduction with Stannous Chloride

A. R. MAIN[1]

Canada Department of Mines and Technical Surveys, Radioactivity Division, 30 Lydia St., Ottawa, Canada

KERN (*2*) reported that stannous chloride reduced uranyl salts after prolonged heating in acid solution, but his results indicated that the reaction was useless for quantitative uranium determinations. In the present work the reaction was made rapid by adding an iron catalyst, and quantitative by adding orthophosphate.

A considerable blank was subtracted from the total titer to correct for the iron. The only source of error associated with this blank was a pipetting error, and this was negligible. Consequently, this large blank did not introduce appreciable error into the method.

Tin does not reduce uranium below the four valency. The oxidation potential of uranium(III) to uranium(IV) is 0.5 volt (*4*); of tin(II) to tin(IV), −0.13 volt (*1*); and of uranium(IV) to uranium dioxide(II), −0.33 volt (*4*).

The use of stannous chloride to reduce uranyl salts eliminates some of the troublesome features encountered with a Jones reductor and other column reductors. Because they are solids and have relatively static and limited reducing areas, column reductors tend to be easily poisoned by even small amounts of many commonly occurring substances, such as phosphate and arsenate. Removal of such substances is often long and costly. The freedom of the stannous chloride reduction from interference by phosphate, bismuthate, and arsenate has resulted in an important saving of labor and time. The rate of reducing samples is about four times that of the Jones reductor.

Table I. The Determination of Indicator Correction Blank

(2.00 Ml. of 0.0200*N* iron solution added to each sample togetherw ith 0.25 ml. of indicator)

99.98% U_3O_8, Mg.	0.02*N* Potassium Dichromate, Ml.		
	Titer found	Theoretical titer; iron plus uranium	Indicator correction by difference
0	2.24	2.00	0.24
20.0	9.39	9.12	0.27
50.0	20.06	19.80	0.26
70.0	27.10	26.92	0.18
100.0	37.87	37.60	0.27
100.0	37.86	37.60	0.26
150.0	55.60	55.40	0.20
150.0	55.62	55.40	0.22

After reduction by stannous chloride, samples may be left to stand for several hours in the cold until it is convenient to titrate them because the reduced uranium and iron are protected from air oxidation by the excess stannous ion.

REAGENTS

Standard uranium solution. A standard solution of uranyl sulfate was prepared by dissolving 10.0000 grams of uranium oxide (previously dried at 105° to 110° C.) in 30 ml. of concentrated nitric acid. About 30 ml. of 1 to 1 sulfuric acid were added and the solution was fumed to dryness. The uranyl sulfate residue was dissolved and diluted to 1 liter with water in a volumetric flask. The uranium oxide was labeled MS-ST U_3O_8, 99.93% pure.

Iron catalyst solution. A 0.02*N* iron solution was prepared by dissolving 0.5585 gram of iron wire in 20 ml. of concentrated hydrochloric acid. The iron was oxidized by a few drops of hydrogen peroxide. The solution was diluted to 500 ml. with water in a volumetric flask.

Stannous chloride solution. A solution of stannous chloride was prepared by dissolving 25 grams of C.P. stannous chloride dihydrate in 50 ml. of concentrated hydrochloric acid and diluting to 500 ml. with water.

Mercuric chloride solution. A saturated solution of mercuric chloride was prepared and stored over the excess salt.

Diphenylamine–sulfonic acid indicator. A 0.005*M* solution of indicator was prepared by stirring 1.6 grams of C.P. barium diphenylamine sulfonate into 500 ml. of water, and 5 ml. of concentrated sulfuric acid were added. The precipitate was allowed to settle overnight before it was filtered off.

Potassium dichromate solution. A 0.02*N* solution was prepared by dissolving 1.9615 grams of reagent grade potassium dichromate in water and diluting to 2 liters in a volumetric flask.

Ferric chloride solution. An 8% solution was prepared by dissolving 160 grams of ferric chloride sexihydrate in water and diluting to 2 liters.

Phosphoric–sulfuric acid mixture. Three volumes of C.P. 85% phosphoric acid were mixed with one volume of C.P. concentrated sulfuric acid.

EXPERIMENTAL AND DISCUSSION

The reduction of uranium was successfully catalyzed by 2.00 ml. of 0.02*N* iron solution over a convenient range of time and reagent concentrations. The minimum necessary amount of iron has not been evaluated. The results of experiments, shown in part in Table IV, indicate that 1 ml. of the iron solution is as satisfactory as 2 ml.

The titration correction blank needed for the iron catalyst is 2.00 ml. of 0.02*N* potassium dichromate. The error associated with this blank is negligible and is the error resulting from the use of a 2-ml. pipet to dispense the 0.02*N* iron solution.

The uranous ion was titrated with dichromate solution according to the method of Kolthoff and Lingane (*3*).

The amount of stannous chloride required to give complete reduction is calculated from the estimated maximum uranium content of the sample to be determined. One milliliter of stannous chloride reduces 50 mg. of uranium and is oxidized by 2 ml. of mercuric chloride. An excess of 1 ml. of stannous chloride over a calculated volume required was employed.

The effect of variable amounts of mercurous chloride precipitate on the titration of ferrous iron using diphenylaminesulfonic acid indicator was tested and found to be negligible. This confirms the observation of Sarver and Kolthoff (*5*).

The procedure used was as follows: The samples to be reduced were contained in a 500-ml. Erlenmeyer or other convenient flask. The volume was brought to about 10 ml. with water. Two milliliters of iron catalyst solution were added by pipet. Twenty to 25 ml. of concentrated hydrochloric acid and 4 ml. of 1 to 1 phosphoric acid were added from a graduate. The flask was covered with a watch glass and heated to 96° to 99° C. on a hot plate. The calculated volume of stannous chloride was added and mixed by gently swirling the flask. Heating was continued for a further 10 to 15 minutes. The flask was cooled and set aside until ready for titration. Twenty milliliters of mercuric chloride solution were added. The precipitate was allowed to stand at least 2 minutes before 20 ml. of 8% ferric chloride were added. The mixture was diluted to 250 to 300 ml. with water and a lump of dry ice was added to provide an oxygen-free atmosphere during titration. Fifteen milliliters of phosphoric-sulfuric acid mixture and 0.25 ml. of diphenylaminesulfonic acid indicator were added. The solution was titrated with 0.02*N* potassium dichromate.

The indicator blank was determined over a range of uranium concentrations varying from 0 to 150 mg. as shown in Table I. The total theoretical titer for the uranium and iron present was subtracted from the titer found, to obtain the indicator correction. The stoichiometric volume of 0.02*N* dichromate required to oxidize 0.25 ml. of 0.005*M* diphenylaminesulfonic acid is 0.25 ml. Sarver and Kolthoff (*5*) employed 0.01*N* dichromate to determine the indicator correction for variable volumes of 0.005*M* diphenylaminesulfonic acid. Recalculation of their results to apply to 0.02*N* dichromate shows that about 0.22 ml. of dichromate would

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[1] Present address, Canada Department of National Health and Welfare, Occupational Health Division, 200 Kent St., Ottawa, Canada.

be needed as a correction blank for 0.25 ml. of 0.005*M* diphenylaminesulfonic acid. The indicator correction actually found was 0.24 ± 0.03 ml. of 0.02*N* dichromate. Table I gives the values obtained for the indicator correction, as well as a measure of the precision which may be expected from the method. The results were obtained with a 50-ml. buret.

Table II shows the accuracy obtained in the range of uranium contents given in Table I. A blank of 2.24 ml. was subtracted from the titer found to obtain the uranium titer.

Table II. Accuracy of Determination of Uranium by Reduction with Stannous Chloride

99.93% U_3O_8, Mg.	0.02*N* $K_2Cr_2O_7$, Ml.		% Theoretical Titer
	Uranium titer found	Theoretical uranium titer	
20.0	7.15	7.12	100.4
50.0	17.82	17.80	100.1
70.0	24.86	24.92	99.7
100.0	37.62	37.60	99.9
100.0	37.63	37.60	99.9
150.0	55.38	55.40	100.0
150.0	55.36	55.40	99.9

Low results were frequently obtained on samples having a titer greater than 30 ml. The error was proportional to the time required for titration. It was assumed that air progressively oxidized the ferrous iron during titration. To prevent this error, small lumps of dry ice were added to the titration flask to provide an oxygen-free atmosphere during the titration. For example, a titration which required 5.5 minutes to complete gave a titer of 55.35 ml. in the absence of carbon dioxide and a titer of 55.62 ml. in the presence of carbon dioxide. The theoretical titer was 55.64 ml.

Table III shows the effect of acidity, iron, and phosphoric acid on the reduction of uranium by stannous chloride.

The iron acted as a catalyst to the reaction. Its presence in small amounts increased the percentage of uranium reduced in 15 minutes from 26.1 to 97.8 as shown in Table III. However, in the absence of phosphoric acid, even prolonged heating (45 minutes) failed to increase appreciably the percentage of uranium reduced beyond 97.8%. Evidently the reaction reached equilibrium short of quantitative reduction.

Table III. Effect of Acidity, Iron, and Phosphoric Acid on Reduction of Uranium by Stannous Chloride

(Each sample contained equivalent of 103.6 mg. of U_3O_8. Reduction heating time was 15 minutes)

Acid Normality	H_3PO_4, Mg.	Fe Added, Mg.	% Theoretical Titer
	Effect of Iron		
6	0	0	26.1
6	0	5.6	97.8
	Effect of Phosphoric Acid		
6	1400	0	38.0
6	700	5.6	99.8
6	1400	5.6	100.0
6	7000	5.6	100.1
	Effect of Acidity		
3	1400	5.6	95.0
10	1400	5.6	99.9

Phosphoric acid, in the absence of iron, caused an increase of 12% in the uranium reduced in 15 minutes as shown in Table III. The small increase in the rate of reduction by phosphate present in 40 times the uranium concentration was not considered to be of a catalytic nature, but was tentatively attributed to the formation of a uranous phosphate complex. According to this hypothesis, the increased oxidation potential caused by the lowered uranous ion concentration should push the reaction toward more complete uranium reduction. The addition of phosphoric acid did result in quantitative uranium reduction as shown in Table III, under "effect of phosphoric acid." The effects of the phosphoric acid and iron were separated on the basis of the interpretation and data given above.

Table IV. Effect of Reduction Time

(Each sample contained 100 mg., 99.93% U_3O_8)

Reduction Time, Min.	Fe Added, mg.	% Theoretical Reduction
1	1	88
	2	89
2	1	93
	2	95
5	1	99.8
	2	99.9
10	1	100.0
	2	99.9

Table V. Effect of Various Substances on Determination of Uranium by Stannous Chloride

(Each sample contained 100 mg. of 99.93% U_3O_8 in addition to substance added)

Substance Added	Substance Added, Mg.	Ml. of Titer[a] 0.02*N* $K_2Cr_2O_7$	% Theoretical Titer
......	....	35.60	100.0
$NaAsO_3$	5	35.62	100.1
$NaAsO_3$	25	35.70	100.2
$NaAsO_3$	50	35.76	100.4
$HClO_4$	6000	35.57	99.9
H_2SO_4	9200	35.64	100.1
Na_2WO_4	20	35.60	100.0
$KMnO_4$	20	35.58	99.9
$Ce(SO_4)_2$	20	35.53	99.8
NH_4OH	1000	35.67	100.2
C_5H_5N	1000	35.58[b]	100.0
$NaBiO_3$	20	35.60	100.0
$CoCl_2$	20	35.63[b]	100.1
$(NH_4)_6Mo_7O_{24}$	12.5	43.20[b]	121.0
$CuSO_4 \cdot 5H_2O$	40	42.00[b]	118.0
Na_3VO_4	20	41.61[b]	116.0
$TiCl_4$	20	38.64[b]	108.5

[a] After subtraction of 2.24, iron and indicator correction.
[b] Recalculated from 0.05*N* $K_2Cr_2O_7$.

The amount of phosphate present and the acidity used do not appear to be critical over a wide range.

Table IV shows the effect of varying reduction times on the reduction of uranium by stannous chloride.

Complete reduction was obtained after 5 minutes as shown in Table IV. The reduction time was extended an additional 5 to 10 minutes to ensure complete reduction.

Table V shows the effect of various substances on the determination of uranium by stannous chloride.

The effect of milligram amounts of nitrate on the reduction of 100 mg. of uranium oxide (U_3O_8) by 3.5 ml. of stannous chloride solution was investigated. In the presence of 5 mg. of nitrate, the titer was 99.8% of theoretical. With 10 mg. of nitrate, 96.2% of the theoretical titer was obtained. Larger amounts of nitrate gave progressively lower results. It was concluded that small amounts of nitrate do not interfere with the method, but that amounts in the order of 10 mg. and more do interfere by giving low results.

Table VI gives results obtained on unknown uranium samples and compares with them values obtained by a fluorometric method (*7*). The samples contained uranium, phosphate, sulfate, sodium, chloride, and small amounts of iron and arsenate. Normally the iron would be removed before estimating the uranium. As it is quantitatively reduced and reoxidized with uranium, an alternative method may be used in which the iron is determined separately and the uranium estimated by correcting for the iron. When the amount of iron is small, in the order of 1 mg. or less per sample (equivalent to 0.9 ml. of 0.02*N* potassium dichromate), and when nickel, cobalt, and copper are absent, the colorimetric ferron method (*6*) may conveniently and accurately be used to determine and correct for the iron. The samples included in Table VI and Table VII all contained small amounts of iron, as shown, and were free from "ferron" inter-

Table VI. Comparison of Results Obtained by Stannous Chloride Reduction and by a Fluorimetric Method

(Uranium by stannous chloride method estimated by correcting for separately determined iron)

Sample No.	Stannous Chloride Reduction, Grams/Liter			Fluorometer, G./Liter
	Fe	U_3O_8 1	U_3O_8 2	U_3O_8
1	0.074	6.63	6.63	6.64 ± 0.04
2	0.061	6.57	6.59	6.56 ± 0.04
3	0.059	6.61	6.63	6.65 ± 0.06
4	0.054	6.59	6.63	6.50 ± 0.08
5	0.061	5.96	5.98	5.93 ± 0.07
6	0.057	6.04	6.02	6.0 ± 0.1
7	0.068	5.99	..	5.97 ± 0.09
8	0.073	6.39	6.39	6.4 ± 0.2

Table VII. Precision of Stannous Chloride Method

(Uranium estimated by correcting for separately determined iron)

Sample No.	0.02*N* Dichromate, Ml.			U_3O_8, %	
	Iron correction	Uranium titer 1	Uranium titer 2	1	2
1	0.36	55.25	55.35	77.5	77.6
2	0.27	54.84	54.79	76.9	76.9
3	0.34	56.22	56.27	78.9	78.9
4	0.23	54.33	54.48	76.2	76.4
5	0.30	54.46	54.41	76.4	76.3
6	0.29	54.27	53.87	76.1	75.6
7	0.17	51.86	52.16	72.8	73.2
8	0.16	53.91	53.97	75.6	75.7

ferences. The uranium in these samples was estimated by correcting for the iron by the ferron colorimetric method. The duplicates for the iron determination did not deviate by more than ±1%; the average agreement was ±0.48%. In terms of milliliters of 0.02*N* dichromate titrant, the error amounted, on the average, to ±0.004 ml. This error is insignificant compared with errors associated with estimating the end point and reading the buret. Consequently, Table VII gives a fair measure of the precision which may be expected from the stannous chloride method.

A 10-ml. aliquot (containing approximately 60 mg. of uranium oxide equivalent to 20 ml. of 0.02*N* dichromate) was used to obtain each value shown in Table VI. The average titer subtracted to correct for the iron was 0.56 ml.; the range was 0.48 to 0.66 ml.

The samples in Table VII were similar in content to those of Table VI, except that they contained magnesium and calcium in addition to the other substances. The samples contained, on the average, 0.15% of iron, equivalent to 0.27 ml. of 0.02*N* dichromate. The correction applied to each titration, in addition to the uranium titer, is shown in Table VII.

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Determination of the Short-Lived Decay Products Of Radon in Natural Waters

P. K. KURODA

Department of Chemistry, University of Arkansas, Fayetteville, Ark.

YUJI YOKOYAMA

University of Tokyo, Tokyo, Japan

IT HAS long been established that the major portion of natural radioactivity of rain water is caused by the decay products of radon, but not by radon itself (*3, 7, 9, 11, 12*). In other words, in fresh rain water there is an excess of decay products the radioactivity of which has an "apparent" half life of some 30 minutes. This is in sharp contrast with the fact that fresh spring waters usually show a deficiency of decay products (*6, 8*). Although many papers on the determination of radon and radium have been published, practically nothing has been done on the quantitative determination of the short-lived decay products. The general impression has been that the equilibrium between radon and its short-lived decay products always should be established in water, because of the short half lives of the decay products.

Methods for use of short-lived radioactive elements in natural waters as tracers in nuclear-geochemical studies have been developed by the authors during the past several years, and some of the results have been published in preliminary reports (*6–9*). The present paper describes the analytical procedures used by the authors in the studies of natural waters both in Japan and in the United States.

EXPERIMENTAL

Apparatus. A Lauritsen-type electroscope (*8, 10*) of the Institute of Scientific Research, Tokyo, was used for the determination of the decay products, especially in the field work. Measurements were also made with a loop-line windowless Geiger counter (*1*) and a 2.9 mg. per cm.^{2} end-window Geiger counter (*3*) in the study of the radioactivity of rainfall. An I.M.-type fontactoscope (*5*) of the Institute of Scientific Research was used for the determination of radon in water.

Procedure. A simple evaporation method was used except when the concentration of the decay products in the sample of water was low. The natural radioactivity of rain water varies between 10^{-9} and 5.10^{-8} curie per liter, and the radon content of most spring waters varies between 10^{-11} and 10^{-6} curie per liter. The evaporation method is usable with concentrations higher than 10^{-9} curie per liter. When the concentration was lower than 10^{-9} curie per liter, the decay products were coprecipitated with lead sulfide.

For the determination of radium B, C in rain water, the water sample (1 to 10 ml.) was collected as quickly as possible, the volume was measured, and the water was transferred to a small dish (surface area 19.6 sq. cm.) and evaporated to dryness. The time consumed in each step was recorded and the radioactivity measurement was begun immediately after evaporation. As the salt content of rain water is low (up to a few micrograms per milli-