SPECTROPHOTOMETRIC DETERMINATION OF CALCIUM IN URANIUM USING GLYOXAL BIS-(2 — HYDROXYANIL)

ALCÍDIO ABRÃO

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INSTITUTO DE ENERGIA ATÔMICA
Caixa Postal 11049 (Pinheiros)
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by

Alcídio Abrão
Divisão de Radioquímica
Instituto de Energia Atômica
São Paulo - Brasil

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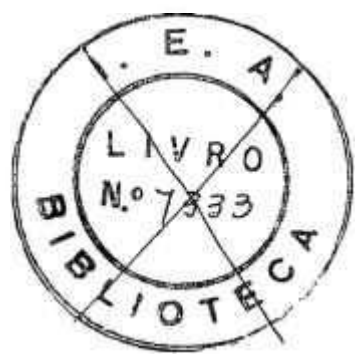

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RESUMO

A determinação de micro quantidades de cálcio em sais de uranila e óxidos de urânio de pureza nuclear é feita colorimétricamente. O urânio é separado primeiramente por:

a) extração com fosfato de tributila-tetracloreto de carbono,
b) absorção do complexo aniônico de sulfato de uranila em resina aniônica, ou
c) precipitação do urânio com água oxigenada.

Após a separação do urânio o complexo vermelho de cálcio-glioxal é extraído em cloroformio e medido a 535 mu. A interferência dos últimos traços de urânio, formando com glioxal um complexo violeta, é eliminada com hidroxilamina.

A lei de Beer é obedecida de 0 a 18 microgramos de cálcio.

RÉSUME

La détermination du calcium en micro quantités dans les sels d'uranyle et dans les oxydes d'uranium de pureté nucléaire a été faite par colorimétrie.

Aprés la séparation de l'uranium par extraction avec phosphate de tributyle-tétra chlorure de carbone, ou fixation du complexe anionique de sulfate d'uranyle dans une résine échangeuse d'anions, ou encore précipitation de l'uranium par le peroxyde d'hydrogène, le complexe rouge calcium-glyoxal bis-(2-hydroxianil) est extraid avec du chloroforme et mésuré à 535 mu. L'interférence des derniéres traces d'uranium qui forment un complexe violet avec le glyoxal, est eliminée par l'hydroxilamine.

La loi de Beer est valable entre 0 e 18 microgrames de calcium.

SUMMARY

A colorimetric method for the determination of micro-quantities of calcium in nuclear grade uranyl salts and uranium oxides is presented. After the separation of uranium by:

a) solvent extraction with tributyl phosphate-carbon tetrachloride,

b) absorption of the anionic complex uranyl sulphate on an anionic resin, or

c) precipitation of the uranium with hydrogen peroxide, the red complex calcium-glyoxal bis-(2-hydroxyanil) is extracted with chloroform and measured at 535 mu. The interference of the last traces of uranium giving a violet complex with glyoxal is eliminated with hydroxylamine chloride.

The Beer's law is obeyed from 0 to 18 micrograms of calcium.

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Spectrophotometric Determination of Calcium in Uranium Using Glyoxal Bis-(2-Hydroxyanil)

SIR: Glyoxal bis-(2-hydroxyanil) (hereafter glyoxal) is a specific reagent for spot test detection of calcium (*1*). The spectrophotometric determination of calcium using this reagent was applied by Williams and Wilson (*3*) for solutions of calcium in the presence of common cations including magnesium, strontium, and iron.

Nuclear pure ammonium diuranate and uranium oxides (UO_3, UO_2, and U_3O_8) have been analysed in our laboratory for their calcium content with this reagent, after the separation of the uranium with hydrogen peroxide precipitation (*2*), tributyl phosphate (TBP) extraction in nitric acid, or retention of the uranyl sulfate complex on an anionic ion exchange resin(sulfate form).

EXPERIMENTAL

Apparatus. Measurements were made with a Hilger spectrophotometer (Hilger & Watts, Ltd., London), using 1-cm. matched, square cells. Conical glass centrifuge tubes (12 cm. of height and 12-ml. capacity, with glass stopper) were used for the color extraction.

Reagents. Glyoxal (E. Merck Ag. Darmstadt). Make a 0.4% w./v. solution of glyoxal in ethyl alcohol. Prepare this solution fresh daily.

Prepare a color developing solution by dissolving 10.0 grams of sodium hydroxide and 0.5 gram of sodium carbonate in 100 ml. of water.

Ion exchange column. Transfer 5 ml. of Nalcite SAR (30–50 mesh) anionic ion exchange resin to a glass tube (8-mm. i. d.) column and condition the resin by passing 25 ml. of 1*M* H_2SO_4 and wash with 50 ml. of water.

Procedure. SEPARATION OF URANIUM.

Precipitation of Uranium by Hydrogen Peroxide.

Use uranyl nitrate solution prepared by dissolving the samples (U_3O_8, UO_2, UO_3, or ammonium diuranate calcinated to U_3O_8) with minimum amount of 6*M* HNO_3 and dilute to desired volume with water. The optimum pH of the final solution is 1–3.

Pipet 2 to 10 ml. of uranyl nitrate containing 100 to 500 mg. of U_3O_8 (2 to 14 μg. of calcium) into a centrifuge tube, add 1 ml. of 30% hydrogen peroxide, mix thoroughly with a glass rod and keep in the refrigerator for 20 minutes. Centrifuge and pour the supernatant through a Whatman 41 filter (previously washed with water), recovering the filtrate directly into a platinum crucible (to avoid calcium from glass). Add 2–3 drops of 30% hydrogen peroxide to the centrifuge tube and make the volume 5–7 ml. with demineralized water, mix the precipitate thoroughly with a glass rod and centrifuge again. Collect the second supernate using the same filter. Evaporate the filtrate to 3–5 ml. on a hot plate, transfer to a 25-ml. volumetric flask and make up to the mark with water. Use aliquots of this solution for the determination of calcium.

Extraction of Uranium with Tributyl Phosphate.

To 2 ml. of uranyl nitrate solution (100 mg. of U_3O_8), add 5 ml. of 6*M* HNO_3 and extract 5 times with 1 ml. of 20% TBP in CCl_4, and finally wash the aqueous phase twice with 2 ml. of

pure CCl_4. Filter the aqueous phase through a Whatman filter paper previously washed with water. Evaporate the aqueous phase to dryness using a platinum crucible, after adding one drop of $HClO_4$. Wash the crucible using 2 ml. of water containing one drop of 2*M* HCl and transfer the solution into a 10-ml. volumetric flask. Take an aliquot for the determination of calcium.

Ion-exchange Separation.

Use uranyl sulfate solution prepared by fuming uranyl nitrate solution with minimum amount of sulfuric acid for complete elimination of nitric acid and finally dilute with water to a desired volume. In the case of ammonium diuranate, dissolve 5.0 grams of ammonium diuranate of nuclear purity on a hot plate with 1*M* H_2SO_4 adding the last amounts of the acid drop by drop; transfer the solution to a 100-ml. volumetric flask and dilute to the mark with water. The pH of this solution should be 1–2.

Dilute an aliquot of the uranyl sulfate solution containing 100 mg. of U_3O_8 to 10–12 ml. with water and percolate through the anionic exchanger column with a flow rate of 5–8 drops per minute. Wash the column with 10 ml. of water. Collect the effluent and wash into a platinum crucible and evaporate to dryness. Add 1 drop of 1*M* H_2SO_4 to the platinum crucible and transfer the content to a centrifuge tube using 2 ml. of water dropwise.

To prepare the column for the next experiment elute the resin with 25 ml. of 1*M* HNO_3 and wash with 25 ml. of water, 25 ml. of 1*M* H_2SO_4, and 50 ml. of water, successively.

Extraction and Estimation of Calcium. For the color development and extraction of calcium, pipet 2 ml. of solutions obtained in any of the above steps, into the centrifuge tube, add 2 drops of 10% hydroxylamine hydrochloride, stopper, and mix thoroughly. Add 2 ml. of glyoxal solution, mix well, and add 0.5 ml. of color-developing solution. Finally, add 4 ml. of chloroform, stopper, and extract the calcium–glyoxal complex inverting the tube about 20 times. (It is essential to do the extraction like this since violent mixing results in a decrease in the absorbance, thereby giving lower values for calcium. A similar behavior has been observed also when the organic phase is filtered. The reasons for both have not been investigated.) Centrifuge for one minute (2400 r.p.m.) and remove the supernate using a pipet. Transfer the organic phase into the spectrophotometer cell and measure the absorbance at 535 mμ using chloroform in the other cell.

For the determination and standard curve, develop the color and extract the glyoxal–calcium complex of two centrifuge tubes one at a time and make the measurements immediately.

Reagent Blank. Prepare a reagent blank using the same amounts of reagents. Develop the color and measure the absorbance exactly as for the calibration curve. Subtract this value from the determination for the exact correction.

Calibration Curve. Prepare a standard curve using 2-ml. aliquots of the solutions containing 1, 2, 3, 4, 5, 6 and 7 μg. of calcium per ml., and follow the procedure given for the extraction of calcium for the determination of the absorbance of the calcium complex. Plot calcium in micrograms against absorbance.

RESULTS AND OBSERVATIONS

Table I shows typical results of the determination of calcium in one batch of nuclear grade uranium. The results are in good agreement for the three different methods used for the separation of uranium. However, the hydrogen peroxide method is preferred to the other two because it is more simple, less time consuming, and the blank corrections are small.

For the TBP extraction a relatively large amount of HNO_3 is used and because even C.P. nitric acid contains considerable amounts of calcium, the reagent blank correction is higher than in the hydrogen peroxide or ion exchange separation procedures. With TBP extraction the last traces of TBP have to be washed carefully with CCl_4; otherwise the phosphate ions produced by the decomposition of TBP lower the calcium values.

In the anion exchange resin separation, the flow rate for the small column used has to be controlled and the acidity of the sulfate solution is critical, the optimum pH being 1–2. Finally, there is a relatively large volume of solution to be evaporated.

Table II contains the results of the determination of calcium in the same batch of uranium analyzed by this procedure after the separation of uranium by precipitation with hydrogen peroxide. In these analyses the recovery of calcium is controlled by adding a spike of calcium.

Table III shows the results of calcium determination performed using uranyl nitrate solution with negligible content of calcium. This solution is prepared by dissolving the uranium oxide which was obtained from nuclear grade uranium by hydrogen peroxide

Table I. Calcium in Uranyl Nitrate Solution (H_2O_2 and TBP Procedures) and Uranyl Sulfate Solution (Ion Exchange Procedure)

Procedure	No. of determinations	Ca/U_3O_8 Av., p.p.m.	Ca/U_3O_8 Std. dev.
H_2O_2	5	46.0	1.6
	3	44.0	1.7
	4	46.8	1.9
	5	46.4	2.1
	5	42.4	2.1
	6	47.6	4.1
Ion-exchange	6	46.8	1.9
	5	48.0	1.8
TBP	4	46.5	3.7
	4	44.8	1.0

Table II. Calcium in Uranyl Nitrate Solution (H_2O_2 Procedure)

Calcium, μg. Total	Added	Found	Ca/U_3O_8 P.p.m.	Average	Std. dev.
9.4	5.0	4.4	44		
9.7	5.0	4.7	47		
4.6	...	4.6	46		
4.8	...	4.8	48	46.8	1.9
4.9	...	4.9	49		
4.8	...	4.8	48		
9.4	5.0	4.4	44		
9.6	5.0	4.6	46		
9.5	5.0	4.5	45	46.4	2.1
4.8	...	4.8	48		
5.3	...	5.3	53		
4.6	...	4.6	46		
5.2	...	5.2	52		
7.6	3.0	4.6	46		
9.2	5.0	4.2	42	47.6	4.1
4.3	...	4.3	43		
4.5	...	4.5	45		
8.0	4.0	4.0	40		
9.1	5.0	4.1	41		
9.3	5.0	4.3	43	42.4	2.1

Table III. Calcium in Uranyl Nitrate Solution (H_2O_2 Procedure), Previously Purified by H_2O_2 Precipitation

Group	Calcium μg. Total	Added	Found	Ca/U_3O_8 p.p.m
A	0.1	...	0.1	1
	0.2	...	0.2	2
	0.2	...	0.2	2
	0.1	...	0.1	1
B	4.8	5.0	...	...
	5.2	5.0	0.2	2
	4.9	5.0	...	...
	5.0	5.0	...	...
	5.1	5.0	0.1	1

precipitation, and subsequent calcination.

In the three separation techniques there always remain traces of uranium that interfere by imparting a violet color to the chloroform glyoxal extract. Color development experiments were made which showed that when 100 to 500 mg. of uranium were used, 0.2 to 5.0 mg. remained after separation by the three methods suggested. When hydroxylamine was added, the same experiments showed no interference. The experiments were made with or without calcium present and uranium was detected in the organic phase, chloroform, after evaporation and destruction of organic matter with HNO_3–HCl and evaporation to dryness, addition of 3–4 drops of acetic acid and 2 drops of 3% potassium ferrocyanide solution. In those experiments in which hydroxylamine was present no uranium was detected.

It has been observed that the chloroform extract of calcium–glyoxal complex starts fading after 5–10 minutes and for a series of determinations the last readings give systematically lower results. To avoid this, the color development and extraction are carried out only on two samples at a time.

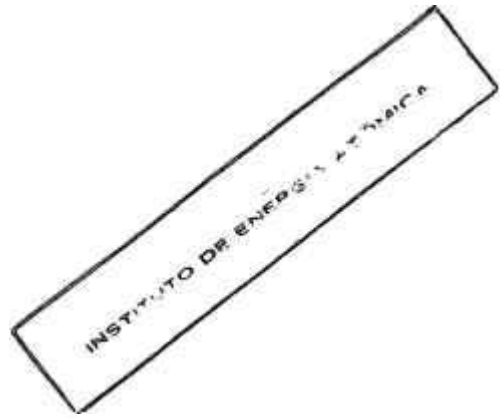
Calcium is usually and routinely determined by flame photometry, which is a relatively insensitive method compared with the spectrophotometric one. Beer's law is obeyed from 0 to 18 μg. of calcium.

LITERATURE CITED

(1) Goldstein, D., Stark-Mayer, C., *Anal. Chim. Acta*, **19**, 437 (1958).
(2) Rodden, Clement J., "Analytical Chemistry of the Manhattan Project," Vol. **VIII-1**, p. 18 McGraw-Hill, New York, 1950.
(3) Williams, T. Kenneth, Wilson, R. John, ANAL. CHEM. **33**, 244 (1961).

ALCÍDIO ABRÃO

Radiochemistry Division
Instituto de Energía Atômica
São Paulo, Brazil



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