BILJEŠKE   NOTES

Spectrophotometric Determination of Uranium in the Presence of Alkaline Earths*

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A spectrophotometric method for the determination of uranium in the presence of an excess of alkaline earths was needed to perform investigations of the precipitation systems uranyl nitrate — sodium carbonate — alkaline earth chlorides[1,2]. Hök's method[3] for the spectrophotometric determination of uranium by extraction of uranium (VI) from a perchloric acid solution (pH about 3) into a solution of 8-hydroxyquinoline in chloroform and measuring the absorbance of the complex at 450 mμ, seemed convenient for our purpose. The interference of alkaline earth ions with the determination of uranium by Hök's method has not yet been investigated. The influence of barium, strontium, calcium and magnesium chloride is the subject of this paper.

EXPERIMENTAL

All spectrophotometric measurements were performed using the Hilger Watts Model Uvispec 700—307 spectrophotometer and absorption cells of 1 cm optical path lenght.

Chemicals used

All chemicals used were analytical grade.
1. Concentrated $HClO_4$.
2. 0.05 N $HClO_4$ solution.
3. 2N $BaCl_2$ solution, 5N $SrCl_2$, $CaCl_2$ or $MgCl_2$ solution.
4. 1.5% solution of 8-hydroxyquinoline in chloroform.

Procedure

In order to investigate, whether the presence of barium, strontium, calcium and magnesium chloride in large excess has any influence on uranium determination by Hök's method ,the following experiments were performed: Known amounts of uranyl nitrate solution (containing $1 \times 10^{-4} - 3.4 \times 10^{-3}$ mg. atoms of uranium) were evaporated to dryness with 2 — 3 drops of concentrated $HClO_4$. The residue was dissolved in 1 ml. of 0.05 N perchloric acid solution and transferred to a separatory funnel, rinsing the evaporation disk with 2×0.5 ml. of 0.05 N perchloric acid solution. 0.5 ml. of the solution of the respective alkaline earth chloride (2N barium chloride, 5N strontium, calcium or magnesium chloride solution) was added and uranium was

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extracted twice with 4 ml. of 1.5% solution of 8-hydroxyquinoline in chloroform. The extracts were collected in a 10 ml. volumetric flask and made up with chloroform. After at least 1 hour the absorbance was measured at 425 mµ against a blank, obtained in the same manner without addition of uranium.

RESULTS AND DISCUSSION

Calibration lines for the determination of uranium in the presence of barium, strontium, calcium or magnesium chloride in excess were obtained by performing test analyses in the manner described. Beer's law was proved to be valid in the concentration range investigated. The straight lines obtained were analysed by the least-squares method and molar extinction coefficients were calculated.
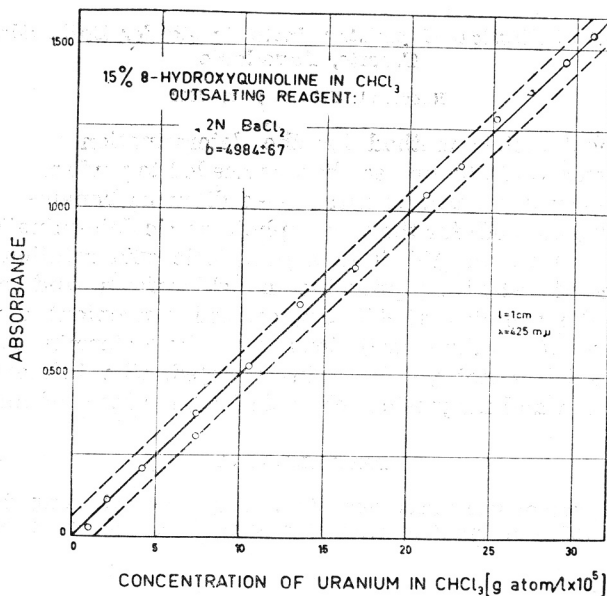

Fig. 1. The regression of the concentration C of uranium in CHCl₃ [g-atom/1×10⁵] upon absorbance at 425 mµ and 99% confidence limits for predictions of C. 2N barium chloride added before extraction.

Fig. 1. shows the results of uranium determination, obtained when 2 N barium chloride solution was added before extraction. The absorbance is plotted against the concentration C of uranium in CHCl$_3$ [g-atom/l × 10⁵] and the linear regression together with the 99% confidence limits for predictions of C are presented.

Fig. 2. shows the variation of the standard error, and the coefficient of variation with the concentration of uranium in CHCl$_3$, in the above case.

In Table I. the results of the statistical analyses of all four straight lines are listed. Molar extinction coefficients, standard errors and coefficients of variation are comparable.

In the 5th row of this Table results obtained when all experimental data were calculated together are listed. The molar extinction coefficient obtained

TABLE I

| Alkaline earth chloride added	Concentration range [g-atom U/l CHCl$_3$×10^5]	Standard error [g-atom U/l CHCl$_3$×10^6]	Coefficient of variation	Molar extinction coefficient	Intercept on y axis
1. 2N BaCl$_2$	1.0 — 31.5	4.58 — 4.97	45.75 — 1.58	4984 ± 67	—
2. 5N MgCl$_2$	1.0 — 34.0	4.74 — 5.15	47.36 — 1.51	4736 ± 58	—
3. 5N CaCl$_2$	1.0 — 33.6	2.42 — 2.58	24.22 — 0.77	4626 ± 27	—
4. 5N SrCl$_2$	1.0 — 33.6	4.79 — 4.88	47.91 — 1.45	4478 ± 104	0.03 ± 0.02
5. All data calculated together	1.0 — 34.0	7.28 — 7.43	72.8 — 2.19	4723 ± 43	—
6. Calculated from Hök's results[3]	2.1 — 21	—	—	4750	—
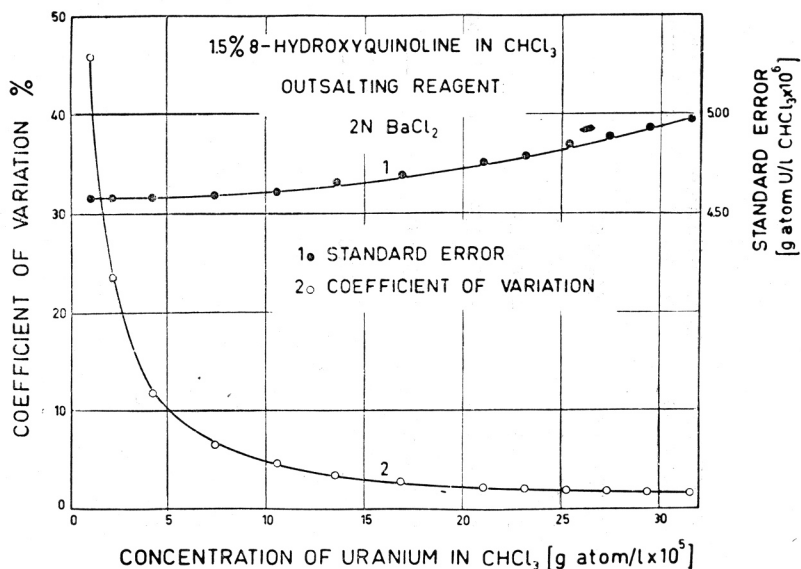
Fig. 2. Standard error (curve 1) and coefficient of variation (curve 2) of the concentration of uranium in CHCl₃ [g-atom/l×10⁵], plotted against uranium concentration. 2N barium chloride added before extraction.

by this calculation agrees within experimental error with the one which could be calculated from the calibration line, published by Hök[3] (row 6, table I).

It is evident that practically none of the alkaline earth chlorides investigated has any influence on the determination of uranium by Hök's method.

Conclusion

It was proved that under the conditions described, a large excess of alkaline earths has practically no influence on the determination of uranium with 8-hydroxyquinoline in slightly acid medium. Owing to its sensitivity and accuracy, the method described can be recommended for the analyses of microamounts of uranium in the presence of a large excess of alkaline earths.

REFERENCES

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IZVOD

Spektrofotometrijsko određivanje urana u prisutnosti zemnoalkalija

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Dokazano je, da stroncijev, barijev, kalcijev i magnezijev klorid u velikom suvišku ne smeta spektrofotometrijskom određivanju mikro-količina urana pomoću 8-hidroksikinolina u slabo kiseloj sredini[3]. Tabelirani su rezultati statističke obrade

pravaca, dobivenih određivanjem urana uz prethodni dodatak velikog suviška pojedinog zemno-alkalijskog klorida. Statističkom obradom svih eksperimentalnih podataka dobiven je molarni ekstinkcioni koeficijent $\varepsilon = 4723 \pm 43$, koji se dobro slaže sa molarnim ekstinkcionim koeficijentom za određivanje urana istom metodom bez prisustva drugih metala. Posljednji iznosi $\varepsilon = 4750$, a dobiven je preračunavanjem podataka iz objavljenog baždarnog pravca B. Hök[3].

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