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SPECTROPHOTOMETRIC DETERMINATION OF URANIUM WITH SORBOHYDROXAMIC ACID AS REAGENT

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Sorbohydroxamic acid forms with uranium an orange red, water soluble complex. The mole ratio of uranyl ion to compound is 1 to 1 under the investigated conditions. The formation constant of this chelate was also determined by the Likussar—Boltz method at a constant ionic strength of $0.1\,M$ at 30°C as 2.10×10^{3}. The recommended procedure obeys Beer's law between 3.98 *ppm* and 166.6 *ppm* of uranyl ion at *p*H 3.8±0.1. Tolerances to cerium (IV) and thorium have been investigated. The procedure for the determination of uranium are made more specific by applying preliminary extraction of uranium by ether.

The great importance of uranium in the production of nuclear energy and in military application call for a vivid interest among the analytical chemists since 1935. The ever increasing number of analytical methods for this element has been appeared in the analytical literatures year by year. The analytical papers concerning uranium has reached 1 to 2 percents of the total analytical literature in the world in these years[1]. The trend shows the importance of the problem as well as the earnest demand for more accurate, selective, rapid and sensitive method are still in fashion.

Uranium forms stronger complexes, usually as UO_2^{2+}, with oxygen containing reagents rather than with nitrogen containing ligands[2]. The strongest complexes are likely to be formed where bonding is through adjacent oxygen atoms at least one of which is anionic. A number of such organic reagents has been suggested as colorimetric reagents for uranium. Examples include dibenzoylmethane, chromotropic acid, tiron, salicylic acid, sulfosalicylic acid, alizarin red S., thoron, cresotic acid and so on[2].

Hydroxamic acid contains the reactive group, —CO—NHOH which form complex with metal ions through vicinal oxygen. It is to be expected to form a stable complex with uranium as explained above. Some of hydroxamic acids, such as salicylhydroxamic acid[3], benzohydroxamic acid[4] has been already used for the determination of uranium. Since sorbohydroxamic acid has a conjugated system of double bonds, its higher reactivity with metal ion and the greater absorbance of its complex are to be expected. The present investigation is undertaken in

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view of the above consideration.

EXPERIMENTAL

Reagents

Standard solutions of uranium (VI) were made by dissolving uranyl nitrate (A. R.) in distilled water and standardized by EDTA titration5). An aqueous solution of sorbohydroxamic acid was prepared and used.

All other reagents employed were of analytical reagent quality.

Instrument

The spectrophotometric measurements were carried out on a Hitachi model 624 digital spectrophotometer connected with Hitachi model QD_{15} recorder in 10 *mm* cuvettes. The *p*H of the solution was measured with Radiometer titrator equipped with saturated calomel (Type K 401) and glass (Type G 202B) electrodes. The electrodes were checked against Merck Buffer-Titrisol (*p*H 4.00 and 7.00).

RESULTS AND DISCUSSION

Spectrum behavior and effect of *p*H on uranyl-sorbohydroxamic acid complex

The absorption spectra of the orange red uranyl-sorbohydroxamic acid chelate at various *p*H were taken against reagent blank as shown in Fig. 2 and uranium blank as shown in Fig. 3. The absorbance of the complex has its maximum at 385 *nm*. The maximum absorbance of the reagent was in the region lower than 380 *nm* and it has practically very little absorption above 400 *nm* as shown in Fig. 1.

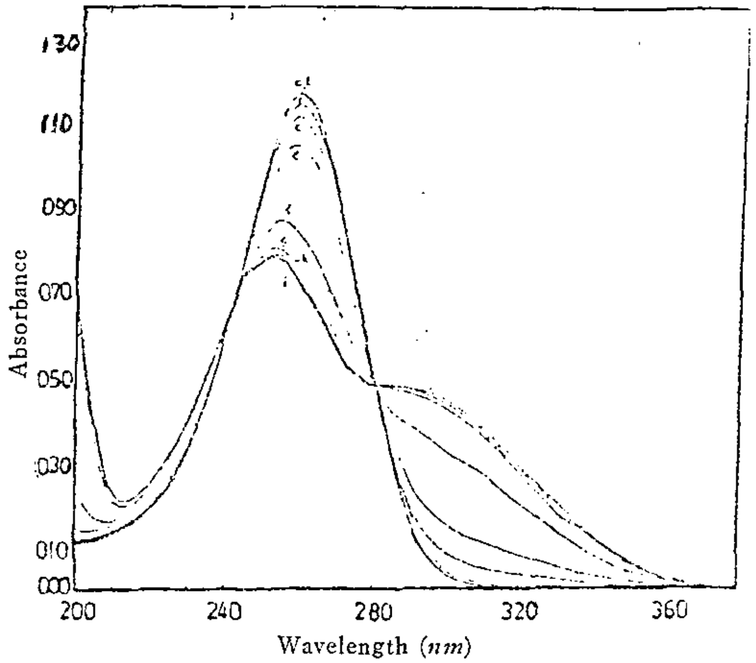

Fig. 1. Absorption spectra of sorbohydroxamic acid at different *p*H.
$C_R=4.00\times10^{-5}\,M$, $\mu=0.10\,M$
*p*H: a = 2.75, b = 3.25, c = 6.95, d = 7.91, e = 8.37,
f = 9.22, g = 10.08, h = 10.9, i = 11.48

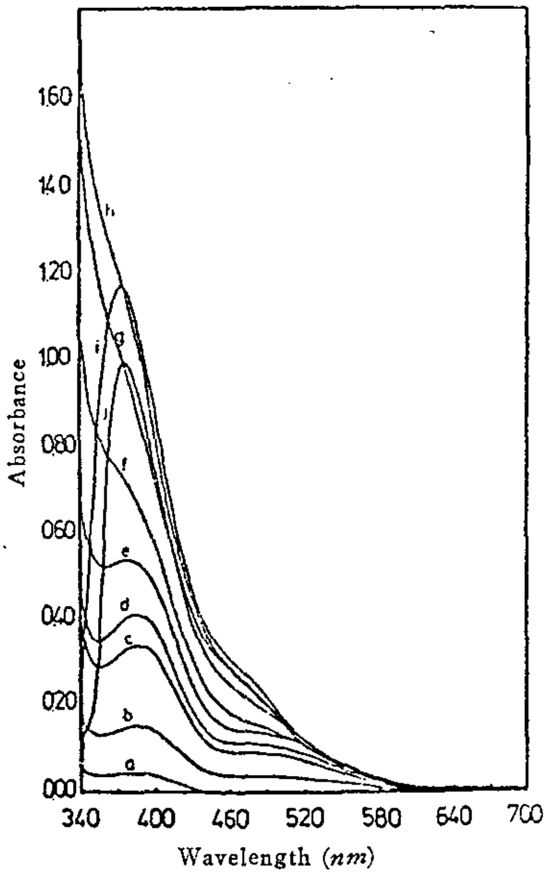

Fig. 2. Absorption spectra of uranyl-sorbohydroxamic acid complex at different pH.
Composition: $(UO_2^{2+})=1.12\times10^{-4}M$, $C_R=2.00\times10^{-3}M$
pH: a =3.20, b =3.85, c =4.35, d =4.68, e =5.40, f =6.30, g =7.20, h =8.00, i =8.85, j =9.70

For the absorbance measurements of the orange red chelate, the wavelength 385 *nm* was found to be workable, and all the measurements were made at this wavelength. The decrease in the concentration of the complex at low *p*H may be due to the competition of hydrogen ions with uranyl ions for sorbohydroxamic acid, while the effect of high *p*H is probably due to the tendency for uranyl ions to combine with hydroxyl ions. The *p*H of the uranyl salt solution was adjusted by the addition of 0.1 *N* sodium hydroxide or 0.1 *N* hydrochloric acid, since the usual buffers were found to interfere with the color of the complex.

Stability of the color of the complex

The color of the complex was found to be stable and no change could be observed after keeping the complex for 48 hours.

Effect of the amount of sorbohydroxamic acid on the absorbance of uranium (VI) chelate

A study of the effect of reagent concentration at *p*H 3.85 and *p*H 6.00 and 385 *nm*

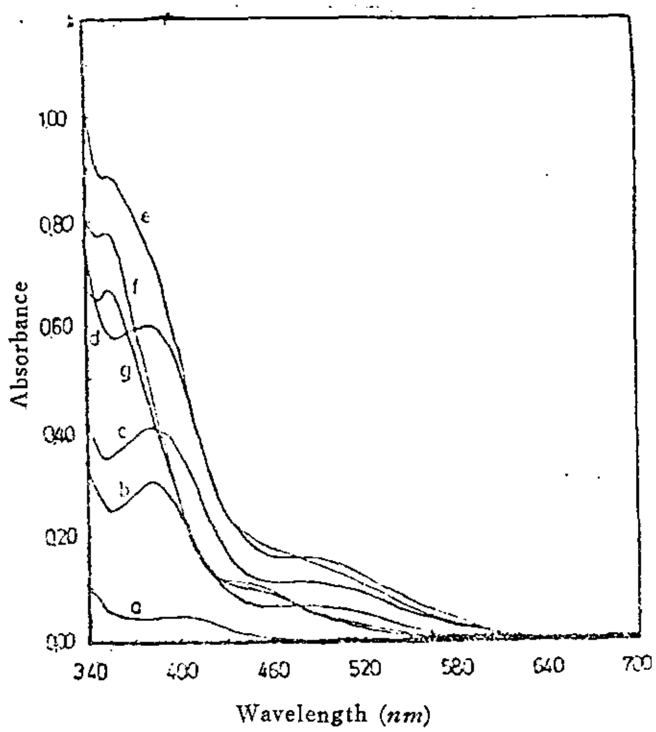

Fig. 3. Absorption spectra of uranyl-sorbohydroxamic acid complex at different *p*H.
Composition: $(UO_2^{2+})=1.12\times10^{-3}M$, $C_R=4.00\times10^{-4}M$
*p*H: a =2.30, b =3.50, c =4.80, d =4.55, e =4.90,
f =5.70, g =6.62

indicated that variations in the reagent concentration did not change the maximum absorption as shown in Fig. 4 and Fig. 5. Under these conditions, the complex was found to contain uranium (VI) and sorbohydroxamic acid in 1:1 molar ratio.

Composition and formation constant of uranyl-sorbohydroxamic acid chelate

The "normalized absorbance" concept[6] has been utilized in the continuous variation plot method of determining the composition of metal chelates and the formation constant. The continuous variation plot for uranyl-sorbohydroxamic acid chelate employing a normalized absorbance scale was shown in Fig. 6 and Fig. 7. It is a 1:1 complex which was in accordance with the previous result.

The conditional constant of the chelate was determined according to the following equation,

$$K_c=\left[\frac{(m+n)}{C_M+C_R}\right]^{(m+n-1)}\cdot Y\cdot[(m+n)x-mY]^{-m}\cdot[(m+n)(1-x)-nY]^{-n}$$

where m, n represents the mole number of metal and ligand respectively and

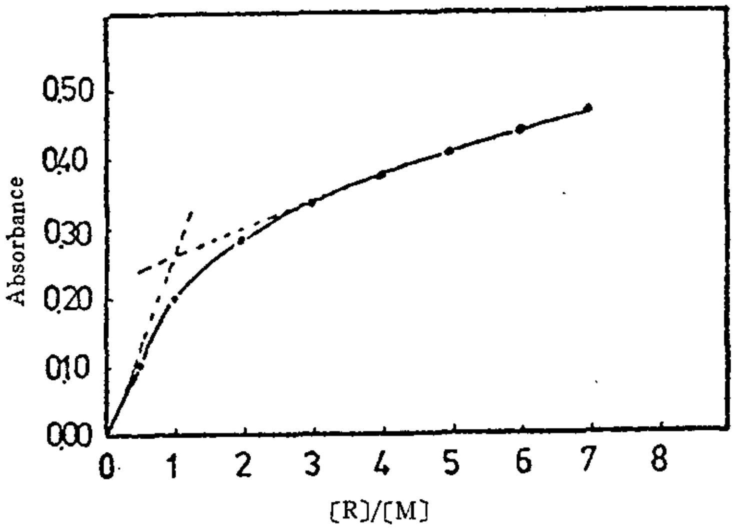

Fig. 4. Variation in the absorbance of the complex solution with change in molar ratio of sorbohydroxamic acid and uranyl nitrate.
$pH=3.85$ $(UO_2^{2+})=2.79\times10^{-4}\,M$

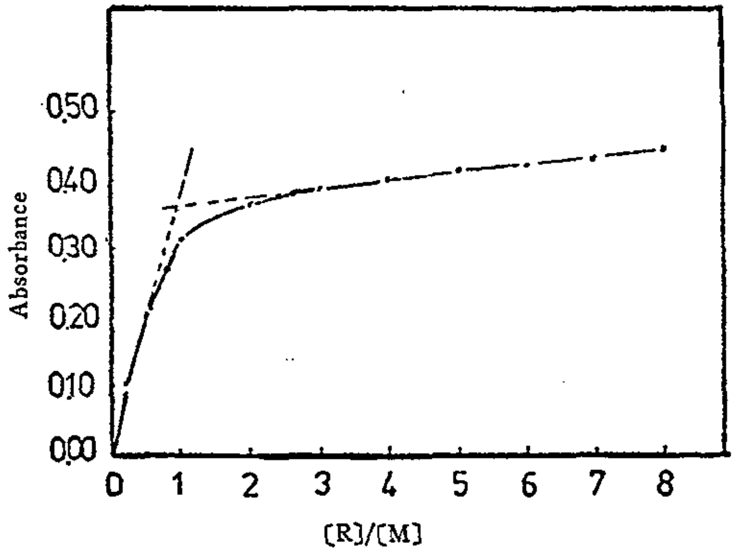

Fig. 5. Variation in the absorbance of the complex solution with change in molar ratio of sorbohydroxamic acid and uranyl nitrate.
$pH=6.00$ $(UO_2^{2+})=4.73\times10^{-4}\,M$

$$x=\frac{C_M}{C_M+C_R}, \qquad Y=\frac{[A_T-(A_T)_R]}{[(A_T)_{max}-(A_T)_R]}$$

$(A_T)_R$: the absorbance of the reference solution

$(A_T)_{max}$: It is obtained by measuring the absorbance of a solution containing a definite excess of ligand and a metal concentration $(C_M)_{max}$. The metal concentration selected for mesurement of $(C_M)_{max}$ is equivalent to that corresponding to the mole fraction of metal at the stoichiometric composition of complex—i. e., the maximum in the Y vs. mole fraction plot.

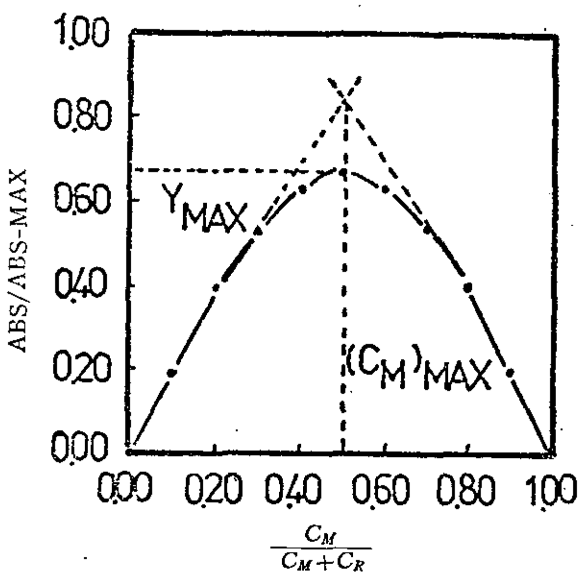

Fig. 6. Continuous variations plot for uranyl-sorbohydroxamic acid complex. ($Y_{max}=0.67$)
$C_M+C_R=5.58\times10^{-4}$ M, pH=3.85,
$\mu=0.10$ M, $\lambda=385$ nm, Temp.: 30°C

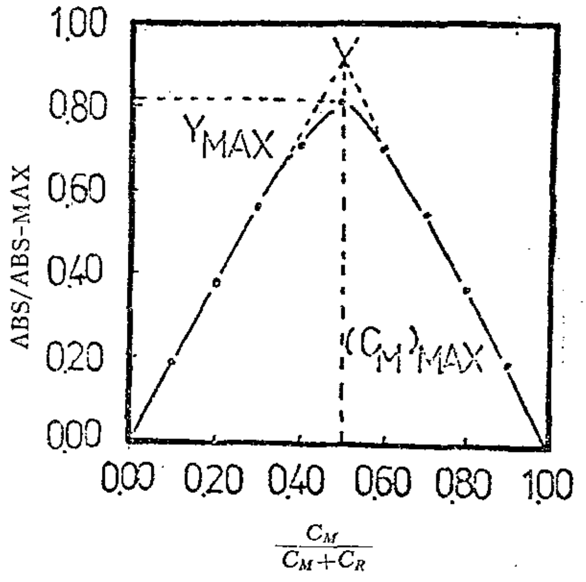

Fig. 7. Continuous variations plot for uranyl-sorbohydroxamic acid complex. ($Y_{max}=0.82$)
$C_M+C_R=9.46\times10^{-4}$ M, pH=6.00,
$\mu=0.10$ M, $\lambda=385$ nm, Temp.: 30°C

The total molarity of the system, C_M+C_R, was 5.58×10^{-4} M at pH 3.85 and 9.46×10^{-4} M at pH 6.00. The conditional constant, K_c obtained was 2.40×10^4 and 5.36×10^4 respectively. The fraction of free sorbohydroxamic acid present as anion form, L, in the experimental condition is

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$$\alpha=\frac{[\mathrm{L}]}{C_{HL}}=\frac{K_a}{[\mathrm{H}^+]+K_a}$$

where $K_a=10^{-8.80}$ 7).

The formation of metal-sorbohydroxamic acid chelates can be represented by $UO_2^{2+}+L^-=UO_2L^+$. Hence, the formation constant is obtained as follows;

$$K_f=\frac{[\mathrm{UO_2L^+}]}{[\mathrm{UO_2^{2+}}][\mathrm{L^-}]}=\frac{K_c}{\alpha}$$

for case I. (at pH 3.85) $\alpha=10^{-4.95}$, thus $K_f=2.10\times10^9$ and for case II. (at pH 6.00) $\alpha=10^{-2.8}$.

Since the measurements were made at pH 6.00, the following hydrolysis of uranyl ion should be taken into consideration.

$$UO_2^{2+}+H_2O=UO_2(OH)^++H^+$$

The hydrolysis constant, $\log K_h=-4.2$ for uranyl ion8) was used in calculation, then

$$\beta=\frac{[\mathrm{H}^+]}{[\mathrm{H}^+]+K_h}=10^{-1.8}$$

Thus, the formation constant, K_f is represented by

$$K_f=K_c\cdot\frac{1}{\alpha\cdot\beta}=\frac{5.36\times10^4}{10^{-2.8}\times10^{-1.8}}=2.10\times10^9$$

Analytical application

According to Rooden9), it is only in rare cases the uranium can be determined without prior separation from interfering elements. Because of the nonspecific nature of hydroxamic acid, a preliminary separation of uranium is necessary. The solubility of uranium nitrate in ether has been used for years for the separation of uranium from many elements10). Hence, the Holcomb and Yoe method11) was made for the extraction of uranyl nitrate. This procedure gives good precision and accuracy as stated in the literature. The procedure may be applied to prepare the sample solution. According to their method, the sample solution is treated as follows:

To a uranium containing solution (the primary requisite is the complete conversion of the uranium to its nitrate) and 1 *N* nitric acid in separatory funnel are added about 10 grams of ammonium nitrate per 5 *ml* of solution (containing 2.5 to 9 *mg* of uranium). An equal or slightly greater volume of ether is added to the funnel and the mixture is shaken thorughly and then allowed to stand. The ether layer is transferred to a beaker containing water. The extraction procedure is repeated for a total of four extractions. After the extraction process, remove the ether layer above the water by careful evaporation on a steam bath. After neutralization of the aqueous solution with sodium hydroxide, make the solution slightly acidic with nitric acid before the addition of sodium carbonate.

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An aliquot of this solution is then treated with sorbohydroxamic acid according to the followidg recommended procedure.

Recommended procedure

The following procedure may be proposed for the spectrophotometric determination of uranium ion with sorbohydroxamic acid.

To a suitable aliquot containing 99.5-4165 *μg* of uranium ion is added an excess of reagent (5 *ml* of 1×10^{-2} *M*). The *p*H of the solution is adjusted to 3.8±0.1 with 0.1 *N* hydrochloric acid or 0.1 *N* sodium hydroxide solution. Total volumes of the aqueous are then made to 25 *ml* by the addition of water. The absorbance is measured at 385 *nm* and the amount of uranium ion is obtained from the calibration curve drawn under identical condition.

Calibration curve

Fig. 8 shows the concentration-absorbance plots at 385 *nm* at *p*H 3.8. The concentration of sorbohydroxamic acid in the experimənt was fixed at 2.0×10^{-3} *M*. The uranyl-sorbohydroxamic acid systen conforms to Beer's law over the concentration range 3.98 *μg/ml* to 166.6 *μg/ml* of the metal.

The precision of the procedure is quite high and the absorbances are reproducible.

Since the only elements that are extracted appreciably with uranium under the conditions used are cerium (IV) and thorium[9], the effect of the two ions in the determination of uranium (VI) ions has been studied by preparing synthetic solution

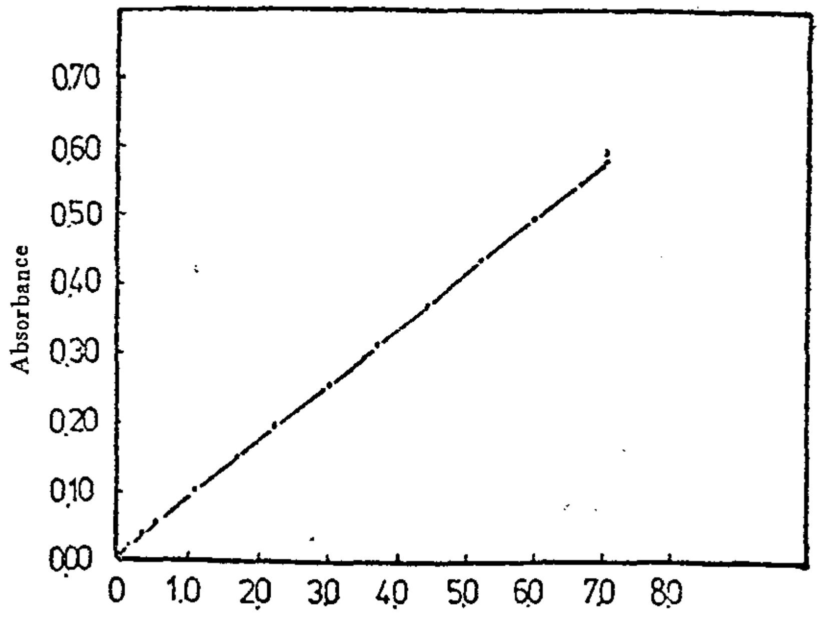

Fig. 8. Validity of Beer's low.
$u=0.10\,M$, $C_R=2.0\times10^{-3}M$. pH=3.8

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with varying amounts of foreign ions. Using 11.9 *ppm* of uranium ion, it is found that the presence of 7.56 *ppm* of cerium and 1.16 *ppm* of thorium in the sample, did not cause deviation of more than ±2% in absorbance.

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