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THE ESTIMATION OF URANIUM IN TRIBUTYL PHOSPHATE SOLUTIONS

AN A. E. R. E. REPORT

E. FURBY
G.J. ASHWORTH

MINISTRY OF SUPPLY
HARWELL, BERKS.
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THE ESTIMATION OF URANIUM IN TRIBUTYL PHOSPHATE SOLUTIONS.

by

E. Furby and G. J. Ashworth.

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ABSTRACT

The estimation of uranium in tributyl phosphate solutions by the standard hydrogen peroxide colorimetric method is discussed, and experimental details of a method are given. An alternative procedure by means of thiocyanate is also described, and some comparisons are drawn. The methods discussed are suitable for quantities of uranium down to 200 micrograms in the presence of the tributyl phosphate dissolved in the aqueous extracting solutions.

A.E.R.E. Harwell.

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DECEMBER, 1950.

CONTENTS

APPENDICES

ILLUSTRATIONS

1. Introduction

The following work was undertaken as a consequence of difficulties encountered in attempts to estimate uranium in tributyl phosphate solutions during a recent uranium purification run on the Micro Air-Lift apparatus. The precise nature of the trouble was, at the time, difficult to assess, but its effect rendered the results so inconsistent as to be worthless. It was decided therefore, to consider the problem under the following headings:-

(a) Transfer of uranium from the organic layer into an aqueous solution.

(b) Modification, if necessary, of the existing peroxide colorimetric method for use with this aqueous solution.

(c) Investigation of the effect of the method of dissolved tributyl phosphate in the aqueous solution.

(d) Examination of an alternative procedure for this determination.

The introduction of an alternative procedure came as a result of the observation of a turbidity when adding caustic soda to the aqueous layer after extraction of the uranium into tributyl phosphate. It had been encountered in some few occasions when analysing butex solutions, and was believed to be due, in some measure, to the dissolved organic phase in alkaline solution. The provision of a method therefore in which the uranium could be determined in acid solution would, it was believed, obviate a recurrence of the difficulty, and of those available the thiocyanate method was chosen to supplement the existing peroxide method. No attempt was made to investigate the method as such; it was used as described elsewhere[1,2].

2. The extraction of uranium from [illegible]

While information is available on the partition of uranium between tributyl phosphate and aqueous solutions[3], little or no data have been published on the stripping of uranium from this solvent. Water has been used in both Canada and the U.S.A., and in this country ammonium sulphate (400 gms/1.) was used in a uranium purification run on a semi-technical scale. It was felt, however, that the introduction of high concentrations of sulphate ion might lead to complications in the subsequent analytical procedures, and it was decided to examine other reagents. Assuming some similarity of tributyl phosphate with butex in its physical effect on uranyl solutions, the examination of sodium carbonate followed as a matter of course, and as a result of some preliminary work alkaline hydrogen peroxide was included in the list of potential stripping agents. The advantages of this latter in view of the analytical method employed in the determination of uranium are self-evident. Finally although existing work has shown that nitric acid assists the transfer of uranium from the aqueous into the solvent layer[3] a 1.0N HNO_3 solution was included for purposes of comparison.

The tributyl phosphate used was a commercial variety supplied by the Chemical Engineering Division, and distilled at a temperature of 116°C - 118°C and 3 mms. pressure, this being the procedure proposed for its use in future semi-technical scale experiments. After washing with 6N nitric acid it was diluted with kerosene, also redistilled (200°C), in the ratio of 20 parts tributyl phosphate to 80 parts of kerosene by volume, again in accordance with standard procedure.

This solvent was stirred for 10 minutes with an equal volume of a standard uranyl nitrate solution containing 10 mgms U/ml. and ~ 1.0N in nitric acid, and after separation of the phases uranium was

determined in the aqueous layer gravimetrically, and by the peroxide and thiocyanate procedures. In the case of the latter two, blank determinations by an identical procedure in the absence of uranium were carried out, and after making the necessary corrections the uranium content of the solvent layer was obtained by difference. Since all subsequent results were based on the stock solution of tributyl phosphate/uranium thus prepared, detailed experimental data for the analysis of the aqueous layer are given in Table I.

TABLE I.

Experimental: 20 mls. of tributyl phosphate solution stirred for 10 minutes with 20 mls. of standard uranyl nitrate solution (10 mgms U/ml.) and 1.0 ml. of conc. nitric acid. Phases separated, and 2.0 ml. aliquot of the aqueous layer taken for colorimetric analysis by means of hydrogen peroxide and ammonium thiocyanate. 10.0 ml. aliquot of aqueous taken for gravimetric determination of uranium. (Precipitation as diuranate and conversion to U_3O_8).

Analytical method.	Absorbancy.	Absorbancy of blank.	Corrected absorbancy.	mgms U in sample	mgms U in aqueous layer.	mgms U in Solvent layer.	mgms U/ml. Solvent.
Peroxide	0.462	0.015	0.447	3.28	34.44	165.56	8.28
Thiocyanate	0.710	0.015	0.695	3.26	34.23	165.77	8.29
Gravimetric				16.3	34.23	165.77	8.29
Average concentration of uranium in solvent layer.							8.29

A comparison of the stripping efficiency of water, N, nitric acid, and 10% ammonium sulphate, was effected by extracting 1.0 ml. of the stock tributyl phosphate/uranium solution twice with 5 mls. portions of these agents. After separation of the aqueous and organic layers uranium was determined on the former by the peroxide and thiocyanate procedures. Some slight modification was introduced after stripping with 10% sodium carbonate; the aqueous layer was neutralised with nitric acid, and a few drops excess acid added, after which the solution was boiled to eliminate carbon dioxide. From this point the procedure was identical with that employed for the other stripping agents. In the case of the alkaline peroxide 0.5 ml. of 20 vol. hydrogen peroxide was added to 5 mls. of 10% sodium hydroxide in a separating funnel and, after mixing, 1.0 ml. of the tributyl phosphate uranium stock solution was added. After shaking and allowing the layers to separate the aqueous layer was run into a 50 ml. volumetric flask. The operation was repeated with a further 5 mls. of alkaline peroxide and the aqueous extract added to that in the flask, after which the volume was adjusted to 50 mls. with water and the solution examined on the Spekker Absorptiometer. In all cases blank determinations using identical volumes and procedures with an 80/20 kerosene/tributyl phosphate solution were carried out and Spekker readings were made using a 1 cm. cell, the Chance 556 Filter and the mercury vapour lamp.

Nothing further needs to be added to the experimental details already given with the exception of a note on the actual shaking of the solvent and aqueous layers. Violent shaking over prolonged periods is entirely unnecessary, and, in the case of active solutions, inadvisable. Early experiments failed partly because the two layers had been so

vigorously intermixed that their eventual separation was almost impossible and the aqueous layer on removal remained cloudy. In the experiments mentioned above extraction was quick and very effective, gentle shaking removing the uranium from the solvent layer without difficulty.

The results of the stripping experiments are given in Table II.

Extraction Medium.	Analytical Method.	Absorbancy	Absorbancy of blank.	Corrected Absorbancy	mgms U in aliquot.	Concn of U in sample mgms.	Efficiency of Extraction.	$K = \frac{conc_0}{conc_A}$
1.ON nitric acid	Peroxide	0.265	0.017	0.248	1.73	4.33	52.3	9.1
	Thiocyanate.	0.435	0.013	0.422	1.82	4.55	54.9	8.1
Water	Peroxide	0.394	0.010	0.384	2.80	7.00	84.5	1.8
	Thiocyanate	0.629	0.007	0.622	2.87	7.18	86.6	1.5
10% ammonium sulphate.	Peroxide	0.465	0.013	0.452	3.32	8.30	100.3	
		0.460	0.013	0.447	3.25	8.13	98.5	0.2
	Thiocyanate	0.650	0.010	0.646	2.95	7.38	89.0	1.2
		0.667	0.010	0.657	3.07	7.68	92.6	
10% sodium carbonate.	Peroxide	0.445	0.010	0.435	3.25	8.13	98.5	0.2
	Thiocyanate	0.704	0.007	0.697	3.32	8.30	100.0	-
Alkaline hydrogen peroxide.	Peroxide	0.470	0.017	0.453	3.32	8.30	100.3	-
	-	0.470	0.019	0.451	3.30	8.25	99.6	0.05

3130-6

It will be noted that ammonium sulphate, sodium carbonate, and alkaline hydrogen peroxide are all effective as stripping agents under the conditions of the experiment, and that a good agreement is obtained with the results. The figures also indicate that water could be equally effective if used in larger volumes. Some inconsistency was observed when using the thiocyanate method with the ammonium sulphate strip, but since this method was used largely to supplement the standard procedure and not with the intention of superceding it, this apparent failure of the thiocyanate method was not pursued.

3. Spectrophotometric data for uranium/alkaline peroxide and uranium/thiocyanate complexes as applied to the determination of uranium in the presence of tributyl phosphate.

Many workers have investigated the peroxide method for the determination of uranium and experimental details and the absorption spectrum of the complex have been published[4,5,6]. While however thiocyanate has to some extent replaced peroxide in America[1] it has not been so widely used in this country and it was felt that the spectrophotometric data might with advantage be included in this work.

The absorption spectra of the thiocyanate and peroxide complexes with their respective reagent blanks in the presence of tributyl phosphate are shown in Fig. 1. They were determined on a Unicam instrument. It is seen from these curves that the reagent blanks containing dissolved tributyl phosphate cease to absorb significantly above 3500Å so that the Chance Filter No. 556 which has its maximum transmission at a wavelength of 3650Å, may be used with the Spekker Absorptiometer to give the optimum sensitivity with this instrument. A lower blank absorption may be obtained by using the Chance OVI/Wratten 2 combination, isolating the mercury line 4047Å, but the curve shows that the lower blank does not compensate for the decreased sensitivity using this combination. In this latter connection it will be observed that the sensitivity of the two methods at the wavelength 4047Å is very similar (molar extinction coefficients $\sim 0.8 \times 10^3$) whereas measured at the wavelength 3650Å the thiocyanate method has almost twice the sensitivity (molar extinction coefficient 3×10^3 for thiocyanate, 1.6×10^3 for peroxide). The above confirms work of a similar nature carried out by Beamish and Curragh[2].

In Fig. 1 are also shown the absorption spectrum of 80/20 kerosene tributyl phosphate and the transmission data for the Chance 556 and Chance OVI/Wratten 2 combination filters.

A plot of absorbancy against uranium concentration for the two methods is shown in Fig. 2. The data was obtained using a Chance 556 Filter, 1 cm. cell, and mercury vapour lamp.

4. Conclusions

From the data given in Table II it is evident that either method is satisfactory for use with tributyl phosphate solutions. Of the two, however, the peroxide method is preferred as being much quicker and equally accurate for the range of concentrations within which it is expected to be used. It has been shown that dissolved tributyl phosphate in the aqueous layer after extraction does not materially affect the results obtained by either method under the conditions stated.

Since blank determinations are of the order of 0.02 the accuracy of the peroxide method using a 1 cm. cell on the Spekker is not good with quantities of uranium less than 0.5 mgm. It can, however, be improved by using a 4 cm. cell, when reasonable accuracy (± 20%) has been obtained on quantities as low as 0.2 mgm. The thiocyanate procedure, owing to its higher specific extinction, is more successful when used with amounts of uranium of this order.

Finally should it be advisable at a future date for reasons as yet unknown to change over to the thiocyanate method, extraction of the uranium is quick and effective, and the procedure presents no difficulties.

Details of the two methods in their application to tributyl phosphate solutions are given in Appendices A and B.

5. Acknowledgment

The assistance of Mr. J. Bridge in some of the spectrophotometric work, is acknowledged.

6. References

1. AERE/C/R.495 A. A. Smales, A. H. Gillieson, R. G. Monk, E. J. Wadman.

2. Anal. Chem. 19, 1949, p.609 - Colorimetric determination of uranium with thiocyanate - J. E. Curragh and F. E. Beamish.

3. AERE/C/M.84 - E. Glueckauf.

4. Colorimetric Determination of Traces of metals - E. B. Sandell. Interscience Pub. New York. 1944.

5. AERE/C/R.344 The Spectrophotometric determination of uranium using Hydrogen Peroxide - A. A. Smales and E. Furby.

6. CRL/A.E.21. Aug. 1948 (Miss) M. R. Begg, A. F. Williams, and G. A. Wood.

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APPENDIX A

The determination of Uranium in Tributyl phosphate solutions by the Peroxide Absorptiometric Method.

1. Solutions. Sodium hydroxide - 10% solution in glass-distilled water.
Hydrogen peroxide - 20 vol. It is advisable to prepare fresh each time by diluting 100 vol. with glass-distilled water.

2. Procedure.

(1) Add 0.3 ml. of hydrogen peroxide to 5.0 mls. of sodium hydroxide in a small separating funnel and mix.

(2) Pipette sample containing 1-8 mgms. of uranium and add to alkaline peroxide in funnel.

(3) Shake gently for about 1 min (a) and allow to stand for 5 mins. so that aqueous and solvent layers may separate.

(4) Drain off the lower aqueous layer into a 50 ml. volumetric flask. Add 3 mls. of water, swirl gently and again drain off into the volumetric flask (b).

(5) Repeat the extraction by the addition of a further 2 mls. of caustic soda and 0.2 ml. of hydrogen peroxide (c), extract and wash as in (3) and (4).

(6) Make up volume to mark with water (d) and examine on Spekker using Chance 556 Filter, 1 cm. cell, and mercury vapour lamp.

(7) Make the necessary blank correction and determine uranium content of sample in mgms U/ml. from calibration curve.

Notes.

(a) The extraction is quick and efficient and violent shaking is unnecessary besides causing difficulty in the separation of the aqueous and organic layers.

(b) the water wash is for the purpose of removing caustic soda containing uranium from the stem of the separating funnel.

(c) Add the peroxide first. It is unlikely that a precipitate will form on the addition of the second 0.5 ml. of peroxide. Should it do so it will immediately dissolve on addition of the sodium hydroxide.

(d) It is essential to use glass distilled water throughout.

Calibration Curve.

Treat known volumes of a standard uranium solution, the uranium content of which has been determined gravimetrically, with 0.5 ml. of 20 vol. hydrogen peroxide and 7 mls. of 10% caustic soda in a 50 ml. volumetric flask. Shake, make up to 50 mls. with glass-distilled water and allow to stand for 10 minutes. Determine the absorbancy of the solution on the Spekker using a 556 Filter, 1 cm. cell, and mercury vapour lamp.

Determine the absorbancy of the reagents in the absence of uranium.

Plot the concentration of uranium against absorbancy after deducting the blank from the latter.

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[redacted]

APPENDIX B

The Determination of Uranium in Tributyl phosphate by the Thiocyanate absorptiometric method.

1. Solutions. Sodium carbonate - 10% solution in water.
Ammonium thiocyanate - 608 grams per litre.
Stannous chloride - Dissolve 10 grams of stannous chloride in 20 mls. of concentrated hydrochloric acid and dilute to 100 mls. with water.

2. Procedure.

(1) Pipette sample containing 1-5 mgms. of uranium into a small separating funnel.

(2) Add 5 mls. of sodium carbonate soln. and shake gently (a) for about 1 min, Allow to stand for 5 mins. so that aqueous and solvent layers may separate completely.

(3) Drain off the lower aqueous layer into a 50 ml. beaker. Add 3 mls. of water, swirl, and add the aqueous layer to the contents of the beaker (b).

(4) Repeat pars. (2) and (3) with a further 5 mls. of sodium carbonate combining the extracts with the previous ones.

(5) Neutralise the sodium carbonate with nitric acid (c) and add 2 or 3 drops in excess.

(6) Boil to remove CO_2. Cool and transfer to 50 ml. volumetric flask.

(7) Add 0.2 ml. of nitric acid, 0.2 ml. of stannous chloride (d), shake and then add 10 mls. of thiocyanate reagent.

(8) Make up to 50 mls. with water and examine on Spekker using 556 filter, 1 cm. cell, and mercury lamp.

(9) Make the necessary blank (e) correction and determine uranium content of the sample in mgms U/ml. from a calibration curve.

(a) The extraction is quick and effective and violent shaking is unnecessary besides causing difficulty in the separation of the aqueous and organic phases.

(b) The water wash serves to remove residual sodium carbonate containing uranium from the stem of the separating funnel.

(c) A small piece of litmus paper assists here.

(d) To reduce iron either in sample or in reagents.

(e) The extinction of the blank may be determined by treating a volume of TBP in keresene equal to that of the sample according to pars. (2) - (8).

Calibration Curve.

Treat known volumes of a standard uranium solution, the uranium content of which has been determined gravimetrically, with the reagents as in para (7) and make up volumes to 50 mls. Determine the absorbancy of the solutions on the Spekker using the 556 filter, 1 cm. cell, and mercury vapour lamp.

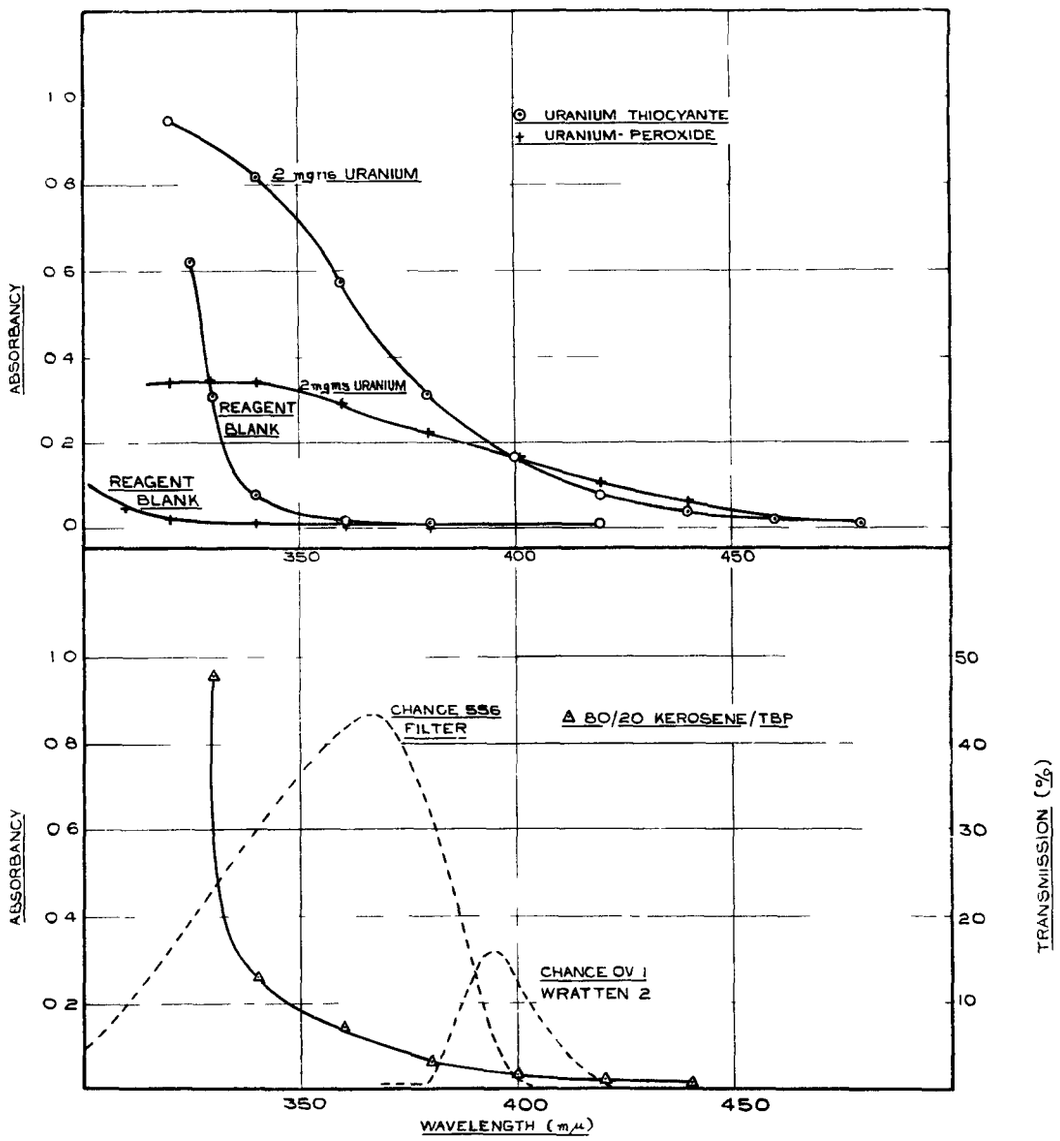
Determine the absorbancy of the reagents in the absence of uranium.

Plot the concentration of uranium against absorbancy after deducting the reagent blank from the latter.

[redacted]

3130-10

ABSORPTION SPECTRA OF U/CNS⁻ AND U/H_2O_2(ALKALINE) COMPLEXES WITH THEIR RESPECTIVE REAGENT BLANKS (WITH T B P).



ABSORPTION SPECTRUM OF 80/20 KEROSENE / T B P WITH TRANSMISSION CURVES (PARTIAL) FOR CHANCE 556 AND CHANCE OVI / WRATTEN 2 FILTERS

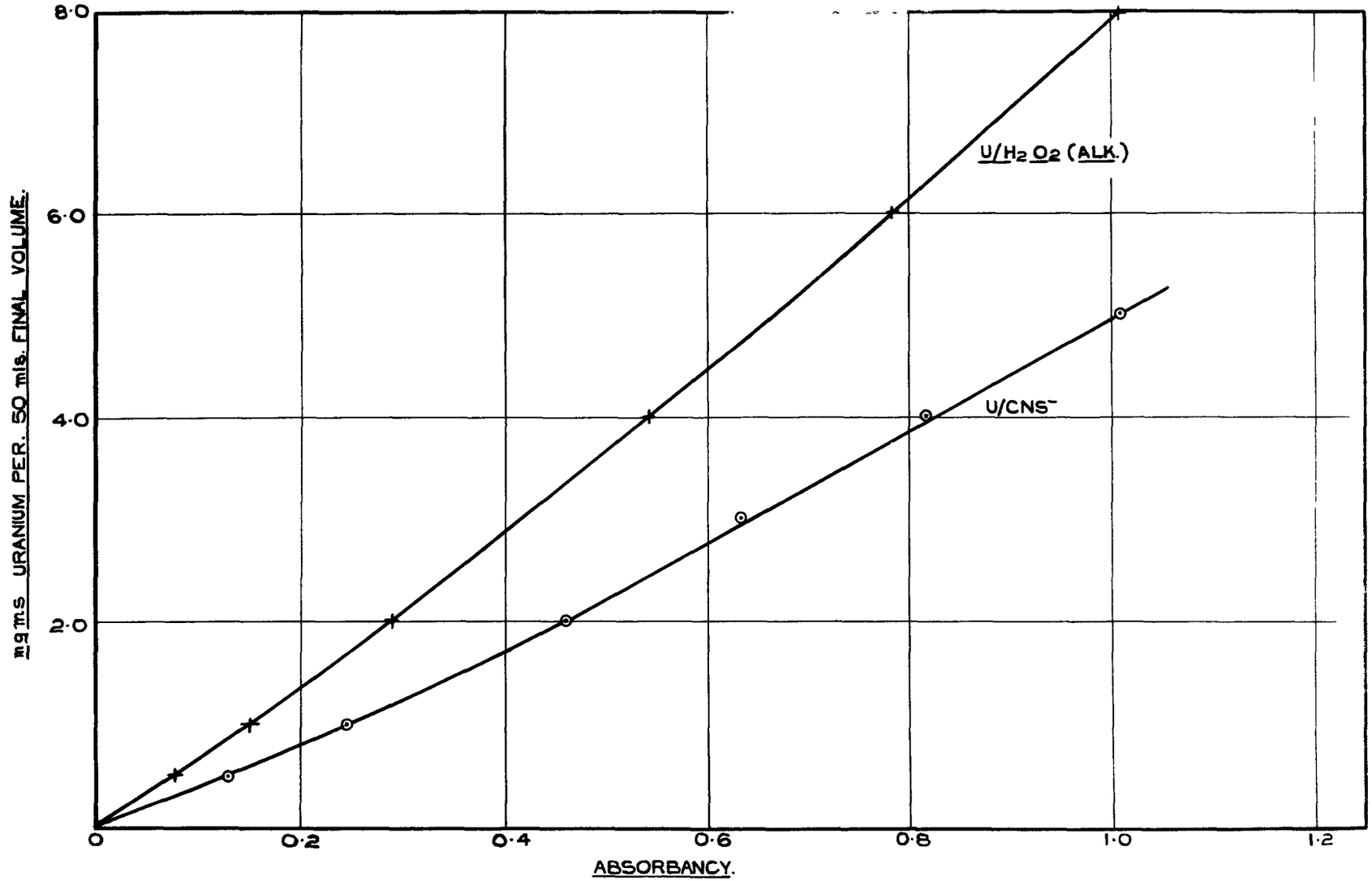


FIG. 2. SPEKKER CALIBRATION CURVES (BLANK CORRECTED) FOR U/CNS⁻ & U/H_2O_2 (ALK) COMPLEXES IN FINAL VOLUMES OF 50 mls.
CHANCE 556 FILTER, 1cm CELL, MERCURY VAPOUR LAMP.