

THE EXTRACTION OF URANIUM AND ITS PHOTOMETRIC DETERMINATION WITH OXINE AND DIBENZOYLMETHANE

J. ADAM and R. PŘIBIL

*Analytical Laboratory, Institute of Geological Sciences,
Charles University, Prague 2, and
Analytical Laboratory, J. Heyrovský Institute of Polarography,
Czechoslovak Academy of Sciences, Prague 1*

Dedicated to honour the memory of Professor J. Hanuš on the occasion of the centenary of his birthday.

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A highly selective extraction of uranium from a medium of sulphuric acid (pH 1.5–4) and sodium sulphate, with a chloroform solution of trioctylamine (Alamine S-336), was worked out. Uranium is determined directly in the extract with oxine by measuring the absorbance at 480 nm or 380 nm, according to the expected concentration. Beer's law holds for concentrations up to 250 μg , or 83 μg , in 1 ml of extract. For microgram amounts, the reaction with dibenzoylmethane was used. Beer's law holds up to a concentration of 20 μg in 1 ml of extract. The latter method allows determination of traces of uranium in very unfavourable concentrations of accompanying elements (at least to the ratio 1 : 10 000).

For the photometric determination of uranium, a considerable number of reagents of varying sensitivity are known. However, most of the reagents have quite low selectivity, so that they can be used only after appropriate treatment of the analysed sample. Complications from accompanying interfering elements can be eliminated in principle either by masking with appropriate complexing substances (*e.g.* EDTA or DCTA) or by separation of the uranium: for the separation of only uranium from thorium, Korkisch¹ gives 879 references in his review. Very often, chromatographic separation on ion exchangers is recommended². A second method is based on the extraction of uranium with appropriate extractants^{3–5}.

During the study of the extraction properties of trioctylamine and trioctylmethylammonium chloride (Alamine S-336, Aliquat 336-S)^{6,7}, we found that uranium can also be easily extracted from a medium of sulphuric acid by a chloroform solution of these amines. The extraction proceeds quantitatively, not only for traces, but also for greater amounts of uranium. Under optimum conditions, the aqueous phase does not contain uranium after the extraction, as was shown polarographically. Uranium was also not detected with sensitive reagents.

In this work, trioctylamine was used for the extraction of uranium. A colour reaction with an appropriate reagent can be developed immediately in the separated extract. Both oxine and the very sensitive reagent for uranium, dibenzoylmethane, were used. There is no doubt that further reagents, such as PAR or Arsenazo III, could also be used. The above described reagents were chosen mainly because, at the

measured wavelengths, they themselves either do not absorb, or absorb only slightly. The different sensitivities of the chosen reactions permitted the development of two procedures based on the reaction with oxine and one using dibenzoylmethane. Oxine (Ox) has low sensitivity as a reagent for uranium, since it forms insoluble oxinates suitable for gravimetric determination with a long series of elements. With uranium it also forms the insoluble oxinate, $\text{UO}_2\text{Ox}_2\text{HOx}$, which is easily extracted from weakly acidic or basic media.

The reaction of uranium with oxine has been studied in detail by a number of authors. Attention has mostly been paid to observance of the optimal pH for the extraction⁸⁻¹². The selectivity of the oxine reaction for uranium can be substantially increased by using EDTA to mask interfering elements. This was initially used by Přebil and Sedlář¹³ for the separation and gravimetric determination of uranium. As a screening agent for the colorimetric determination of uranium with oxine, EDTA was used by Kirby and Crawley¹⁰ during the analysis of reactor alloys with bismuth. Motojima^{11,14} also studied in detail the screening ability of EDTA during the extraction of uranyl oxinate. More useful appears to be prior extraction of uranium, for example with tributyl phosphate¹⁵ or triphenylarsine oxide¹⁶. The colour can afterwards be developed in the isolated extract with a chloroform solution of oxine. Dibenzoylmethane (DBM) is a much more sensitive reagent than oxine for uranium, and was proposed for the determination of uranium simultaneously and independently by Přebil and Jelínek¹⁷ and Yoe, Will, and Black¹⁸. The former method is based on the extraction of uranium from a neutral EDTA medium by an ethyl acetate solution of DBM. During the latter method, uranyl nitrate is initially extracted with ether. Both methods in their original form are somewhat lengthy, involving several extractions, careful maintenance of pH, *etc.* The reaction itself has been thoroughly studied, and a large number of modified procedures have been published for the determination of uranium, differing mainly in the choice of extraction agents¹⁹⁻²¹. Much more useful are methods depending on prior extraction of uranium with appropriate extractants and development of the colour reaction directly in the organic phase. In connection with the DBM reaction, for the extraction of uranium were used, *e.g.*, tri-*n*-octylphosphine oxide in cyclohexane²², tributyl phosphate in ethyl acetate²³, or in isooctane^{24,25}, or in *n*-hexane²⁶. Some reactions require the use of expensive extraction agents. Also, optimum conditions for extraction are not always simple, such as, *e.g.*, maintaining the molarity of acids in a narrow range, or using a high concentration of salting out materials (*e.g.* a saturated solution of aluminium nitrate, *etc.*). Many extractions must be repeated several times, sometimes the extracts must be freed of traces of coextracted elements, *etc.*

EXPERIMENTAL

Reagents and Apparatus

0.05M uranium sulphate was prepared by dissolving 2.120 g of uranyl acetate, $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ (Lachema, Brno), in a small amount of water and evaporating almost to dryness after adding sulphuric acid (1 : 1). The damp residue was dissolved in 100 ml of distilled water. The content of the solution was checked gravimetrically. Prepared from this stock solution, a $5 \cdot 10^{-3}\text{M}$ diluted solution contained 1.1901 mg uranium per ml, and a $5 \cdot 10^{-4}\text{M}$ diluted solution contained 119 μg uranium per ml. A 5% solution of trioctylamine was prepared by dissolving 50 g Alamine S-336 (General Mills Inc., Kankakee, Illinois, USA) in 1 kg of chloroform, *p.a.* The solution was used without further purification. A 1% solution of oxine was prepared by dissolving 1 g of the material (Lachema, Brno) in 100 ml of chloroform, *p.a.* A 1% solution of dibenzoylmethane

was prepared in an analogous way from the prepurate of the firm Fluka A. G. Buchs SG, Switzerland. The remaining solutions, such as saturated sodium sulphate, 1M sulphuric acid, 1M sodium hydroxide, and a series of solutions of metal sulphates and others, were prepared in the usual manner from chemicals of p.a. purity.

The spectrophotometer VSU-1 (Zeiss, Jena) was used for photometric measurements. Glass and silica optics and 1 cm cuvettes were used. For pH measurements was used the Precision pH meter OP-205 (Radelkis, Hungary) and glass electrodes from the same firm.

RESULTS AND DISCUSSION

Extraction of Uranium as the Uranyl Sulphate

During preliminary tests it was ascertained that uranium is extracted quantitatively with chloroform solutions of Alamine only from acid sulphate media, and we assume this to be the complex anion $\text{UO}_2(\text{SO}_4)_2^{2-}$. The optimum pH for the extraction is 1.5–4 in the presence of sodium sulphate. Acetates, chlorides, and nitrates lower the efficiency of the extraction. Permissible limits for chlorides and nitrates are 0.4 g NaCl and 0.4 g KNO_3 per 100 ml of solution. Fluorides and phosphates also interfere. The former can be removed already during the preparation step by evaporating with sulphuric acid; phosphate can be precipitated *e.g.* with a solution of bismuth or zirconium.

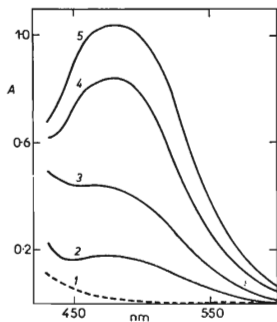


FIG. 1

Absorption Curves of Extracted Uranyl Oxinate.

Visible region. 1 Blank, 2—5 0.2, 0.5, 1.0, 1.5 ml of $5 \cdot 10^{-3}$ M uranium.

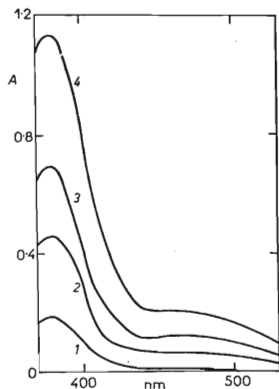


FIG. 2

Absorption Curves of Extracted Uranyl Oxinate

Near UV region. 1—4 0.5, 1.0, 1.5, 2.0 ml $5 \cdot 10^{-4}$ M uranium.

For microgram to milligram amounts, it proved to be satisfactory to add to a neutral solution of uranyl sulphate 2 ml of saturated sodium sulphate, 1.5 ml of 1M sulphuric acid, and to dilute the solution to 25 ml with redistilled water. The solution was shaken for 1–2 minutes with 5 or 10 ml of the Alamine solution in a 150 ml separatory funnel. The organic phase was then separated and the aqueous phase was extracted with 10 ml of pure chloroform. In the aqueous phase, traces of uranium were not detected by sensitive reactions. In further experiments, in which uranium was extracted according to the described procedure, it was demonstrated that it can be extracted quite selectively even in the presence of high concentrations of most elements, where their screening is almost impossible and where even recommended extraction methods fail due to coextraction of further trace elements.

The Determination of Uranium as the Oxinate at 480 nm

In preliminary tests it was ascertained that, after extraction with a chloroform solution of Alamine, uranium reacts directly in the extract with solid oxine. The extract exhibits a maximum in the visible region of the spectrum at 480 nm. The sensitivity is less than with measurement in the UV region, but, under the conditions described below, does not necessitate the preparation of a blank (Fig. 1).

For determining the absorption curves (Fig. 1), 0.2–1.5 ml of the $5 \cdot 10^{-3}$ M uranium solution were pipetted into a 150 ml separatory funnel, 2 ml saturated sodium sulphate were added, along with 1.5 ml of 1M sulphuric acid and it was diluted to 25 ml with water. It was extracted for 2 min with 5 ml of a chloroform solution of Alamine. After separation of the phases, the extract was filtered through a dry filter into a 1 cm cuvette. To the extract was added 3–5 mg of solid oxine, the cuvette was closed with a ground glass stopper and the contents was shaken. The spectrum was measured in the region 430–600 nm against an Alamine solution. Absorption curves for four uranium concentrations are given in Fig. 1. The dotted line (Fig. 1) shows the absorbance of 10 mg of oxine in 5 ml of Alamine, which is for normal measurements negligible. Beer's law holds for concentrations of 0.3–1.3 mg/5 ml. However, quantities up to 1.6 mg/5 ml extract can be read from the calibration curve. The same method was followed for the determination of uranium in the presence of various elements (Table I). Together with uranium are also extracted chromate, vanadate, and molybdate. The first two can be reduced by ascorbic acid. Small amounts of molybdenum up to 1 mg do not disturb the determination.

The Determination of Uranium as the Oxinate at 380 nm

Uranyl oxinate exhibits a very pronounced absorption maximum at 380 nm. Measurement in this region affords a much more sensitive method than determination at 480 nm. According to the values of the molar absorption coefficients, A_{480} 850, A_{380} 5600), the method is roughly 7 times more sensitive. However, at

TABLE I
The Colorimetric Determination of Uranium with Oxine at 480 nm

Added		Found mg U	Relative error %	Metal : U
mg U	mg metal			
0.595	11.5 Fe	0.600	+0.84	
0.595	11.5	0.610	+2.5	
0.595	57	0.630	+5.8	100
1.190	11.5	1.230	+3.3	
1.190	37	1.190	—	
1.190	345	1.230	+3.3	290
1.190	25 Cu	1.220	+2.5	
0.595	50	0.610	+2.5	
0.595	126	0.620	+4.2	
0.595	126	0.610	+2.5	
1.190	506	1.185	-0.5	425
0.595	50 Co	0.615	+3.4	
1.190	50	1.195	+0.4	
1.190	495	1.190	—	416
0.595	247	0.615	+3.3	416
1.190	500 Ni	1.195	+0.5	400
0.595	81 Sc	0.610	+1.0	
0.595	162	0.615	+3.3	300
1.190	20 Ce(III)	1.195	+0.4	
0.595	40	0.600	+0.84	
1.190	197 Th	1.195	+0.4	166
1.190	205 As	1.190	—	
0.595	205	0.610	+2.5	344
0.595	133 Cr(VI)	0.610 ^a	+2.5	
1.190	267	1.195 ^a	+0.4	225
1.190	25 V(V)	1.165 ^a	-2.2	
0.595	100	0.600 ^a	+0.84	186
0.595	1.20 Mo(VI)	0.630	+5.8	2

^a Reduced with ascorbic acid before the extraction.

380 nm it is also necessary to allow for the absorption of oxine and thus measurement against a blank is necessary. During measurement of spectra and verification of Beer's law, 1 to 5 ml of $5 \cdot 10^{-4}$ M uranyl sulphate was pipetted into a 150 ml separatory funnel, 2 ml of saturated sodium sulphate was added along with 1.5 ml of 1M sulphuric acid, and the solution was diluted to 25 ml. The extraction was carried out with 10 ml of Alamine solution. After separation of the phases, 5 ml of chloroform extract was transferred to a 50 ml separatory funnel, exactly 1 ml of a 1% chloroform solution of oxine was added, and shaken 1 min. The chloroform extract was filtered through a dry filter directly into a 1 cm cuvette and measured in the region 340–540 nm against a blank. In Fig. 2 are collected the appropriate spectra. Beer's law holds for uranium concentrations to $83 \mu\text{g}$ per ml of extract (Fig. 4). A series of determinations of uranium in the presence of normally interfering elements was carried out. With regard to the sensitivity of the method, uranium can be quite reliably determined in much more favourable ratios, *e.g.* next to iron to the ratio 1 : 2000, next to yttrium and the rare earths to the ratio 1 : 3,000 and so forth.

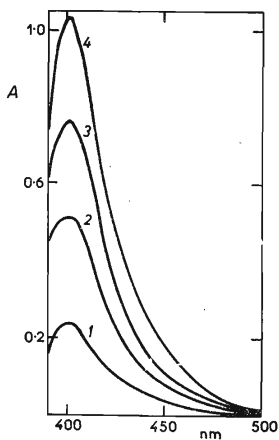


FIG. 3
Absorption Curves of UO_2 -DBM Complex in Alamine
1—40.5, 1.0, 1.5, 2.0 ml $5 \cdot 10^{-4}$ M uranium.

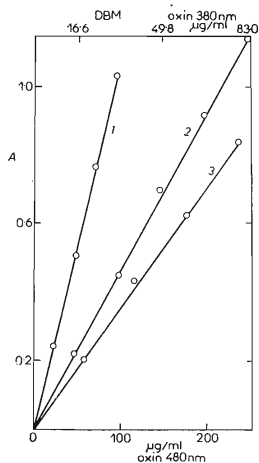


FIG. 4
Applicability of Beer's Law for the Colorimetry of Uranium with Oxine and Dibenzoylmethane
1 Dibenzoylmethane 400 nm; 2 oxine 380 nm; 3 oxine 480 nm.

The Determination of Uranium with Dibenzoylmethane (DBM)

As was already mentioned in the preceding paragraphs, uranyl sulphate can be easily extracted by a single extraction with a chloroform solution of trioctylamine, which is produced in large quantities and is very cheap²⁸. The conditions of this extraction are the same as has already been described. Dibenzoylmethane begins to considerably absorb light at 395 nm. Thus it is necessary to carry out measurements at 400 nm against a blank.

TABLE II
The Colorimetric Determination of Uranium with Dibenzoylmethane at 400 nm

Added		Found µg U	Relative error %	Metal : U
µg U	mg metal			
119	60 Fe	119	—	500
60	60	57	-5	1 000
119	200 Y	122	+2.5	1 680
119	400	120	+0.84	3 360
60	400	61	+1.6	6 720
119	50 Co	120	+0.84	420
119	100	121	+1.7	840
60	100	61	+1.6	1 680
119	100 Ni	121	+1.7	840
60	100	62	+3.3	1 680
119	250 Cu	123	+3.3	2 100
60	250	60	—	4 200
119	100 Ce(III)	123	+3.3	830
60	100	61	+1.6	1 660
119	100 V(V)	124	+4.2	830 ^a
60	100	63	+5	1 660 ^a
119	150 Cr(VI)	120	+0.84	1 240
60	150	61	+1.6	2 480

^a Reduced with ascorbic acid before the extraction.

Procedure: Extraction with 10 ml of Alamine is carried out in the same way as was described initially in the results section of the work. 5 ml of the extract is pipetted into a 50 ml separatory funnel, and exactly 1 ml of a 1% chloroform solution of DBM is added. After mixing, the chloroform is filtered through a small dry filter directly into a 1 cm silica cuvette and measured at 400 nm. A blank is carried out in the same way. Beer's law holds for concentrations up to 20 μg in 1 ml of extract. In Fig. 3 are collected absorption curves for various concentrations of uranium. With regard to the sensitivity of the method, uranium can be determined in the presence of high concentrations of accompanying elements (Table II). Limiting concentrations couldn't even be determined in several cases due to insufficient solubility of the metal compound.

The usefulness of the described method depends upon their sensitivity. Fig. 4 illustrates the latitude of the applicability of Beer's law for all three procedures.

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