UNCLASSIFIED

AAEC/E 29
COPY NO

AUSTRALIAN ATOMIC ENERGY COMMISSION
RESEARCH ESTABLISHMENT
LUCAS HEIGHTS

A NEW ION EXCHANGE METHOD FOR ENRICHMENT OF URANIUM AND THE DETERMINATION OF URANIUM IN SOLID SAMPLES

by

J. Korkisch, A. Farag and F. Hecht

Translated by

H.M.J. Meyer

from

Mikrochimica Acta, 3, 415–425 (1958)

Sydney, August, 1958.

AAEC/E 29

UNCLASSIFIED

AUSTRALIAN ATOMIC ENERGY COMMISSION

A NEW ION EXCHANGE METHOD FOR ENRICHMENT OF URANIUM AND THE DETERMINATION OF URANIUM IN SOLID SAMPLES

by

J. Korkisch, A. Farag and F. Hecht

Translated by

H. M. J. Meyer

from

Mikrochimica Acta, 3, 415–425 (1958)

CONTENTS

1. INTRODUCTION

The investigations carried out by M. Susic, I.J. Gal and E. Cucker (1) proved that uranium can be determined polarographically, using hydrochloric acid containing ascorbic acid, immediately after decomposition of the ore, without separation of the foreign ions. The ascorbic acid acts as a complexing agent for uranium and many of the foreign ions which interfere with the polarographic determination. In this, the uranium concentration of the test solution should be greater than 5×10^{-5} molar.

The separation and quantitative determination of very small amounts of uranium is very important. For this reason the different behaviour of some cations with ascorbic acid was used to develop an ion exchange method for the separation of microgram or milligram quantities of uranium for bivalent iron and a large number of other elements. The strongly basic anion exchanger "Amberlite IRA–400" (ascorbate form) was used.

When a hydrochloric acid solution containing uranyl ions is treated with ascorbic acid and adjusted to a pH of 4–4.5 with ammonia, a yellow–brown negatively charged uranium (VI) ascorbate complex will be formed.

I.J. Gal (2) discovered that the $NH_4^+(UO_2(OH)_2(C_6H_7O_6))$ compound was formed in the pH range 5–7. The same author also found by spectrophotometry (3), that the uranyl ascorbate complex has, depending on the acidity; a positive or no charge at all in the pH range below 3.

The uranyl ascorbate complex formed in the pH range 4–4.5 is very stable in solution and is strongly adsorbed on the ion exchanger. It was found that up to 1000 μg uranium can be adsorbed on the exchange column (shown in fig. 1) without exceeding the adsorption capacity, even with a flow rate of 1 ml/min. Milligram quantities of uranium can be separated quantitatively from any amount of iron using larger exchange columns. The elements titanium, zirconium, thorium, vanadium, molybdenum and tungsten behave similarly to uranium.

Experiments are being carried out to evaluate analytically these experimental results and the data obtained will be published in further reports.

Alkali metals, alkaline earth metals, Al, Pb, As(III), Bi(III) Zn, rare earths, Cr (III), Mn(II), Fe(II), Co and Ni, were analysed in a similar manner and formed, in contrast to uranium, either neutral or positively charged ascorbic acid complexes. These elements can thus be separated quantitatively from uranium (see table 1). Chloride, sulphate and small amounts of phosphate or fluoride do not interfere with the column process. When very large amounts of elements, which behave similarly to uranium, are present, the uranium might be partly displaced from the exchanger and this separation method cannot then be directly applied. In the presence of these cations or phosphoric acid, the uranium must be extracted with ether (E. Hahoffer and F. Hecht (4)), prior to the column process. The precipitation of copper (I) oxide or metallic copper, when copper is present in large quantities, can also be avoided with the ether extraction, as copper (II) ions are practically inextractible with ether.

The following method was developed to determine uranium rapidly and quantitatively in materials containing variable amounts of uranium, such as coal ash, slate and materials produced during technical enrichment of uranium. The final determination of uranium was carried out polarographically using the catalytic nitrate wave (5).

The advantages of this ion exchange method over the two earlier published methods for the determination of uranium in minerals (5, 6), are the very large capacity of the strongly basic anion exchanger "Amberlite" IRA–400 for the uranyl ascorbate complex, and the rapid exchange process. The disadvantages of this method, when directly applied to the decomposed material freed from silicic acid, are the great sensitivity to phosphates and, as mentioned previously, the similar behaviour of uranium and some elements with the exchanger. With the exception of tungsten, only large quantities of these elements interfere with the polarographic determination of uranium. In doubtful cases, the uranium should be extracted with ether prior to the column process.

2. SOLUTIONS AND REAGENTS

(a) Ion Exchanger: The strongly basic anion exchanger "Amberlite" IRA–400 (0.1–0.3mm; Cl–) was cleaned in the usual manner (6).

(b) Standard Uranium Solutions: 20ml of a strong nitric acid uranyl nitrate solution, (containing 0.9994 mg uranium/ml as determined by standardization with 8–hydroxyl–quinoline), were diluted to 100ml with distilled water; 1ml=199.9 µg uranium. 3ml of this solution was diluted to 250ml with 0.01 N nitric acid (A.R.); 1ml=2.39 µg uranium.

(c) Solutions of Other Elements: Standard solutions of other elements were needed.

(d) Ascorbic Acid: Pure ascorbic acid from the "Wiener" pharmaceutical factory was used.

(e) Ammonia Solution: Concentrated ammonia (A.R.) was diluted (1:1) with distilled water.

(f) Hydrochloric Acid Solutions: 0.1, 1.0, 3.0, 5.0, 6.0, 9.0 M and concentrated hydrochloric acid were needed.

3. APPARATUS

(a) Exchange Columns: The ion exchange column (shown in Fig. 1) was filled with the cleaned resin and the resin bed rinsed with 50ml 1N hydrochloric acid. This was followed by distilled water until the effluent was free from acid. The ion exchange column can adsorb quantitatively up to 1000 µg uranium/100ml adsorption solution with a flowrate of 1ml/min. For retention of more than 1mg uranium, similar columns with larger dimensions must be used. For example, a resin bed of 12x150mm can adsorb 25mg uranium.

(b) Polarograph: The measurements were carried out with a "Sargent" polarograph model XXI, with recorder, using a wave specified by D.N.Hume and W.E.Harris (8). The capillary characteristic $m^{2/3}$. $t^{1/6}$ was $1.7 mg^{2/3} sec^{-1/2}$. The electrolysis cell was placed in a thermostatically controlled tank, set at 25° ± 0.1°C.

4. THE POLAROGRAPHIC DETERMINATION OF URANIUM

Take an aliquot containing less than 10 µg uranium from the extracts (see sections 5,7,8,9) (diluting with 1N hydrochloric acid if required) and evaporate to dryness on a waterbath in a tared silica dish. The brown–black residue of the decomposed ascorbic acid is removed by ignition. Then add 5ml 5M hydrochloric acid and again evaporate this solution to dryness on a waterbath. Cool, dissolve the sample in 10ml 0.01M nitric acid and after some time transfer this solution to the polarographic cell. Bubble pure nitrogen through the solution for 10 minutes (to remove dissolved oxygen), and record the polarogram, starting at –0.5V, with 2.0V bridge potential and a sensitivity of 0.04. The plotting and calculations of the calibration curves are fully discussed in earlier reports (5,6,9). One or more elements co–adsorbed with the uranium will be noticeable in the dish as a distinct residue. In these cases an ether extraction should precede the ion exchange process, as the polarographic measurements will be otherwise unreliable. The materials analysed did not form this residue. To determine approximately how much uranium is in the extracts, use about 0.5 or 1ml of the extracts.

5. EFFECT OF pH ON THE ADSORBTION

The pretreated resin bed (see section 3a. and fig. 1) was converted to the ascorbate form with 50ml 1% ascorbic acid, which was adjusted to pH 4 with a few drops ammonia solution (see section 2). 0.5ml of a concentrated standard uranium solution containing 199.9 μg uranium/ml, together with 10ml ferric chloride solution (125mg Fe) were evaporated to dryness on a waterbath in a silica dish. The residue was dissolved in 5ml 5M hydrochloric acid while warming, and the solution transferred to a beaker with 90ml distilled water. 2g. ascorbic acid was added and the pH adjusted to 4 by cautious addition of ammonia solution. The solution was run through the column with a flowrate of 1ml/min. The resin bed was then rinsed with 50ml 1% ascorbic acid adjusted to pH4 and followed by 30ml distilled water. The uranium was then extracted with 100ml 1M hydrochloric acid. An aliquot of 2ml was taken from this extract and the uranium determined polarographically (see section 4); the uranium was quantitatively recovered and iron was not present in the extracts.

Similar experiments were carried out, in which the quantity of ammonia added to the ascorbic acid containing uranium, over a range of pH. These experiments proved that the enrichment of the uranium or its separation from iron could be carried out quantitatively only in the pH range 4-4.5. At pH greater than 4.5 the solution had a violet colour due to the violet ferric ascorbate complex. This complex is also negatively charged and can accordingly be adsorbed on the ion exchanger, but cannot displace the uranium, as the iron complex is less stable. The pH should be kept exactly between 4 and 4.5. A red brown uranium (VI) ascorbate complex will be visible in the bottom of the resin bed, when the solution contains more than 50 μg uranium. The amount of uranium present can be estimated by the colour of the resin bed. This phenomenon is of great use in the estimation of the aliquot needed for the measurements. Titanium is also adsorbed on the exchanger as a red ascorbate complex and can easily be mistaken for uranium. The extract should always be checked for for titanium.

The other co-adsorbed elements produce the following colours in the resin bed; vanadium-green, molybdenum and tungsten-greyish green, zirconium and thorium - no colour.

6. EFFECT OF THE HYDROCHLORIC ACID CONCENTRATION ON THE EXTRACTION

Uranium can be quantitatively eluted with 1M hydrochloric acid or the same amount of 0.1M hydrochloric acid. The uranyl ascorbate complex in contrast with the uranyl acetate complex (5) is far less stable at these hydrochloric acid concentrations, and is no longer negatively charged. The uranium recovery is 48, 18, 40 and 20% using 3, 6, 9 and 12M hydrochloric, respectively, for the extraction.

7. THE DETERMINATION OF THE ADSORBTION CAPACITY OF THE ION EXCHANGE COLUMN

As mentioned in Section 6, the uranyl acetate complex is visible in the resin bed. The determination of the adsorbtion capacity can be carried out easily, as the red brown zone will gradually move upwards, when more uranium is adsorbed. The adsorbtion capacity was determined by carrying out experiments similar to the ones in Section 5, in the pH range 4-4.5, with uranium quantities from 2.39 μg to 1000 μg. The redbrown zone extended over more than half of the resin bed when using 1000 μg uranium, and the effluent contained 1 μg uranium. The flowrate of the adsorption solutions was always 1ml/min. The influence of sodium chloride (which is present in large amounts when the sample is decomposed with sodium carbonate) on the adsorption capacity was also investigated. Up to 3g sodium chloride in 100ml adsorbtion solution did not have any effect on the adsorbtion capacity.

8. EFFECT OF FOREIGN IONS

Large quantities of titanium, zirconium, thorium, vanadium, molybdenum and small amounts of tungsten interfere with the enrichment process and the final polarographic determination of uranium (see table 1). The following anions interfere when present in large quantities; nitrates (ammonium nitrate, which is present in the extract after ether extraction of uranium (4), must be removed by heating the evaporation residue), phosphates and fluorides. The results shown in table 1 were obtained with the method described in section 9. The direct application of this method, without prior ether extraction, is only possible when the ratio of the interfering ions to uranium is less than 10:1. The ratio is valid for all previously mentioned elements except tungsten which interferes within the ratio of 1:1. Ferric and thorium nitrate, small amounts of lead, magnesium, calcium nitrate, cerium and traces of other rare earth metals should be extracted with ether. (E. Hahoffer and F. Hecht (4)). Thorium interferes with the polarographic determination only when the ratio of thorium to uranium is greater than 10:1, which only occurs with high–grade thorium minerals and monazite sand. Satisfactory results however were obtained for some samples using the direct method (see table 2). The method cannot be directly applied to determine uranium in water, in contrast with a recently published method for rapid determination of uranium in ocean and river waters (10). The reason for this is that there is probably more tungsten than uranium in these samples. Experiments to separate thorium and tungsten from uranium without any further separation process are being carried out. Such a method would make it possible to determine uranium and thorium separately in the same sample, using simultaneous ascorbate enrichment.

9. METHOD

(a) Preparation of the resin bed

Distilled water is run through the resin bed (fig. 1), previously rinsed with 50ml 1M hydrochloric acid, until the effluent is free from acid. The resin is then converted to the ascorbate form with 50ml 1% ascorbic acid solution, which is adjusted to a pH 4–4.5 with a few drops of ammonia solution. The ascorbic acid solutions must be freshly prepared, as they decompose fairly rapidly.

(b) Adsorption process

The evaporated uranium sample solution (residue of the sample decomposed with sodium carbonate or acids, freed of silicic acid; or an evaporated, ignited ether extract) is dissolved in 5ml 5M hydrochloric acid with slight warming and diluted with 45ml distilled water. After about 2 hours, filter and rinse the filtered residue with 25ml 0.1M hydrochloric acid. Add to this solution,(now about 75ml) 2g ascorbic acid dissolved in 25ml distilled water and adjust the pH to 4–4.5 by careful addition of ammonia solution. Pass the solution through the column with a flowrate of 1ml/min.

(c) Rinsing process

Now rinse the resin bed with 50 ml 1% ascorbic acid solution with a pH 4–4.5 and follow with about 30 ml distilled water.

(d) Extraction of the uranium

Extract the uranium immediately with 100ml 1M hydrochloric acid into a 100ml volumetric flask.

(e) Quantitative determination of the uranium

Take an appropriate aliquot from the extract and determine the uranium polarographically, as described in section 4. The analytical results shown in table 2 were obtained by this method.

* Note: The sodium chloride content after the decomposition should be less than 3 g.

The results on six of the above mentioned samples (marked *) were checked with a recently published method (5). The uranium in these check analyses was extracted and separated from the co-extracted ions (see section 7) by ion exchange using the acetate complex. The results obtained with this method agreed with the above mentioned ones to ± 8%. The ion exchange process using the acetate complex can be directly applied in most cases, without prior use of ether extraction and especially when there is less than 42 μg uranium in the 120ml adsorption solution (5) and large amounts of phosphoric acid are not present. Very small aliquots of the ether extract were used in the above mentioned six samples. The separation of milligram quantities of uranium on a larger column was carried out in similar manner, but the uranium was extracted with 200ml 1N hydrochloric acid. The extract was evaporated to dryness on a waterbath in a silica dish and the ascorbic acid removed by ignition. The residue consisting of uranium (VI) oxide was dissolved in 10ml 5N hydrochloric acid and this solution again evaporated to dryness on a waterbath. The residue was then dissolved in a few ml 1N hydrochloric acid and the uranium quantitatively determined as oxinate (11).

The results given in table 3 show that uranium can be quantitatively separated from iron. To determine the iron in the effluents an aliquot was taken and the iron (III) precipitated as cupferronate after adding the required amount of hydrochloric acid and a few drops hydrogen peroxide. The iron cupferronate was ignited and the iron weighed as Fe_2O_3.

The method is already in use in our laboratories as an exercise for the separation of different cations with ion exchangers. A fresh resin bed is used for each experiment.

10. SUMMARY

A simple, rapid, and quantitative ion exchange method has been developed, which permits the separation of microgram as well as milligram quantities of uranium as a negatively charged ascorbate complex, from a large number of cations and anions by means of the strongly basic anion exchanger "Amberlite IRA-400" (ascorbate).

This method is applicable following ether extraction or it may be applied directly, and because of the extremely high capacity of the ion exchanger used for the uranyl ascorbate complex, it is possible to determine uranium in materials whose uranium content is 0.0001 to 0.1% higher.

TABLE 1

EFFECTS OF CATIONS AND ANIONS ON THE DETERMINATION OF URANIUM

CATIONS

CATIONS	COMPOUND	QUANTITY IN mg.	μg. URANIUM	% RECOVERED URANIUM	REMARKS
Fe^{3+}	chloride	125	4.8	101	
Th^{4+}	nitrate	12	4.8	–	Was retained
rare earth	oxide mixtures	100	4.8	98	
Co^{2+}	nitrate	10	4.8	95	
Ni^{2+}	sulphate	10	4.8	105	
Al^{3+}	sulphate	50	4.8	93	
Mg^{2+}	nitrate	50	4.8	102	
Ca^{2+}	nitrate	1000	9.6	100	
V^{5+}	vanadate	10	4.8	–	Retained as a green complex.
Mo^{6+}	molybdate	10	4.8	–	Retained as a grey green complex.
As^{3+}	oxide	20	4.8	97	
Cu^{2+}	sulphate	10	4.8	100	Brown residue on the column.
Cr^{3+}	sulphate	20	4.8	102	
Bi^{3+}	chloride	10	4.8	104	Forms a yellow positively charged complex.
Zr^{4+}	oxychloride	10	2.4	–	Was retained.
Mn^{2+}	nitrate	10	2.4	100	
Pb^{2+}	nitrate	1	2.4	101	
W^{6+}	tungstate	10	2.4	–	Retained as a grey green complex.
Ti^{4+}	oxysulphate	10	2.4	–	Retained as a red complex.
Zn^{2+}	sulphate	10	2.4	97	

ANIONS

ANION	COMPOUND	QUANTITY IN mg.	μg. URANIUM	% RECOVERED URANIUM
nitrate	calcium nitrate	1000	9.6	100
sulphate	ammonium sulphate	1000	9.6	104
fluoride	sodium fluoride	10	9.6	100
phosphate	phosphoric acid	1	9.6	98
chloride	sodium chloride	1000	9.6	97
,,	,, ,,	1000	1000.0	104
,,	,, ,,	3000	9.6	100
,,	,, ,,	3000	1000.0	105
,,	,, ,,	5000	9.6	98
,,	,, ,,	5000	1000.0	50

TABLE 2

RESULTS OF URANIUM ANALYSIS OF DIFFERENT MATERIALS

Type of Sample	μg. uranium/g found
Coal ash 1*	195.1
,, 2	495.0
,, 3*	500.0
,, 4	95.5
,, 5*	1400.0
Slate	65.0
Powdered rock 1*	936.0
2*	728.0
3*	692.0

TABLE 3

EFFECT OF IRON ON THE URANIUM DETERMINATION

mg. Uranium Taken	mg. Fe Taken	Mg. Uranium Recovered	mg. Fe Recovered
9.99	50.5	9.98	50.3
19.98	100.0	20.01	100.3
21.96	120.5	21.80	119.5
24.84	760.0	24.52	759.1

LITERATURE REFERENCES

1. M. Susic, J. Gal and E. Cucker, Analyt. Chim. Acta 11, 586, (1955).
2. I.J. Gal, Bull. Inst. Nuclear Sci. "Boris Kidrich" 6, No. 110, 173 (1956). (Laboratory of physical chemistry, Belgrade).
3. I.J. Gal, International Conference on the peaceful uses of Atomic Energy, Geneva, 1955, A/Conf. 8/P/966.
4. E. Hahoffer and F. Hecht, Mikrochim. Acta (Wien) 1954, 412.
5. F. Hecht, J. Korkisch, R. Patzak and A. Thiard, Mikrochim, Acta (Wien) 1956, 1283.
6. J. Korkisch, M.R.Zaky and F. Hecht, Mikrochim. Acta (Wien) 1957, 435.
7. O. Samuelson, Ion exchangers in analytical chemistry, New York: Wiley; Stockholm; Almqvist and Wiksell. 1953. S.95.
8. D.N.Hume and W.E.Harris. Ind. Eng. Chem. Analyt. Ed. 15, 465, (1943).
9. J. Korkisch Dissertation, Universität Wien, 1957.
10. J. Korkisch, A. Thiard and F. Hecht, Mikrochim. Acta (Wien) 1956,1422.
11. F. Hecht and W. Reich – Rohrwig. Mh. Chem. 53/54, 596 (1929)

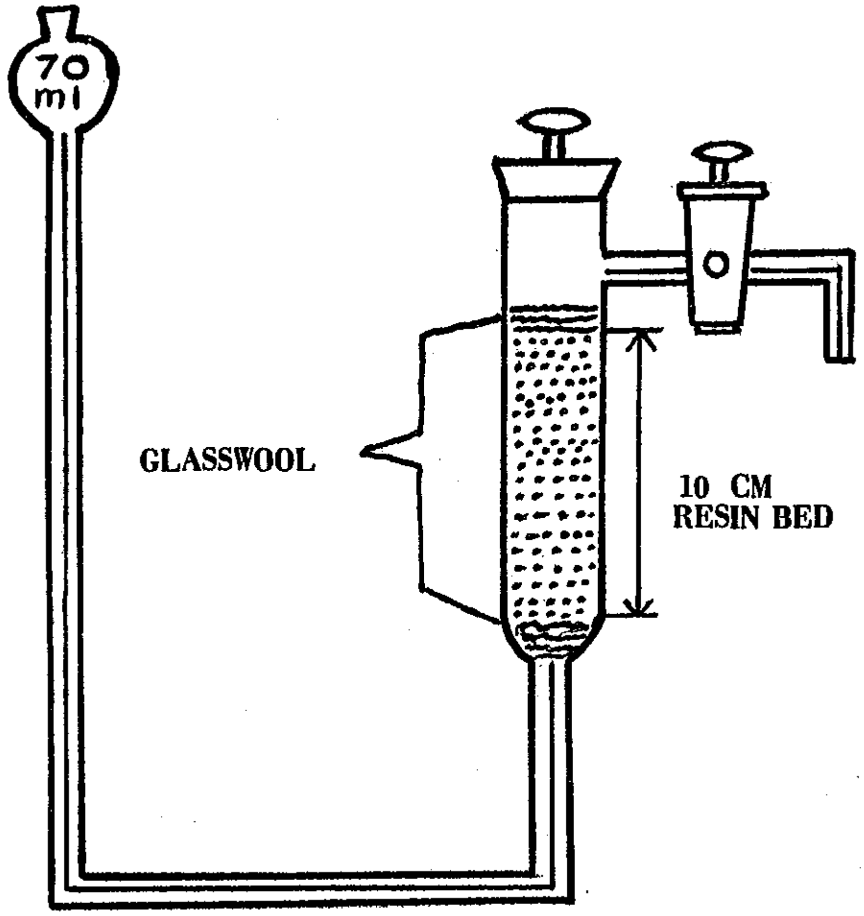

FIG.1. ION EXCHANGE COLUMN