A Rapid Method for the Determination of Uranium

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A method is given for the determination of uranium in solutions with a low concentration of uranium and a high concentration of iron, aluminium, magnesium and sulphate. The uranium is selectively adsorbed from sulphate solutions at $\text{pH} = 2$ by a strongly basic anion exchanger, *e.g.* Dowex 2, in sulphate form. The influence of pH, sulphate concentration and valence state of uranium was studied.

The adsorbed uranium is eluted with dilute hydrochloric acid and determined spectrophotometrically.

The spectrophotometric method using sodium hydroxide and hydrogen peroxide for the uranium determination has been modified to give accurate results even in the presence of certain amounts of iron.

A method has been developed by which a determination of uranium in aqueous solutions containing down to 0.001 % U together with a number of other metal ions can be made in $1\frac{1}{2}$ —2 hours. The method has been used as a routine method in the central analytical laboratory of AB Atomenergi, Stockholm, Sweden, for the last few years with satisfactory results.

The method is based on the fact that, when a solution containing uranium sulphate passes through a column of a strongly basic anion exchanger, *e.g.* Dowex 2, the uranium is selectively adsorbed by the ion exchanger. The adsorbed uranium can be eluted by different agents and determined by a suitable method.

The spectrophotometric determination of uranium in a solution of NaOH and H_2O_2 ¹ proved to be satisfactory in this case. By following the procedure given below, moderate concentrations of iron, chromium, vanadium, molybdenum, manganese and phosphate do not interfere.

The degree of adsorption of hexavalent uranium on a strongly basic anion exchanger from a solution containing sulphate is dependent on the hydrogen ion concentration and the concentration of the sulphate. (Figs. 1 and 2.) A quantitative adsorption from a solution of uranyl sulphate is obtained, when the pH of the solution is higher than about 1.2. In the presence of a concentration of 200 g NaHSO_4 /litre, a quantitative adsorption of the uranium occurs when the pH is about 2 or higher. A practical upper limit for the useful pH-

Fig. 1. The influence of pH on the adsorption of uranium. A 20 ml column of Dowex 2 in sulphate form was used. Grain size: 0.2–0.4 mm. Flow rate: 4–5 ml/min. Curve A: 248 mg uranium (VI) as sulphate in aqueous solution + H_2SO_4 for the adjustment of pH. Volume of solution: 65 ml. Curve B: 248 mg uranium (VI) as sulphate in aqueous solution + 16 g Na_2SO_4 + H_2SO_4 for the adjustment of pH. Volume of solution: 65 ml.

Fig. 2. The influence of the concentration of Na_2SO_4 on the adsorption of uranium (VI) at pH = 1. A 20 ml column of Dowex 2 in sulphate form was used. Grain size: 0.2–0.4 mm. Flow rate: 4–5 ml/min. Aqueous solutions of 248 mg uranium (VI) as sulphate + varying amounts of Na_2SO_4 + H_2SO_4 for the adjustment of pH. Volume of solution: 65 ml.

range is about 4, above which precipitation phenomena take place. Since those solutions, which are subject to routine determinations of uranium and for which the present method was developed, contain a concentration of sulphate equivalent to about 200 g NaHSO_4 /l, pH equal to 2 was chosen for the preliminary experiments on the adsorption of uranium.

Uranium(IV) is not adsorbed quantitatively from a sulphate solution under those conditions which secure a quantitative adsorption of uranium (VI), (Fig. 3).

The presence of chloride ion decreases the adsorption of uranium (Table 1).

The adsorbed uranium is eluted in a suitable manner with dilute hydrochloric acid. As seen from Fig. 4 the volume required for 98 % recovery of the adsorbed uranium is about the same for concentrations of 1 : 20, 1 : 10 and 1 : 5. When hydrochloric acid 1 : 1 was used, 75 ml eluted about 5 % of the adsorbed uranium. Further addition of the latter elutriant effected practically no elution. The residual uranium was retained by the ion exchanger as a chloride complex.

The adsorption of chromium and vanadium, which both severely interfere with the spectrophotometric determination of uranium with NaOH and H_2O_2 ,

Fig. 3. The influence of the concentration of Na_2SO_4 on the adsorption of U(IV) at $\text{pH} = 2$. A 5 ml column of Dowex 2 was used. Grain size: 0.2–0.4 mm. Flow rate: 4–5 ml/min. Aqueous solutions of 9.6 mg U(IV) as sulphate + varying amounts of Na_2SO_4 + H_2SO_4 for the adjustment of pH. Volume of solution: 60 ml.

Fig. 4. The influence of the concentration of HCl on the elution of 248 mg uranium adsorbed on 20 ml Dowex 2, 0.2–0.4 mm, in sulphate form. Flow rate: 4–5 ml/min.

was found to be nil at $\text{pH} = 2$, provided that chromium was present as chromium(III) and vanadium as vanadium(IV). Iron(II) is not adsorbed but iron(III) is partially retained by the ion exchanger. More than 90 % of the trivalent iron passes through the ion exchanger without being adsorbed, when

Table 1. The adsorption of uranium(VI) as sulphate by 20 ml Dowex 2, 0.2–0.4 mm, in sulphate form. Flow rate: 4–5 ml/min. The solutions had a volume of 65 ml, a $\text{pH} = 2$ and contained 248 mg U(VI) and also Na_2SO_4 and NaCl .

g Na_2SO_4	g NaCl	% Uranium adsorbed
15.5	0.4	99.5
15	0.8	98.2
14.5	1.2	96.2
14	1.6	82.0
13	2.5	69.3
12	3.5	58.6
10	4.9	31.2
8	6.6	27.1
6	8.2	20.0
4	9.9	13.0
2	11.5	24.9
0	13.2	26.5

Table 2. The adsorption of iron(III) from sulphate solutions.

mg Fe ³⁺ added	g Na ₂ SO ₄ added	Iron adsorbed	
		mg	%
100	—	22	22
200	—	36	18
300	—	56	19
400	—	51	13
100	6	6	6
200	6	11	6
300	6	18	6
400	6	18	5

the iron solution contains a sulphate concentration about equal to the concentration of sulphate in the solutions in question. (Table 2.) The experiments were made on a column of 20 ml Dowex 2, 0.2—0.4 mm, in sulphate form. The flow rate was 4—5 ml/min. The iron was adsorbed from solutions with a volume of 60 ml, containing sulphuric acid to establish a pH of 2, different amounts of iron(III) sulphate and in some cases 6 g Na₂SO₄. The results obtained are given in Table 2.

Even small amounts of iron interfere in the spectrophotometric determination of uranium using sodium hydroxide and hydrogen peroxide, as seen in Table 3.

It was found that, if the iron present is masked as hexacyanoferrate(II), the interference of the iron on the spectrophotometric determination of uranium, using the sodium hydroxide and hydrogen peroxide method, is eliminated in the case of small amounts of iron and diminished in the case of larger

Table 3. Spectrophotometric determinations of uranium in solutions containing sodium hydroxide, hydrogen peroxide and varying amounts of iron. The determinations were made with a Beckman spectrophotometer model B at 3 900 Å using 5 cm cells.

Added to 50 ml solution mg U	mg Fe	U found mg	Difference %
2.14	0.05	2.23	+ 4.4
2.14	0.10	2.33	+ 8.8
2.14	0.10	2.29	+ 6.8
2.14	0.15	2.35	+ 9.9
2.14	0.20	2.42	+ 13.3
2.14	0.25	2.50	+ 16.7
2.14	0.30	2.57	+ 19.9
2.14	0.30	2.56	+ 19.7
2.14	0.45	2.82	+ 32.0
2.14	0.50	2.86	+ 33.5
2.14	0.75	3.38	+ 57.8
2.14	0.75	3.28	+ 53.3
2.14	* 2.00	3.03	+ 41.4
2.14	* 3.00	2.99	+ 39.5
2.14	* 4.00	2.96	+ 38.5

* The solution was centrifuged before the photometric determination.

Table 4. Spectrophotometric determinations of uranium from solutions containing tartaric acid, potassium cyanide, sodium hydroxide, hydrogen peroxide and varying amounts of iron. The determinations were made with a Beckman spectrophotometer model B at 3 900 Å using 5 cm cells.

Added to 50 ml solution mg U mg Fe		U found mg	Difference %
2.34	0.4	2.34	± 0
2.34	0.6	2.35	+ 0.4
2.34	0.8	2.36	+ 0.9
2.34	1.0	2.36	+ 0.9
2.34	1.2	2.38	+ 1.7
2.34	1.4	2.39	+ 2.1
2.34	1.6	2.37	+ 1.3
2.34	1.8	2.39	+ 2.1
2.34	2.0	2.39	+ 2.1
2.50	0.4	2.50	± 0
2.50	0.6	2.50	± 0
2.50	0.8	2.51	+ 0.4
2.50	1.0	2.51	+ 0.4
2.50	1.2	2.53	+ 1.2
2.50	1.4	2.53	+ 1.2
2.50	1.6	2.54	+ 1.6
2.50	1.8	2.54	+ 1.6
2.50	2.0	2.55	+ 2.0
18.95	4	19.10	+ 0.8
18.95	7	19.03	+ 0.4
18.95	10	19.22	+ 1.4
18.95	13	19.35	+ 2.1
18.95	15	19.78	+ 4.4
18.95	18	19.86	+ 4.8

amounts of iron. Experiments were carried out to test the masking effect. Tartaric acid was first added to solutions containing hexavalent uranium and varying amounts of trivalent iron, followed by additions of potassium cyanide, sodium hydroxide and hydrogen peroxide. The latter reduces the hexacyanoferrate(III) to hexacyanoferrate(II). Results are to be found in Table 4.

EXPERIMENTAL

The apparatus used for the separation of uranium is of a common type. It can accommodate 5 ml of the ion exchange resin. The diameter of the column is 10 mm.

Aqueous solutions

Hydrochloric acid:	1 : 10
Sodium sulphate:	10 %
Sulphosalicylic acid:	10 %
Sodium dithionite (hyposulphite):	2.5 %
Sodium hydroxide:	50 %
Sodium hydroxide:	5 %
Iodine:	0.1 N containing 25 g KI per litre
Tartaric acid:	25 %
Potassium cyanide:	20 %
Hydrogen peroxide:	4 %

Procedure

The ion exchanger consisting of 5 ml Dowex 2, grain size 0.1–0.2 mm, is washed with HCl 1 : 10 until 45 ml of the effluent gives a blank only slightly higher than that obtained from 45 ml of the acid itself. The ion exchanger is then transformed into the sulphate form by washing with 25 ml of the sodium sulphate solution.

The solution taken for an analysis may contain 1–20 mg of uranium. Its volume ought not to exceed 50 ml and the stoichiometric concentration of SO_4 ought not to exceed 75 mg per ml.

The pH of the test solution is adjusted to 1–1.5 and thereafter 0.25 ml of sulphosalicylic acid is added. The solution is heated to about 40° C and sodium dithionite is carefully added until the red colour disappears. Another suitable reducing agent can alternatively be used. The solution is boiled 2–3 minutes and allowed to stand 5 minutes to cool. Four ml of the iodine solution is then added to ensure that the uranium is quantitatively present in the hexavalent state. The small percentage of iron simultaneously reoxidized does practically not interfere.

The solution is boiled for 1–2 minutes to expel the excess of iodine and cooled. The pH is then adjusted to 1.9–2.1 with 5 % sodium hydroxide. If the concentration of sulphate exceeds the above-mentioned value, an appropriate volume of water is added. The solution is now passed through the anion exchanger. After complete percolation the ion exchanger is washed twice with 25 ml water. The uranium is then eluted with 45 ml hydrochloric acid. When performing routine analyses it is practical to work with about twenty ion exchanger columns simultaneously.

If a rapid determination is desired the percolation and the washing can be accelerated by suction, which must be so regulated that the time of percolation is not shorter than 5 minutes. The elution must be carried out without suction.

The solution containing the eluted uranium is evaporated to 20–25 ml. In turn 2 ml tartaric acid, 2 ml potassium cyanide, 6 ml 50 % sodium hydroxide and 3 ml hydrogen peroxide are mixed with the solution. The mixture is then heated till bubbles of oxygen appear, cooled to room temperature, transferred to a 50 ml measuring flask and diluted to the mark with distilled water.

Table 5. Comparison of results of uranium determinations in test solutions according to the ion exchange method and the continuous ether extraction method.

Uranium added mg	Ion exchange method Uranium found mg	Difference %	Extraction method Uranium found mg	Difference %
7.27	7.24	– 0.4	7.08	– 2.6
7.27	7.18	– 1.2	7.08	– 2.6
7.27	7.27	± 0.0	7.15	– 1.7
7.27	7.12	– 2.2	7.13	– 1.9
7.27	7.28	+ 0.1	7.12	– 2.1
7.27	7.23	– 0.6	7.15	– 1.7
7.27	7.18	– 1.2	—	—
7.27	7.33	+ 0.8	—	—
7.27	7.24	– 0.4	—	—
7.27	7.24	– 0.4	—	—
0.727	0.730	+ 0.4	0.742	+ 2.1
0.727	0.790	+ 8.7	0.727	± 0.0
0.727	0.768	+ 5.6	0.663	– 8.8
0.727	0.790	+ 8.7	0.685	– 5.8
0.727	0.768	+ 5.6	0.663	– 8.8
0.727	0.830	+ 14.2	0.685	– 5.8
0.727	0.730	+ 0.4	0.709	– 2.5
0.727	0.790	+ 8.7	0.682	– 6.2

Table 6. Comparison of results of uranium determinations by the ion exchange method and the continuous ether extraction method.

Uranium concentration found	
Ion exchange method g/l	Extraction method g/l
0.006	0.006
0.026	0.022
0.034	0.032
0.054	0.053
0.069	0.068
0.116	0.119
0.148	0.141
0.184	0.181
0.196	0.193
0.291	0.287
0.296	0.289
0.306	0.302
0.364	0.363
0.370	0.360
0.414	0.406
0.457	0.450
2.63	2.58
2.83	2.77

In a Beckman spectrophotometer model B the extinction at 3 900 Å is determined for this solution.

Of the hydrochloric acid 45 ml are taken and evaporated to 20–25 ml and treated in exactly the same manner as the test solution. The resulting solution is used as reference in the spectrophotometric determination of uranium.

The method was tested on two especially prepared solutions, and the results compared with the results obtained according to a continuous ether extraction method² combined with the above spectrophotometric method of determining uranium. One litre of each solution contained 15.5 g Fe²⁺, 1.5 g Fe³⁺, 11 g Al, 5 g Mg, 3.5 g K, 0.1 g V and 0.005 g Cr, all as sulphates, together with 55 g H₂SO₄ and 6 g Na₂HPO₄. The solutions thus contained a stoichiometric concentration of 170 g/l SO₄. One solution contained 0.290 g/l uranium(VI) as sulphate and the other 0.0145 g/l uranium(VI) as sulphate. The results obtained are given in Table 5.

From the first solution 25 ml were taken for every analysis, corresponding to 7.27 mg U. The ion exchange method gave on the average an error of –0.6 % and the continuous ether extraction method –2.1 %.

From the second solution 50 ml were taken for every analysis corresponding to 0.727 mg U. The ion exchange method showed on the average a positive error, namely + 6.5 %. On the other hand the continuous ether extraction method yielded on the average a negative error, –4.8 %.

In the latter case, where the concentration of iron was 17 g/l and that of uranium 0.0145 g/l, there were 1 170 times as much iron as uranium in the solution, and the amount of iron adsorbed by the ion exchanger was larger

than the total amount of uranium in the solution taken for an analysis. The ratio between the concentrations of iron and uranium in the eluate would thus be unfavourable for the spectrophotometric determination of uranium (*vide supra*), and positive errors were to be expected.

A number of solutions, *e.g.* obtained at research work, containing different concentrations of uranium, was analysed by the ion exchange method and by the continuous ether extraction method combined with the spectrophotometric determination of uranium. Table 6 shows some results.

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