UNCLASSIFIED

AAEC/E.19.

A NEW ION EXCHANGE METHOD FOR THE DETERMINATION OF URANIUM IN PHOSPHATE ROCKS, COAL ASHES, BAUXITES ETC.

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CONTENTS

1. INTRODUCTION

The determination of microgram quantities of uranium in phosphate rocks by a single separation process, in the presence of large quantities of the cations iron (III), aluminium, calcium, magnesium etc. was, until recently, a difficult micro-analytical problem. It was thought possible under certain conditions to determine uranium quantitatively in phosphate rocks, with the earlier published method for rapid determination of uranium (6) by carrying out a single column process, using the strongly basic anion exchanger "Amberlite" IRA–400 (NO_3–). A critical study of this method proved however, that an accurate uranium determination with reproducible values was only possible with materials low in phosphate.

For this reason and to avoid the ether extraction of uranium (E. Hahoffer and F. Hecht (1), the following method was developed for rapid and quantitative determination of microgram quantities of uranium in phosphate rocks, etc. The uranium is retained by the strongly basic anion exchanger "Amberlite" IRA–400 (Cl^-) as a negatively charged uranium (VI) chloride complex from a 4N hydrochloric acid solution, which contains ascorbic acid. The ions present in the sample, such as the alkaline metals, the alkaline earth metals, aluminium, chromium etc., and large quantities of phosphoric acid do not interfere with the column process, as they are generally not absorbed on the exchanger. Ferric ions present are converted to the bivalent state (Ferrous) with ascorbic acid so efficiently, that after rinsing the resin with 4N hydrochloric acid containing ascorbic acid, the effluent contains only a small amount of iron. The extract of the next elution of the uranium with 1N hydrochloric acid contains still less bivalent iron. The quantitative separation of uranium from iron can be carried out within the limits of the ratio Uranium:Iron = 1:10,000. The separation of phosphoric acid and the abovementioned cations, present at the same time, takes place quantitatively within any arbitrary ratio.

The following method, developed in our laboratories (2,4,5,6), presents therefore a valuable supplement to the enrichment and separation method for microgram and milligram quantities of uranium.

The final determination of uranium was done polarographically using the catalytic nitrate wave, and in some cases fluorimetrically (see table 4).

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 (7).

B. Standard uranium solutions : 20ml of a strong nitric acid uranyl nitrate solution, containing 0.9994 mg uranium/ml, standardised with 8-hydroxyquinoline, were diluted to 100ml with distilled water; 1ml ≈ 199.8 µg uranium 3ml of this solution was diluted to 250ml with 0.01N nitric acid (A.R.); 1ml ≈ 2.39 µg uranium.

C. Solutions of other elements: Standard solutions of a large number of elements were needed.

D. Ascorbic acid: Pure ascorbic acid from the "Wiener" pharmaceutical factory was used.

3. APPARATUS

The separation processes were carried out with ion exchange columns having dimensions as stated in our earlier publications (2,4,6). The polarograph used in the final quantitative determination of uranium, the accurate measurement conditions and the evaluation of the polarogram are also published in earlier reports (2,3,4,5). The fluorimeter used for the fluorimetric determination of uranium is fully discussed in another article(8).

4. EXPERIMENTS ON SEPARATION OF URANIUM FROM PHOSPHORIC ACID AND IRON WITH DIFFERENT HYDROCHLORIC ACID CONCENTRATIONS

5ml of a ferric chloride solution (100 mg Fe) and 1g ammonium hydrogen phosphate together with 4ml. of a standard uranium solution, containing 2.39 μg uranium/ml., were evaporated to dryness on a waterbath. The residue was dissolved in 100ml. 5N hydrochloric acid while gently warming; this solution was cooled to room temperature and within one hour treated with portions of ascorbic acid to reduce the iron until the colour of the solution did not change. 5g ascorbic acid was necessary for this treatment. The fairly dark yellow solution, (unreduced ferric ions, existing as ferric chloride complex), was run through the resin bed, which was pretreated with 50ml 5N hydrochloric acid solution containing ascorbic acid. The resin was rinsed with 100ml 5N hydrochloric acid containing ascorbic acid after the adsorption was finished.

The uranium was then extracted with 100ml 1N hydrochloric acid. 10ml of this extract was evaporated to dryness in a silica dish on a waterbath. The residue was ignited to remove the ascorbic acid and after cooling the dish the residue was dissolved in 10ml 4N hydrochloric acid and this solution evaporated again to dryness on a waterbath. Polarographic measurements were carried out and the uranium was found to be quantitatively recovered.

The extract contained many ferric ions, owing to the incomplete reduction of ferric to ferrous chloride in the adsorption solution, but no trace of phosphoric acid. Using 4N hydrochloric acid, the quantity of iron in the extract was so low that the separation of uranium from iron was then practically quantitative. When phosphoric acid was absent, the uranium could be recovered quantitatively and without interference. Similar experiments with 3N, 1N and 0.1N hydrochloric acid showed, that while in these cases the iron (iii) was completely reduced, 25% of the uranium was adsorbed on the exchanger with 3N and none at all with 1N and 0.1N hydrochloric acid. To determine if an increase in the chloride concentration improved the adsorption of the uranium chloride complexes on the exchanger, the 3N, 1N and 0.1N hydrochloric acid solutions were saturated with ammonium chloride and three similar experiments were carried out.

The results of these experiments showed that the uranium was retained by the exchanger for 74, 63 and 60% respectively from the ammonium chloride saturated 3N, 1N and 0.1N hydrochloric acid solutions. All these experiments proved that the best results can be obtained with 4N hydrochloric acid. All following experiments were carried out by using this hydrochloric acid concentration.

5. EFFECT OF CHLORIDE-IONS

The adsorption of uranium (VI) complexes on the exchanger, and the separation of uranium from iron and phosphoric acid in 4N hydrochloric acid which contained various amounts of ammonium chloride was investigated. 100 μg uranium, 100mg iron and 1g ammonium hydrogen phosphate was used in these experiments, which were done in a similar manner to the tests mentioned previously. Ammonium chloride was added to the five 4N hydrochloric acid solutions giving respectively, nil ¼, ½, ¾ and completely saturated solutions. The uranium was recovered quantitatively in all cases. The adsorption solution was slightly yellow when using 4N hydrochloric acid without ammonium chloride. The colours of the solutions with ammonium chloride were more distinct. These experiments proved again, that iron was not present in sufficient quantities, after the separation of uranium from iron and phosphoric acid, to interfere with the polarographic determination, when using 4N hydrochloric acid without ammonium chloride. The interference of iron, which occurred in the experiment of the uranium determination in the extract with 4N hydrochloric acid (saturated with ammonium chloride), was relatively small, yet greater than in all other experiments. To get a complete separation of uranium from iron, the adsorption solution should not be stronger than 4N with respect to hydrochloric acid and contain the smallest amount of chloride ions. It is advisable to decompose 0.5g or less of the sample with only 5-6 times this quantity of soda, to restrict the increase of the chloride concentration when separating the silicic acid with hydrochloric acid.

6. DETERMINATION OF THE ADSORPTION CAPACITY OF THE ION EXCHANGE COLUMNS

The procedure quoted in section 8 (ii), was carried out with uranium concentrations of 100-200 μg in 100ml. adsorption solution, in the presence of 100mg iron and 1g ammonium hydrogen phosphate. The flowrate was 0.75ml/min. The results of this experiment are shown in fig. 1. From fig. 1 it can be seen that up to 400 μg uranium can be quantitatively adsorbed on the exchanger.

7. INTERFERENCE OF FOREIGN IONS

Large quantities of the ions Mo^{6+}, W^{6+}, Sn^{4+}, NO_3^- interfere with the column process and with the final polarographic determinations of uranium as shown in table 1. In these cases the method cannot directly be applied and the uranium must first be extracted with ether (E. Hahoffer and F. Hecht (1) and separated from these ions by methods which we have recently published (2,4).

The interfering ions can displace the uranium from the column or make final polarographic determination impossible. No interference occurred in our tests of phosphate rocks (see table 2) and other materials (see table 3). The interference of tungsten on the catalytic nitrate wave gave a characteristic curve and such a curve is shown in fig. 2 to make this clear. The small preliminary stage shows the start of the uranium wave. The catalytic nitrate wave of the tungsten overlaps this and indicates too great a quantity of uranium. When this curve is compared with the uranium curve of the analysed phosphate rocks, coal ashes, etc., (see fig. 3), the difference is quite clear.

When curves are obtained similar to the one in fig. 2 or completely different from the one in fig. 3 (a tendency is not important), without visual differences in the column, the uranium must be determined fluorimetrically or an ether extraction must precede the column process.

8. PROCEDURE

(i) Decomposition of sample

0.5g or less of the material is decomposed with 2.5-3g anhydrous sodium carbonate in a platinum crucible. After destruction of the carbonates with 4N hydrochloric acid evaporate the solution in a large porcelain dish to complete dryness on the waterbath. The residue is dissolved two or three times in a few ml 4N hydrochloric acid and these solutions each time evaporated to dryness.

(ii) Column process

(a) Preparation of the resin bed. The resin is rinsed with 50ml 1N hydrochloric acid and then treated with 50ml 4N hydrochloric acid containing 1g ascorbic acid.

(b) Adsorption procedure. The complete dry residue (from section 1) is dissolved in 50ml 4N hydrochloric acid while slightly warming on the water bath (even better after allowing to stand for some time at room temperature) and the silicic acid filtered off (filter and funnel are rinsed with 4N hydrochloric acid).

The filtered residue is then rinsed with 50ml 4N hydrochloric acid and ascorbic acid added in portions to the filtrate within one hour. In most cases 2g ascorbic acid will be sufficient. The temperature of the filtrate must not be higher than 20°C; the column process must be carried out at a temperature lower than 20°C. The solution is then run through the pre-treated column with a flowrate of 0.75ml/min.

(c) Rinsing of Column. The resin is now rinsed with 50-100ml 4N hydrochloric acid containing 1-2g ascorbic acid depending on the original iron content in the sample.

(d) Extraction of the Uranium. The uranium is then immediately extracted with 100ml 1N hydrochloric acid into a 100ml volumetric flask.

(iii) Quantitative determination of the Uranium

(a) Polarographically. Take an aliquot containing between 10 μg and 0.1 μg uranium from the 100ml extract. Transfer this aliquot to a silica dish and evaporate to dryness on the waterbath. The residue is then ignited to remove the ascorbic acid. After cooling the dish, dissolve the residue in 10ml 4N hydrochloric acid and evaporate again to dryness on the waterbath. Now add 10ml 0.01N nitric acid and determine the uranium quantitatively by using the catalytic nitrate wave (2,4,6). The results of experiments carried out in this manner, are shown in tables 1,2,3 and 4.

(b) Fluorimetrically. When the uranium must be determined fluorimetrically for comparison or for reasons given in section 7, take an aliquot, which contains between 60 μg and 0.5 μg uranium from the 100ml extract and proceed as in section (iii) a. After cooling the dish, rinse the residue with 5ml 4N hydrochloric acid into a platinum crucible and evaporate this solution to complete dryness on the waterbath. Then add to the crucible 5g of a mixture containing sodium carbonate, potassium carbonate and sodium fluoride in the ratio 45:45:10. This mixture is then fused in an electric furnace at 580-650°C (preferable at 640°C) for 20 minutes. After this time take the crucible out of the furnace (taking care to hold it upright) and cool completely to room temperature. When the crucible is turned over a fused cake is obtained, similar in shape to the bottom of the crucible. Care should be taken, that all the crucibles used have the same shape and dimensions. The fused cake is kept in a desiccator overnight and the measurements are done the next day. The existing calibration curve is first checked against a blank and standard cakes (which keep for months) and the uranium content of the fused cakes is then derived from this curve. In all cases divert the bottom part away from the photocell (as the impurities sink to the bottom as carbonates).

From the experimental data given in table 2 it can be seen, that this method has given good results with all the samples analysed.

9. SUMMARY

The simple, rapid and quantitative ion exchange method described makes it possible to determine with great accuracy Uranium in phosphate rocks, coal ashes, bauxites, etc., using a single column process. Uranium forms a negatively charged uranium (VI) chloride complex in a 4N hydrochloric acid solution containing ascorbic acid, which is adsorbed quantitatively on the strongly basic anion exchanger "Amberlite" IRA-400 (Cl^-) in contrast with most other elements. After rinsing the resin with 4N hydrochloric acid, which contains ascorbic acid, the uranium is then extracted with 1N hydrochloric acid. The uranium in the extract is determined polarographically using the catalytic nitrate wave (2) or fluorimetrically. Results from this method compare favourably with those from methods in current use.

We wish to express our thanks to Dr. E. Tomic, who assisted us greatly with the preparation of the fluorimetric determination of the uranium, the apparatus, test values and calibration curves.

TABLE 1

INFLUENCE OF FOREIGN IONS ON THE URANIUM DETERMINATION

	ION	QUANTITY OF THE RESPECTIVE IONS mg	URANIUM TAKEN g	URANIUM RECOVERED %
	Ca^{2+}	100	9.56	100
	Mg^{2+}	100	9.56	97
	Mn^{2+}	100	9.56	99
	Al^{3+}	50	9.56	100
	Fe^{3+}	100	9.56	98
	Th^{4+}	10	9.56	100
(x)	W^{6+}	2.5	9.56	198
(xx)	Mo^{6+}	5.0	9.56	–
	V^{5+}	10	9.56	100
	Zn^{2+}	20	9.56	103
	Cu^{2+}	20	9.56	96
	Bi^{3+}	20	9.56	95
	Co^{2+}	10	9.56	100
	Ni^{2+}	10	9.56	94
	Cr^{3+}	10	9.56	101
	Ti^{4+}	10	9.56	93
	Pb^{2+}	20	9.56	95
	Sn^{4+}	10	9.56	–
(o)	Rare earth	100	9.56	100
(oo)	NO_3^-	100	9.56	98
	SO_4^{2-}	500	9.56	100
	F^-	100	9.56	97

(x) The interference of tungsten is shown in fig. 2

(xx) Molybdenum is adsorbed as a yellow coloured complex and extracted partly with 1N HCl.

(o) Oxide mixtures used, as mentioned earlier (2,6).

(oo) 1 or more grammes of nitrate interfere with the column process by reaction with the ascorbic acid.

TABLE 2

URANIUM DETERMINATION IN PHOSPHATES AND SILICATE ROCKS

Material	Results in μg Uranium/g	Results by other methods in μg uranium/g	Difference %
Superphosphate	33.0	32.0	3.0
Superphosphate	46.0	42.0	9.5
North African Ca–phosphate	79.2	85.0	7.3
South African Fe–phosphate	18.0	17.5	2.8
South American Al--phosphate	7.5	7.5	0.0
Silicate–rock Sample 1	13.0	11.5	13.0
” ” ” 2	8.0	8.3	3.0
” ” ” 3	2.0	2.1	5.0
” ” ” 4	1.7	1.5	13.3
” ” ” 5	2.7	2.7	0.0

TABLE 3

URANIUM DETERMINATION IN BAUXITES AND COAL ASHES

Material	Results in μg Uranium/g	Material	Results in μg Uranium/g
Bauxite 1	7.1	Bauxite 8	15.7
” 2	18.5	Coal Ash 1	50.0
” 3	12.3	” ” 2	1500.0
” 4	12.4	” ” 3	3.9
” 5	24.5	” ” 4	6.8
” 6	29.4	” ” 5	9.4
” 7	0.7	” ” 6	92.0

TABLE 4

URANIUM DETERMINATION IN COAL ASHES

Material	μg Uranium/g determined fluorimetrically	μg Uranium/g determined polarographically	Difference %
Coal Ash I	740	736	0.5
" " II	700	680	2.9
" " III	720	681	5.7
" " IV	80	78	2.5
" " V	170	157	8.2

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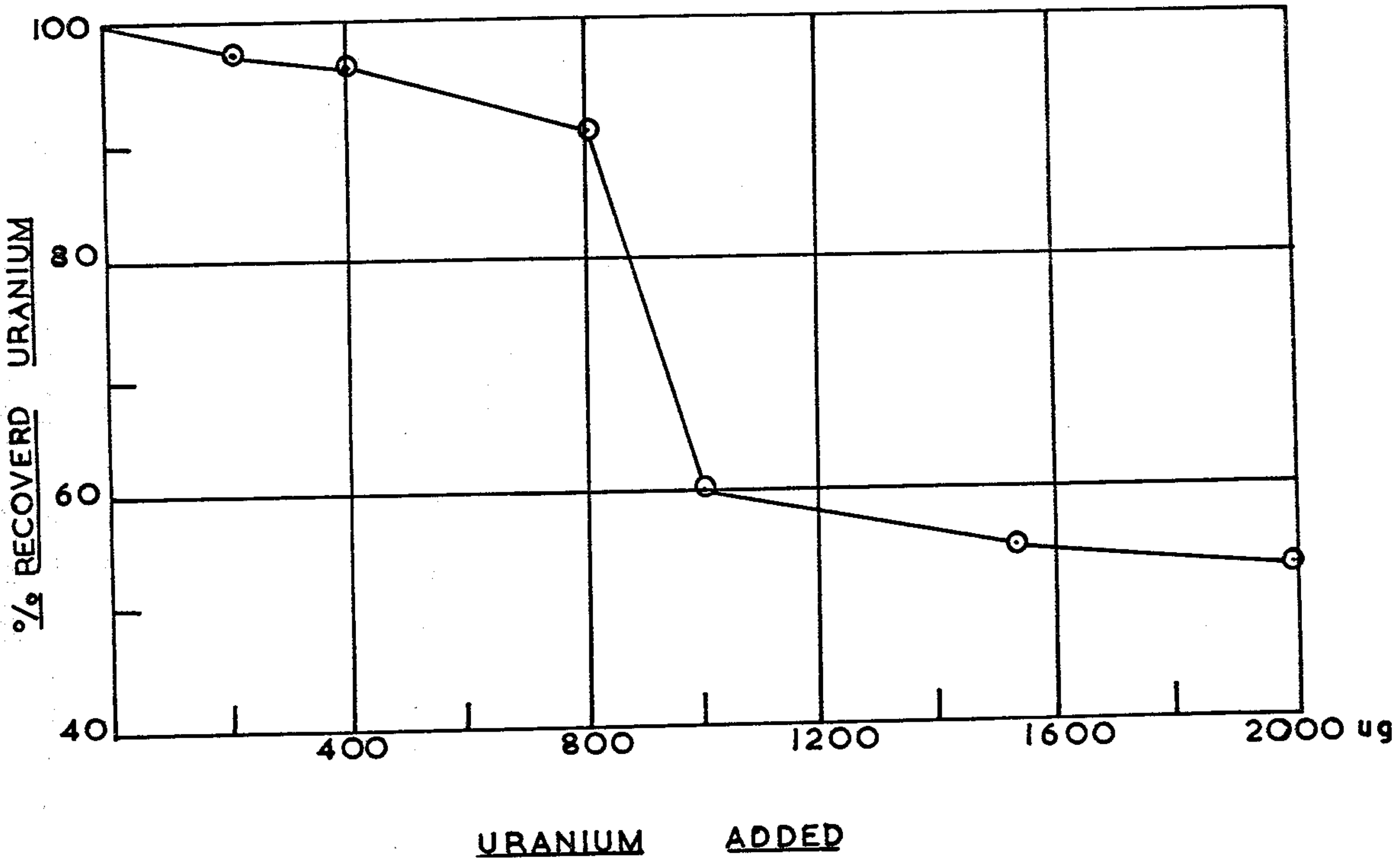

FIGURE 1.

RELATIONSHIP BETWEEN URANIUM QUANTITY ADSORBED ON EXCHANGER AND APPLIED QUANTITY.

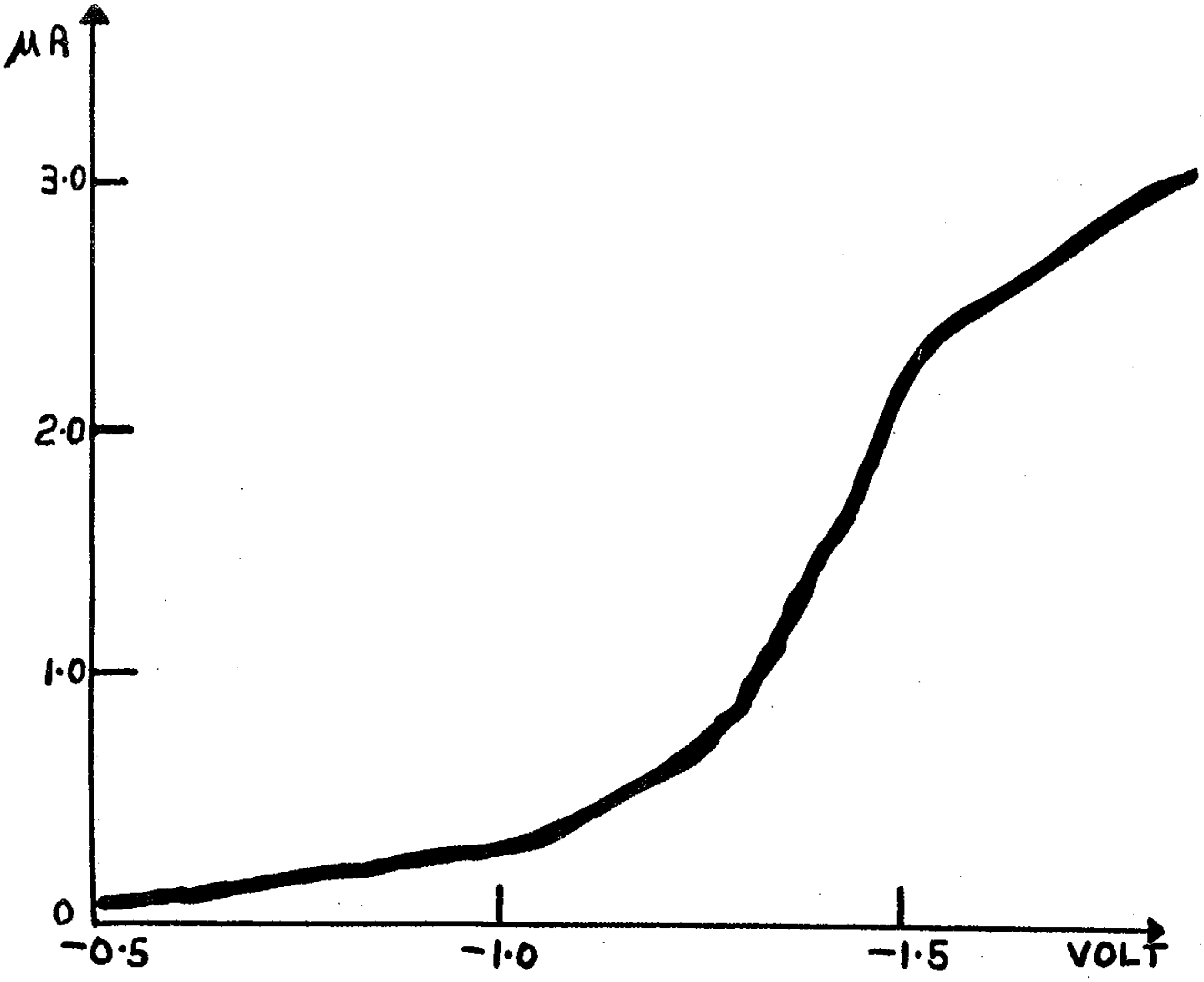

FIGURE 2.

Interference of Tungsten on the polarographic uranium determination.

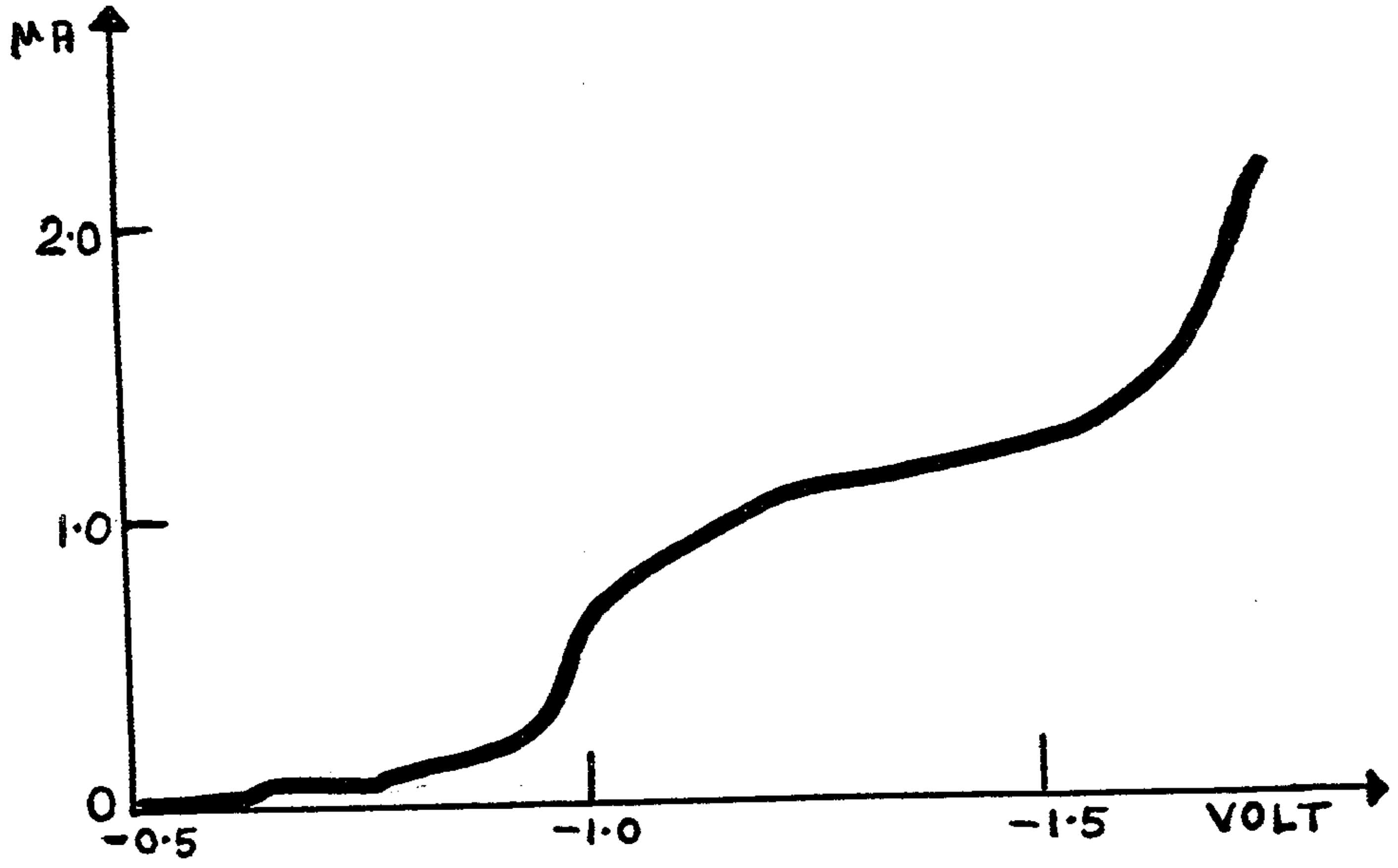

FIGURE 3.

Polarographic uranium determination.