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A SPECIFIC METHOD FOR THE DETERMINATION OF URANIUM IN ORES BY CATHODE RAY POLAROGRAPHY

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Summary

A method is presented for the specific determination of uranium in ores by cathode ray polarography. The uranium is separated by a simple and rapid mercury–cathode electrolysis, then determined polarographically in a base electrolyte in which vanadium, titanium and tungsten do not interfere. Application of the method to the analysis of ten standard uranium ores is shown.

CONTENTS

1. INTRODUCTION

In recent years polarographic procedures have been extensively applied to the determination of uranium in ores. Among the many base electrolytes employed may be mentioned the acid–tartrate method of LEWIS and OVERTON(1, 2,)the acid–oxalate method of LEGGE(3,) and the ascorbic acid method of SUSIC(4.) While some doubt appears to exist regarding the selectivity of these base electrolytes towards uranium(5,)the acid tartrate and the ascorbic acid base electrolytes appear to be the most selective of those available. A systematic study of interferences in these two methods indicated, however, that they may not, in general, be directly applied to the determination of uranium in ores. Considering the low concentrations of uranium frequently present in these ores, and the wide variety of foreign elements associated with uranium, it is usually necessary to separate the uranium from the bulk of the impurities. Vanadium, in particular, interferes seriously in most polarographic determinations of uranium(6, 7, 8,) and is also difficult to completely separate from uranium prior to the determination (9).

The methods most commonly used for the purification of the uranium solution are chromatography (10) solvent extraction(11,)and ion–exchange(12.) Chromatography and solvent extraction suffer from the disadvantage that large amounts of organic solvents are employed which must be completely removed before the polarographic determination. The anion exchange separation of uranium on a strongly–basic resin from dilute sulphate solutions(12)is apparently the most selective available, but difficulty was experienced in this laboratory in obtaining complete recovery and good separation of the uranium at the same time. A mercury cathode separation of uranium appears ideal where a polarographic finish to the determination is contemplated, since a large number of foreign elements are removed, the operation is simple and rapid, and the solution comes in contact only with glass, mercury and platinum. In this paper a procedure is described, using a small mercury cathode cell, which allows the uranium to be separated in less than one hour by the "constant current" electrolysis technique. A base electrolyte has been developed in which elements not removed by the mercury cathode electrolysis, do not interfere in the polarographic determination of uranium. This base electrolyte is considered the most selective yet developed for uranium, and combined with a previous mercury cathode separation, the method appears specific for uranium in ores processed in this country.

2. APPARATUS

A linear–sweep cathode ray polarograph equipped with an electrode stand and constant temperature water bath, from Southern Instruments Computer Division, Surrey, England, was used for the experimental work. This instrument is of the DAVIS type (13,) with a voltage sweep rate of 0.3 volt per second, a sweep time of 2 seconds and a delay period of 5 seconds. A polarographic cell employing a mercury pool anode was used throughout. All polarographic measurements were made at 25°C.

Mercury Cathode Electrolysis Cell. This cell is illustrated in Fig. 1. An aliquot of the solution may be withdrawn from the cell, without interrupting the electrolysis, by means of a pipette inserted through the air–condenser socket. The surface of the mercury may be stirred with a magnetic stirrer, or alternatively, by vibration.

3. REAGENTS

Base Electrolyte Stock Solution. Dissolve the following reagents in demineralised water, and dilute to 1 litre; tribasic ammonium citrate (194g), citric acid monohydrate (84g), ammonium oxalate monohydrate (14.2g), disodium ethylene diamine tetraacetate dihydrate (37g), sodium chloride (5.85g). The chemicals used should be the purest grade available.

This stock solution was purified by controlled-potential mercury cathode electrolysis, using a cell of 1.5 litre capacity(14,)a cylindrical platinum-gauze anode, and a silver-silver chloride reference electrode. The potential of the mercury cathode was maintained by a manually operated circuit at -0.8 v versus the reference electrode for five hours. The purified solution was filtered into a polythene storage bottle.

The pH of this solution should be 4.7 at 25°C.

1.0M Ascorbic Acid. High purity 1-ascorbic acid from C.S.R. Chemicals Pty. Ltd., Sydney, was used for the preparation of this solution. Dissolve 17.6g of ascorbic acid in water and dilute to 100 ml. This solution should be prepared fresh daily.

All other chemicals used were of A.R. quality.

4. PROCEDURE FOR THE DETERMINATION OF URANIUM IN ORES

Weigh a suitable amount of the very finely ground ore directly into a small platinum dish. Add 5 ml of conc. HNO_3 and 5 ml of 50% H_2F_2. Swirl gently, and evaporate the solution just to dryness. Add further 5 ml portions of HNO_3 and H_2F_2 and repeat the evaporation until solution of the ore is complete. Add sufficient 72% $HClO_4$ to make the sample solution, when diluted to volume, 0.1 N in $HClO_4$. Heat to fumes of $HClO_4$ for a few minutes, then cool and dilute to volume with water in a volumetric flask. The sample solution should be between 10^{-5} and 2×10^{-4} molar in uranium.

Transfer about 15 ml of solution to the mercury cathode cell. Electrolyse at 6 - 9 V (1.5 a) for 40 - 60 min. Remove the air condenser and withdraw a 5 ml aliquot of the solution while electrolysis is still proceeding. Transfer to a small, dry, stoppered flask and cool under a tap to room temperature. Pipette a 2 ml aliquot into a 10 ml volumetric flask. Add 2 ml of 1.0M ascorbic acid, one drop of 5 M NaOH, and mix. Add 5 ml of the base electrolyte stock solution and dilute to volume with water. Immediately transfer about 3 ml of this solution to a polarographic cell and pass nitrogen gas through the solution at a slow rate for 5 - 10 min. Using a start potential of zero volts, measure the peak current occurring at about -0.28 V v.Hg pool anode. Under the same conditions record the peak current due to a standard uranyl perchlorate solution of approximately the same concentration as the unknown. After correction of the results for residual current, which should be less than 0.01 μa, the uranium content of the ore may be calculated.

5. THE MERCURY CATHODE SEPARATION

Using the cell, and the procedure described, it was found that large amounts of copper, iron, molybdenum, tin and other metals could be removed from the solution in less than 30 min. It is interesting to note that if the uranium concentration is kept below 5×10^{-4}M no net reduction of uranium occurs during the electrolysis in 0.1N $HClO_4$. This phenomenon does not occur with dilute uranium solutions in 0.1 N H_2SO_4 nor with more concentrated uranium solutions in 0.1 N $HClO_4$. Here considerable reduction occurs during electrolysis, and the solution must be reoxidised before the polarographic determination is carried out. It is believed the presence of a small amount of oxidising agent, e.g. chlorine formed by the decomposition of some perchloric acid, is sufficient to reoxidise the dilute uranium solution.

6. COMPOSITION OF THE BASE ELECTROLYTE

Of the elements which remain in solution with uranium after a mercury cathode electrolysis, vanadium, titanium and tungsten are most likely to interfere in the subsequent polarographic determination of uranium. The interference of vanadium has been shown(6)to be partly due to oxidation of pentavalent uranium by tetravalent vanadium.

$$UO_2^{+} + VO^{+2} + 2H^{+} = UO_2^{+2} + V^{+3} + H_2O$$

The regenerated uranyl ions are then available for further reduction, leading to erroneously high diffusion currents. Since considerable amounts of vanadium are commonly encountered in uranium ores, this interference is serious. Many previously published base electrolytes for uranium were investigated, but none could tolerate even moderate amounts of vanadium.

It is known(15,16) that vanadium, particularly VO^{+2} and V^{+3}, forms strong complexes with ethylenediamine tetraacetic acid (E.D.T.A.). In a base electrolyte consisting of ascorbic acid and E.D.T.A. no reduction wave for vanadium is evident, and vanadium up to 200 times the uranium concentration may be present before interference occurs. This base electrolyte is quite selective towards uranium, but unfortunately even small amounts of titanium interfere. By adding citric acid and maintaining the pH at 4 –5, the titanium reduction wave is shifted to a very negative potential, and an ascorbate – E.D.T.A. – citrate base electrolyte will tolerate large concentrations of titanium. In this medium, however, a double uranium wave is obtained, the first wave representing the reduction of the uranyl ion to the pentavalent state, and the second wave, occurring at a slightly more negative potential, is probably due to disproportionation of the pentavalent uranium.

$$UO_2^{+2} + e = UO_2^{+} \qquad (1)$$

then $$2\,UO_2^{+} + H^{+} = UO_2^{+2} + UO(OH)^{+} \qquad (2)$$

By adding a small amount of ammonium oxalate, a single uranium wave is again obtained, its height being equal to the sum of the two previous waves. The oxalate ion forms strong complexes with both hexavalent and tetravalent uranium(17,) and apparently accelerates reaction (2).

The final composition of the base electrolyte is then:

0.2M ascorbic acid, 0.4M ammonium citrate, 0.2M citric acid, 0.05M ammonium oxalate, 0.05M E.D.T.A. and 0.05M sodium chloride. The sodium chloride is added to enable a mercury–pool anode to be used.

While this base electrolyte is admittedly complex, this is no disadvantage, as the constituents, with the exception of ascorbic acid, are stable and compatible, and a concentrated stock solution may be prepared and stored indefinitely. Small variations in the composition of the base electrolyte do not affect the determination. If the uranium concentration is below 10^{-4}M, a particularly well–formed wave is obtained with a very flat base line (Fig. 2). With larger amounts of uranium the wave becomes drawn out and ill defined.

7. STUDY OF INTERFERENCES

Table 1 shows the effect of diverse ions in the ascorbate, acid–tartrate, and the citrate–oxalate–E.D.T.A.–ascorbate ("mixed") base electrolytes for the determination of uranium using a Cathode Ray polarograph and a Hg–pool anode.

The 1M H_2SO4, 0.05M sodium tartrate base was prepared as directed by SHALGOSKY(2) (no maximum suppressor), and the ascorbate base was 0.5M ascorbic acid containing 0.05M sodium chloride and adjusted to pH 3.7. The final solutions contained 8 x 10^{-4}% uranium, and 8 x 10^{-2}%, 8 x 10^{-3}%, 8 x 10^{-4}% and 8 x 10^{-5}% respectively of the particular element for the concentration levels 100 : 1, 10 : 1, 1 : 1 and 0.1 : 1 element to uranium. The table shows the concentration level at which interference ($>$ 2% error in peak current) first occurs.

Whenever possible the foreign elements were added as the perchlorates, prepared by solution of the element or its oxide in perchloric acid.

It may be seen from the table that Bi^{+3}, Cr^{+6}, Cu^{+2}, Fe^{+3}, Mo^{+6}, Sn^{+6}, Sn^{+2}, Ti^{+4}, V^{+5} and W^{+6} interfere seriously in the acid–tartrate method. Using the ascorbate base electrolyte at pH 3.7, Bi^{+3}, Cu^{+2}, Mo^{+6}, Pb^{+2}, Sn^{+2}, Te^{+6}, Tl^{+1}, V^{+5}, and W^{+6} interfere seriously. With the "mixed" base Cr^{+6}, Cu^{+2}, Fe^{+3}, Mo^{+6}, Sn^{+2} and Tl^{+1} interfere. Tungsten does not interfere if it is less than 50 times the uranium concentration. If more than 5 mg of aluminium is present in the final solution a double wave is obtained, presumably due to the removal of oxalate ions by Al^{+3}. While iron is reduced completely by ascorbic acid, on the addition of the base electrolyte a ferric wave gradually reappears. This is probably due to the formation and oxidation of a ferrous – E.D.T.A. complex, which is known to be very rapidly oxidised by air(18.)

In addition to the cations shown, the "mixed" base electrolyte was found to be unaffected by large amounts of sulphate, chloride, nitrate and phosphate.

8. COMPARISON OF BASE ELECTROLYTES

Table 2 compares the peak potentials and sensitivities of the acid–tartrate, ascorbate and "mixed" base electrolytes at a uranium concentration of 2×10^{-5}M. It is seen that at the uranium concentration used, the "mixed" base electrolyte is somewhat more sensitive than the other two.

TABLE 1

Interference of diverse cations in the ascorbate, tartrate and "mixed" base electrolytes for the determination of uranium. Showing the concentration level, 100:1, 10:1, 1:1 or 0.1 : 1 corresponding to foreign element: uranium, at which interference first occurs. Uranium conc. in all cases 8 x 10^{-4}%.

ION	ASCORBATE	TARTRATE	"MIXED"
Al^{+3}	nil	nil	nil **
As^{+3}	nil	nil	nil
Bi^{+3}	1:1	10:1	nil
Ca^{+2}	nil	nil	nil
Cd^{+2}	nil	nil	nil
Ce^{+4}	nil	nil	nil
Co^{+2}	nil	nil	nil
Cr^{+6}	nil	1:1	10:1
Cu^{+2}	1:1	0.1 : 1	0.1 : 1
Fe^{+3}	nil	10:1 *	10:1
Mg^{+2}	nil	nil	nil
Mn^{+2}	nil	nil	nil
Mo^{+6}	0.1 : 1	0.1 : 1	1:1
Ni^{+2}	nil	nil	nil
Pb^{+2}	0.1 : 1	nil	nil
Sb^{+3}	100:1	100:1	nil
Sn^{+2}	0.1 : 1	0.1 : 1	10.1 *
Te^{+6}	0.1 : 1	nil	nil
Th^{+4}	nil	nil	nil
Ti^{+4}	100:1	1:1	nil
Tl^{+1}	10:1	100:1	1:1
V^{+5}	1:1	0.1 : 1	nil
W^{+6}	0.1 : 1	1:1	100:1
Zn^{+2}	nil	nil	nil
Zr^{+4}	nil	nil	nil

* Peak potential altered

** Double wave obtained

TABLE 2

Comparison of peak potentials and sensitivities of the tartrate, ascorbate and "mixed" base electrolytes for the determination of uranium.

Base Electrolyte	Peak potential in volts versus Hg pool anode (0.05M chloride)	$K = \frac{ip}{c}$ μa/ millimole/litre * for a UO_2^{++} conc. of 2×10^{-5} mole/litre
Tartrate	– 0.38	13.4
Ascorbate	– 0.27	13.0
"Mixed"	– 0.28	14.1

* ip = peak current for m = 1.14 mg/sec.
t = 6.5 sec.

9. RELATIONSHIP BETWEEN URANIUM CONCENTRATION AND PEAK CURRENT

It may be seen from Table 3 that peak current is proportional to concentration in the "mixed" base electrolyte if the uranium concentration is below 4×10^{-5}M. Above this value the peak current becomes proportionally less, the reduction wave gradually assumes an irreversible nature, and the peak potential shifts to more negative values.

10. ANALYSIS OF ORES

Table 4 shows the results obtained on ten samples of uranium ores by the polarographic method described above. The results on ores No. 1 – 7 are compared with those obtained by an independent research organisation using the classical method consisting of a cellulose column separation of the uranium from nitric acid–ether solution, followed by spectrophotometric determination with hydrogen peroxide. Ores No. 8 – 10 were analysed fluorometrically by an independent laboratory.

In addition to uranium, ores No. 1 – 7 were found to contain silica (25 – 85%), iron(5 – 65%), vanadium (0.2 – 2.0%), copper (0.05 – 0.2%), and small amounts of the following elements:

Al, Pb, Cr, Ti, Mo, Ni, Ag, Au, Bi, W and Mn.

To test the precision of the procedure outlined, ten portions of ore No. 5 were carefully analysed. The results gave a standard deviation (n–1) of 1.9%.

TABLE 3

Relationship of Peak current to concentration of uranyl ion in the "mixed" base electrolyte at 25°C.

UO_2^{++} conc. C. mole/litre	Peak current ip μa	K = $\frac{ip}{C}$ μa/millimole/litre
1×10^{-3}	9.80	9.80
5×10^{-4}	5.11	10.3
2×10^{-4}	2.22	11.1
1×10^{-4}	1.21	12.1
5×10^{-5}	0.658	13.2
4×10^{-5}	0.559	14.0
2×10^{-5}	0.282	14.1
1×10^{-5}	0.142	14.2
5×10^{-6}	0.0705	14.1
2×10^{-6}	0.0280	14.0
1×10^{-6}	0.0141	14.1
5×10^{-7}	0.0070	14

TABLE 4

Application of the "mixed" base electrolyte polarographic method for uranium to the determination of uranium in ores.

Ore No.	Reference Method % U_3O_8	"Mixed base" polarographic method % U_3O_8	Difference %
1	8.3	8.3	–
2	7.6	7.5	–1.3
3	0.72	0.73	+1.4
4	0.65	0.65	–
5	0.55	0.55	–
6	0.42	0.44	+4.8
7	0.34	0.35	+2.9
8	0.037	0.046	+24
9	0.020	0.025	+25
10	0.011	0.014	+27

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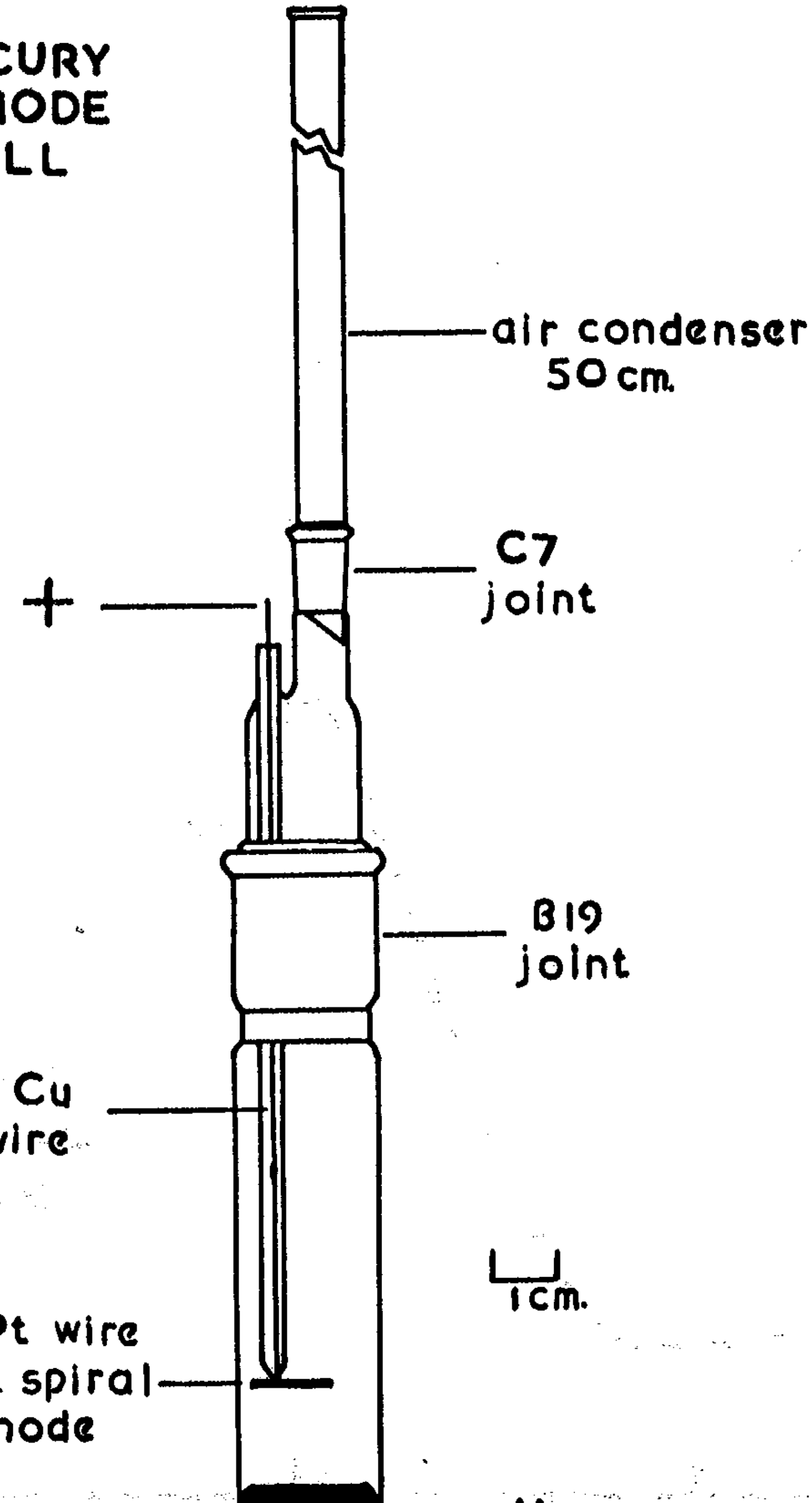
FIG 1

MERCURY CATHODE CELL



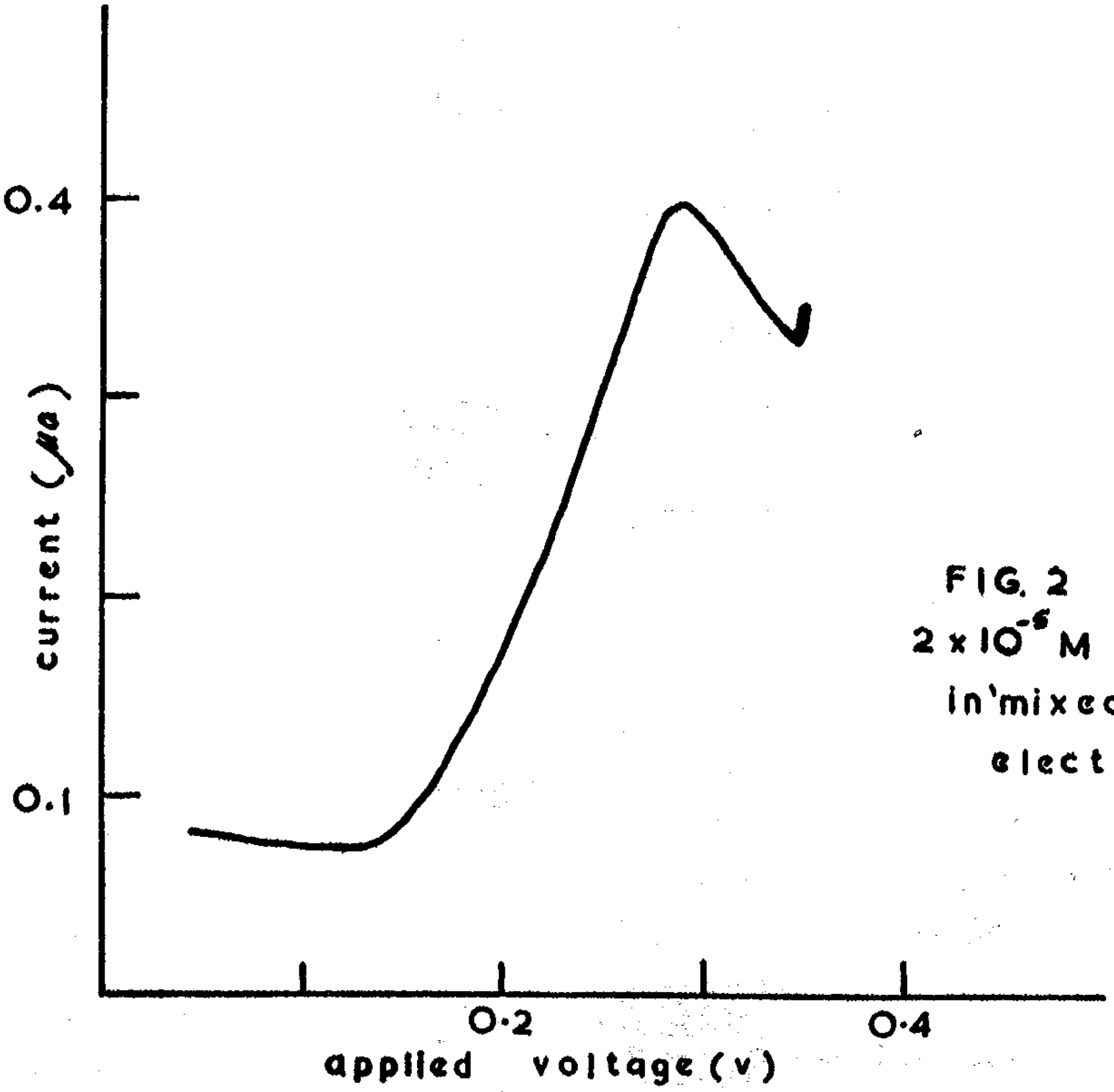


FIG. 2
2×10^{-6} M uranium
in 'mixed' base
electrolyte