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Polarographic Determination of Potassium in Uranium Compounds

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The A. C. polarographic method is proposed for the determination of potassium in precipitates of the system: uranyl nitrate-potassium hydroxide-potassium nitrate. Samples containing potassium and uranium were dissolved in 4 M nitric acid, present uranium was removed by continuous extraction with tetrahydropyrene. After mineralization with concentrated nitric acid and hydrogen peroxide, the samples were dissolved in supporting electrolyte: 0.075 M tetramethylammonium hydroxide and 0.075 M tetramethylammonium chloride. From 2.8 to 28 μg of potassium per ml. could be determined with a standard error of 0.4 μg K/ml. The lowest gramatomic ratio K/U was 3.5×10^{-5} i. e. 5.6 ppm of K in U.

INTRODUCTION

In a previous paper¹ we described some phenomena found in the precipitation system: uranyl nitrate-potassium hydroxide-neutral electrolyte. The polarographic method seemed to be very convenient for the determination of small amounts of potassium in the formed uranium precipitates. The presence of uranium interferes with the polarographic determination of potassium, therefore the continuous extraction method with tetrahydropyrene² was used for removal of uranium.

EXPERIMENTAL

A. C. and D. C. polarograms were recorded using the Cambridge Polarograph Pen Recording Type, in connection with the Cambridge Univector Unit. The chemical operations (dissolution, extraction, and mineralization) were performed in quartz dishes to prevent contamination with sodium from glass. For the same reason, the polarographic cells used were made from perspex. The chemicals used were analytical grade, solutions were prepared in bidistilled water obtained from a quartz apparatus (*Jena Cat. No. 5335 Wasser Bidestillator nach Zelner*). However, technical grade tetramethylammonium chloride, Eastman Organic Chemicals (Practical), was used for the preparation of the supporting electrolyte. The procedure of quantitative separation of uranium was the following: samples containing potassium and uranium were dissolved in bidistilled nitric acid (up to 4 M). Continuous extraction with tetrahydropyrene in microextractors³ was performed during 50 minutes. The aqueous phase from the extraction vessels was evaporated, dissolved in 4 M bidistilled nitric acid and extracted again during the next 50 minutes. After this procedure, uranium was quantitatively separated from potassium remaining in the aqueous phase.^{2,4} The aqueous phase was evaporated on quartz dishes using an IR lamp. A few drops of bidistilled nitric acid and hydrogen peroxide were added to samples in order to decompose traces of tetrahydropyrene. Special care must be taken during this process because organic substances could affect the shape of the polarographic curve. After the evaporation, the samples were dissolved in the supporting electrolyte and the polarograms were recorded.

Preparation of the supporting electrolyte

A 1 M solution of commercial tetramethylammonium chloride was converted to a 1:1 mixture of tetramethylammonium chloride and hydroxide by pouring it through Dowex X-1⁵ anion exchanger. The obtained mixture was purified in the following manner: the solution was evaporated to small volume *in vacuo* on a Craig rotatory evaporator at 30° C. The residual solution was purified by electrolysis at constant potential on a Hg cathode.⁶ The electrolysis was performed in a plastic vessel during 45 minutes at a constant potential of -2.3 volts vs. S. C. E., connected with salt bridge filled with electrolysing solution. The solution was quickly decanted into a plastic flask and stored. After electrolysis the solution is free from impurities which could interfere with the polarographic determination of potassium. The supporting electrolyte was prepared by simple dilution with bidistilled water.

RESULTS AND DISCUSSION

The D.C. and A.C. polarographic behaviour of potassium was investigated after the removal of uranium by the described method. The polarographic wave obtained by the D.C. method was ill-defined and it was impossible to read out the limiting current. The A.C. polarographic peak of potassium had a better characteristic although the shape of the peak was not as good as in pure systems⁷. The A.C. polarographic peaks of potassium are shown in Fig. 1. The height of the A.C. peak was measured as the difference between a top of a curve and a horizontal tangent of the left part of the curve. The height of the peaks obtained in such a way was reproducible.

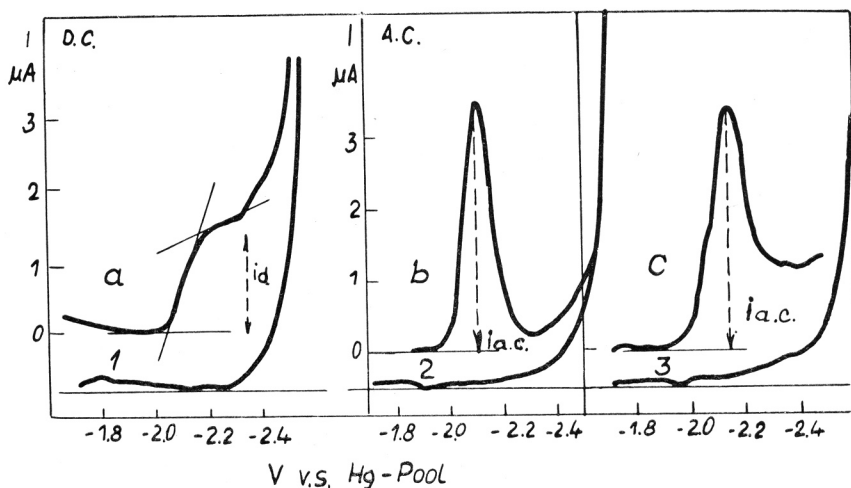


Fig. 1. Typical D.C. and A.C. polarographic curves of potassium:

- a) D. C. polarogram of 23.4 $\mu\text{g K/ml}$
- b) A. C. polarogram of 23.4 $\mu\text{g K/ml}$
- c) A. C. polarogram of 23.4 $\mu\text{g K/ml}$ after removal of 1 g. of uranium, 1, 2, 3 curves of supporting electrolyte.

As the polarographic reduction of potassium takes place at very negative potentials, the drop time is changing very markedly with the potential. The drop time in dependence on potential of Hg dropping electrode is listed in Table I. The height of mercury reservoir was constant at 25 cm. It is evident that the drop time in the measuring intervals was not shorter than the critical value of 1.5 sec.⁸

TABLE I.
The Drop Time in Dependence on Potential of Hg Dropping Electrode

V (volts)	-1.0	-1.1	-1.2	-1.3	-1.4	-1.5	-1.6
t (sec/drop)	7.1	6.8	6.6	6.3	5.9	5.6	5.3
	-1.7	-1.8	-1.9	-2.0	-2.1	-2.2	-2.3
	5.2	4.8	4.5	3.5	3.2	3.0	1.8

The obtained regression of concentration of potassium upon the A.C. polarographic current (after the removal of 1 g. of uranium) can be expressed as:

$$y = (0.160 \pm 0.002) \cdot x \quad (1)$$

where y concentration of potassium in $\mu\text{g K/ml}$

x A.C. polarographic current in μA .

The regression line has the slope of 0.16 when passing through the origin which indicates that no loss of potassium occurred during the preparation of the samples. In Fig. 2. the relationship between the concentration of potassium (in $\mu\text{g K/ml}$) and the A.C. polarographic current (in μA) is given. Fig. 3. shows the standard error (curve 1), and the relative standard error (curve 2) as functions of the concentration of potassium.

Each result is a mean value of two parallel recorded polarograms.

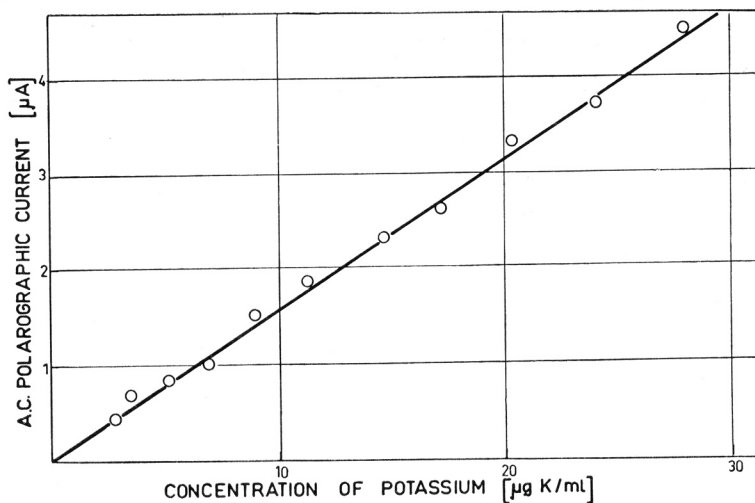


Fig. 2. The regression of potassium concentration upon A. C. polarographic current.

The presence of sodium and earth alkalies interferes with the determination of potassium by the described method. The range of proportionality of the regression line was obtained from 2.8 to 28 $\mu\text{g K/ml}$. A higher dilution with the supporting electrolyte is recommended, since it will also lower the amount of organic impurities and better defined polarograms can be obtained. The lowest ratio of K/U is 5.6 ppm in the analyzed concentrates (the gramatomic ratio was 3.5×10^{-5}).

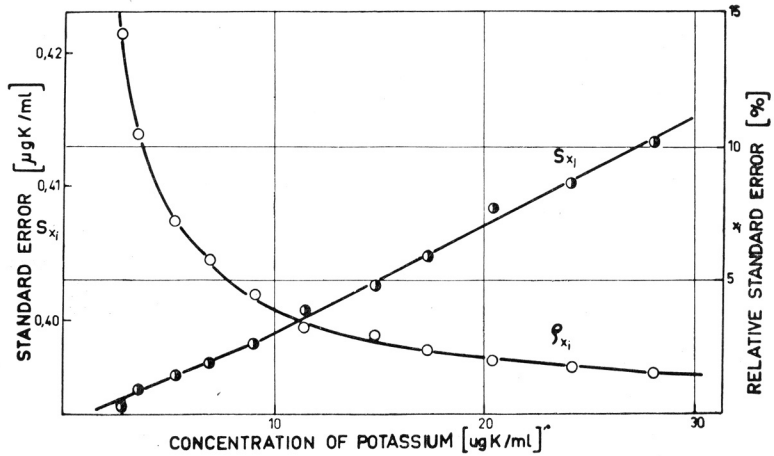


Fig. 3. The standard error (curve 1) and the relative standard error (curve 2) as functions of the concentration of potassium.

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IZVOD

Polarografsko određivanje kalija u uranovim spojevima

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Predložena je A. C. polarografska metoda određivanja kalija u talozima sistema: uranil nitrat-kalijev hidroksid-kalijev nitrat. Uzorci koji su sadržavali kalij i uran otopljeni su u 4 M dušičnoj kiselini, a uran je separiran kontinuiranom ekstrakcijom sa tetrahidropiranom. Nakon mineralizacije sa koncentriranom dušičnom kiselinom i vodikovim peroksidom, uzorci su otapani u osnovnom elektrolitu: 0,075 M tetrametilamonijum hidroksid — 0,075 M tetrametilamonijum klorid. Kalij se može odrediti od 2,8—28 $\mu\text{g K/ml}$ uz standardnu pogrešku od oko 0,4 $\mu\text{g K/ml}$. Najniži gramatomski odnos kalija prema uranu iznosi $3,5 \times 10^{-5}$ tj. 5,6 ppm kalija u uranu.

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ZAGREB

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