

ON THE INCREASE OF SENSITIVITY AND SPECIFICITY IN THE OSCILLOPOLAROGRAPHY OF URANIUM

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INTRODUCTION

The aim of the present paper is to investigate the oscillopolarographic activity and the specificity of the reaction for uranium and various metal ions. Recently, MATYSIK¹ has proposed a selective, semi-quantitative method for the rapid determination of uranium based on the high degree of oscillopolarographic selectivity of the compounds that uranium forms with phenols. Similarly, KALVODA AND JUAN² have observed that the oscillopolarographic sensitivity increases when the substance being studied is sparingly soluble or forms complexes with the supporting electrolyte.

The behaviour of uranium in both organic and inorganic supporting electrolytes is examined, and also the influence of complexing agents on the incision in the curve, $dE/dt = f(E)$.

EXPERIMENTAL

Both the quantitative and qualitative determinations were made on a Krizick P576 Polaroscope. The curve, $dE/dt = f(E)$, is presented on the screen of the cathode-ray tube of this instrument. The position of the incisions is expressed³ by means of the quantity, Q . The sensitivity of the qualitative test is expressed by means of the quantity, pD .

Qualitative analysis and discussion

The oscillopolarographic behaviour of U(VI) in both inorganic and organic supporting electrolytes is examined and in each case a study made of the conditions that make the reaction specific.

Inorganic supporting electrolytes. Both cathodic and anodic incisions are obtained in 0.1 *M* solutions of the inorganic acids, H₃PO₄, HCl, and HClO₄; the anodic incisions ($pD = 6.2$) are more sensitive than those of the cathodic branch ($pD = 4.7$) (see Fig. 1).

In HClO₄, the following cations form incisions: Cu(II), Cd(II), Pb(II), Bi(III), Zn(II), Fe(III), Sn(II), Mo(VI), V(V) and Cr(III). Table 1 shows that in the qualitative determination of U(VI) in 0.1 *M* HClO₄, only Zn(II), V(V) and Cr(III) interfere; they are eliminated by using potassium ferrocyanide, urotropine and benzidine, respectively.

If these interfering elements are eliminated, perchloric acid can be used as a specific reagent for the detection of uranium at a concentration of $0.02 \mu\text{g/ml}$. This medium is unsuitable when quantitative results are required because the depth of the incision is not proportional to the concentration of uranium.

In $0.1 M$ HCl, U(VI) produces two cathodic and one anodic incision, of which the anodic is more sensitive ($pD = 5.7$). Many metallic ions, such as Zn(II), Cr(III) and V(V), act as depolarizers and interfere in the detection of U(VI). The effect of Zn can be eliminated with $\text{K}_4\text{Fe}(\text{CN})_6$, that of the other ions, with urotropine.

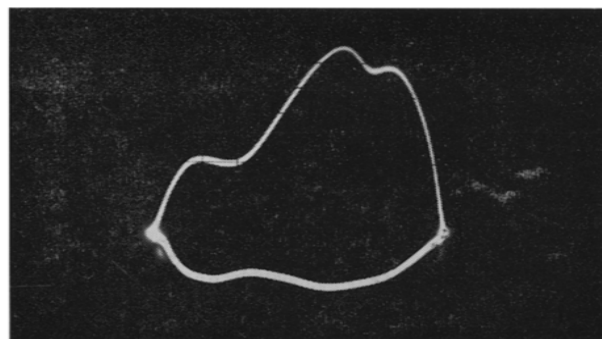
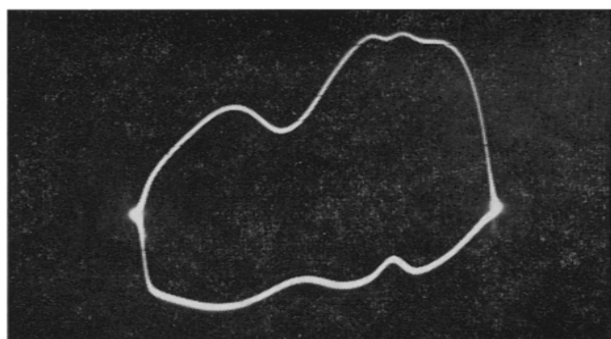


Fig 1. $0.05 \text{ ml } 10^{-2} M$ U(VI) in 6 ml of HClO_4 $0.1 M$; d.c. = 4 mA ; a.c. = 0.25 mA .

Fig 2. $0.08 \text{ ml } 10^{-2} M$ U(VI) in 6 ml TEA ($0.1 M$)-HCl ($0.1 M$) in $1:5$ proportion ($\text{pH} = 1$); d.c. = 4 mA ; a.c. = 0.15 mA .

TABLE I

SUPPORTING ELECTROLYTE, PERCHLORIC ACID $0.1 M$

	Q_c	Q_a	pD	Observations
U(VI)	—	0.63	6.2	
Pb(II)	0.45	0.41	5.4	
Cu(II)	—	0.18	5.9	
Cd(II)	—	0.40	5.7	
	0.54	—	5.4	
Bi(III)	—	0.12	5.4	
Zn(II)	—	0.67	5.9	Eliminated with $\text{K}_4\text{Fe}(\text{CN})_6$
	0.81	—	5.6	
Fe(III)	0.12	0.054	5.3	
Sn(II)	—	0.30	5.2	
	0.30	—	5.0	
Mo(VI)	0.30	—	4.4	
V(V)	0.83	—	5.0	Eliminated with urotropine
Cr(III)	0.81	—	5.7	Eliminated with benzidine
Ni, Al, La, Th	—	—	—	Inactive

Note: Besides the anodic incision, $Q_a = 0.63$. U(VI) produces two cathodic incisions ($Q_c = 0.63$ and $Q_c = 0.81$) of inferior sensitivity.

Effect of complex-forming agents on inorganic supporting electrolytes. When triethanolamine (TEA) is added to supporting electrolytes consisting of inorganic acids, it reduces the sensitivity but has the great advantage of eliminating interference due to other ions.

In a base solution of 0.1 *M* HCl and 0.1 *M* TEA in the proportion of 5 : 1, none of the 16 cations examined interferes in the detection of U(VI) (see Table 2 and Fig. 2).

Organic supporting electrolytes. Supporting electrolytes based on organic acids have a number of advantages in the detection of U(VI). The incision of the curve $dE/dt = f(E)$ is ample and clear, and in general, the sensitivity is greater in organic supports. In media consisting of organic acids one anodic and two cathodic incisions are produced.

TABLE 2

SUPPORTING ELECTROLYTE, HYDROCHLORIC ACID (0.1 *M*)-TRIETHANOLAMINE (0.1 *M*)

	Q_c	Q_a	pD	Observations
U(VI)	0.76	—	4.4	
Pb(II)	0.34	0.34	5.4	
Cd(II)	0.36	0.34	5.4	
Bi(III)	0.10	0.14	5.4	
Cu(II)	—	0.20	5.6	
Zn(II)	0.69	—	5.6	
Mo(VI)	0.30	—	4.5	
Sn, V, Ni, Cr, Fe, Al, La, Zr, Th	—	—	—	No depolarizing activity

Q_c = cathodic incision, Q_a = anodic incision.

In 0.1 *M* tartaric acid, 10^{-2} *M* U(VI) produces two cathodic incisions and one anodic. At lower concentrations (10^{-3} *M*), only the anodic incision is formed. In this medium, Bi(III), Ni(II), Zn(II) and Cr(III) interfere. The interferences caused by these ions can be eliminated as described below. Other cations, although they may produce incisions, do not affect the detection of U(VI).

In 0.1 *M* citric acid also, are formed one anodic and two cathodic incisions, of which the anodic is the most sensitive ($pD = 6.1$) (see Fig. 3). Table 3 shows that the following ions interfere in the detection of U(VI): Ni(II), Zn(II), Mo(VI) and Cr(III). The interferences caused by these ions can be eliminated by adding reagents of a strong complex-forming character.

In 0.1 *M* ascorbic acid, the following ions interfere in the detection of U(VI):

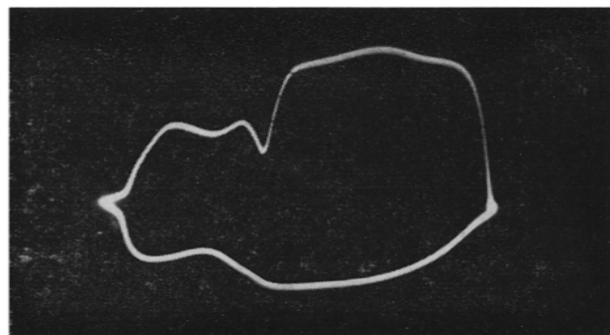
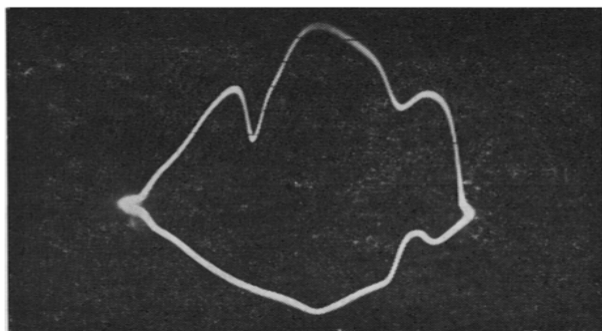


Fig. 3. 0.15 ml 10^{-3} *M* U(VI) in 6 ml citric acid 0.1 *M*; d.c. = 2 mA; a.c. = 0.1 mA.

Fig. 4. 0.15 ml $5 \cdot 10^{-3}$ *M* U(VI) in 6 ml TEA (0.1 *M*)-tartaric acid (0.1 *M*), pH = 5-8.

Pb(II), V(V), Al(III) and Zn(II). Other ions, although they may produce incisions, do not affect the determination of U(VI); Fe(III), Co(II), Cr(III), Mo(VI), La(III) and Zr(IV) are not reduced.

Effect of complex-forming substances on organic supporting electrolytes. In order to increase the specificity and sensitivity of the reaction being studied, triethanolamine (T.E.A.) was added to the organic supporting electrolytes. This increases the sensitivity and at the same time is an excellent reagent for eliminating interference caused by other ions.

TABLE 3
SUPPORTING ELECTROLYTE, CITRIC ACID 0.1 M

	Q_c	Q_a	pD	Observations
U(VI)	—	0.75	6.1	
Cu(II)	0.21	0.21	5.3	
Pb(II)	0.42	0.44	5.4	
Ni(II)	0.78	—	5.5	
Bi(III)	0.32	—	5.4	
	—	0.23	5.1	
Zn(II)	0.74	0.73	5.6	
Cd(II)	—	0.52	5.7	
	0.49	—	5.4	
Fe(III)	0.09	—	5.3	
Mo(VI)	0.37	—	5.1	
Cr(III)	0.78	—	5.3	
Sb(V)	0.20	—	4.7	
Zr, La, Th	—	—	—	No depolarizing activity

Note: If the concn. of U(VI) is 10^{-2} – 10^{-3} M, there are 2 cathodic and one anodic incisions ($Q_c = 0.37$; $Q_c = 0.78$ and $Q_a = 0.75$) ($pD = 5.7$). In more dilute solutions, 10^{-4} M, only the anodic incision is produced.

In a mixture of 0.1 M tartaric acid and 0.1 M TEA in the proportion 2 : 4 at pH = 5–8, the specificity of the reaction is excellent. Only one clear, characteristic and sensitive cathodic incision is formed at -0.61 V (S.C.E.), $Q_c = 0.36$ and $pD = 6.1$ (see Fig. 4). The addition of TEA eliminates the interferences caused by Zn(II), Ni(II) and Cr(III) that appear if pure tartaric acid is used. However, the pH must be higher than 4 or Pb(II) and Bi(III) begin to interfere. The interferences caused by these ions, even at pH 4, can be eliminated as shown in Table 4. The interferences caused by the Pb(II) incision disappears on the addition of 1 ml of a 0.1 M solution of EDTA + 1 ml of citric acid, to 6 ml of original solution. If too little EDTA is added, the Pb(II) incision is displaced to $Q_c = 0.75$. Similar results are obtained at pH = 4 by the addition of citrate, citric acid and EDTA.

The interference caused by Bi(III) can be eliminated by adding thiourea at pH = 5, or citric acid and EDTA, when the incision of Bi(III) is displaced to $Q_c = 0.49$, or citric acid and hydroxylamine, when the incision of Bi(III) is displaced to $Q_c = 0.23$ and $Q_a = 0.09$. Under these experimental conditions using TEA with tartaric acid as supporting electrolyte U(VI) has been detected in the presence of 17 other ions.

In a mixture of 0.1 M citric acid and 0.1 M TEA in the proportion of 3 : 3 at pH = 4, only one cathodic incision is formed, $Q_c = 0.41$ and $pD = 5.6$ (see Fig. 5).

TABLE 4

SUPPORTING ELECTROLYTE, TARTARIC ACID (0.1 M)—TRIETHANOLAMINE (0.1 M)

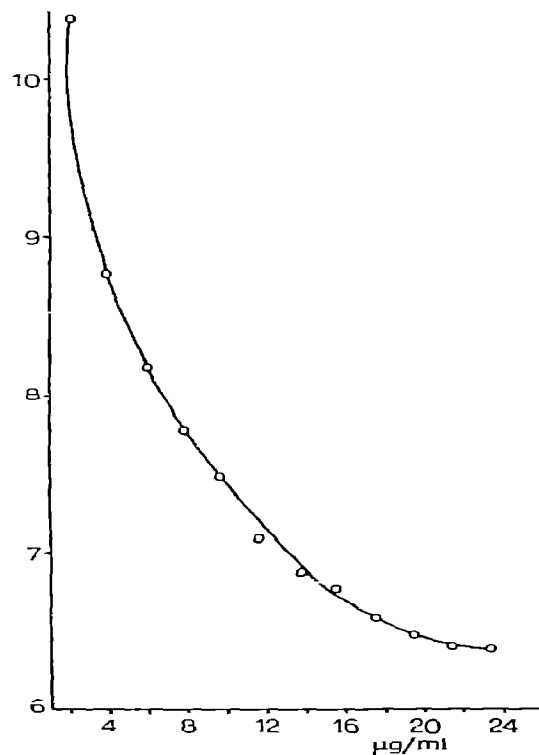
	Q_c	Q_a	pD	Observations
U(VI)	0.36	—	6.1	pH = 1-4
	0.41	—		
	0.36	—	6.1	pH = 5-8
Cu(II)	0.18	0.21	5.9	Suppressed with 1 ml EDTA, 0.1 M + 1 ml citric acid, 0.1 M
Pb(II)	0.36	—	5.1	
	—	0.29	5.0	
Zn(II)	—	0.47	5.6	
	0.72	—	5.1	
Bi(III)	0.40	0.12	5.4	Suppressed with thiourea
V(V)	0.16	—	6.0	
Sn, Mo, Fe, Al, Ni, Cr, La, Zr, Th	—	—	—	Inactive

Note: At pH values below 4, uranium produces two incisions of the same sensitivity which are very close to each other ($Q_c = 0.36$ and $Q_c = 0.41$); furthermore, Pb and Bi interfere. Between pH 5 and pH 8 there is only one incision ($pD = 6.1$) and no interference.



Fig. 5. 0.04 ml 10^{-2} M U(VI) in 6 ml TEA (0.1 M)—citric acid (0.1 M) in 3 : 3 proportion (pH = 4); d.c. = 3 mA; a.c. = 0.15 mA.

Fig. 6. Calibration curve for 10^{-2} M U(VI) in TEA (0.1 M)—tartaric acid (0.1 M) medium at pH = 5-8; d.c. = 4 mA; a.c. = 0.05 mA.



The addition of TEA eliminates the interferences produced in a supporting electrolyte of citric acid alone but Pb(II) interferes and must be eliminated by EDTA.

In a mixture of 0.1 M ascorbic acid and 0.1 M TEA in the proportion of 3 : 4 at pH = 6, U(VI) produces only one cathodic incision: $Q_c = 0.34$ and $pD = 4.7$.

The TEA eliminates the interferences that occur when ascorbic acid only is used except for the incision produced by Pb(II); this can be eliminated by adding 10^{-1} M EDTA.

Supporting electrolytes based on substances with a strong complex-forming nature. Strongly complex-forming substances, EDTA, TEA, pyridine and TAN (tetra-acetic nitrile), afford a wide selection for dealing with the depolarizing activity of the metallic ions. A number of ions that in ordinary conditions produce marked incisions in the curve, $dE/dt = f(E)$, are made completely inactive in such supporting electrolytes. With supporting electrolytes of 0.1 M EDTA with 0.1 M TEA in the proportion of 5 : 1 and pH = 5, U(VI) can be detected in the presence of 16 other ions (see Table 5). In this medium, the only interfering ion is Cu(II), the incision of which is displaced to $Q_c = 0.49$ by adding potassium ferrocyanide.

TABLE 5
SUPPORTING ELECTROLYTE, EDTA (0.1 M)–TEA (0.1 M)

	Q_c	Q_a	pD	Observations
U(VI)	0.34	—	4.7	
Pb(II)	—	0.34	5.1	
Bi(III)	0.45	—	5.4	
Cr(III)	—	0.72	5.0	
*Cu(II)	0.34	0.18	5.2	Displaced with $K_4Fe(CN)_6$
Sb(V)	0.61	—	4.7	
Sn(II)	—	0.009	5.2	
V(V)	—	0.67	5.0	
Zn, Ni, Al, Fe, Mo, Co, Cd, La, Zr, Th	—	—	—	Inactive

* = interfering

Q_c = cathodic incision, Q_a = anodic incision

In pyridine with TAN, U(VI) forms only one cathodic incision: $Q_c = 0.40$ and $pD = 4.7$. There are no interferences, although Cu(II), Pb(II), Cd(II) and Bi(III) ions produce incisions.

Both the TEA–EDTA mixture and the TAN–pyridine mixture have given excellent results in the detection of U(VI) in the presence of 17 other ions.

Quantitative results

The supporting electrolyte chosen from those studied, for the quantitative determination of uranium, was 0.1 M tartaric acid with 0.1 M triethanolamine.

The only interferences, which are caused by Pb(II) and Bi(III) ions, can be eliminated or displaced as described in the previous section, without disturbing the curve, $dE/dt = f(E)$. The depth of the incision is proportional to the concentration of uranium, as can be seen in the calibration curve (see Fig. 6). Determinations can be made between 2 and 24 $\mu\text{g/ml}$ of U(VI) in this support, with an error of $\pm 1\%$.

SUMMARY

The behaviour of uranium in both organic and inorganic supporting elec-

trolytes is examined, and also the influence of complexing agents on the incision in the curve, $dE/dt = f(E)$.

The addition of TEA to supporting electrolytes consisting of organic acids increases the sensitivity and the selectivity. The reaction becomes specific when the following are added to the supporting electrolyte: EDTA, thiourea, or substances that precipitate the interfering ions (e.g., $K_4Fe(CN)_6$). It has been possible to detect U(VI) in the presence of 16 different ions.

The behaviour of uranium has also been studied in complex-forming media: EDTA-TEA, pyridine and tetra-acetic nitrile. Specific reduction of uranium was obtained in these media in the presence of 17 other ions. In every case, the incision corresponds to the reduction of a complex absorbed on the surface of the electrode.

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