Polarography of uranium by the catalytic nitrate wave

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ion (2), it seems reasonable to suspect that an alkaline cyanide solution might be able to remove silver from less stable complexes of silver. If such is the case, it should be of advantage in the analysis of trace quantities or organic bound silver in that preliminary wet ashing or dry ashing could be avoided. To test this hypothesis a mild silver protein, "Argyrol," was analyzed gravimetrically and found to contain 21.7% silver. An aqueous solution of this material was prepared to give

samples containing 10.9 μg of silver in 10.00 ml of solution which was also $10^{-3}M$ in sodium cyanide and $0.1M$ in sodium hydroxide. Analysis was then carried out according to the standardization procedure given above. Triplicate results gave 9.94, 10.3, and 9.78 μg of silver, respectively, for an average value of 10.0 μg corresponding to a precision of 2% and an error of 8%.

(2) I. M. Kolthoff and J. T. Stock, J. Am. Chem. Soc., 78, 2081 (1956).

Polarography of Uranium by the Catalytic Nitrate Wave

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THE CATALYTIC ACTION of uranyl ion on the reduction of nitrate ion at the dropping mercury electrode was first reported by Kolthoff, Harris, and Matsuyama in 1944 (1). Since this wave is about 100 times higher than the normal polarographic wave, Crompton, Tichenor, and Young in 1949 (2) explored the possibility of utilizing it in determining traces of uranium. They concluded that the wave is highly susceptible to interference by minute amounts of anions and cations. It was only in 1955 that Hecht et al. (3) made use of this wave in determining traces of uranium in surface waters after a careful separation of uranium from other ions by strongly basic anion exchange resins. Since little work was done in this area, and we were interested in determining traces of uranium in sulfuric acid solution, we studied the catalytic wave in this medium.

EXPERIMENTAL

Stock solutions of uranyl acetate, sodium nitrate, sulfuric acid, and nitric acid were prepared. Different solutions of known concentrations of uranyl ion, nitrate ion, and sulfuric acid were prepared by dilution, and then polarographed. Solutions of nitric acid containing variable amounts of uranyl ion were also prepared and polarographed. A Sargent-Heyrovsky Polarograph Model XII was used, dropping times were 1 drop/3 seconds, and the temperature was controlled in a water bath at 25° C.

RESULTS

In sulfuric acid medium the following points were observed: At low NO_3^- concentration $(0.0001-0.001M)$ the limiting current when plotted against the uranyl ion concentration shows an adsorption curve (Figures 1a and 1b). At $[NO_3^-]$ = $0.01M$, the limiting current is a nonlinear function of uranyl

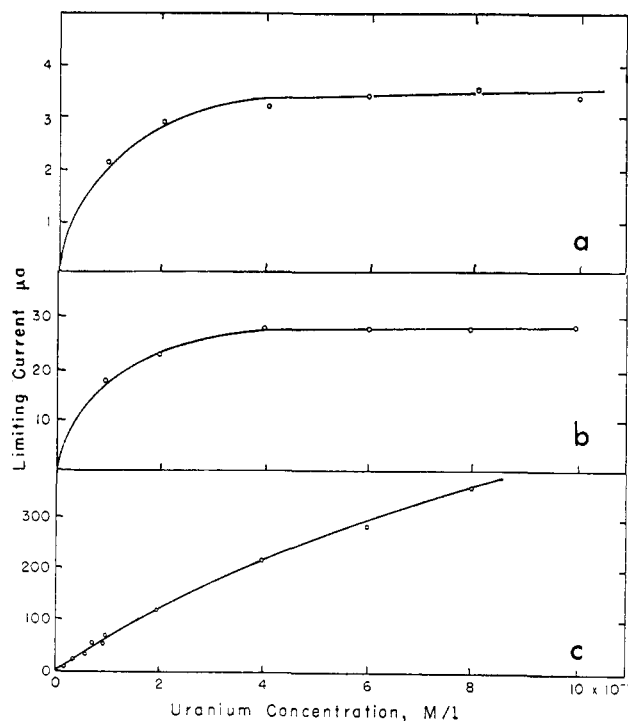(1) I. M. Kolthoff, W. E. Harris, and G. Matsuyama, J. Am. Chem. Soc., 66 1782 (1944).
(2) C. E. Crompton, R. L. Tichenor, and H. A. Young, U. S. At. Energy Comm. Rept. AECD 2704 (1945); declassified 1949.
(3) F. Hecht, J. Korkisch, R. Patzak, and A. Thiard, Mikrochimica Acta, 1956, 1283.

Figure 1. Effect of uranium concentration on the limiting current

a) $[NO_3^-]$ = $0.0001M$, $[H_2SO_4]$ = $0.1M$
b) $[NO_3^-]$ = $0.001M$, $[H_2SO_4]$ = $0.1M$
c) $[NO_3^-]$ = $0.01M$, $[H_2SO_4]$ = $0.1M$

ion concentration (Figure 1c). However, under these conditions, it is possible to determine uranium in this medium with reproducibility ±5%. The half-wave potential varies with the NO_3^- concentration as shown in Table I. At $[NO_3^-]$ = $0.1M$ or higher, the half-wave potential becomes more negative and apparently coincides with the decomposition of the acid. For this reason the wave is completely distorted and is of no analytical value.
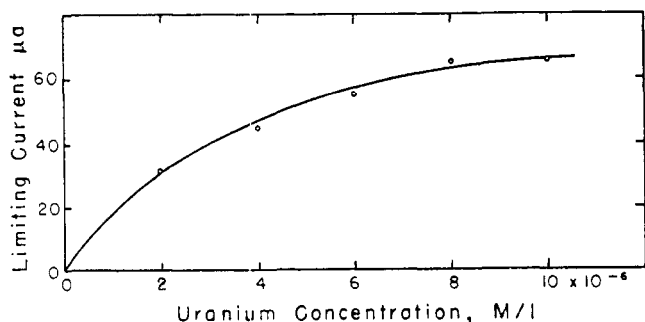
Figure 2. Effect of uranium concentration on the limiting current

$[HNO_3] = 0.1M$

In absence of H^+ ions, neither the nitrate ion nor the uranyl ion are reduced at the dropping mercury electrode. A small concentration of acid is necessary for the reaction to take place while above $0.05M$ H_2SO_4, the limiting current decreases as shown in Table II.

In $0.1M$ HNO_3, the limiting current when plotted against the uranyl ion concentration shows also an adsorption curve (Figure 2). For comparative purposes the plot of the limiting current against UO_2^{+2} concentration in $0.1M$ H_2SO_4 in absence of nitrate ion—i.e., a normal polarographic wave—is shown in Figure 3; a straight line is obtained over a wide concentration range.

DISCUSSION AND CONCLUSIONS

A catalytic wave may arise from the following mechanism (4):

$$O + ne^- \rightarrow R \qquad (1)$$

$$R + Z \rightarrow O \qquad (2)$$

were O is an oxidized species in solution, R is the reduced species, and Z is an oxidizing agent capable of oxidizing R back to O thus forming a catalytic cycle. This catalytic cycle causes a great increase in the diffusion current. In the present study O and R are the uranium species, and Z is the nitrate ion.

It appears, however, that the $U-NO_3^-$ wave is not a true catalytic wave since no linear proportionality between the uranium concentration and the limiting current exists. Most probably the species R is adsorbed on the mercury surface. This can be deduced from Figure 1 which suggests an adsorption isotherm. If this is the case, then when the concentration of Z is very small, the amount of R removed from the mercury surface according to Reaction 2 will also be small. Therefore the free surface available for Reaction 1 to take place will also be small. Thus, although more of O is formed,
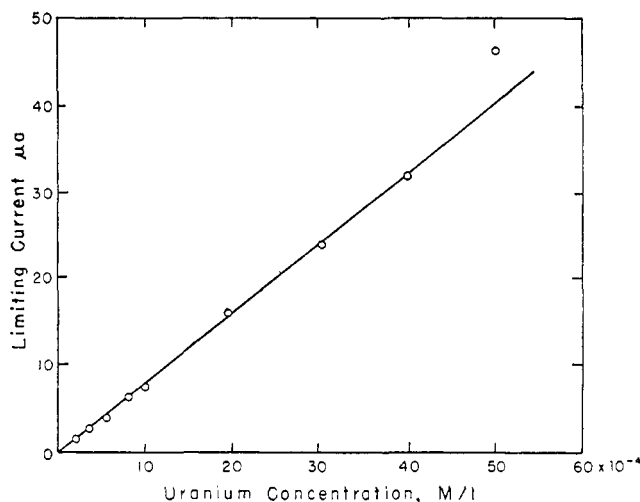
(4) L. Meites, "Polarographic Techniques," p. 182, Interscience, New York, 1965.

Figure 3. Effect of uranium concentration on the limiting current in $0.1M$ $H_2SO_4 \cdot E^{1/2} = -0.55$ volt $vs.$ the mercury pool

Table I. Effect of $[NO_3^-]$ on Half-Wave Potential
(as measured against the mercury pool)

NO_3^-, M	$E^{1/2}$, volts
0.0001	-1.45
0.0010	-1.50
0.0100	-1.55

Table II. Effect of H_2SO_4 Concentration

$[UO_2^{+2}] = 1 \times 10^{-4}M$, $[NO_3^-] = 0.01M$

H_2SO_4, M	Limiting current, μa.
0.000	0.0
0.005	65.0
0.010	66.3
0.050	84.0
0.100	68.2
0.500	25.2

yet it cannot be reduced at the mercury drop because the free surface is small. Therefore, at low concentrations of Z the limiting current will be practically the same although O is increasing. In a true catalytic wave R is oxidized as soon as it is formed.

ACKNOWLEDGMENT