# DETERMINATION OF CHROMIUM BY MEANS OF FILM VOLTAMPEROMETRY

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UDC 543.257.5:546.76

A study has been made of the processes of electroreduction of the ion $CrO_4^{2-}$ ($Cr_2O_7^{2-}$), and of electrodissolution of the precipitate formed in phosphate and ammoniacal buffer solutions, and in 0.01 N sulfuric acid. Conditions have been established for the determination of $10^{-4}$% of chromium in $Na_2WO_4$.

The determination of elements of variable valency, with their preliminary concentration as hydroxides on a graphite electrode, has been described [1].

In the work described below we investigated the process:

$$CrO_4^{2-} + 4H_2O + 3e \rightleftarrows \underset{\downarrow}{Cr(OH)_3} + 5\,OH^-$$

in buffered and unbuffered solutions, over a wide range of pH, and selected conditions to ensure maximum sensitivity for the method.

The experimental technique and preparation of the electrode have been described previously [2].

Figure 1 shows cathodic polarization curves for the electroreduction of $CrO_4^{2-}$ ions in phosphate and ammoniacal buffer solutions. The half-wave potentials were close to −0.35 V in the first case, and to −0.45 V in the second case. Subsequent anodic polarization of the electrode, with a linearly changing electrode potential, was accompanied by the appearance of a maximum in the derivative of the anode current with respect to time, shown on the corresponding differential curve. This indicated the formation on the electrode of a sparingly soluble compound, during the anodic cycle. The maxima on the curves were well defined, so that differential anodic curves were mainly used in the subsequent work.

Some Characteristics of the Reaction $CrO_4^{2-} + 4H_2O + 3e \rightleftarrows \underset{\downarrow}{Cr(OH)_3} + 5\,OH^-$

| Composition of solution | Half-wave potential for the reduction of Cr(VI) $\varphi_{1/2}$, V | Electrolysis potential, $\varphi_{el}$, V | Potential of the max. of electrodissolution of $Cr(OH)_3$, $\varphi_T$, V | Min. determinable concentration, $C_{min}$, g-ion/liter |
|---|---|---|---|---|
| 0.1-N $NaOH + CrO_4^{2-}$ | −0.80 | −1.00 | +0.10 | — |
| 0.4-M $NH_4Cl$ + 0.1-M $NH_4OH + CrO_4^{2-}$ | −0.45 | −0.70 | +0.60 | $4\cdot10^{-8}$ |
| $KH_2PO_4 + NaOH + CrO_4^{2-}$ (pH = 8) | −0.35 | −0.70 | +0.70 | $1\cdot10^{-7}$ |
| 0.05-M $Na_2B_4O_7 + CrO_4^{2-}$ (pH = 9.2) | −0.70 | −1.00 | +0.60 | $2\cdot10^{-7}$ |
| $C_3H_4(OH)(COOH)_3 + NaOH + CrO_4^{2-}$ (pH = 5.2) | −0.35 | −0.50 | +0.70 | $1\cdot10^{-6}$ |
| 0.1-M $CH_3COOH$ + 0.1-M $CH_3COONa + CrO_4^{2-}$ | −0.10 | −0.50 | +0.90 | $2\cdot10^{-6}$ |
| 0.4-M $NH_4Cl$ + 0.1-M $NH_4OH$ + 1-M $KCl + CrO_4^{2-}$ | — | −1.20 | +0.95 | — |
| 0.01-M $K_2SO_4 + H_2SO_4$ + Cr(VI) (pH = 2.5) | +0.15 | −0.30 | +1.15 | $1\cdot10^{-5}$ |

Donets Branch of the All-Union Scientific-Research Institute for Chemical Reagents and Specially Pure Chemicals. Translated from Zavodskaya Laboratoriya, Vol. 33, No. 4, pp. 400-402, April, 1967. Original article submitted June 9, 1966; revised October 3, 1966.

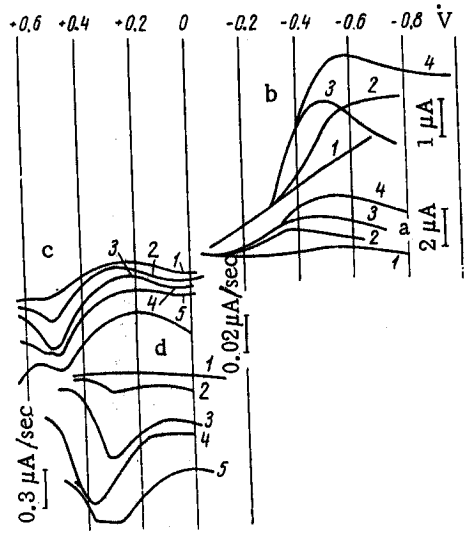


Fig. 1. a, b) Polarograms for the reduction of chromate ions; c, d) anodic differential polarization curves, obtained after electrolysis of the solutions at various potentials: c) $KH_2PO_4$ + NaOH containing $7 \cdot 10^{-6}$ g-ion of $CrO_4^{2-}$ per liter; 1) $\varphi_{el} = -0.5$, 2) $-0.8$, 3) $-0.9$, 4) $-1$, 5) $-1.5$ V; d) ammoniacal buffer containing $8 \cdot 10^{-5}$ g-ion of $CrO_4^{2-}$ per liter, 1) $\varphi_{el} = -0.2$, 2) $-0.35$, 3) $-0.7$, 4) $-0.9$, 5) $-1.2$ V; $\tau$ = 1 min and 30 sec for c) and d) respectively; v = 600 mV/min.

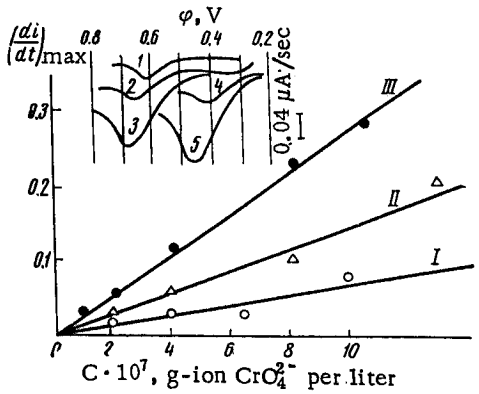


Fig. 2. Relation between maximum of derivative of anodic current with respect to time and $CrO_4^{2-}$ concentration in solution: I) $KH_2PO_4$ + NaOH; II and III) ammoniacal buffer. Also shown are the corresponding polarization curves, 1, 2, and 3 for the first case, 4 and 5 for the second, $\varphi_{el} = -0.9$ V; $\tau$ = 10, 15, and 30 min for 1, 2, and 3 respectively; v = 600 mV/min.

It is evident from the lower part of the figure that the maximum concentration of the element in phosphate and ammonia buffers was observed at $-0.9$ V. The anodic curves recorded after electrolysis of the solutions at potentials more negative than $-1.0$ V, were branched and less suitable for measurement. The potentials of maximum concentration coincided with the corresponding region of limiting current electroduction. The great difference in potential between the anodic and cathodic processes was due to the low rate of the electrode reaction.

It is clear from Fig. 2 that the maximum of the derivative of the current for electrodissolution of the precipitate was directly proportional to the concentration of $CrO_4^{2-}$ ions in the solution.

The maximum sensitivity, $4 \cdot 10^{-8}$ mole/liter, could be obtained by concentrating chromium from an ammonical buffer solution. An increase in the rate of change of voltage was accompanied by an increase in the maximum of the derivative of the anodic current with respect to time.

An increase in the duration of electrolysis, of solutions containing small quantities of $CrO_4^{2-}$ ions, was accompanied by an increase in the maximum of the derivative of the anodic current with respect to time. However, in the electrolysis of more concentrated solutions ($C_{CrO_4^{2-}} > 10^{-5}$ g-ion/liter), the reference electrode was rapidly passified by a film of the compound, so that growth in the value of $(di/dt)_{max}$ was prevented.

An increase in the concentration of ammonium hydroxide from 0.1 to 0.8 N, while the ammonium chloride concentration was kept constant, led to a reduction in the maximum of the derivative of the anodic current with respect to time. Ions of $Cl^-$ and $NO_3^-$ considerably shifted the potential for electroreduction of the $CrO_4^{2-}$ ion in an ammoniacal buffer solution, in the negative direction.

Chromium in acid solution began to concentrate at a potential of $-0.1$ V. The maximum in the derivative of the anodic current with respect to time achieved its highest value when the preliminary electrolysis was carried out at $-0.5$ V, and decreased towards zero as the potential for preliminary electrolysis was made more negative.

Figure 3 shows that the maximum of the derivative of the anodic current with respect to time was linearly related to the concentration of $Cr_2O_7^{2-}$ ions. The sensitivity for the determination of chromium (VI) in an acid medium was lower, as would be expected [3], than under the conditions described above.

The table shows half-wave potentials for the reduction of Cr(VI) ions at a graphite electrode in various solutions, the potentials of the maxima of anodic polarization curves for the electrodissolution of chromium (III) hydroxide, electrolysis potentials, and minimum determinable concentrations of Cr(VI).

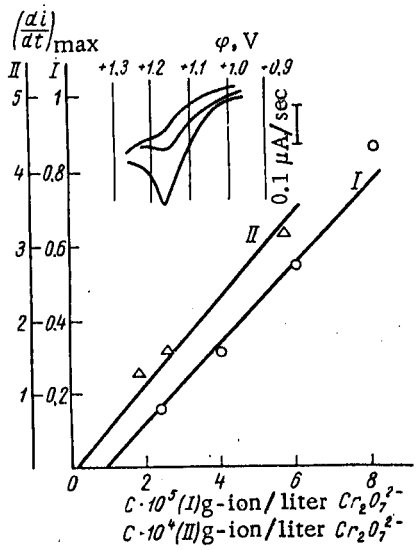


Fig. 3. Relation between the maximum of the derivative of the anodic current with respect to time and the concentration of $Cr_2O_7^{2-}$ in 0.01 M $H_2SO_4$. Also shown are the differential polarization curves corresponding to the first case; $\varphi_{el}$ = −0.5 V; $\tau$ = 2 and 1 min for I) and II) respectively.

Chromium determination was not affected by the presence of comparable amounts of cadmium, copper, antimony, tin, or nickel. For the determination of $8 \cdot 10^{-6}$ g-ion $CrO_4^{2-}$ per liter, there was no interference by five times as much lead, or four times as much $Bi^{3+}$.

On the basis of the above investigations, a method was developed for the determination of chromium (VI) as an impurity in sodium tungstate.

A 1 g sample of $Na_2WO_4$ was weighed to a precision of 0.01 g, ignited at 700°C for 3 to 4 h, and dissolved in 20 ml of water. The solution was adjusted to pH 8 with nitric acid and transferred to the electrolyzer. The working surface of the graphite electrode was previously cleaned with fine emery paper.

Electrolysis at −1.0 V was carried out for 15 min. The stirrer was then stopped, the potential was set manually to zero, the solution was allowed to settle, and an anodic polarization curve was recorded from zero to +1.0 V, with the potential changing at 0.019 V/sec. The maximum current for electrooxidation of chromium (III) hydroxide was observed at a potential of +0.60 V.

The sensitivity for determination of chromium under the selected conditions was $10^{-4}$%.

## LITERATURE CITED

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