AMPEROMETRIC TITRATION USING A PERMANGANATE REFERENCE ELECTRODE

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Permanganate solution is suggested as a reference electrode during amperometric titration with a platinum electrode. SO_4^{2-}, Pb^{2+}, Zn^{2+}, and Zr^{4+} have been titrated without applying external emf.

The possibility has already been demonstrated of using a rotating platinum electrode in solutions of different redox systems as a reference electrode [1]. We have used a permanganate solution as an electrode of this type in the work described here.

Permanganate ions are reduced at positive potentials on platinum [2], the reduction potential being dependent to a considerable extent on the acidity of the medium, since

$$E_{MnO_4^-/Mn^{2+}} = E_0 + \frac{0.058}{5} \times \lg \frac{[MnO_4^-][H^+]^8}{[Mn^{2+}]}.$$

Consequently, by using a solution of permanganate of reasonably high concentration in acid, alkali, or neutral media as the electrolyte in the reference electrode, it is possible to prepare a series of reference electrodes with a given potential value.

We used an ordinary rotating platinum wire electrode 5 mm long and 0.5 mm in diameter in sulfuric acid solutions of potassium permanganate, and a similar platinum electrode as the reference electrode. A PPTV-1 potentiometer was used for measuring the potential of the reference permanganate electrode. All measurements were made relative to a mercury sulfate electrode (E = 0.68 V). It was found that the reference electrode indicated can be used at permanganate concentrations higher than $2 \cdot 10^{-1}$ M at which electrode polarization ceases in practice. The potential of such an electrode is 1.5 ± 0.04 V,* depending on the sulfuric acid concentration (Fig. 1).

We used a saturated permanganate solution which corresponds to a concentration of about 1 M. Having a very high positive potential, and being at the same time the cathode, such a reference electrode permits titration of a large number of materials without applying an external emf, use being made of the diffusion current of ions which are oxidized at less positive potentials on platinum. We have used this reference electrode for titrating a number of materials.

Titration on the Basis of the Oxidation Current of Lead

Heyrovsky and Berezitskii [3] have suggested amperometric (polarometric) determination of SO_4^{2-} ions as lead sulfate. This titration is usually carried out on a dropping mercury electrode on the basis of the lead reduction current. It can also be carried out on a rotating platinum electrode at a potential of +1.3-1.5 V, using the current from the oxidation of lead to its tetravalent state. As a result, however, of passivation of the indicator electrode by a film of lead dioxide, the current drops significantly under these conditions† and the titration curve becomes diffuse.

We have titrated 1-0.14 mg of sulfuric acid with lead acetate solution on the basis of the oxidation of lead on a rotating platinum electrode without applying an external emf, by using a permanganate reference electrode. In order to stabilize the pH of the solution being titrated during titration, we added 4-5% of acetic acid to it beforehand

*Here and for the rest of the paper, potential values are given relative to the normal hydrogen electrode.

† The authors of [4] suggest using a galvanometer with a very high sensitivity.

Potential Differences between Reference and Indicator Electrodes

Test ion	Mercury-iodide electrode*		Permanganate electrode**	
	external emf, E_v	difference $E_v - E_{ref.e}$	Indicator electrode potential $E_{ind.e}$	difference $E'_{ref.e} - E_{ind.e}$
SO_4^{2-} with lead acetate and Pb^{2+} with dichromate	+1.3	1.28	+1.48	0.02
Zn^{2+} with ferrocyanide	+1.0	0.98	+1.45	0.05
Zr^{4+} with cupferron	+1.05	1.03	+1.45	0.05

*Reference electrode potential 0.02 V ($E_{ref.e}$).
**Reference electrode potential 1.5 V ($E'_{ref.e}$).

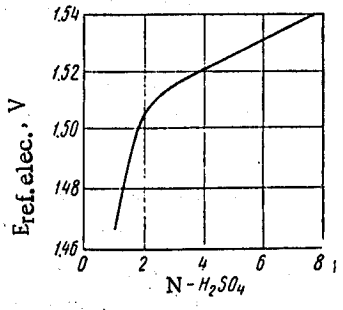

Fig. 1. The relationship between the potential of a reference permanganate electrode and H_2SO_4 concentration.

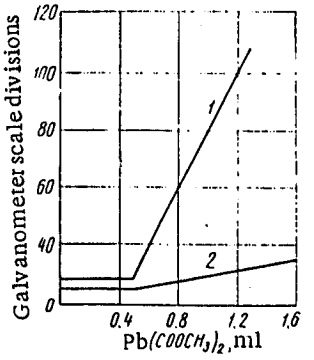

Fig. 2. Titration curves of 0.5 mg of sulfuric acid with lead acetate solution.

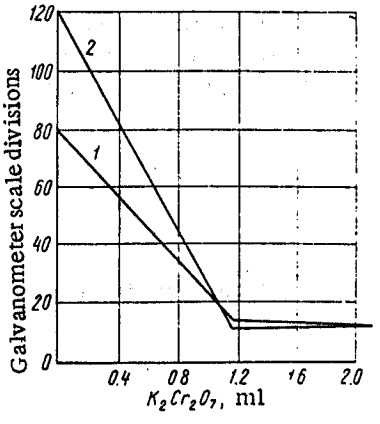

Fig. 3. Titration curve of 4.10 mg lead with dichromate.

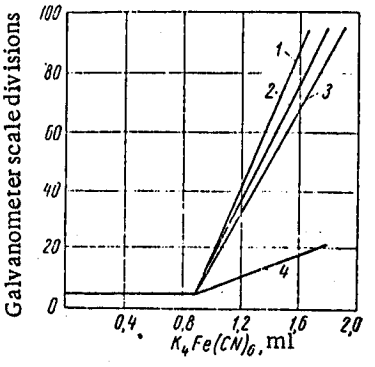

Fig. 4. Titration curves of 2 mg of Zb with potassium ferrocyanide in absence of aluminum (curves 1 and 3) and in presence of 160 mg of Al (curves 2 and 4).

and used an 0.01 N lead acetate solution, containing the same amount of free acetic acid as the titrant. Fifty to sixty percent of ethanol was added to the solution being titrated in order to suppress the solubility of the lead sulfate formed. The total volume of solution titrated was 25 ml.

Figure 2 shows titration curves without (curve 1) and with application of an external emf (curve 2). In the first case, the maximum relative error for determining 0.2 mg of H_2SO_4 was not more than 10%. On using a mercuric iodide reference electrode, an ill-defined titration curve with a "diffuse" end point was obtained.

Lead was also determined by titration with dichromate; the curve obtained is shown in Fig. 3.

Titration of Zinc and Zirconium in the Presence of Aluminum

Aluminum affects titration strongly because of the adsorption of aluminum hydrolysis products on the platinum electrode [3]. It has already been pointed out that interference from aluminum is appreciably weaker under certain conditions. We assumed that this phenomenon is related to the value of the indicator electrode potential which affects percentage aluminum adsorption on the electrode.

Using a permanganate reference electrode, we titrated zinc with ferrocyanide in an 0.02 N sulfuric acid supporting electrolyte in the presence of 80 times its amounts of aluminum, without applying an external emf. Under these conditions, aluminum hardly interferes at all (Fig. 4, curves 1 and 2), while on applying an external emf of +1.0 V during titration, aluminum strongly affects the current value (curves 3 and 4).

A similar phenomenon is observed on titrating zirconium with cupferron. We titrated from 0.1 to 0.5 mg of zirconium in the presence of 200 times its amount of aluminum; this is not practically feasible under ordinary amperometric titration conditions [5].

It is obvious that these facts are related to a decrease in the difference between the potential of the permanganate reference electrode (cathode) and the potential of the anode process which occurs on the indicator electrode.

The penultimate column in the table contains the measured values of the indicator electrode potentials at the titration end point. A comparison of these results with the polarograms for the oxidation of lead, ferrocyanide, and cupferron taken under the conditions given above for these cases, showed that the indicator electrode potential corresponds to the beginning of oxygen evolution. Since the potential at which oxygen is evolved depends on the acidity of the medium, the potential difference between the permanganate reference electrode and the anode is determined by the composition of the solution being titrated.

The current increases sharply after the titration end point; it is accordingly determined by two simultaneously occurring processes – oxidation of the titrating ion and anodic evolution of oxygen. The decrease in potential difference favorably affects titration for still one more reason. The transport of charged particles is proportional to the potential gradient; consequently, adsorption on the anode of colloidal particles of $Al(OH)_3$, which carry a negative charge in this case, will be smaller than on applying an emf of about 1.0 V.

LITERATURE CITED

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