Amperometric Titrations. IV. The Use of Metal Electrode of High Negative Potential and its Application to the Determination of Sulfur in Pyrite

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In the previous paper,⁽¹⁾ the authors reported on the use of reference electrodes having high negative potential, *e. g.* the mercuric sulfide electrode ($E = -0.8$ volt *v. s.* S. C. E.) in the short-circuited amperometric titration of some organic reagents with copper sulfate.

In the present paper, some fundamental experiments on the short-circuited amperometric titration by the use of metal electrode of high negative potential, especially of metallic zinc-potassium chloride electrode, are presented and their application to the determination of sulfur in pyrite after its oxidation to sulfate is reported.

Experimental.

In amperometric titrations, different from the polarographic method where the electrolytic current is a function of the electrode potential, the current is a function of the concentration of the reducible ion in question, and the potential of the indicator electrode is invariant, so in spite of the change in the composition of the titrating solution, the potential of the opposite electrode (anode) must be kept constant while the titration is carried out. In the polarographic method, the mercury pool is generally used as anode of the constant electrode potential, and the potential of dropping electrode is proportional to the applied voltage. In amperometric method, however, if the naked mercury pool is used as the opposite electrode, a very indefinite result is apt to occur. The example is shown in the argentometric titration of cyanide (see Fig. 1). From curve 1 in Fig. 1, where the mercury pool is used as the opposite electrode, the end point is difficult to be determined. The reason is clearly shown by tracing the change of the electrode potential of mercury pool electrode, which is shown by curve 2 in the Fig. 1. As is shown in the curve, the mercury pool electrode has a highly negative potential in the original cyanide solution, but it comes to have a highly positive potential in excess of silver ion against the saturated calomel

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(1) M. Ishibashi, T. Fujinaga, this bulletin, **23**, 229 (1950).

electrode and so the amperometric titration curve comes to show irregularity. These effects are thought to occur more or less in all titration reactions. In this case, however, when the separated metallic silver-potassium chloride electrode is used, the titration curve becomes a straight line as is shown in curve 3 in the Fig. 1 and the end point is clearly shown by the cross point of two straight lines (see also Fig. 2)

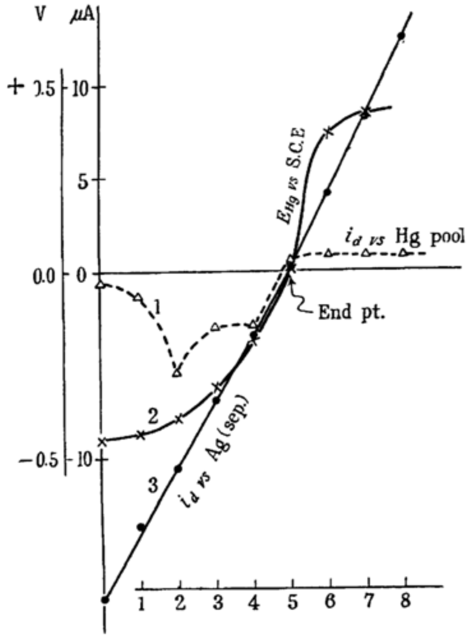

Fig. 1.—Argentometric titration curves of cyanide: curve 1, amperometry using mercury pool as opposite electrode; curve 2, potential change of mercury pool electrode; curve 3, amperometry using separated silver electrode.

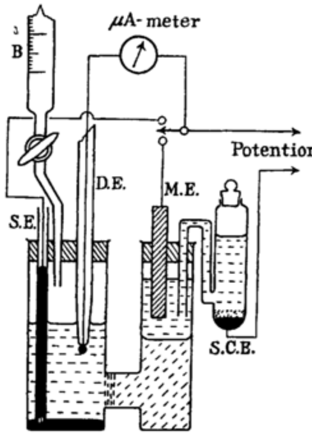

Fig. 2.—Titration cell for the measurement of diffusion current and electrode potential: B, burette; D. E., dropping electrode; M. E., separated metal electrode, S. C. E., saturated calomel electrode; S. E., stationary mercury pool electrode.

These metal electrodes are supposed to be unstable, but from the authors' experiments, an even baser metal like zinc can be used as a stable reference electrode for the amperometric purpose. Table 1 shows the change in the electrode potential of metallic zinc (surface amalgamated) inserted in the anodic solution of potassium chloride, while the cathodic solution containing 10^{-2} M. lead ion is discharged on the dropping mercury electrode for 2.5 hours by short-circuiting both electrodes. In these experiments, 21.1 microamperes flowed continuously, but the electrode potential was kept constant at $E_c = -1.1$ volts *v.s.* S. C. E. So it appears that such natural electrodes are stable and usable for the amperometric titration at E_c of up to −1.1 volts *v. s.* S. C. E. instead of those produced by the battery-potentiometer method. The examples of other metal electrodes and thereby reducible ions are shown in Table 2.

Table 1

Potential of Zinc Electrode

Discharge time, min.	Electrode potential, volts *vs.* S. C. E.	Discharge current, μA
0 (not connected)	−1.120	0
5	−1.122	21.1
60	−1.118	21.1
150	−1.122	20.0

Table 2

Electrode Potential of Some Metal Electrodes

Electrode	Electrode potential, volts *vs.* S. C. E.	Reducible ion
Ag/sat. KCl	−0.08	Ag^+, Hg^+, Fe^{+++}, CrO_4^{--} etc.
Cu/sat. KCl	−0.325	Bi^{+++}
Sb/buffer soln.	−0.1∼−0.6	
Cd/sat. KCl	−0.820	Cu^{++}, $Cu(NH_3)_4^{++}$
Zn/sat. KCl	−1.120	Cd^{++}, Pb^{++}

Determination of Sulfur in Pyrite.

Sulfate can be determined by the amperometric titration with lead nitrate standard solution.⑵ In this titration, the potential of −1.2 volts *v. s.* S. C. E. was applied to the dropping mercury electrode; therefore this outside e. m. f. can be replaced by the zinc-potassium chloride electrode. The apparatus is the same as that shown in Fig. 2 (the calomel electrode and the mercury pool electrode are unnecessary).

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(2) I. M. Kolthoff, Y. D. Pan, *J. Am. Chem. Soc.*, **62**, 3332 (1940).

Reagents Used: Pure sodium sulfate was accurately weighed out and 0.1N-sodium sulfate solution was prepared as the standard of sulfate. The titre was again determined as barium sulfate by the gravimetric method. 0.1N-lead nitrate solution (1 ml. of 0.1N-nitric acid is added per litre of the solution to prevent the hydrolysis of lead nitrate) was prepared and also the concentration was determined as lead sulfate. Other reagents such as nitric acid, sodium hydroxide and alcohol were all c. p. grade.

Procedure: The fundamental experiment was carried out using the standard sodium sulfate and lead nitrate solution. To 10 ml. of 0.1N-sodium sulfate solution is added 10 ml. ethyl alcohol and 10 ml. of water and one drop of 0.1% methyl red, and titration is worked out with 0.1N-lead nitrate standard solution using the same electrode and the titration cell as mentioned above. The procedure is the same as reported in the previous paper.⑴

By the experiments, it is observed that the presence of less than 1N-sodium nitrate does not interfere in this titration. However, the acidity of the titrating solution gives much influence on the results of titration because of the amphotericity of lead ion. So in strong alkaline or acidic medium, the current increases from the beginning of the addition of lead ion, and lead sulfate does not precipitate. Near the *p*H of 9, owing to the coprecipitation of lead oxide with lead sulfate, a larger result is obtained. So, before the titration is carried out, it is preferred to regulate the *p*H of the solution to be about 3 to 5 using nitric acid or sodium hydroxide, and to titrate in 30% alcoholic medium. The recommended procedure for the determination of sulfur in pyrite is, therefore, as follows.

Sample (*ca.* 1 g.) is dissolved in 20 ml. of aqua regia and heated to boiling point and then evaporated to a syrupy state. Nitric acid is then added to the solution and is again concentrated to the same state. After the oxidation of sulfur to sulfate is completed, 20 ml. of water are added to it to dissolve the residue and 10 ml. of sodium hydroxide are added, heated to boiling point, filtered and washed with hot water. The precipitate is dissolved with hot 3N-nitric acid and reprecipitated with sodium hydroxide at boiling state and filtered and washed again. Both filtrates are transferred to a 100 ml. measuring flask and diluted with water to the mark. The aliquot portion is transferred to the cell and neutralized with 3N-nitric acid using phenolephtalein as an indicator. The same volume of alcohol is added to it and the solution is titrated with 0.1N-lead nitrate. The results are shown in Table 3.

Table 3

Determination of Sulfate

No.	0.1N-Na_2SO_4, ml.	Kind of indifferent Salt	0.1N-$PbSO_4$ used (f:1.058), ml.	Error or Result
1	10	None	9.45, 9.45, 9.45	0
2	10	*p*H=3	9.25, 9.30	−2.2%, −1.5%
3	10	1N-$NaNO_3$	9.45	0
4	10	*p*H=9	10.20	+8.0%
5	10	$pH{>12 \atop <1}$	not found	....
6	Pyrite(0.05 g.) (S=25.71%)		7.48 7.54 7.50	S=25.71% 25.58% 25.44%
7	Pyrite(0.10 g) (S=3.56%)		2.14 2.14 2.16	S= 3.63% 3.63% 3.66%

Conclusion

The amperometric titration of sulfate with lead nitrate standard solution by the use of metallic zinc-potassium chloride electrode as an anode was examined and this method was applied to the determination of sulfur in pyrite. A satisfactory result was obtained. These natural electrodes are sufficiently stable and reproducible for the use in short-circuited amperometric titrations.

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