Analytical Chemistry by Means of Organic Compounds XV
Electrolytic Reduction of Organic Reagents at the Dropping Mercury Cathode and its Application to Amperometric Titrations — 8-Hydroxyquinoline (2)

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In the previous paper, the behavior of electrolytic reduction of oxine were investigated and it was seen that the waves of oxine were well-defined in ammoniacal and alkaline medium and ill-defined in acidic medium. These were applicable to the amperometric titration of magnesium, copper, zinc and iron.

Experimental

Titration was carried out with the apparatus shown in Fig. 1. The manipulation of the titration was as follows. A measured volume (usually 20 ml.) of the standard sample solution in the proper medium was introduced into the cell and hydrogen gas was passed through for thirty minutes. The proper e. m. f. was applied to the cell and the current was measured. Alcoholic oxine solution was added successively with a microburette. After each addition the content of the cell was mixed by passing hydrogen gas for half a minute and the current was recorded after it became constant (after one or two minutes). In all cases the values of the current, corrected for the volume change, were plotted against the amount of reagent added. A small ordinary beaker was used as a titration cell, which was not closed when the concentration of metals was larger than about 10^{-3} M However it was necessary to keep on stirring by hydrogen gas, except the case of measurement.

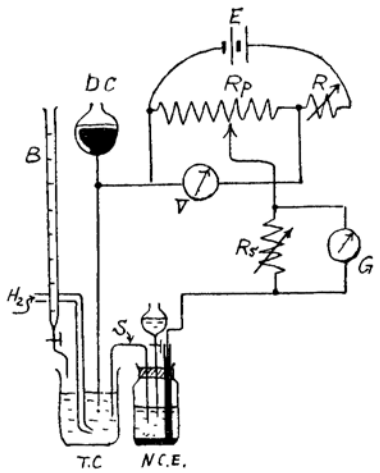

Fig. 1
Apparatus of amperometric titration
E: accumulator
R_p: potentiometer
R: variohm
V: voltmeter
G: galvanometer
R_s: shunt of galvanometer
$D.C.$: dropping mercury electrode
$T.C.$: titration cell
$N.C.E.$: normal calomel electrode
B: burette
S: salt bridge

Titration of Magnesium From the preliminary experiments, it was decided to carry out the titration of magnesium in a medium of ammonium chloride and ammonia. With the normal calomel electrode as anode, the applied e. m. f. was −1.60 V., so the first wave of oxine was used in the titration. In this medium the proportionality of diffusion current of oxine to its concentration was satisfactory (see Fig. 2). Results obtained in the titration of magnesium solutions are given in Table 1. Reverse titration was also agreeable. Calcium, when its amount was very small did not interfere with the titration. When its amount was large, high results were found. However, if ammonium oxalate was added in excess, the correct result was obtained, when separation of calcium oxalate was not necessary before the titration.

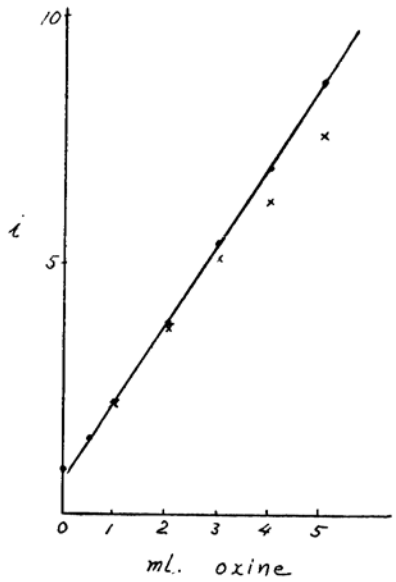

Fig. 2
The proportionality of diffusion current of oxine to its concentration
× observed values
• corrected values

Application of this titration to the analysis of magnesium in aluminium alloy, brine and sea-water were successful (Table 2). Aluminium alloy was dissolved in sodium hydroxide and the residue was dissolved in hydrochloric acid and ammonium hydroxide solution was added in excess. Then hydrogen sulfide was bubbled to precipitate other heavy elements and titrated with oxine without separating the precipitate. These sulfides did not interfere with the titration at this applied potential. Brine contains little calcium. Sea water contains calcium about 0.4 g. per litre, while calcium oxinate is slightly soluble when ammonium salts is present,[1] and by the salt effect of supporting electrolyte and sea-water, the direct titration was possible without adding ammonium oxalate.

Table 1
Titration of magnesium with oxine

No.	Mg used	Ca added	Oxine used	Factor of oxine	Mg found	Error
	mg.	mg.	ml.		mg.	%
1	4.30	0	6.38	0.672	4.287	−0.3
2	6.45	0	9.75	0.672	6.431	−0.3
3	8.60	0	12.77	0.672	8.581	−0.2
4	6.08	0	9.00	0.672	6.048	−0.5
5	4.30	20	6.35	0.672	4.267	−0.7
6	4.30	40	6.35	0.672	4.267	−0.7

* No. 1, 2 and 3 are mean value of several titrations.
* No. 4 is reverse titration (oxine was titrated with magnesium).
* In No. 5 and 6, ammonium oxalate was added in excess before titration.

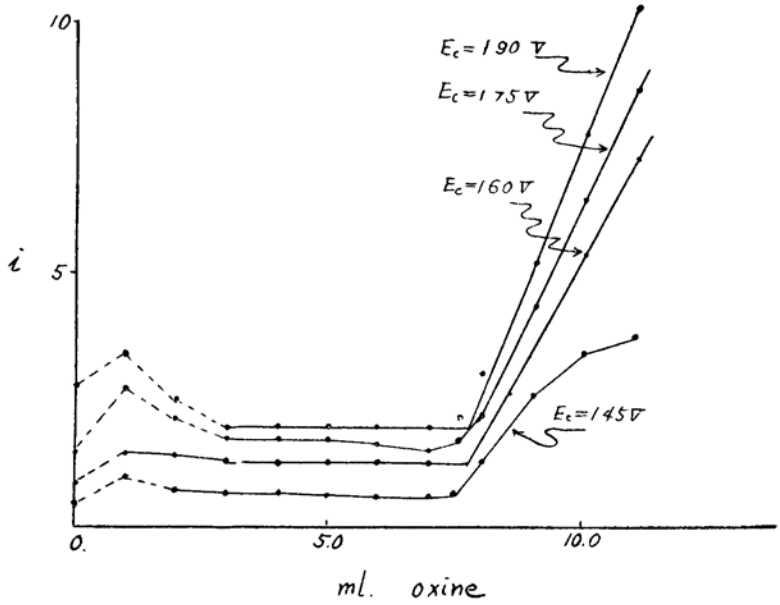

Fig. 3
Titration of magnesium in sea-water with oxine at various applied potentials

These samples were gravimetrically analysed as magnesium pyrophosphate. In this case calcium in sea water was eliminated as calcium oxalate. Sea water used was collected near Suma in the bay of Osaka and its chlorinity was 15.74. The magnesium content obtained in this experiment showed very good coincidence with that calculated from the Wattenberg's

(1) R. Berg, *Z. anal. Chem.*, **71**, 23 (1927)

data[2] (Table 3).

Table 2
Titration of magnesium in various samples

No.	Sample taken	Oxine used ml.	Factor of oxine	Mg found (Ampero.) mg.	Mg found (Gravi.) mg.	Error %
1.	Al-alloy					
	998.1mg.	7.30	0.680	4.964	4.742	+4.0
	1006.1mg	7.05	0.680	4.794	4.778	+0.3
2.	Brine					
	0.20 ml.	28.30	0.672	19.02	19.05	−0.2
	0.10 ml.	14.10	0.672	9.48	9.53	−0.5
3.	Sea water					
	5.00 ml.	8.05	0.680	5.474	5.456	+0.3
	5.00 ml.	8.00	0.680	5.440	5.456	−0.3
	5.00 ml.*	8.00	0.680	5.440	5.456	−0.3

* Calcium was precipitated as calcium oxalate.

Table 3
Magnesium content in sea-water

Mg in kg. of sea-water (by Wattenberg) Cl=19.00 ‰ g.	Mg in ml. of sea-water (calc. from Wattenberg) Cl=15.74 ‰ mg.	Mg in ml. of sea-water (Ampero. titr.) Cl=15.74‰ mg.	Error %
1.280	1.086	1.0882	0.2

Titrations of Iron, Zinc and Copper and Their Differential Titrations Ferric oxinate is quantitatively precipitated from the tartrate solution,[1] but this was not applicable for the titration, because the precipitation is complete only when the excess reagent is added. However we found that ferric iron dissolved in excess of ammonium carbonate reacts stoichiometrically with oxine and this medium is applicable for the titration. Copper was titrated in a medium of ammonium chloride—ammonia at $E_c=-1.60$ V. and sodium acetate-acetic acid at $E_c=-1.40$ V. and also titrated in ammoniacal medium using the rotating platinium wire electrode at $E_c=-0.40$ V. See Fig. 4. Zinc was titrated in the same medium as copper and in 0.1 N-sodium hydroxide at $E_c=-1.80$ V. The reduction of oxine in acidic medium is irreversible and the diffusion current of oxine is only proportional to its concentration in the small concentration range. Therefore, after passing the end point, it is difficult to get a straight line any more.

Next, it was attempted to titrate iron, zinc and copper, differentially when they are present altogether. Sample should be divided into three parts. To the first part we added ammonium carbonate in excess until precipitate of basic carbonate redissolved and titrated at $E_c=-1.60$ V (A cc.). To the second part ammonium chloride and ammonia were added to precipitate ferric hydroxide and the solution was titrated at $E_c=-1.60$ V (B cc.). To the last part, after heating to boiling, sodium hydroxide was added to precipitate copper and iron and the titration was carried out at $E_c=-1.80$ V after cooling the solution (C cc.).

Then the concentration of each component will be calculated from the next equations:

$$[Fe] = X(A-B)$$
$$[Cu] = X(B-C)$$
$$[Zn] = XC$$

In these equations X is the normality of oxine solution. This work, however, is only the preliminary one and the error was about 5% in the determination of zinc and copper. Results are shown in Fig. 5 and Table 4.

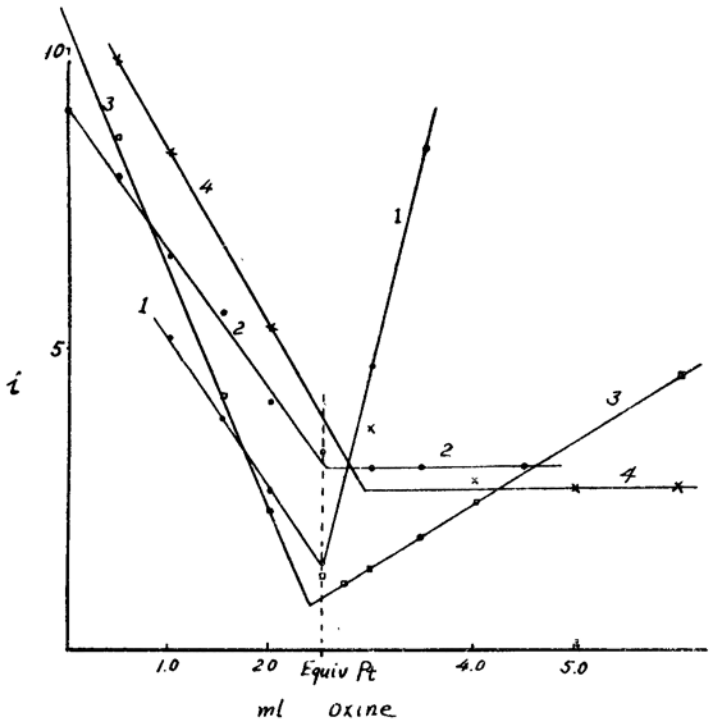

Fig. 4
Titration of copper with oxine
Curve 1 : No. 2 in Table 4 Curve 2 : No. 5 in Table 4
Curve 3 : No. 3 in Table 4 Curve 4 : No. 4 in Table 4
(Pt electrode at $E_c=-0.4$ V)

Summary

Magnesium was directy titrated by the amperometric method. The accuracy was 0.7% or better with 10^{-3} M concentration of magnesium. Its application to the analysis of alloy, brine and sea-water were studied. The interference of calcium and its elimination are described.

(2) H. Wattenberg, *Z. anorg. allgem. Chem.*, **236**, 46 (1938)

Table 4

Titration of coppr, zinc and iron

No.	Metal taken mg.	Medium	Oxine used mg.	Conc. of oxine N	Metal found mg.	Error %
1.	3.369 Cu	Amm. chl	5.00	0.0211	3.353	− 0.4
2.	1.685 Cu	Amm. chl.	2.48	0.0211	1.663	− 0.3
3.	0.1685 Cu	Amm. chl.	2.42	0.00211	0.1622	− 3.2
4.	0.0337 Cu	Amm. chl.	2.90	0.000422	0.0388	+15.04
5.	1.685 Cu	Amm. chl.	2.48	0.0211	1.663	− 1.3
6.	1.685 Cu	Acet. ac.	2.50	0.0211	1.676	− 0.5
7.	1.798 Zn	Amm. chl.	2.60	0.0211	1.793	− 0.3
8.	1.798 Zn	Acet. ac.	2.59	0.0211	1.791	− 0.4
9.	1.798 Zn	Sod. hyd.	2.60	0.0211	1.793	− 0.3
10.	1.033 Fe	Amm. carb.	2.64	0.0211	1.042	+ 0.9
11.	1.685 Cu 1.798 Zn	Amm. chl.	5.12	0.0211	.....	+ 0.0
12.	1.685 Cu 1.798 Zn	Sod. hyd.	2.44	0.0211	1.683 (Zn)	− 4.7
13.	1.033 Fe 1.685 Cu 1.798 Zn	Amm. carb.	7.75	0.0211	.....	+ 0.01

* In No. 5, the rotating platinium electrode was used.
* In No. 12, copper was precipitated as cupric oxide.

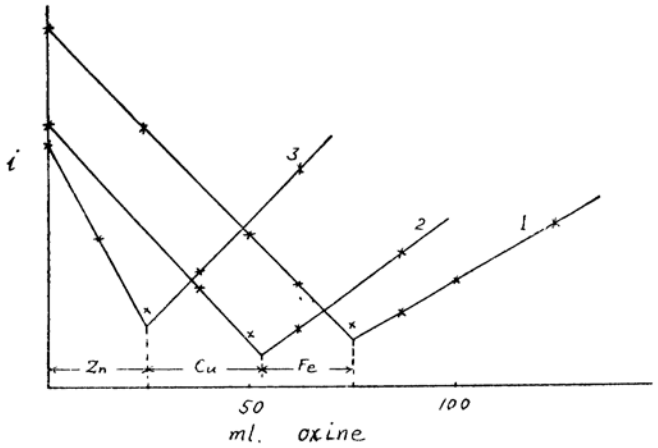

Fig. 5

Titration of mixture of iron, zinc and copper with oxine

Curve 1: in 2 N-$(NH_4)_2CO_3$
Curve 2: in 1 N-NH_4OH, NH_4Cl
Curve 3: in 0.1 N-NaOH

Iron, zinc and copper were also titrated with oxine and their differential titration was investigated.

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