

the range of concentration used in flotation practice.

Gaudin⁹ has shown that the cleanest concentrates are obtained with xanthates containing up to five carbon atoms in the hydrocarbon chain. His experiments on zinc ores indicate that octyl xanthate of itself causes frothing. It is, therefore, probable that part of the longer carbon chain xanthates are removed in the froth without reaction at the mineral surface. Preliminary experiments in this Laboratory with normal hexyl and normal nonyl xanthates indicate that normal hexyl froths much less than does normal nonyl xanthate. Quantitative experiments are under way.

It seems quite probable that if an actual maximum activity calculated on a molar basis occurs, this maximum will be caused by the carrying over of the unreacted collecting agent in the froth. Further, from the data cited, it is believed that such a collector will contain more than seven carbon atoms in the hydrocarbon chain.

The data cited would lead one to surmise that the order of the efficiency of xanthates as collectors for both chalcocite and malachite could have been predicted from the surface tension-concentration data of the several xanthates. However, in arriving at such a generalization it may be necessary to make allowance for the frothing properties of the higher xanthates.

Summary

1. A surface tension apparatus is described which involves Ferguson's principle. The novel

features of the apparatus are the pressure adjusting part and the unified arrangement which readily lends itself to immersion in a thermostat.

2. The surface tension of aqueous solutions of a number of xanthates is reported. A qualitative statement of the results is as follows. (a) The molal lowering of the surface tension is approximately the same for both sodium and potassium ethyl xanthates within the limits of equal solubility. (b) The lowering of surface tension increases in accordance with Traube's rule, as the homologous series of xanthates is ascended from the ethyl group up to and including the nonyl group. (c) Isomeric forms of potassium amyl xanthate differ considerably in their effect upon the surface tension of water. The lowering sequence of the xanthates is as follows in fairly concentrated solutions: (1) *n*-amyl, (2) isoamyl, (3) *s*-butylcarbinyl, (4) methyl-*n*-propylcarbinyl, (5) diethylcarbinyl. (d) In the dilute range the slopes of the surface tension-concentration curves of the isomeric amyl xanthates are in accord with the findings of Swainson and Anderson¹⁰ as to the promoter activity of the isomeric amyl xanthates—secondary, iso, normal.

3. The efficiency of the normal xanthates, ethyl to heptyl inclusive, as collectors for both chalcocite and malachite has been correlated with the surface tension-concentration data of these xanthates.

(10) Swainson and Anderson, *Am. Electrochem.* Preprint, 1931.

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[CONTRIBUTION FROM THE INSTITUTE OF ANALYTICAL CHEMISTRY OF CHARLES UNIVERSITY]

Volumetric Determinations in Strongly Alkaline Solutions. I. The Titration of Cobalt with Ferricyanide

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A number of metals have been determined oxidimetrically with ferricyanide,¹ and we wish to present in this communication the direct oxidimetric titration of cobaltous salts by potassium ferricyanide.

Materials

Potassium ferricyanide solutions were made up 0.1 molar by weight from C. P. salt containing a trace of ferrocyanide and the normality determined both potenti-

metrically² and iodimetrically.³ The solutions were stored in brown bottles and the titer was found to be constant during a week and to lose 0.005 *N* in some three months. The 0.05 and 0.01 *N* solutions were prepared by dilution and analysis.

Potassium iodide, sodium thiosulfate, potassium permanganate, and other solutions were prepared from average pure salts and standardized by the usual methods.

Cobalt Salts and Solutions.—Cobalt sulfate heptahydrate (Kahlbaum-Schering) was used in preliminary

(1) Tomíček, *Rec. trav. chim.*, **44**, 410 (1925); Furman and Evans, *This Journal*, **51**, 1128 (1929); Hahn, *Z. angew. Chem.*, **40**, 349 (1927); del Fresno and Valdés, *Z. anorg. allgem. Chem.*, **183**, 251 (1929).

(2) E. Müller and O. Diefenthaler, *Z. anorg. allgem. Chem.*, **135**, 265 (1924).

(3) I. M. Kolthoff, *Pharm. Weekblad*, **59**, 66 (1922).

work and found to contain traces of nickel and alkali metals, so cobalt sulfate was prepared from pure cobalt free from these metals. Fifteen grams of Kahlbaum metallic cobalt was warmed with 125 cc. of pure dilute sulfuric acid until nearly dissolved, cooled and filtered into 96% ethanol. The minute crystals of pure salt thus obtained were separated on a filter plate, washed with 96% ethanol and dried at room temperature. Its composition as a hexahydrate was proved by treatment in the "dehydratograph"⁴ and a gravimetric dehydration in a furnace at not over 420°.

Anal. Calcd. for $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$: H_2O , 41.09. Found: H_2O , 41.06, 41.03, 41.05.

The dehydrated salt was used in the final experiments on the accuracy of the titration. For other work a stock solution was made up from the hydrated salt and its concentration ascertained by evaporating a portion and weighing the salt residue.

Copper and zinc sulfates, ammonium metavanadate, ammonium hydroxide and other salts and reagents were of average purity and cobalt free. Nickel sulfate was of c. p. quality but contained cobalt.

The technically pure cobalt and some cobalt-containing steels were kindly given to us by Ing. F. Wald, Chief of the Analytical and Research Laboratory of Vitkovice Means, Steel and Iron Corporation, Čs. R. The meteorite samples came from the Mineralogical Institute of Charles University in Prague through the kindness of Dr. F. Ulrich.

Apparatus

The apparatus⁵ included a titration vessel of some 170 cc. volume, closed by a rubber stopper with openings for platinum spiral electrode, potassium chloride siphon tube connecting to the calomel electrode, buret, carbon dioxide in- and outlet tubes, thermometer, and small funnel for introducing the required ammonia solution. The carbon dioxide was prepared from marble and hydrochloric acid and purified by washing first with concentrated titanous chloride saturated with sodium acetate and then with water. Solutions were measured in calibrated pipets and burets or in a microburet if the volume was small. Iron was separated by the method of J. W. Rothe in a special separatory funnel.⁶

Titration of Cobalt

Known solutions of cobalt sulfate were titrated potentiometrically with potassium ferricyanide in the presence of sodium or potassium hydroxide or carbonate, potassium cyanide or ammonium hydroxide, in an atmosphere of carbon dioxide. Potassium cyanide gave an irregular jump in potential. The best results were obtained with ammonium hydroxide, as the solution did not become turbid and complete oxidation is indicated by a sharp and well-reproducible change in potential. Atmospheric oxidation of the cobalt

may become serious at elevated temperatures. Large quantities of ammonium chloride, sulfate or nitrate are harmless and seem to have a beneficial stabilizing effect on the potential near the end-point.

In the preferred procedure, 20–30 cc. of 0.05 *M* cobalt chloride, sulfate or nitrate is placed in the titration vessel, the stopper inserted, the vessel immersed in ice (to below 10°) and a slow stream of air-free carbon dioxide bubbled through for ten to fifteen minutes. Then 40–60 cc. of 10% ammonia is added through the funnel to give a 3 *N* concentration at the end-point, and the solution cooled again. Finally 0.1 or 0.05 *M* potassium ferricyanide is added until the potential breaks. Upon adding ferricyanide the color becomes dark red and deepens with further additions. The titration may be made rapidly, as the potential becomes steady quickly after each addition until near the end-point, at which perhaps a minute may be necessary to give a constant reading. The inflection potential under the conditions specified is 0.00 volt as related to the saturated calomel electrode.

The removal of air by passage of carbon dioxide before adding the ammonia is quite important, as is also the order of procedure; the addition of potassium ferricyanide before ammonia should be avoided as it gives a brown precipitate which does not dissolve in excess ammonia. The 3 *N* concentration of ammonia at the end seems most suitable although a greater concentration does no harm. The 0.1 and 0.05 *N* potassium ferricyanide solutions are preferable to a 0.01 solution, which gives a slow titration and prolonged end-point.

A typical titration is illustrated in Fig. 1.

Numerous cobalt determinations were made, using varying volumes of reagent, and agreeing and reproducible results were obtained, as is shown in the table.

TABLE I

$\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$, g.	0.1 <i>N</i> $\text{K}_3\text{Fe}(\text{CN})_6$, cc. Calcd.	Used	Diff., %
0.4391	16.69	16.70	+0.06
.4648	17.67	17.66	– .06
.4794	18.22	18.21	– .06
.3967	15.08	15.07	– .07
.2949	11.21	11.22	+ .09
.2932	11.14	11.14	.00

Titration of Cobalt in the Presence of Nickel and Other Metals.—Experiments with cobalt-free nickel sulfate showed that nickel does not

(4) S. Škramovský, *Coll. Czechoslovak. Chem. Comm.*, **5**, 6 (1933).

(5) I. M. Kolthoff and O. Tomíček, *Rec. trav. chim.*, **43**, 780 (1924).

(6) W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, 1929, p. 108.

react with the ferricyanide or affect the electrode potential, and it also has been found that an excess of nickel salt does not interfere with the titration of small amounts of cobalt. For example, 5 g. of ordinary nickel sulfate was titrated and found to contain 0.04% of cobalt while 5 g. of Schering-Kahlbaum nickel sulfate hepta-

hydrate showed 0.008% of cobalt (both calculated as $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$). Metallic nickel may be analyzed by dissolving in hydrochloric acid and following the same procedure as for metallic cobalt.

Although the properties of nickel are similar to those of cobalt, nickelous ion forms an ammonia complex which does not oxidize under the conditions of the experiment, whereas cobaltous ammonia complexes are not known and the cobalt is therefore readily oxidizable, making the ferricyanide titration possible.

TABLE II

0.1 N CoSO ₄ , cc.	Substance added	G.	Ca. 0.1 N K ₃ Fe(CN) ₆ , cc. (av. of 3)	Diff., cc.
1	0.97
5	4.97
10	9.96
10	Zinc sulfate, cryst.	0.5	9.97
10	Same	1.0	9.97
10	Same	2.0	9.97
5	Same	1.0	4.97
1	Same	2.0	0.97
10	Ferrous ammonium sulfate,	0.5	9.68	-0.28
10	Same cryst.	1.0	9.40	-0.56
10	Same with tartaric acid, 1 g.	0.5	9.97
5	Same, 2 g.	1.0	4.97
5	Same, 3 g.	2.0	4.98
1	Same, 3 g.	2.0	0.97
10	Sodium arsenate	0.5	9.96
10	Same	1.0	9.97
10	Same	2.0	9.96
5	Same	0.5	4.97
1	Same	1.0	0.97
10	Copper sulfate, cryst.	0.5	9.96
10	Same	1.0	9.97
10	Same	2.0	9.97
5	Same	0.5	4.97
1	Same	2.0	0.97
10	Potassium chromic sulfate,	0.05	9.97
10	Same cryst.	.5	9.83	-0.13
10	Potassium chromate, cryst.	.5	9.97
10	Same	1.0	9.96
5	Same	1.0	4.97
1	Same	2.0	0.98
10	Ammonium molybdate	0.5	9.97
10	Same	1.0	9.97
5	Same	1.0	4.96
1	Same	2.0	0.97
10	Ammonium metavanadate	0.2	9.97
10	Same	.5	9.96
5	Same	.2	4.95
1	Same	.5	0.95
10	Nickel sulfate heptahydrate	1.0	9.97	+0.01
10	Same (0.008% Co)	3.0	9.97	+ .01
10	Same	5.0	9.98	+ .02
10	Same	10.0	9.99	+ .03
5	Same	5.0	4.99	+ .02
5	Same	10.0	5.00	+ .03
1	Same	10.0	1.00	+ .03
10	Nickel sulfate heptahydrate	1.0	9.98	+ .02
5	Same (0.04% Co)	5.0	5.01	+ .05
1	Same	10.0	1.10	+ .13
0	Same	5.0	0.07
0	Same	10.0	.13

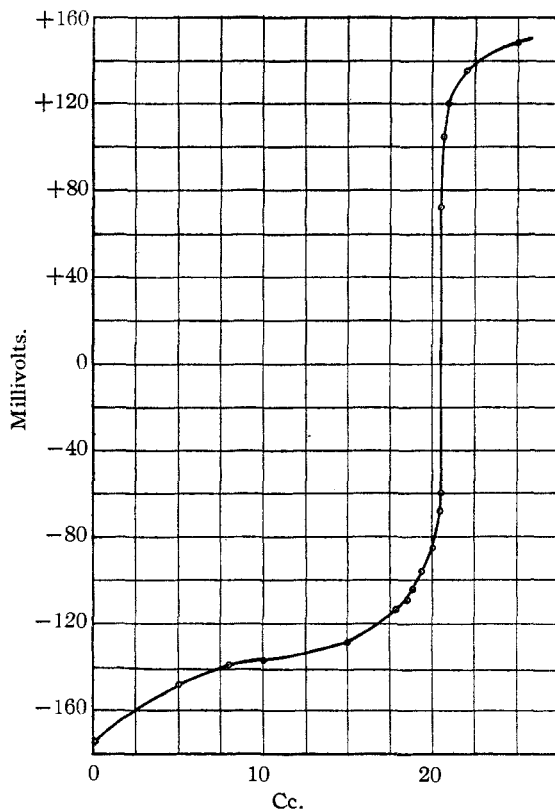


Fig. 1.—The titration curve of cobaltous salt by ferricyanide in 3 normal ammonia (calcd. inflection at 20.65 cc.; observed, 20.64 cc.).

Divalent copper and zinc and pentavalent arsenic do not interfere, while ferrous iron and trivalent arsenic must be absent. A small amount of ferric ion is harmless but a large amount is troublesome, as the hydroxide which precipitates adsorbs cobaltous ion. A reasonable amount of ferric ion may be suppressed by adding tartaric acid, but when much is present, as in the analysis of iron alloys, it must be removed by the Rothe⁶ method (the zinc oxide process is not applicable here). Hexavalent chromium and

molybdenum and pentavalent vanadium do not interfere, nor does chromic ion (which oxidizes only in strongly alkaline hydroxide medium) except for the adsorbing effect of its hydroxide. Manganese if present should be removed as manganese dioxide, as it reacts with ferricyanide. Its determination by ferricyanide titration will be presented in a later paper.

Practical Analytical Application.—In order to test the method, analyses were made of (1) technical cobalt, (2) special steel 139, (3) special steel 333 and (4) samples of meteorite. In general the procedure was to dissolve the sample of cobalt or alloy (about 5 g.) in dilute hydrochloric acid, oxidize the iron with boiling nitric acid, make up to 500 cc. and titrate aliquot portions. Iron was suppressed by tartaric acid in the cobalt samples and in the case of alloys removed by the Rothe method. Manganese was separated as manganese dioxide by oxidation with ammonium persulfate in slightly acid solution with silver as catalyst. The other constituents of the alloys were determined by standard methods.⁷

TABLE III

	ANALYSES OF COBALT AND ALLOYS				
	Tech. cobalt (Co + Ni, 99%)	Steel No. 139		Steel No. 333	
		Calcd.	Found	Calcd.	Found
Co	98.03	2.16	2.09	0.20	0.22
Cr	...	2.30	2.36	1.23	1.21
Cu	1.15	Undetd.
Mn	0.46	7.67	7.64
Ni	...	1.68	1.72	8.30	8.34
V	...	0.10	0.11
W	...	8.25	8.24

(7) I. M. Kolthoff and O. Tomiček, *Rec. trav. chim.*, **43**, 447 (1924); W. Hiltner and C. Marwan, *Z. anal. Chem.*, **91**, 401 (1933).

The meteorite samples were from a meteorite found September 18, 1909,⁸ at Teplá near Mariánské Lázně in the Czechoslovak Republic. The material was partly as shining filings and the rest in larger pieces from which filings were prepared on a lathe. The samples were not quite homogeneous but the cobalt content agrees very well.

TABLE IV

Sample, g.	ANALYSES OF THE METEORITE			Notes
	Filings used in 1-5, larger pieces in 6-10			
	Co, %	Ni, %	Fe, %	
5.00	0.45	} Fe removed by Rothe method
4.00	.43	
1.500	.45	Fe by tartaric acid
0.4995	.43	7.20
1.0225	.45	7.40	88.03
1.3773	.43	} Fe by addn. of tartaric acid
1.4965	.44	
0.5070	.44	8.97	...	
.5119	.42	9.24	...	
1.1196	.48	8.60	91.04	

Summary

1. A new, rapid, simple, potentiometric titration of cobalt with ferricyanide has been described.

2. The method is not interfered with by large amounts of nickel or by Cu^{II} , Zn^{II} , As^{V} , Fe^{III} , Cr^{III} , chromate, molybdate or metavanadate. Manganese and large amounts of ferric ion must be absent.

3. The application of the method to some alloys and samples of a meteorite is given.

PRAGUE, CZECHOSLOVAKIA RECEIVED SEPTEMBER 10, 1934

(8) B. Ježek, *Rozpravy II. tr. české akademie*, **33**, No. 12 (1923); *Bull. int. Acad. Sci. Bohême*, 1923; analysis by J. St. Štěrba-Böhm: Fe, 88.80; Co, 1.95; Ni, 7.47; Ca, 0.70; Mg, 0.52; P, 0.25; C, 0.35; Si and S, traces.