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1. *Conditions for Estimating Antimony by the Permanganate Method: Potentiometric Titration.*

By W. Pugh.

The method most in use for the estimation of antimony in its alloys is that of Low (*J. Amer. Chem. Soc.*, 1907, **29**, 66) or one of its modifications [Demorest, *J. Ind. Eng. Chem.*, 1913, **5**, 842; McCabe, *ibid.*, 1917, **9**, 42; Shaw, Whittemore, and Westby, *ibid.* (*Anal. Edn.*), 1930, **2**, 402], involving titration by permanganate in acid solution. When using solutions of pure antimony, however, the author was unable to get consistent results.

Until recently, the method was often regarded as empirical and factors were given for use with it (see, *e.g.*, Sutton, " Volumetric Analysis," 1924, p. 159), but this is doubtless due to the erroneous atomic weight in use for antimony (120·2) until 1921; with the new value of 121·76 (Willard and McAlpine, *J. Amer. Chem. Soc.*, 1921, **43**, 797) this objection disappears, for it is now possible to obtain concordant standardisation of permanganate on antimony and on sodium oxalate. Under the proper conditions, the author obtains agreement by the two methods to within 1 part in 3,000.

The condition necessary for this agreement is essentially the proper adjustment of the relative quantities of sulphuric and hydrochloric acids used. Too little of the latter leads to low results on account of the precipitation of a basic antimony salt, and too much leads to the reduction of permanganate by chloride ions, with liberation of chlorine, and the end-point becomes barely perceptible. When the ratio of the two acids is properly adjusted, the oxidation of tervalent antimony proceeds stoicheiometrically according to the equation $4MnO_4' + 5Sb_2O_3 + 12H^{\cdot} \longrightarrow 4Mn^{\cdot\cdot} + 5Sb_2O_5 + 6H_2O$, and the estimation of antimony becomes one of the simplest and most accurate of volumetric processes.

Potentiometric Titration.—The effect of varying the quantities and the ratio of the two acids on the accuracy of the method was investigated by potentiometric titration. A stock solution was made by dissolving 2·9736 g. of Kahlbaum's Sb in 30 c.c. of conc. H_2SO_4, diluting it, boiling off traces of SO_2, and making it up to 500 c.c. with 125 c.c. of conc. HCl and H_2O. The $KMnO_4$ was standardised with this solution, and found to be 0·09062*N*; against $Na_2C_2O_4$ it was 0·09060*N*.

For the electrometric titration, 20·00 c.c. of the Sb solution, in an initial vol. of 180 c.c., were taken in every case. This initial vol. contained measured amounts of conc. HCl and of conc. H_2SO_4 which had previously been diluted and boiled to expel SO_2. The titrations were made at room temp. (15—17°) and the liquid was stirred mechanically.

A bright Pt wire dipping into the liquid constituted one half-element; the other was the satd. HgCl electrode connected through an agar-agar–KCl bridge. The *E.M.F.* of the combination was measured after each addition of $KMnO_4$. In Table I, *E* is the *E.M.F.*, it being assumed that the potential of the satd. HgCl is zero.

In every titration, except two where the acid concn. was so low that the solution was cloudy, the potential assumed a steady value immediately over the whole titration up to the equivalence point. Beyond this point a fairly rapid upward drift set in, probably owing to interaction between $KMnO_4$ and HCl. The change of potential in the neighbourhood of the equivalence point is very large, being about 300 millivolts. Since the titration readily shows the influence of $[H^{\cdot}]$ it is well adapted to illustrate the principles of oxidation potentials.

In every case, the $KMnO_4$ colour change is coincident, to within 0·02 c.c., with the potentiometric end-point, the colour change being slightly delayed.

In Table I are the results of three complete titrations. Numerous others were carried out under different conditions of acidity and these are summarised in Table II, where the influence of the ratio H_2SO_4 : HCl is clearly seen. Some of the results are also plotted in the fig. The theoretical titre is 21·56 c.c.

Titration of 20 *c.c.* Sb *soln.* (0·09769*N*) *with* $KMnO_4$ (0·09062*N*).

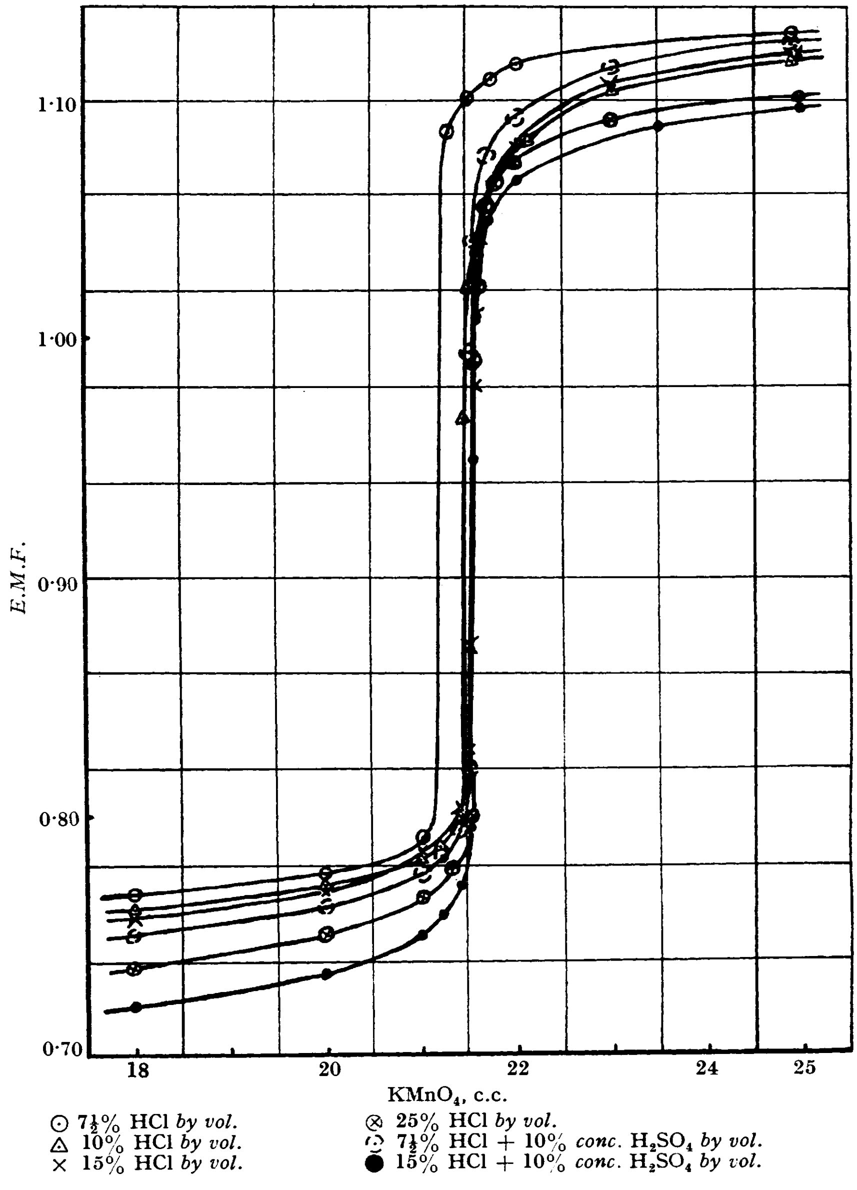

Table II shows that low results are obtained when the [H˙] is low. On the other hand, above a certain min., the amount of acid has no influence on the accuracy of the electrometric titration, although the colour change becomes less readily detectable as the Cl′ ion concn. increases. In order, therefore, to get accurate results in the volumetric estimation of Sb it is necessary to adjust the quantities of HCl, within certain limits, according to the quantity of H_2SO_4 present. These limits. according to the data in Table II, are set out in Table III for a total vol. of 200 c.c. :

TABLE I.

20 C.c. of antimony solution; final volume, 200 c.c.

	Solution A.		Solution B.		Solution C.	
$KMnO_4$, c.c.	*E.*	$\Delta E/\Delta C$.	*E.*	$\Delta E/\Delta C$.	*E.*	$\Delta E/\Delta C$.
5	—		0·690		0·684	
10	0·730		0·710		0·704	
15	0·746		0·728		0·722	
20	0·768		0·758		0·752	
21·00	0·786		0·770		0·766	
21·20	0·792		0·780		0·776	
21·40	0·804		0·790		0·788	
21·44	0·810		0·792		0·796	
21·48	0·828	450	0·794	50	0·806	250
21·52	0·872	1100	0·810	400	0·838	800
21·56	0·984	2800	0·968	3950	1·006	4200
21·60	1·012	700	1·006	950	1·042	900
21·64	1·036	600	1·020	350	1·056	350
22·0	1·084		1·080		1·08	
23·0	1·106		1·100		1·10	
25·0	1·119		1·112		1·11	

Solution A contained 30 c.c. of conc. HCl.
Solution B contained 40 c.c. of conc. HCl.
Solution C contained 20 c.c. of conc. HCl + 20 c.c. of conc. H_2SO_4.

TABLE II.

20 C.c. of antimony solution; initial volume, 180 c.c.

C.c. of conc. acid present.				
H_2SO_4.	HCl.	Titre.	Error, %.	Duration of colour.
1	15	21·35	−1	2—3 min.
1	20	21·45	−0·5	1—2 min.
1	30	21·54	−0·1	1 min.
1	40	21·56	±0·0	30 sec.
1	50	21·56	±0·0	20 sec.
1	60	21·57	+0·05	evanescent
5	20	21·50	−0·3	1 min.
5	30	21·55	−0·05	30 sec.
5	40	21·55	−0·05	5 sec.
10	10	21·33	−1·1	1—2 min.
10	15	21·44	−0·6	1 min.
10	20	21·52	−0·2	30 sec.
10	30	21·55	−0·05	20 sec.
10	40	21·57	+0·05	evanescent
20	5	21·32	−1·2	2—3 min.
20	10	21·50	−0·3	1 min.
20	15	21·54	−0·1	30 sec.
20	20	21·56	±0·0	15 sec.
20	30	21·57	+0·05	evanescent
30	5	21·54	−0·1	30 sec.
30	10	21·56	±0·0	15 sec.
30	15	21·57	+0·05	5 sec.

TABLE III.

Conc. H_2SO_4, c.c.	0	10	20	30
Conc. HCl, c.c.	30—50	30—35	15—20	10—15

Estimation of Antimony in Lead–Tin Alloys.—The best solvent for such alloys is boiling conc. H_2SO_4, which dissolves Sn as Sn^{IV} and Sb as Sb^{III}. In such a solution, Demorest (*loc. cit.*) and McCabe (*loc. cit.*) estimate the Sb by addition of excess of $KMnO_4$ and back-titration with $FeSO_4$. This method is empirical and is liable to give results for Sb which are high by 1%. This is due to the fact that in absence of HCl the reduction of $KMnO_4$ by $Sb^{\cdots}$ ion does not proceed quantitatively to $Mn^{\cdot\cdot}$ except under special conditions, any departure from these leading to partial reduction to tervalent Mn.

In view of the great accuracy of the estimation in the presence of HCl, as shown by the electrometric titrations, the author has adapted the method for antimony alloys. In any method involving the use of H_2SO_4 for solution, considerable error may be caused by occlusion of Sb salts in the pptd. $PbSO_4$. Three methods of avoiding this were tested.

Method I. A suitable wt. of the alloy (containing about 0·1 g. of Sb) was decomp. with 20 c.c. of conc. H_2SO_4 and 5 g. of fused Na_2SO_4 until the residue was quite white. After cooling, 50 c.c. of H_2O were added and the whole was boiled for 5 min. to expel SO_2. 20 C.c. of conc. HCl were then added, and the liquid well shaken, diluted to 180 c.c., cooled to 15°, and titrated with $KMnO_4$ to a pink flush.

Method II. The alloy was dissolved completely in 20—50 c.c. of conc. H_2SO_4, according to the amount of Pb present, the liquid cooled, diluted to 100 c.c. and set aside. The clear solution was decanted from $PbSO_4$ and boiled for 5 min. to expel SO_2. The $PbSO_4$ was boiled with the appropriate vol. of conc. HCl (see Table III) and an equal vol. of H_2O. When the $PbSO_4$ was completely in solution, it was washed into the main bulk of Sb solution, cooled to 15°, and titrated with $KMnO_4$.

Method III. The procedure was that of method II, but the liquid was titrated hot (40—60°), the addition of $KMnO_4$ being slow to prevent loss of chlorine; near the end-point, a few drops of methyl-orange were added, and the titration continued to the discharge of the indicator colour. The end-point was perfectly sharp and very little Pb salt separated.

These three methods were tested on mixtures of the pure metals, with the results shown in Table IV. Three commercial alloys were then selected, alloy II being heavily contaminated with Cu and Fe. The results on these are in Table V.

For the mixtures, the results by method I are inconsistent; and for the alloys, they are low as well. The results by method II are higher but still inconsistent: some Sb either remains undissolved or is coprecipitated with the Pb salt on cooling. Method III is therefore recommended as giving the best results; it is also the quickest for routine purposes. Sn may be determined in the same solution by reduction and titration with I; Pb and Cu may be determined in separate portions of the alloy. A complete analysis of the three alloys gave the following results:

TABLE IV.

Content, %.			Sb taken, g.	Method.	Sb found, g.	Content, %.			Sb taken, g.	Method.	Sb found, g.
Pb.	Sn.	Sb.				Pb.	Sn.	Sb.			
—	—	100	0·1191	I	0·1191	85	4	11	0·1210	I	0·1209
			0·1200	I	0·1200				0·1208	I	0·1202
			0·1203	III	0·1204				0·1204	I	0·1180
			0·1217	III	0·1218				0·1213	II	0·1213
65	12	23	0·1209	I	0·1213				0·1208	II	0·1205
			0·1201	I	0·1201				0·1208	II	0·1208
			0·1219	I	0·1216				0·1196	III	0·1194
			0·0613	I	0·0610				0·1191	III	0·1191
40	—	60	0·1220	I	0·1226				0·1191	III	0·1189
			0·1194	III	0·1193						
			0·1200	III	0·1199						

TABLE V.

Sb, found, %; and method.

Alloy I.			Alloy II.			Alloy III.		
I.	II.	III.	I.	II.	III.	I.	II.	III.
22·43	22·66	22·90	9·27	9·42	9·85	15·27	—	15·36
22·41	22·65	22·95	9·21	9·43	9·81	15·20	—	15·38
22·34	22·61	22·85	8·80	9·51	9·83	—	—	15·37
22·57	22·47	22·90	—	9·77	9·80	—	—	15·35
22·40	—	—	—	9·60	—			
			—	9·38	—			

	Pb.	Sn.	Sb.	Cu.	Fe.	Total.
Alloy I	63·6	13·42	22·90	—	—	99·92
,, II	85·0	3·98	9·83	0·95	0·14	99·90
,, III	78·9	5·70	15·36	—	—	99·96

SUMMARY.

1. The oxidation of tervalent antimony by potassium permanganate has been followed potentiometrically and found to be stoicheiometric under the proper conditions.

2. The essential condition for correct results when titrating in the cold is to adjust the amount of hydrochloric acid according to the amount of sulphuric acid present.

3. The method gives low results in the presence of lead because the lead sulphate occludes considerable amounts of antimony sulphate.

4. This source of error is obviated in the modified method described, according to which the lead sulphate is maintained in solution in the presence of hot hydrochloric acid and the solution is titrated at 40—60° with permanganate, with methyl-orange as indicator.

UNIVERSITY, CAPE TOWN.

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