79. *The Determination of Small Amounts of Aluminium in Spelter.*

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The aluminium content of spelter has an important bearing on its behaviour in hot-dip galvanising. Existing methods for the separation and determination of small amounts of aluminium have been improved and adapted to the analysis of spelter.

In the modern " hot-dip " galvanising process, aluminium is added to the galvanising bath in order to improve the appearance, uniformity, and flexibility of the coating. At the same time, the thickness of the coating may be decreased, depending on the amount of aluminium added.

A rigid control of the aluminium contents of the bath—ranging from 0·01 to 0·1%—has to be maintained, so an accurate and rapid method of determination is required. The bath made up from spelter according to B.S.S. 222 should contain not more than 1·25% of lead, 0·07% of iron, 0·02% of tin, 0·02% of antimony and arsenic, and 0·25% of cadmium, the remainder being zinc.

The separation of aluminium from large amounts of zinc by ammonia is troublesome and unsatisfactory. The elimination of interfering elements can be achieved with the help of a mercury cathode cell (Scherrer and Mogerman, *J. Res. Nat. Bur. Stand.*, 1938, **21**, 106) but necessitates special equipment, and the complete removal of zinc from a larger sample of spelter takes several hours.

Kolthoff and Stenger and their co-workers (*J. Amer. Chem. Soc.*, 1934, **56**, 812; *Ind. Eng. Chem. Anal.*, 1942, **14**, 797) introduced ammonium benzoate as an analytical reagent which separates aluminium from zinc, cadmium, and iron(II), but small amounts of zinc are co-precipitated. With the help of this reagent, a method has been adopted, based on the following separations. Lead and tin remain undissolved when the sample is treated with a dilute sulphuric–hydrochloric acid mixture in the presence of excess of zinc. Aluminium, together with iron(III), is precipitated as benzoate and subsequently freed from iron and co-precipitated zinc by treatment with hydrogen sulphide in ammoniacal tartrate solution (Haslam, *Analyst*, 1933, **58**, 270). Aluminium is finally precipitated as the 8-hydroxyquinoline derivative and estimated volumetrically.

Experimental.

Special Solutions.—(i) Ammonium acetate, 500 g./l. (ii) Ammonium benzoate, 100 g./l., with addition of 1 mg. of thymol. (iii) Ammonium benzoate wash-liquid : 100 ml. of reagent (ii) diluted to 1 l. ; for use, 2 ml. of glacial acetic acid are added to 100 ml. of this solution, which is used hot, since benzoic acid separates at room temperature. (iv) Ammoniacal tartrate solution : 30 g. of tartaric acid and 150 ml. of ammonia (*d* 0·88) in 1 l. (v) Ammonium sulphide–tartrate wash-liquid : a solution of 1 g. of tartaric acid in 200 ml. of water is saturated with hydrogen sulphide, and 2·8 ml. of ammonia (*d* 0·88) are added. (vi) " Oxine " reagent : 10 g. of 8-hydroxyquinoline are treated with 25 ml. of glacial acetic acid diluted with an equal volume of water and made up to 500 ml. (vii) Standard 0·1N-potassium bromate–bromide solution : 2·784 g. of potassium bromate and 13 g. of potassium bromide in 1 l. (1 ml. = 0·2248 mg. of aluminium). (viii) 0·1N-Sodium thiosulphate solution : 25 g. of the pentahydrate and 2 g. of borax in 1 l. (ix) Indigo-carmine indicator : 0·5 g. in 100 ml. of water. (x) Stabilised starch solution : 2 g. of soluble starch made into a smooth paste with a little cold water and poured with constant stirring into 500 ml. of boiling water containing 0·6 g. of salicylic acid; boiling is continued for 2 mins., and the solution cooled to room temperature.

Procedure.—For amounts of 0·02—0·1% of aluminium, 5 g. of fine magnetted drillings are gently heated in a 400-ml. conical beaker with 25 ml. of 1 : 4 sulphuric acid and 25 ml. of 1 : 9 hydrochloric acid. When the evolution of hydrogen has ceased, 1 g. of pure zinc is introduced, and the liquid warmed for 5 mins. The solution is then filtered through a 9-cm. Whatman filter-paper No. 41 into a 400-ml. conical beaker, and beaker and filter are washed five times with 10 ml. of water. The filtrate is cooled, and after addition of 4 ml. of solution (i), 5N-ammonia is added in portions of 1 ml. with constant shaking, until a distinct turbidity remains. To the turbid solution 3 or 4 drops of glacial acetic acid are added, but no attempt is made to dissolve the slight precipitate which collects at the bottom of the vessel. Slowly and with constant stirring, 20 ml. of reagent (ii) are added. The liquid is heated and kept gently boiling for 5 mins. with occasional stirring. The precipitate is allowed to settle somewhat and is then filtered hot on an 11-cm. Whatman filter-paper No. 41. If the first portion is turbid, it should be refiltered. After the beaker and filter have been washed five times with hot wash-liquid (iii) and once with hot water, the precipitate is dissolved on the filter-paper with 50 ml. of hot ammoniacal tartrate solution (iv), and the filter-paper washed with a hot mixture of 5 ml. of solution (iv) and 45 ml. of water.

The filtrate and washings, collected in the beaker in which the benzoate precipitation took place, are heated just below boiling point, and a rapid current of hydrogen sulphide is passed through for 5 mins. Half a macerated Whatman accelerator and 3 ml. of ammonia (*d* 0·88) are added, and after the solution has been shaken and gassed for 2 mins. the precipitate is allowed to settle in a warm place. It is then filtered off on an 11-cm. Whatman filter-paper No. 41, and beaker and filter are washed five times with 10 ml. of wash-liquid (v). The filtrate and washings are collected in a 400-ml. conical beaker, heated to 90°, and an excess of oxine reagent (vi) (shown by a yellow colour of the liquid) is added slowly and with constant stirring. Heating at 90° is continued until the precipitate coagulates, and it is allowed to settle in a warm place for 15 mins. The complex is then collected on an 11-cm. Whatman filter-paper No. 540, and beaker and filter are washed with hot water until the washings are colourless. The precipitate is dissolved on the filter with 50 ml. of hot 1 : 1 hydrochloric acid into the beaker in which the oxine precipitation took place, and the filter is washed with 50 ml. of hot water. The volume is adjusted to 150 ml., and the solution cooled to room temperature. After addition of three drops of indicator (ix), standard bromate–bromide solution is run in slowly from a burette until the colour changes to pure yellow, and then 3—5 ml. are added in excess. About 1 g. of potassium iodide is introduced, and the liberated iodine is titrated with thiosulphate solution, 5 ml. of starch solution being used as indicator. The thiosulphate solution is standardised against the bromate–bromide solution. Correction is made for the bromine consumption of the indicator; for this purpose, the same amount of the indicator solution as used in the estimation is added in a " blank " titration. The time for the estimation is 2½ hours.

Results.—All experiments were carried out upon 5·000 g. of Prime Western Spelter of the following composition : lead, 1·05; iron, 0·015; tin, 0·01; cadmium, 0·18%; remainder, zinc. Various amounts of pure aluminium were added, and the results are shown in the following table.

Aluminium taken :		Titration.				
g.	*i.e.*, % on 5-g. sample.	0·1N-$KBrO_3$–KBr, ml.	0·1N-$Na_2S_2O_3$, ml.	Diff., ml.	Al, found, g.	Error, g.
Nil	Nil	—	—	—	Nil	—
0·0012	0·024	9·05	4·60	4·45	0·0010	−0·0002
0·0024	0·048	15·95	4·85	11·10	0·0025	+0·0001
0·0036	0·072	19·85	4·30	15·55	0·0035	−0·0001
0·0048	0·096	25·00	4·10	20·90	0·0047	−0·0001

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