AN IMPROVEMENT IN THE METHOD OF SEPARATING ZINC FROM
NICKEL BY SULPHURETTED HYDROGEN IN A SOLUTION CON-
TAINING GALLIC ACID.

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I HAVE recently made some experiments to see if a more reliable method of separating zinc from nickel could be devised than those which are usually used. The separation of zinc from nickel in a solution faintly acidified with HCl never gives accurate results, as the zinc sulphide always contains appreciable amounts of nickel and the zinc is seldom completely precipitated, and it is well known that zinc sulphide is one of the most difficult precipitates to wash owing to its tendency to give turbid filtrates. Methods involving the use of cyanides and sulphocyanides are objectionable owing to the poisonous nature of the vapour of prussic acid that is

liberated. The succinic acid method is not satisfactory, as it is necessary to have a saturated solution of the succinic acid, which sometimes crystallizes in the filter when filtering off the zinc sulphide.

I have found that if to a neutral or faintly acid (with H_2SO_4) solution of zinc and nickel, containing from 0.3 gramme to 0.6 gramme of each metal, 2 grammes of gallic acid dissolved in hot water be added, and then H_2S passed through the perfectly cold and diluted solution, the zinc is precipitated as perfectly white sulphide not containing a trace of nickel. The zinc sulphide settles readily, can be filtered through a single Swedish filter-paper, and washed easily and rapidly; the filtration and washing seldom take more than half an hour, the filtrate is perfectly clear, and contains the whole of the nickel.

The details of the method are as follows: To the solution of the two metals containing not more than 0.6 gramme of each, preferably in sulphate solution, sodium carbonate solution is added until a faint precipitate persists in the solution on stirring; this is dissolved by adding a drop of dilute sulphuric acid. The solution is diluted to about 300 c.c. with cold water, 2 grammes of gallic acid dissolved in water are added, and the solution mixed; a fairly rapid current of H_2S is passed through the solution for half an hour, after which it is filtered through a single Swedish filter-paper, the precipitate washed four or five times with cold water, and then dried in the steam-oven. The precipitate is transferred as completely as possible to a Rose crucible, the paper, burnt to a complete ash in a coil of platinum wire, is then added, the precipitate, sprinkled with a little pure sulphur, ignited over a Bunsen flame for five minutes in a current of purified dry hydrogen, and weighed as ZnS .

The nickel may be estimated in the filtrate from the zinc sulphide as follows, but the instructions given must be carefully carried out, or low results will be obtained: The solution is evaporated down in an open beaker on a hot-plate until it is reduced to about 15 c.c.; the cover is then replaced on the beaker, which is taken from the hot-plate and allowed to cool; 30 c.c. of strong HNO_3 are added, and the cover is kept on the beaker, which, when the first effervescence has ceased, is replaced, still covered, on the hot-plate. The solution, which is dark brown, is boiled until it again becomes green; the cover is then rinsed, 1 c.c. of H_2SO_4 added, and the solution boiled down almost to dryness in a 6-inch porcelain dish on a water-bath. It is heated over gauze with a Bunsen burner until the sulphuric acid is volatilized, then more strongly to decompose the small amount of organic matter left, allowed to cool, the residue boiled with water containing a little sulphuric acid, and filtered. The filtrate received in a 500 c.c. Jena glass beaker; the residue is washed once with dilute sulphuric acid, and then four times with water; 10 c.c. of strong ammonium hydrate are added, then 3 grammes of ammonium oxalate dissolved in water, and the solution is diluted to about 300 c.c. It is heated to about 40°C ., and electrolysed with three Bunsen cells or their equivalent. The solution is kept at about 40°C . during the electrolysis, which is complete in three or four hours, the end of the process being ascertained by the addition of ammonium sulphide in the usual manner. The platinum cone is well washed, first with cold water and then with alcohol, dried in the steam-oven, and weighed. Care must be taken that all the alcohol is driven off; sometimes the nickel deposit is only

free from alcohol after drying for half an hour. This method gives very accurate results if the above instructions are carefully carried out.

Unless, after the evaporation with sulphuric acid, the mass of nickel sulphate and organic matter is thoroughly charred, the organic matter will contain from 10 to 30 milligrammes of nickel, which cannot be washed out; hence the necessity for strongly heating after the sulphuric acid is driven off. The addition of ammonium oxalate causes the nickel to form a silvery deposit, and not a black deposit as when ammonia only is added.

The following results were obtained in sulphate solution :

ZINC.				NICKEL.		
No.	Taken.	Found.	Error.	Taken.	Found.	Error.
	Gramme.	Gramme.				
1	·2714	·2701	— ·0013	about ·3 gramme		—
2	·3097	·3096	— ·0001	"		—
3	·6194	·6195	+ ·0001	"		—
4	·4045	·4032	— ·0013	"		—
5	·1300	·1304	+ ·0004	"		—
6	·9291	·9287	— ·0004	·1210	·1188	— ·0022
7	·3251	·3248	— ·0003	·3065	·3065	nil
8	·3251	·3267	+ ·0016	·1226	·1219	·0007

In Nos. 1 to 5 the nickel was from 10 to 30 milligrammes too low, owing to the organic matter not having been destroyed. The following results were obtained in a nitrate solution :

ZINC.				NICKEL.		
No.	Taken.	Found.	Error.	Taken.	Found.	Error.
	Gramme.	Gramme.		Gramme.	Gramme.	
1	·2985	·2962	— ·0023	·2671	·2674	+ ·0003
2	·2985	·2960	— ·0025	·1085	·1098	+ ·0013
3	·1194	·1183	— ·0011	·2671	·2666	— ·0005

And the following in a chloride solution :

ZINC.				NICKEL.		
No.	Taken.	Found.	Error.	Taken.	Found.	Error.
	Gramme.	Gramme.		Gramme.	Gramme.	
1	·2999	—	—	·2169	·2146	— ·0023
2	·2999	·2975	— ·0024	·0867	·0864	— ·0003
3	·1199	·1190	— ·0009	·2169	·2160	— ·0009

I have also made experiments to see if zinc could be separated from cobalt, iron, aluminium, and manganese in a neutral solution containing 2 grammes of gallic acid. The following results were obtained :

Metal.	Taken.	Found.	Metal.	Taken.	Found.
	Gramme.	Gramme.		Gramme.	Gramme.
Zinc	·3251	·3322	Cobalt	·4042	·402
Zinc	·3251	·3250	Iron	·3204	·3213
Zinc	·3251	·3277	Aluminium	·2922	·2919
Zinc	·3251	·3245	Manganese	·4716	·4719

It is seen from these experiments that iron, aluminium, and manganese are completely separated, but a little cobalt is precipitated with the zinc. The zinc sulphide had a greenish colour.

For the analysis of German silver and similar alloys about 1 gramme of the alloy is treated with nitric acid, the excess of acid boiled off and the solution diluted. Any tin oxide is filtered off. The filtrate is diluted to 300 c.c., and 5 c.c. HCl added. H_2S is passed through to precipitate copper and lead; the sulphide precipitate is redissolved, reprecipitated with H_2S , and filtered; the copper being estimated volumetrically or electrolytically. The filtrates are boiled down to dryness with sufficient H_2SO_4 to convert the zinc and nickel into sulphates. The solution is taken up with water, neutralized with Na_2CO_3 till a faint precipitate persists in the solution, then 1 drop of dilute sulphuric acid is added to redissolve the precipitate and 2 grammes of gallic acid. The solution is diluted to 300 c.c., and the zinc precipitated as sulphide; the remainder of the process being conducted in the manner described above. As these alloys seldom contain more than small amounts of tin, lead, iron, aluminium, manganese, and cobalt, these metals are best estimated in a separate portion, using 5 grammes of the alloy.

In order to see if small amounts of nickel could be separated from comparatively large amounts of zinc, I took a solution containing about 3 grammes of zinc with 0·0245 gramme of nickel, added 8 grammes of gallic acid, and passed H_2S to saturation; filtering off the zinc sulphide. The filtrate was boiled down and the gallic acid destroyed with 70 c.c. of HNO_3 , followed by evaporation to dryness with 1 c.c. of H_2SO_4 and the strong heating of the residue. The residue was redissolved in water containing a little dilute H_2SO_4 neutralized with Na_2CO_3 , 1 drop of dilute H_2SO_4 added, 2 grammes of gallic acid, and H_2S again passed; a small amount of ZnS came down, which was filtered off, and the filtrate again evaporated with HNO_3 and H_2SO_4 . The residue was taken up with water containing a little H_2SO_4 , filtered, and electrolysed after adding ammonia and ammonium oxalate; 0·0254 gramme nickel was found.

This method can, therefore, be used for estimating the small amount of nickel usually present in commercial brasses by taking 7 grammes of brass, separating the copper with H_2S , and then evaporating with sufficient H_2SO_4 to convert the zinc, etc., into sulphates, separating the zinc by a double precipitation with H_2S , as

described above, and estimating the nickel and iron in the filtrate. My assistants, Messrs. L. E. Dance and L. J. Meyrick, have assisted me in these experiments.

DISCUSSION.

Mr. ALLEN said that, while the use of a fixed organic acid like gallic acid certainly effected complete separation, trouble would probably arise, as the author had himself found, unless great care was exercised. He (Mr. Allen) had used habitually two processes for the separation of zinc from nickel in alloys. Formerly he used to convert the two metals into double cyanides, then passing sulphuretted hydrogen, and obtaining a perfectly white, slimy precipitate of pure sulphide of zinc, which was difficult to treat afterwards, requiring to be redissolved and being difficult to wash. The separation, however, was good. For many years past he had used a process devised by Mr. Thomas Bayley, in which, after neutralization of the solution with sodium carbonate (ammonium salts must not be present), twice its bulk of ordinary acetic acid was added, sulphuretted hydrogen being then passed through the liquid. The sulphide of zinc came down, not in a slimy condition, but as a granular precipitate, which was easily filtered. The nickel in the filtrate was present as sulphate, and it was only necessary to evaporate the liquid in order to get rid of all the acetic acid, when the nickel could be determined without difficulty by any of the ordinary methods. The sulphide of zinc could be treated with sulphuric acid and converted into sulphate, which was the most convenient form in which to weigh either zinc or nickel. A larger weight was obtained, and either sulphate would withstand a dull red heat without decomposition, though in the case of nickel an obvious change to black oxide took place if overheating occurred. Zinc sulphate, however, was not so readily decomposed by heat. He had used to a limited extent the sulphocyanide process. The zinc came down quite well in an acid solution to which potassium sulphocyanide had been added; but in this case also difficulty arose owing to the presence of another fixed organic acid—namely, free thiocyanic acid.