

mate is purified by fusing a chemically pure article and pouring upon a tile. The factor of the thiosulphate solution is taken every two or three days. The periodide analyzed is weighed by difference, from a weighing bottle into a No. 3 beaker, taking 0.150 to 0.600 gram. Of alcohol from ten to fifteen cc. are added. All the periodides so far obtained are soluble in cold alcohol, but with much difference in the readiness and abundance of this solubility, and this property governs the speed of the estimation. The crystals can be broken under a flat end of a rod, and if not readily soluble, the titration is commenced before solution is completed, keeping down the excess of the iodine-like color. At the end starch can be used as an indicator, but after practice this is not necessary, as the extinction of the iodine-like color can be read to within one drop of the thiosulphate. The burettes had been calibrated and were used with a table of corrections. Other solvents have been tried but alcohol proves far the best for the crystals in titration. Two to four titrations have been made and the average given in each estimation. The agreement of the titrations is represented by a few quotations: of the pyridine methyl diiodide, 37.01, 37.24, 36.48, 37.17; pyridine methyl triiodide, 78.55, 78.84.

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## ON THE ANALYSIS OF ALLOYS OF LEAD, TIN, ANTIMONY AND ARSENIC.<sup>1</sup>

BY LAUNCELOT ANDREWS.

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THE experiments described in the present paper were carried out under my direction during the last winter by Mr. Earl Durfee. Part of them were suggested by Drown's investigation of the separation of tin from lead by repeated evaporations with concentrated hydrochloric acid, but were carried out previous to the publications of Jannasch,<sup>2</sup> and of Jannasch and Schmitt<sup>3</sup> on the same subject. All experiments referred to here, relate to the analysis of an alloy containing in round numbers eighty per cent. lead, thirteen per cent. antimony, seven per cent. tin. The exact composition of this metal will be given later.

<sup>1</sup> Read at the Springfield meeting.

<sup>2</sup> *Ber. d. chem. Ges.* 27, 3335.

<sup>3</sup> *Ztschr. anal. Chem.*, 9, 274.

## FIRST METHOD.

The attempt was made to drive off all tin and antimony as chlorides according to Drown. To this end one gram of the alloy was dissolved in aqua regia and evaporated to dryness, heating the residue to  $200^{\circ}\text{C}$ . The latter was moistened with about four cc. fuming hydrochloric acid and evaporated as before, the whole operation being repeated five times. The remaining lead chloride was, however, not free from tin and antimony. A series of attempts were then made to effect a separation by treating the alloy with bromine and hydrochloric acid gas, in varying forms of apparatus and at various temperatures. The details of these experiments need not be given, since they either failed to give a complete separation or were affected by practical faults of one kind or another.

On the other hand, no difficulty was found in completely volatilizing all the tin and antimony by heating the alloy directly, without previous solution, in a current of hydrochloric acid gas which had passed through concentrated nitric acid. The process was carried out as follows: Hydrochloric acid gas, evolved in a slow and steady stream by allowing the fuming acid to flow through a capillary tube into concentrated sulphuric acid, passes first through a flask containing ten cc. of nitric acid of 1.50 sp. gr. and then through a combustion tube of large diameter, thirty cm. long, containing a porcelain boat with the alloy in the form of turnings. The current of gas on leaving the combustion tube traverses a Volhard absorption flask, charged with a solution of potassium bromide and kept cold during the process. The combustion tube is covered with an asbestos tent and heated by means of an Argand burner to  $210^{\circ}\text{C}$ . The amount of the alloy used in each experiment was a half gram, and in two hours, during which time the operation required no attention whatever, the separation was complete and the snow-white residue in the boat was completely soluble in boiling water, while the distillate in the receiver was free from lead. The lead was weighed as sulphate. The receiver contained the antimony and tin and a little arsenic. To it was added the solution obtained by rinsing the unheated part of the combustion tube with hydrochloric acid. The small amount of arsenic present was easily separated from

the contents of the receiver by distillation according to Gooch and Phelps.<sup>1</sup> After the removal of the arsenic, tin and antimony were separated by Carnot's method,<sup>2</sup> which was found to be excellent.<sup>3</sup>

The process as described may be modified by attacking the alloy with nitric acid first, in a two-necked flask, then evaporating in a current of hydrochloric acid gas and heating in the same as before. The quantitative results are concordant, but the modified process is less convenient and requires decidedly more time.

## ANALYTICAL RESULTS.

	I. Gram.	II. Gram.	III. Per cent.	IV. Per cent.
Alloy taken .....	0.5000	0.5000	....	....
Lead sulphate.....	0.5849	0.5853	....	....
Lead found.....	0.3988	0.3991	79.75	79.82
Antimony trisulphide...	0.0925	0.0925	....	....
Antimony found.....	0.0661	0.0661	13.21	13.21
Stannic oxide .....	0.0434	0.0437	....	....
Tin found .....	0.0342	0.0344	6.84	6.88
Arsenic (volumetrically)	0.0006	0.0007	0.12	0.14
Total.....			99.92	100.05

## SECOND METHOD.

It has been observed that when various kinds of anti-friction metal or type metal were boiled with hydrobromic acid or with mixtures of hydrochloric acid and potassium bromide, the antimony remained undissolved, the arsenic distilled off and all the other constituents of the alloy went into solution. A more critical examination of the matter showed that, under the conditions named, in the presence of air, a small amount of the antimony dissolved, but that the undissolved portion was free from lead and tin. On the theory that the partial solution of the antimony was due to the oxidizing action of the air, it seemed likely that the addition of a powerful reducing agent, such as hydriodic acid, would prevent the loss of antimony, a view which was

<sup>1</sup> *Ztschr. anal. Chem.*, 7, 123.

<sup>2</sup> *Ztschr. anal. Chem.*, 88, 650.

<sup>3</sup> In this method, the solution, containing an oxalate and free oxalic acid and much ammonium chloride, is boiled with sodium thiosulphate. Beside the precautions given by the originator of the method, it is essential to success that the solution be boiled violently until one-fourth is boiled away, and that, finally, the acid be in excess as regards thiosulphate.

confirmed by an experiment in which potassium iodide took the place of the bromide.

One gram of the metal, in turnings, after boiling for one hour with hydrochloric acid of 1.10 sp. gr. and potassium iodide, (about one gram) was entirely disintegrated. The antimony remained undissolved as a dark gray powder. It was filtered from the boiling solution through a Gooch filter, washed with boiling water until free from lead iodide, dried, mixed with sulphur and gently ignited in a stream of carbon dioxide. This conversion into sulphide is needful because the finely divided antimony obstinately retains either water or hydrogen, in consequence of which the results come about seven-tenths per cent. too high if the metal is weighed directly.

## ANALYTICAL RESULTS.

	I.	II.
Metal taken.....	1.0000	1.0000 grams.
Antimony weighed direct....	0.1385	0.1375
Antimony trisulphide.....	0.1827	0.1833
Antimony calculated.....	<u>0.1305</u>	<u>0.1310</u>
Antimony .....	13.05	13.10 Per cent.

The subjoined table presents a summary of the results obtained by the different methods of analysis of the same alloy. Column I gives the results obtained by tedious but exact methods, not described in this paper but employed for a control. Column II gives the figures obtained by the first method above described. Column III those of the second method. Column IV the mean of all of the results.

## SUMMARY.

	I.	II.	III.	Mean.
	Per cent.	Per cent.	Per cent.	Per cent.
Arsenic.....	0.13- 0.12	0.12	0.14- 0.13	0.128
Antimony.....	13.13-13.15	13.21-13.21	13.05-13.10	13.14
Tin .....	6.83- 6.84	6.84- 6.88	.....	6.85
Lead.....	79.87-79.95	79.75-79.82	.....	<u>79.85</u>
Total.....	.....	.....	.....	99.97

In conclusion, I wish to draw attention to a convenient device for maintaining temperatures lying between 200° and 500° which are difficult to secure with certainty by means of a Bunsen or even in some cases by the ordinary forms of air-bath. The

device consists simply of an ordinary Argand gas burner with chimney, as made for illuminating purposes, with the addition of a simple hood or tent of asbestos and sheet-iron to go over the top of the chimney and confine the heat. It is surprising what a wide range of temperatures this simple apparatus gives command of. It is very perfectly adapted for the ignition of antimonous sulphide in carbon dioxide, an operation which can be carried out with great nicety at  $400^{\circ}$ , but which is difficult and uncertain when a Bunsen burner is used as the source of heat. Many other operations, distillations, digestions, etc., are carried on advantageously in this way, the great merit of the arrangement consisting in the superior control of the temperature. It is, for example, well adapted to the conversion of calcium oxalate into carbonate.

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### THE DETERMINATION OF GRAPHITE IN PIG-IRON.<sup>1</sup>

BY P. W. SHIMER.

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THE purpose of this note is to call attention to a source of error in the determination of graphitic carbon, made by the usual method of solution in hydrochloric acid. Although the method is tedious, because of the necessary treatment of the separated carbon with caustic potash, alcohol and ether, the text-books seem to give it preference; and it is, perhaps, used more generally than the method of solution in dilute nitric acid. Solution in hydrochloric acid usually gives higher graphitic-carbon results than solution in nitric acid, and many, therefore, consider it more trustworthy, the inference being that the lower results obtained by nitric acid are due to the loss of some of the finely-divided graphite by reason of the oxidizing action of the solvent. But, experiments made in Dr. Drown's laboratory, about seventeen years ago, showed no appreciable oxidation of graphite in the fifteen or twenty minutes' boiling required for the solution of a sample of pig-iron.

The point I desire to bring out here is, that the high results in graphitic carbon obtained by solution in hydrochloric acid are due to the presence, in the graphitic residue, of titanium carbide,<sup>2</sup>

<sup>1</sup> To be read at the Atlanta meeting of the American Institute of Mining Engineers.

<sup>2</sup> See *Trans. Am. Inst. Min. Eng.*, 15, 455.