

upon to make accurate determinations of aluminium when present in such minute proportion as 0·01 per cent., or one part in 10,000 of iron or steel.

We hear frequently that aluminium steels have been searched for aluminium by analysts in this and other countries, and that they have failed to find any present. Some metallurgists have in consequence been led to believe that none is really present, and that aluminium in some mysterious way benefits the steel, and as soon as it has done its work straightway passes out of it into the slag.

In exceptional cases it is probable that steel to which aluminium has been added may not contain it in the finished ingot, but in every case when such steel has been examined in our laboratory we have detected it, and the quantity has been determined. I am therefore very much afraid that in many cases where it has not been found it was really present, and the fault was not so much that of the analyst as of the methods given in his text-books which he followed, and which, although well adapted for removing practically all the aluminium or alumina from compounds of iron and aluminium, yet fail to remove the last traces. It is these last traces which we have now to deal with, and our methods of analysis must be so modified that we can be perfectly certain we obtain any trace of aluminium present.

The only book to my knowledge giving any detailed reliable method for the determination of aluminium in iron and steel is that of Mr. Andrew A. Blair, entitled "The Chemical Analysis of Iron," but although the method is a correct one, as I have proved by making a trial with it, it is so tedious and prolonged (taking three days to make the determination) that I believe it will never be generally used in the works laboratory of the iron and steel maker.

The method I use in the laboratory of Messrs. Pattinson and Stead, Middlesbro', is very much shorter than that of Mr. Blair, and gives very correct results if followed out exactly on the lines of the description which follows:—

Re-agents, &c., required—

- (1.) Pure hydrochloric acid.
- (2.) Ammonia.
- (3.) Pure sodium hyposulphite (sat. sol.)
- (4.) Sodium or ammonium phosphate (sat. sol.)
- (5.) Sodium hydrate, free from alumina and silica. That prepared from sodium is best.
- (6.) Washed filter-paper of C. Schleicher and Schüll,  $\frac{1}{4}$  in. and 5 in.

Method of analysis:—Weigh off 11 or 22 grms. of the iron or steel to be examined; the smaller quantity is preferable unless less than 0·01 per cent. of aluminium is expected.

Dissolve the 11 grms. in 44 cc. strong hydrochloric acid or the 22 grms. in 88 cc. on the sand bath in a 600 cc. beaker. When dissolved evaporate to dryness and re-dissolve residue in HCl and hot water: filter off from silica, collecting the filtrate in a 500 cc. beaker, and wash the silica clean. Let the total bulk of the filtrate and washings not exceed 200 cc.

To separate the alumina from the main bulk of the iron, add 3 cc. of the phosphate solution, then dilute ammonia till the free acid is neutralised—this point is readily known by a small quantity of phosphate of iron and alumina remaining insoluble after repeatedly shaking the solution. Add HCl drop by drop till the solution is clear, and then set the beaker on the bath to boil. As soon as the boiling commences add a large excess of the sodium hyposulphite solution (50 cc. is sufficient), and continue boiling till the solution does not give off  $\text{SO}_2$ . If there is doubt whether or not there is excess of hyposulphite, add a few more cc., and if this does not give a precipitate of sulphur, sufficient hyposulphite has been added.

The smell of sulphur must not be mistaken for  $\text{SO}_2$ , as the former is always present. One hour's boiling will eliminate all the  $\text{SO}_2$ . The precipitate must now be collected on a 5 in. washed filter-paper, and be well washed with boiling water to free it from all soluble iron and other salts.

Dissolve all soluble matters out of the precipitate by pouring over it 5 cc. HCl, and 5 cc. boiling water, allowing the solution to collect in the beaker in which the alumina was originally precipitated. Wash out of the filter all soluble matters with a small nozzle on the wash-bottle. The matter left on the filter will be all sulphur, and may be thrown away.

The solution must now be transferred to a platinum dish, and evaporated to dryness over a beaker of boiling water. When dry, add 2 grms. of pure sodium hydrate, placing it on the bottom of the dish, and then add about 1 cc. of boiling water to partially dissolve the hydrate. Place the dish over the flame of a Fletcher's rose burner till the mass is in a state of tranquil fusion. Allow to cool, and add 50 cc. boiling water, and place the dish and contents over a Bunsen burner, and boil for five minutes.

More water must be added so that the total bulk measures exactly 110 cc. Filter off the insoluble oxides through a  $\frac{1}{4}$  in. washed dry filter-paper. The first portions which pass through will be unclear, and must therefore be refiltered.

When 100 cc. (= 10 grms. of steel) have passed through, measure that quantity off exactly, and reject the insoluble matter and the remainder of the solution.

Neutralise the NaHO with HCl till the solution reddens blue litmus paper, and add 3 cc. sodium phosphate, and then hyposulphite of soda in large excess.

Boil till all  $\text{SO}_2$  has been expelled, and add 2 cc. ammonium acetate, boil for two minutes longer, and filter through a  $\frac{1}{4}$  in. washed filter. Wash well with boiling water till the washings are free from chlorides, burn off wet or dry and weigh.

The precipitate I have found consists of  $\text{AlPO}_4$ , and therefore contains 22·36 per cent. of aluminium.

This process, it will be seen, consists of a combination of several already well-known methods, with this very important difference that excess of phosphoric acid is added to the iron solution to produce a compound more insoluble than free alumina. If no phosphate is present, it is only after boiling for several hours that the last traces of  $\text{Al}_2\text{O}_3$  are precipitated. The  $\text{Al}_2\text{O}_3$  as phosphate may also be separated from a neutral or acid ferrous solution by boiling with ammonium acetate, but a much larger amount of iron is precipitated than when hyposulphite is used.

The following results will show the effect of adding a phosphate, compared with those obtained when no phosphate is added.

Four portions of 10 grms. each of pure iron were mixed with sufficient alum to equal 0·064 per cent. aluminium.

Aluminium found—

	Per Cent.
Hypsulphite with phosphate, boiling $\frac{1}{2}$ hour .....	0·063
" without " " " .....	0·028
" " " " 2 hours.....	0·065
Acetate of ammonia (no phosphate) .....	0·045
" " (with phosphate) .....	0·062

The description of this method is somewhat lengthy, but the determination can easily be made in 12 hours.

## ON THE ESTIMATION OF SULPHUR IN PYRITES.

BY G. LUNGE.

It is no wonder that the estimation of sulphur in pyrites, a commodity of which annually at least two million tons are got, at least one million of which is sold by analyses, should be very carefully treated. Although the value of pyrites has so much declined since, some years ago, Messrs. Chance first proved the possibility of recovering the entire sulphur of alkali waste, yet the sums involved in this trade, owing to the immense quantities concerned, are very large, and warrant the demand of accuracy in establishing the sale price of any large parcel of pyrites.

For a number of years the methods of decomposing pyrites for analysis by fusion with alkaline carbonates, nitrates, and so forth, have been in most laboratories replaced by decomposition in the wet way, employing the mixture first proposed by me, namely, three or four parts of nitric acid of sp. gr. 1.4 to one part of strong hydrochloric acid. This operation is much more easily carried out than the decomposition by fusion in the dry way; it succeeds with ordinary care even in the hands of less experienced chemists, who would not obtain sufficiently accurate results by the process of fusion, with its concomitant risks of loss by spurning in getting the mass out of the crucible, &c. It takes altogether only about half the time of that required for an analysis in the dry way; no platinum crucibles are spoiled, and no chance of error is introduced by the sulphur contained in coal-gas. The fact that the decomposition in the wet way leaves untouched the sulphur of barium sulphate and, apart from a very slight quantity, that of galena, is precisely a recommendation of it in comparison with the dry method, which estimates also the useless sulphur of the first-mentioned minerals.

This, no doubt, explains the preference shown by most practical chemists for the decomposition of pyrites in the wet way. As practised universally before, and very frequently even now, that method certainly contains a source of error in the large quantity of iron present. It had long been known that it is hardly possible, when precipitating barium sulphate in solutions containing iron, to obtain a precipitate free from the latter, and tedious prescriptions were made for purifying such precipitates after ignition, which, I am bound to say, could not be carried out by any but very skilled operators without incurring mechanical losses, and which, moreover, rarely succeeded in their object. I have shown in one of my former publications (*Zeits. Anal. Chem.* **19**, 419) that it is quite possible to get the iron out of the precipitate in the wet state by means of energetic treatment with strong hydrochloric acid; but this causes the dissolution of somewhat considerable quantities of barium sulphate which can be recovered only by circuitous and lengthy methods.

Fresenius (*Zeits. Anal. Chem.* **19**, 53) has treated the point in question somewhat in detail. He states that by the wet method as carried out according to prescriptions in my "Treatise of the Manufacture of Sulphuric Acid and Alkali" results were obtained about 1 per cent. lower than by the (lengthy and troublesome) dry method described by himself, which he ascribes to the solubility of barium sulphate in ferric chloride. He certainly neglected to take into account the fact, pointed out by me both before and after, that the dry method includes the sulphur of heavyspar and galena, *purposely* left out by the wet method; this would no doubt have reduced the real difference between his and my method to a much smaller figure. But I do not doubt that there is such a difference, for my own very careful experiments, described in the above-mentioned paper, did show an average error of 0.18 per cent. in the wet method as practised *then*, in comparison with the results obtained by the improved process which I had worked out in consequence of Fresenius' objection, and which consists in removing the iron by means of ammonia previously to precipitating the sulphur, and operating in such manner that no trace of sulphuric acid is left in the ferric hydrate, and that the analysis is detained only about an hour by this additional operation, as we shall see hereafter.

The cause of the error incurred in the presence of salts of iron has been fully investigated by Jannasch and Richards (comp. the abstract of their paper in this Journal, 1889, p. 819), and has been satisfactorily explained by them. They have, however, arrived at a very misleading conclusion, namely, "that 'Lunge's method' is not sufficiently accurate, and that the dry way prescribed by Fresenius should be employed for all purposes requiring scientific precision." Jannasch and Richards had made a serious mistake in conducting that part of their investigation which refers to a comparison between the methods of Fresenius and my own. They had entirely overlooked the fact that I had, nine years before them and in a paper quoted by themselves (the same which I have mentioned above), modified my method in the above-

mentioned manner, so as to do away with all objections to the wet way of decomposing pyrites by removing the iron by precipitation with ammonia. It is this which is commonly known as Lunge's "new method," which is contained in the "Alkali-Makers' Pocketbook," and which has been adopted in Germany as binding between buyer and seller; but upon *this* method, having omitted to notice it, Jannasch and Richards did not make one single experiment. On the contrary, after I had drawn Professor Jannasch's attention to this fact, he himself tried my "new" method, and expresses himself upon it as follows (*J. prakt. Chem.* [2], **40**, 236):—"By the previous precipitation of the iron at a moderate heat with a slight excess of ammonia, Lunge has rendered his method altogether exact. My attention having been drawn to this fact by Professor Lunge, I have recently employed his method as well as my own with perfectly certain success. The pyrites mentioned in my previous paper, analysed by Lunge's improved method, yielded:—

	Lunge's Method.	Jannasch's Method.
S .....	Per Cent. 52.56	Per Cent. 52.63
Fe .....	45.88	45.69
SiO <sub>2</sub> &c. ....	1.03	1.10
	99.47	99.33

"Since Lunge's method of assaying pyrites is in general use for technical purposes, and consequently of great practical importance, it may be interesting to know that its results are completely concordant with those obtained by an altogether different method."

In a paper published in the *Zeits. f. angew. Chem.* 1889, 473, I have described in detail a number of experiments by which two of my students, Messrs. Barbezat and Obregia, working independently of one another, have investigated a special point in connexion with my improved process, namely, the question whether, as stated by me in my paper of 1880, the precipitate of ferric hydroxide can be entirely freed from sulphuric acid or not; in the latter case my process would, of course, be faulty. They found that if the precipitation of ferric hydroxide took place in the way described in Fresenius and practised in many laboratories, that is, boiling the liquid for some considerable time till the smell of ammonia is all but gone, it is unavoidable to leave some sulphuric acid in the precipitate. If, however, the operation was carried on as described by me in 1881, and again in the "Alkali-Makers' Pocketbook," that is, adding a slight but distinct excess of ammonia, and warming gently for a few minutes, till the precipitate had well settled, and filtering at once, the precipitate proved to be entirely devoid of sulphuric acid, and the results of testing agreed perfectly, both with one another, and with tests made by Fresenius' dry method. This is shown by the following table, which includes a number of assays of the same sample of pyrites according to my old method, that is, precipitating the barium sulphate without previous removal of the iron.

Fresenius' Method.	Lunge's Improved Method.	Lunge's Old Method.
52.46	52.70	52.38
52.40	52.41	52.38
52.31	52.22	51.91
.. .. .	52.20	.. .. .
.. .. .	52.30	.. .. .
Average 52.42	52.40	52.23

