

rhotite by the method described above, using different weights. Some of the results obtained are :

5.00	grams	gave	0.4120	barium	sulphate	=	1.13	per	cent.	sulphur	as	Fe <sub>2</sub> S <sub>3</sub> .
13.74	"	"	1.1300	"	"	=	1.13	"	"	"	Fe <sub>2</sub> S <sub>3</sub> .	
25.00	"	"	2.1570	"	"	=	1.18	"	"	"	Fe <sub>2</sub> S <sub>3</sub> .	

Others were equally concordant.

The method was also applied to the pyrrhotite, as mentioned above, using portions of one gram or one-half gram giving respectively 24.13 per cent. and 24.15 per cent. sulphur as Fe<sub>2</sub>S<sub>3</sub>.

This method is accurate to within two-tenth per cent. on ores containing much or little pyrrhotite. The ore must not be finer than that which will pass through a sixty mesh sieve ; if it is, results will be unreliable.

Another method, which I used until the perfection of this one, is based upon the fact that Fe<sub>2</sub>S<sub>3</sub> gives off hydrogen sulphide with dilute acid, whereas FeS<sub>2</sub> (pyrite) does not. This is reliable when no other sulphides are present, but as most pyrites contain blende the results are usually unreliable.

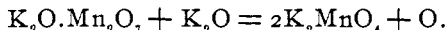
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## DROWN'S METHOD OF DETERMINING SULPHUR IN PIG IRON.

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OF the various evolution methods of determining sulphur in pig iron, Drown's is perhaps the best. Methods in which the sulphur is precipitated in any other form but barium sulphate (cadmium sulphide for instance), are not so convenient for the reason that the sulphur in the graphitic residue must be determined as barium sulphate. A slight drawback, however, attaches to the method in that the evolution of the gas must not be allowed to proceed too rapidly, and it is an object of this note to point out that by the use of potassium hydroxide solution in conjunction with the potassium permanganate solution as an absorbent for the gas, this caution is made unnecessary, and the gas may be passed through the solution as rapidly as it is possible to make it do so, without danger of loss ; a mixed solution of caustic potash and potassium permanganate possessing stronger oxidizing power, than a solution of the latter salt alone. For there is a tendency in such a mixture, even

when no reducing agent is present, to the liberation of an atom of oxygen and a reduction of the potassium permanganate to potassium manganate, by the union of a molecule of potash with a molecule of potassium permanganate.



If a very large excess of caustic potash solution be added to a few drops of potassium permanganate solution, the reduction to green potassium manganate will be seen to take place immediately. But in a mixture of equal or nearly equal parts of the two solutions, the change is very slow and gradual, except a reducing agent be present.

Convenient proportions of the two solutions for use as an absorbent in the determination of sulphur in pig iron are obtained by using in each case six cc. of a caustic potash solution, made by dissolving six sticks of the solid hydroxide in 350 cc. water, and six cc. of a permanganate solution containing about ten grams of the crystallized salt to the liter of water.

These volumes of the two solutions are carefully withdrawn from the bottles containing them by pipettes, so as to avoid getting any of the sediment at the bottom of the bottle; mixed in a small beaker, and drawn into a Troilius bulb, which is then connected with the evolution flask containing the drillings. The solution of the pig iron may be accomplished in five or ten minutes without any hydrogen sulphide passing through the caustic potash and permanganate solution unabsorbed. The purple color of the permanganate gradually changes to the green of the manganate, which latter solution is also a stronger oxidizing agent than permanganate.

Not an inconsiderable convenience also in the use of this mixed solution is in the fact that the oxide of manganese separating out does not adhere to the glass tenaciously, and may be washed out with water instead of requiring to be dissolved out by strong hydrochloric acid and added to the main solution.

The next step in Drown's method is getting the manganese in colorless solution preparatory to the precipitation by barium chloride. This is accomplished by evaporation to dryness with hydrochloric acid, and separation of silica; or by adding enough hydrochloric acid to get the clear solution by the aid of heat, but

without the tedious evaporation to dryness, and afterwards neutralizing the excess of acid with ammonia. The writer would suggest the use of oxalic acid in connection with hydrochloric acid, as by its use the solution of the manganese oxides is effected almost instantaneously and without the use of an excess of hydrochloric acid, a very small amount of the latter sufficing, and the barium chloride precipitation may then at once take place.

In detail: Take 3.4335 grams of the pig iron drillings in a sixteen ounce gas flask and connect with the Troilius bulb containing the mixed solution of caustic potash and potassium permanganate, as described. Pour through the funnel tube dilute hydrochloric acid in not unnecessary amount, and bring quickly to a boil. Then push to a cooler part of the plate and aspirate air through. A convenient arrangement is to have a narrow upright board fastened to the desk, or on a stand next to the filter pump; on the other side of the board stands the iron plate. This upright board, standing edgewise to the plate, is provided with nails or hooks for the support of the Troilius bulbs which are hung one above the other. Three or four determinations can be carried on at once in this way with the greatest possible economy of desk room. The aspirating is done by the filter pump.

Transfer the contents of the Troilius bulb to a small beaker, washing out with water. Filter the solution in the evolution flask through a ribbed filter and wash with hot water. Then punch a hole in the paper and wash the graphite and silica into an evaporating dish. Evaporate to dryness. Add thirty cc. aqua regia. Evaporate to dryness. When dry, add eight to ten cc. dilute hydrochloric acid. Heat, dilute with hot water and filter into the solution washed out of the Troilius bulb. Bring this solution then to a boil, add enough oxalic acid to clear the solution, (a very little will suffice), then five cc. barium chloride solution and boil about an hour. Allow to stand over night. The barium sulphate found, multiplied by four, will give the percentage of sulphur in the pig.

Caustic potash solution always contains considerable amounts of dissolved silica (for instance, in six cc. the amount used in a determination was found to be 0.0051 gram). But it is not

necessary to separate it, as a recent writer in the *Chemical News* has shown that precipitated barium sulphate is not contaminated by silica in solution, and the following experiments also show it. In these experiments a standard solution of sulphuric acid was used; mixed in each case with the amounts of caustic potash solution, and permanganate solution that are used in a regular determination. Instead of using ten cc. of hydrochloric acid, however, twenty cc. was used, but afterwards made alkaline with ammonia, then hydrochloric acid added drop by drop till just acid again, and the solution filtered from the alumina remaining undissolved. Then precipitated by barium chloride. Also the excess of oxalic acid used to bring the manganese oxides into solution was destroyed by permanganate solution before the neutralization and precipitation and the slight excess of permanganate by a piece of fine iron wire and stirring. The barium sulphate found was, for convenience in each case, calculated as though the usual amount of drillings had been taken, and a regular determination had been made.

	Sulphur taken. Per cent.	Sulphur found. Per cent.
No. 1.....	0.237	0.238
“ 2.....	0.121	0.119
“ 3.....	0.057	0.057
“ 4.....	0.029	0.033

To note the effect of precipitating in a strongly acid solution, and one which therefore required no filtration from alumina before precipitating, the following tests were made as before, but with ammonia added to leave five cc. of free hydrochloric acid at time of precipitation, (excess of oxalic acid again destroyed).

	Sulphur taken. Per cent.	Sulphur found. Per cent.
No. 1.....	0.121	0.112
“ 2.....	0.121	0.114
“ 3.....	0.237	0.234
“ 4.....	0.057	0.054
“ 5.....	0.029	0.029
“ 6.....	0.014	0.010
“ 7.....	0.029	0.028
“ 8.....	0.029	0.026
“ 9.....	0.014	0.010

These results show a very marked tendency to lowness. The following were then made, using ten cc. of hydrochloric acid for solution of the manganese oxides (together with oxalic acid, the excess of the latter however, afterward destroyed by adding permanganate solution), and without any after neutralization with ammonia whatever, the solution therefore containing *over* five cc. of free acid, but no ammonium chloride.

	Sulphur taken. Per cent.	Sulphur found. Per cent.
No. 1.....	0.014	0.014
" 2.....	0.029	0.029
" 3.....	0.121	0.115

At this point it was thought well to also try the effect of oxalic acid upon the precipitation. It was feared it might have a solvent action upon the barium sulphate, especially in strongly acid solutions. In other respects the conditions were the same as in the series immediately preceding—ten cc. hydrochloric acid, no ammonia, etc., but excess of oxalic acid *not* destroyed.

	Sulphur taken. Per cent.	Sulphur found. Per cent.
No. 1.....	0.014	0.014
" 2.....	0.029	0.029
" 3.....	0.121	0.118
" 4.....	0.029	0.029
" 5.....	0.060	0.059
" 6.....	0.090	0.090
" 7.....	0.045	0.046
" 8.....	0.060	0.060
" 9.....	0.090	0.090
" 10.....	0.029	0.029
" 11.....	0.014	0.014
" 12.....	0.121	0.119
" 13.....	0.237	0.239

From these results it would seem that the oxalic acid helped rather than hindered the precipitation of barium sulphate.

To see if there was any tendency of barium oxalate to precipitate, a test was made under conditions identical with No. 13, except that the solution was neutralized with ammonia till merely faintly acid before precipitating. Result 0.239 per cent., or just the same as in the strongly acid test. Showing no tendency of barium oxalate to precipitate.

Again, in standard solution equivalent to 0.121 per cent. taken, ten cc. hydrochloric acid added, brought to a boil, and precipitated with barium chloride. Result 0.119 per cent. Then the test repeated twice with addition of oxalic acid. Results, No. 1, 0.120 per cent. ; No. 2, 0.120 per cent.

Thinking perhaps good results could also be obtained by allowing the precipitated barium sulphate to stand only one hour before filtration, the following tests were made (ten cc. hydrochloric acid, no ammonia, excess of oxalic acid not destroyed).

	Sulphur taken. Per cent.	Sulphur found. Per cent.
No. 1.....	0.029	0.024
" 2.....	0.014	0.007
" 3.....	0.029	0.023
" 4.....	0.121	0.115
" 5.....	0.060	0.056
" 6.....	0.045	0.041

Showing that one hour's standing is not sufficient. But the loss seems so uniform that in cases of hurry it would be perhaps safe to allow only one hour for standing, making afterward a correction in the result of 0.005 per cent.

It is important to make a blank or dummy test with the reagents used. In this test use double the reagents and precipitate in nearly neutral solution.

In the regular determinations also precipitations may of course take place in nearly neutral solutions if so desired, and as is usually recommended. The results of the second series, however, may perhaps be taken as a warning against the presence of ammonium chloride in *strongly* acid solutions, and the ammonia should therefore be added to near neutralization if used at all.

In filtering off the barium sulphate it is not advisable to use a rapid filtering funnel, as barium sulphate equal to 0.002 or 0.003 per cent. is more than likely to pass through the filter paper and escape notice in the filtrate, except the liquid be stirred in such a way as to collect it together in the middle of the bottom of the beaker. When hydrochloric acid is spoken of in this article the dilute acid (equal parts water and acid) is meant.