

replaced, however, very satisfactorily by a simple coating of enamel which is fused upon the surface of the tube at the same time that the figures of the scale are produced. The enamel on the rear of the tube, as well as that of the graduation, are totally unaffected after prolonged exposure to high temperatures.

An extended use of these thermometers is to be expected not only in laboratories, but in many branches of chemical industry, such as tar works, petroleum refineries, anilin works, etc.

I would mention in this connection the great help I have experienced in using Mahlke's "thread thermometer" for obtaining accurate readings at high temperatures. This gives the proper correction for the error due to the projection of a part of the mercury column of the thermometer outside of the substance or confined space, the temperature of which is being measured. In the case of long thermometers and high temperatures this error may reach 30° . Mahlke's thermometer is hung alongside the projecting part of a thermometer in use, and is so arranged as to give at once the reading for the number of degrees to be added to the temperature indicated in order to correct the error mentioned.

ON THE ESTIMATION OF SULPHUR IN PYRITES.¹

BY THOMAS S. GLADDING.

THERE are two recognized methods for the estimation of sulphur in pyrites which, with various modifications, are chiefly used by commercial chemists at the present time. These are:

First, the fusion of the ore with a mixture of sodium carbonate and potassium nitrate, solution in water, filtration from iron hydroxide, and precipitation as barium sulphate.

Second, the solution of the pyrites ore in aqua regia, or in aqua regia and bromine, and subsequent precipitation as barium sulphate.

The following investigation was undertaken to determine the relative merits of these two methods and the proper modifications to be observed:

A chemically pure potassium sulphate was examined for

¹ Read before the New York Section, March 9, 1894.

impurities with negative results. 2.7 grams containing about the amount of sulphur found in one gram of high grade pyrites were dissolved in 300 cc. to 400 cc. water, five cc. concentrated hydrochloric acid added, and a ten per cent. barium chloride solution added, at the rate of one drop per second, to the boiling solution. We obtained after standing over night:

Sulphur	0.4960 gram.
"	0.4960 "

Theory requires sulphur 0.4965. This amount of 0.496 gram was taken as the quantity of sulphur contained in 2.7 grams of the potassium sulphate, and the following series of experiments made exactly as above, with the stated additions and modifications. We first investigated the various conditions of the fusion methods.

Series I. With additions of five cc. nitric acid:

Sulphur found	0.5007 gram.
" "	0.5007 "
" "	0.5020 "

The presence of nitric acid produces results too high, from the dragging down of nitrate salts, probably barium nitrate.

Series II. With addition of seventeen grams potassium nitrate:

Sulphur found	0.5066 gram.
" "	0.5102 "

Series III. With addition of fifteen grams of fusion mixture; *viz.*, sodium carbonate and potassium nitrate, and addition of hydrochloric acid to neutrality and five cc. in excess:

Sulphur found	0.5005 gram.
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Series IV. With addition of potassium chloride, 6.5 grams, sodium chloride, seven grams:

Sulphur found	0.4955 gram.
" "	0.4950 "
" "	0.4966 "

No appreciable error either way.

The above series of experiments show that no *nitric* acid nor nitrates should be present in the solution at the time of precipitation. Series IV shows that when all nitric acid is expelled then sodium chloride and potassium chloride in solution will not cause error. We have found, however, that the complete expulsion of all nitric acid is a very difficult and tedious operation,

requiring repeated evaporations to dryness with excess of hydrochloric acid.

The practical difficulty of removing all the nitric acid, and time and labor required, are serious objections to this method.

The following experiments were made to investigate the conditions of the second or aqua regia method.

Series V. With addition of two grams of citric acid :

Sulphur found	0.4960 gram.
" "	0.4960 "

This shows that the citric acid, which is frequently used to keep up any iron present, does not exert a solvent action.

Series VI. With addition of two grams citric acid, and 0.500 gram iron, which is about the amount of iron in one gram of pyrites ore :

Sulphur found	0.4934 gram	-0.4937 gram.
" "	0.4937 "	-0.4933 "
" "	0.4940 "	-0.4937 "
" "	0.4938 "

This shows that the presence of iron causes low results.

The above results were obtained by ignition of the barium sulphate precipitate at low red heat until the filter paper was thoroughly burned. The precipitate was of a buff color.

On exposing the precipitates to a strong blast for several minutes longer they assumed a decided red color and lost weight.

The results were found to be :

Sulphur found	0.4910 gram.
" "	0.4913 "
" "	0.4900 "

We attribute these erroneous results to the unavoidable dragging down of iron salts (probably iron sulphate) with the barium sulphate, and in place of an equivalent amount of barium sulphate. On ignition, this iron sulphate is decomposed, the sulphuric anhydride is expelled, causing low results, and the remaining iron oxide coloring the residue.

This was corroborated by taking 2.7 grams potassium sulphate, precipitating as above, drying the precipitate, brushing from the paper, drying at about 300° C., and adding the ash of the filter paper which had been burned in a separate dish.

Sulphur found	0.4961 gram.
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On heating over the blast-lamp for five minutes we found

Sulphur 0.4880 gram.

It is evident that the presence of iron in the solution is incompatible with accurate results.

We next tried the method of Lunge and Hurter. They precipitate the iron with ammonia and throw down the barium sulphate in the filtrate.

Series VII. With addition of 0.5000 gram iron, precipitation of same with ammonia, and precipitation of barium sulphate in the filtrate:

Sulphur found 0.4944 gram.

“ “ 0.4935 “

These results were too low. On redissolving the ferric hydroxide (on filter paper) with hydrochloric acid, and adding barium chloride to the filtrate, and standing over night, we obtained a precipitate of barium sulphate, giving:

1. Sulphur 0.0020 gram.

2. “ 0.0021 “

Adding these amounts we obtained:

Sulphur 0.4964 gram.

“ 0.4956 “

The most careful washing failed to wash out all sulphur from the ferric hydroxide, and this solution in hydrochloric acid, and the separate recovery of sulphur contained therein, was found necessary.

These results were the most satisfactory yet obtained. The precipitate of barium sulphate was pure white, pulverulent and did not lose appreciable weight on prolonged heating over the blast-lamp. In this respect it differs from all precipitates hitherto obtained, demonstrates its far greater purity, and gives us a fixed and *final* result.

A method recently published instructs as follows: To the solution (about 200 cc.), heated on a steam-bath and containing twenty cc. free hydrochloric acid “add barium chloride solution from a burette, drop by drop, stirring briskly. Add thirty-five cc. and allow the solution to stand one hour on the steam-bath, filter through ten cm. paper and wash three times with hot water Ignite and weigh barium sulphate.” After calculating per cent.

sulphur, add 0.20 per cent. to the result for solubility of barium sulphate in the acidified liquid.

We tested this method using 2.70 grains potassium sulphate, 200 cc. water, twenty cc. hydrochloric acid, and 0.500 gram iron. We obtained :

Sulphur	0.4900 gram.
"	0.4898 "
"	0.4902 "
"	0.4894 "
"	0.4905 "

The average loss was found to be about 0.60 per cent. instead of 0.20 per cent. as stated. The color of the precipitate was light buff. On heating over the blast-lamp for five minutes the precipitate assumed a darker color and lost 0.021 gram in weight so that the percentage of sulphur was reduced about 0.30 per cent. more. Evidently this method does not produce a pure precipitate of barium sulphate.

The following series of comparative analyses on samples of pyrites received for assay, corroborates the above results. The results given under "Fusion Method" were obtained *without* evaporating to dryness to expel all nitric acid. The results given under "Bromine Method, No. 1," were obtained by solution in nitric acid and bromine, evaporation to dryness with hydrochloric acid, taking up with hot water, plus hydrochloric acid, addition of two grams citric acid and precipitation without removing the iron.

In "Bromine Method, No. 2," the iron was removed with ammonia and the barium sulphate precipitated in the filtrate. The ferric hydroxide was dissolved in dilute hydrochloric acid in a separate beaker, heated to boiling, barium chloride added, allowed to stand over night, and the small amount of barium sulphate thus obtained added to the main precipitate.

Samples.	Fusion method.	Bromine method,	
		No. 1.	No. 2.
1	52.50	51.45	51.71
1	52.34	51.30	51.73
1	52.60	51.45	51.71
1	51.34	51.71
1	51.32	51.68
1	51.78

Samples.	Fusion method.	Bromine method.	
		No. 1.	No. 2.
2	40.92	40.50
3	39.90	39.25	39.60
4	40.90	39.72	40.00
5	41.25	40.05	40.40
6	41.80	40.90	41.10
7	40.59	39.71
8	42.54	41.94
9	41.41	40.40

We see from the above that the "Fusion Method" without expulsion of all nitric acid gives results altogether too high, as was to have been expected.

The "Bromine Method," when iron is not removed, gives results too low by 0.20 per cent. to 0.35 per cent. This is in exact agreement with the previous work on pure potassium sulphate. No accurate allowance can be made on this method as the error will vary with the amount of heat applied in igniting the precipitate of barium sulphate.

In the "Bromine Method, No. 2," the precipitated iron hydroxide was redissolved in every case, and an additional amount of sulphur varying from 0.20 per cent. to 0.30 per cent. was obtained.

The insolubility of barium sulphate in the solution of ferric chloride thus obtained was demonstrated by dissolving 0.027 gram potassium sulphate in fifty cc. water, adding five cc. hydrochloric acid and 0.5 gram iron, precipitating hot and allowing to stand over night. We found:

1. Sulphur..... 0.0049 gram.
2. " 0.0050 "
3. " 0.0051 "

The amount actually present was 0.00496 gram.

As a result of the above investigation and of many comparative analyses of pyrites ores extending over several years, we have adopted the following method of assaying pyrites:

1. Grind the ore to an impalpable powder, dry at 100° C., and keep in well-corked bottles. Ten to fifteen minutes drying is sufficient.

2. Weigh one gram, introduce into beaker, cover with watch-glass, and add ten cc. bromine solution, mix by rotating beaker

and allow to stand ten minutes in the cold. Add ten cc. nitric acid, mix as before, and allow to stand ten minutes longer in the cold. Finally place the beaker on a water-bath, containing cold water, heat slowly to boiling, and when solution becomes quiet remove glass after rinsing and evaporate to dryness. Add ten cc. hydrochloric acid, keeping the beaker covered with a glass, and when violent action ceases, again remove the glass after rinsing, and evaporate to dryness once more. Add one cc. concentrated hydrochloric acid and fifty cc. hot water, digest until solution is complete, filter and wash with hot water. The filtrate, about 100 cc., is now saturated with a slight excess of ammonia, allow to stand hot for ten minutes. The precipitated ferric hydroxide is filtered and washed five or six times more on the paper with boiling hot water, the filtrate acidulated with hydrochloric acid in slight excess, heated to boiling and fifty cc. barium chloride solution added, one drop per second to the boiling liquid. The solution is allowed to stand over night, filtered, washed, and ignited, the precipitate of ferric hydroxide is also dissolved in dilute hot hydrochloric acid heated to boiling, and ten cc. barium chloride solution added. It is allowed to stand over night and the barium sulphate thus obtained added to the main precipitate. One filter paper can be used for the two precipitates.

The bromine solution is prepared by dissolving seventy-five grams potassium bromide in fifty cc. water, adding fifty cc. bromine, stirring and adding water to 500 cc. The bromine will nearly all dissolve. Another form of bromine solution used by some is made by saturating aqua regia with bromine. The first solution is the more certain, however, to oxidize all the ore without separation of any sulphur. The barium chloride is in ten per cent. solution.

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