

T H E S I S

on

Sulfur Determinations by Use of
Calcium Hydride

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SULFUR DETERMINATIONS BY USE OF CALCIUM HYDRIDE 1.

Quantitative sulfur determinations are for the most part oxidative in nature. Oxidizing agents such as fuming nitric acid, aqua regia, bromine, hydrochloric acid and potassium chlorate are used to quantitatively convert sulfur or sulfur compounds to sulfates, which sulfates may be precipitated by the addition of barium chloride, and the sulfur content determined by igniting and weighing the barium sulfate.

Methods have been outlined in analytical texts for the quantification of sulfur in hydrogen sulfide by an iodometric process. Aqueous solutions of hydrogen sulfide may be directly titrated with iodine using starch as an indicator, and were it possible to quantitatively convert sulfur or sulfur compounds to water soluble sulfides, the sulfur content of a sample could be easily and quickly determined. Methods have been presented for the determination of sulfur in insoluble sulfates and certain other sulfur bearing materials by the use of calcium hydride⁽²⁾⁽³⁾. When a mixture of calcium hydride and sulfur or sulfur compound is ignited, the sulfur is quantitatively converted to calcium sulfide. On adding a considerable volume of water to the calcium sulfide containing residue followed by acidification, hydrogen sulfide is liberated in solution and may be

directly titrated with standard iodine solution. The sulfur content of the sample is thus determined.

Pyrite has been ignited with powdered iron to form ferrous sulfide⁽⁴⁾. On acidification of the ignited mass, evolution of the generated hydrogen sulfide takes place and is absorbed in ammoniacal cadmium chloride solution. The precipitated cadmium sulfide from the absorption flask is reacidified in a volume of water, and the hydrogen sulfide determined by titration with iodine. Other investigators have used such reductants as barium peroxide with powdered aluminum, strips of magnesium and magnesium powder⁽⁵⁾⁽⁶⁾.

The purpose of this investigation was to further apply the calcium hydride method for the determination of sulfur to a wider variety of sulfur containing substances, with such modifications of method as were deemed necessary.

A discussion of the use of calcium hydride in sulfur determinations may be conveniently divided into three steps: (1) Ignition of calcium hydride and sulfur bearing materials; (2) Digesting of the ignition residue; and (3) Iodimetric evaluation of the sulfur.

(1) Ignition of Calcium Hydride and Sulfur bearing
Material

Calcium hydride is a strong reductant, as calcium

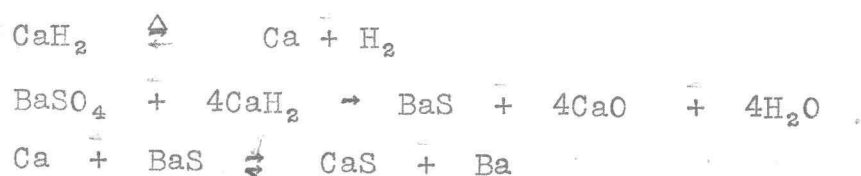
and hydrogen, both reducing substances, are yielded on its decomposition. It may be calculated by using the data of Bronsted⁽⁷⁾ and equation developed and presented by Lewis and Randall⁽⁸⁾ that the free energy of the reaction of calcium and hydrogen is zero at a temperature of about 1000 degrees Centigrade. Complete decomposition would take place at that temperature and considerable decomposition at 600-800 degrees Centigrade. The compound itself is quite stable unless exposed for a time in moist air. It is obtained commercially in small lumps, which are easily ground to fine powder in a pulverizer; a powder of about 150 mesh being used in the present sulfur determinations. The compound is prepared by the direct union of calcium and hydrogen at a temperature of about 500 degrees Centigrade.

As previously mentioned, the temperature of complete decomposition of the calcium hydride is about 1000 degrees Centigrade, but the vapor pressure of the hydride increases rapidly with an increase of temperature, so considerable reduction of an easily reducible sulfur substance is had at temperatures as low as 600 degrees Centigrade.

It is possible with most of the reductions studied in this investigation to completely reduce the sulfur containing substance by ignition in a "pyrex" hard glass test tube. In working with pyrite it was found necessary

to ignite in a small iron crucible and resort to the electric furnace to insure complete conversion of the sulfur in the pyrite to the soluble calcium sulfide. Test tube ignitions were accomplished in the full blast of a "Meker" burner.

Equations for the reactions occurring during the ignition of barium sulfate with calcium hydride might be expressed as follows:



These reactions could be regarded as general ones and would then apply to the reduction of any sulfate. Thio-sulfates, sulfites and such sulfur containing substances would somewhat similarly be converted to sulfide.

During the ignition considerable hydrogen is evolved, so it is practicable to cover the sample and hydride mix with a loosely fitting lid, both to maintain a reducing atmosphere and prevent influx of oxygen. To facilitate the escape of evolved hydrogen, particularly with test tube fusions, the mix is trenched to the bottom of the test tube. As a precautionary measure, a layer of calcium hydride is placed over the mix. It is possible when heating the test tube, to heat the upper part of the tube first, thus decomposing the calcium hydride and insuring a reducing atmosphere before the

lower part of the mix has been sufficiently heated to cause volatilization of the sulfur or sulfur compound and resultant loss.

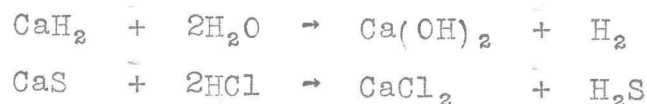
(2) Digestion of the Ignition Residue

The fused mass from the preceding step is easily removed from the test tube or crucible. Reaction of the excess hydride is quite rapid with water. To prevent undue dusting of the material, a small volume of ethyl alcohol is first added, with the subsequent addition of ice and water. On acidification, hydrogen sulfide is generated, which is maintained in solution by virtue of volume of cold water used. Undue agitation at this point would cause loss of the dissolved gas, and a corresponding lowering of results. However, cubes of ice added previous to the addition of acid keeps the solution at a low temperature and greatly increases the solubility of hydrogen sulfide in the aqueous solution. According to Dennis⁽⁹⁾, the solubility of hydrogen sulfide in one volume of water at one atmosphere is as follows:

0°	C	-	4.67	vol.
10°	C	-	3.40	"
20°	C	-	2.58	"
30°	C	-	2.04	"

From the above data it may be calculated that the maximum sulfur contained in one liter of solution

in the form of hydrogen sulfide is 6.77 grams; it is assumed the solution is at one atm. pressure and at a temperature of 0 degrees Centigrade. Experimental conditions would not be as those assumed; however, it is shown that the loss of sulfur from escape of hydrogen sulfide from the solution is a minimum. The reactions involved in treating ignition residue preliminary to titration with iodine are shown by the following equations:



(3) Iodimetric evaluation of the Sulfur

The hydrogen sulfide bearing solution is titrated with .1 N iodine solution, a fresh starch solution being used as an indicator. The hydrogen sulfide solution may be titrated directly, but a better end point is obtained by adding an excess of the iodine and back titrating with sodium thiosulfate. Sulfur liberated in the reaction of hydrogen sulfide with iodine has the property of adsorbing iodine as will be shown by its brown color in the solution, and fading end points. However, this difficulty was alleviated with the back titration procedure. As a precaution, the iodine solution was restandardized from time to time. The equation for the reaction of hydrogen sulfide with iodine

is:



1 cc of N iodine solution is equivalent to .0016 grams of sulfur. The weight of the sample is chosen to require 10-50 cc of iodine solution.

Experimental Details

The procedure in the analysis of a dry powder is as follows: A weighed sample, about .2 gram (sample sulfur content equivalent to 10-50 cc of .1 N iodine solution) is transferred to an eight inch hard glass test tube, and thoroughly mixed with approximately 6 grams of calcium hydride. A long handled spatula is conveniently used in the mixing. The charge is patted down and trenched to the bottom of the test tube, and a layer of hydride (about 2 grams) is placed in a uniform layer over the top of the mix. The charge is brought to a red heat in the full blast of a "Meker" burner, care being taken to heat the top of the tube first. Red heat is maintained for about five minutes, and the contents allowed to cool in the tube. The charge is emptied into a one liter beaker containing about 15 ccs of 95 per cent ethyl alcohol. The test tube is rinsed with water, which is slowly added to the beaker. When the reaction of the excess hydride with water is complete, lumps of

ice are added and about 700 ml. of water. When the solution of the calcium sulfide is complete, (it is not always possible to obtain a clear solution) 100 ml. of concentrated C. P. hydrochloric acid is poured slowly down the side of the beaker. The solution is allowed to stand ten minutes and titrated with .1 N iodine solution, care being taken not to unduly agitate the solution until an appreciable quantity of the iodine solution has been added. An excess of 4 or 5 ml. of the iodine solution is added and back titrated with standard sodium thiosulfate.

In the analysis of a liquid substance, the procedure is slightly modified. (In this investigation liquid lime sulfur spray was the only liquid substance analyzed.) Six grams of the spray solution are made up to 100 ml. in a volumetric flask and 2 ml. aliquots taken for analysis. The aliquots are pipetted to an eight inch hard glass test tube and calcium hydride slowly added until the reaction of the water of the solution with the hydride is complete. The test tube is cooled in running tap water during the addition of the hydride. A total weight of 5 grams of the hydride is added and the contents of the test tube thoroughly mixed, trenched to the bottom of the tube and the layer of hydride placed on the top of the charge. The rest of the procedure is

as with the dry powder.

TABLE I

.25 Gr. of Barium sulfate reduced to sulfide
with Calcium hydride.

$\text{BaSO}_4 = 13.7\% \text{ S theoretical}$

<u>Sample</u>	<u>Wt. of Sample</u>	<u>% S CaH₂ Method</u>
1	.25 g.	10.91
2	.25 g.	10.53
3	.25 g.	13.72
4	.25 g.	13.76

Results in samples 1 and 2 are low due to incomplete reduction of the sulfate. Ignition was accomplished in a "Meker" burner. With samples 3 and 4 a blast lamp was used to secure a higher temperature and as results show complete reduction of the sulfate was had.

TABLE II

Samples of dry lime sulfur spray ignited
with Calcium hydride.

<u>Sample</u>	<u>Wt. of Sample</u>	<u>% S Oxidative Method</u>	<u>% S CaH₂ Method</u>
1	100 mg.	63.87	63.36
2	50 mg.	63.65	63.36
3	100 mg.	63.02	62.48
4	50 mg.	62.84	62.51
5	100 mg.	61.48	61.68
6	50 mg.	61.80	62.13

TABLE III

Check samples of liquid lime sulfur spray ignited with Calcium hydride.

(6 grams of spray solution were made up to 100 ml. with water and 2 ml. aliquots taken for analysis.)

<u>Sample</u>	<u>% S Oxidative Method</u>	<u>% S CaH₂ Method</u>
1	23.89	23.46
2	23.52	23.56

Solvents other than water were used, but results were in error due to the formation of precipitates in solution and the difficulty of securing representative aliquots for analysis.

TABLE IV

Calcium hydride ignitions with various sulfur containing compounds.

<u>Sample</u>	<u>Substance</u>	<u>Wt. of Sample</u>	<u>% S theoretical</u>	<u>% S CaH₂ Method</u>
1	CaS	100 mg.	44.44	36.02
2	CaS	150 mg.	_____	36.12
3	Na ₂ S ₂ O ₃ ·5H ₂ O	200 "	25.80	25.64
4	"	150 "	_____	25.81
5	Cystine	100 mg.	26.67	26.80
6	"	100 mg.	26.53	26.58
7	Free Sulfur	100 mg.	100.00	99.42
8	"	50 mg.	_____	99.64

The results with CaS do not approximate the percentage of sulfur in pure CaS. The salt used was not chemically

pure. On acidification and titration of the hydrogen sulfide, the sulfur content was determined as 35.91%.

With cystine the calcium hydride method results were checked against results as determined by oxidation with sodium peroxide in a "Parr" bomb.

TABLE V

Calcium hydride ignitions with pyrite

<u>Sample</u>	<u>Wt. of Sample</u>	<u>% S Oxidative Method</u>	<u>% S CaH₂ Method</u>
1	500 mg.	42.65	42.33
2	500 mg.	35.78	35.65

The above results were obtained without evolution of the hydrogen sulfide and are subject to error due to the interference of iron in the iodimetry of the process.

*Note: More work is to be done on the analysis of pyrite.

DISCUSSION OF RESULTS

It is seen from tables I, II, III and IV that the calcium hydride method for the determination of sulfur may be applied to organic as well as inorganic substances, also to liquid and solid sulfur containing substances. Barium sulfate, pyrites of iron and organic sulfur are quantitatively converted to sulfide by ignition with calcium hydride, pointing to possible diversity of use of the method on numerous sulfur containing materials. Lime sulfur sprays containing calcium polysulfide, calcium thiosulfates and free sulfur are readily converted to the water soluble sulfide by test tube ignitions.

SUMMARY

(1) The use of calcium hydride in the determination of sulfur has been extended to include several diverse types of sulfur bearing substances.

(2) Modification and improvement of method has been instituted in the making of numerous check determinations.

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