A STUDY OF THE EFFECT OF CHANGES OF PROCEDURE IN A STANDARD SULFATE DETERMINATION

by

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A Thesis Submitted for Partial Fulfillment for the Degree of

BACHELOR OF SCIENCE

in

CHEMISTRY

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Blacksburg, Virginia
1952

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ACKNOWLEDGMENT

The author wishes to acknowledge and express his indebtedness for the encouragement and helpful advice of Professor E. V. Russell, Jr.

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June 1952

INTRODUCTION

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It is desirable to know the amount of sulfur present in ores before a study can be satisfactorially made on the ores. In the case of ores of a very high sulfur content, this is especially important. The ores found in some old iron mines in Virginia are of this type. They contain approximately 25% sulfur.

In previous attempts to determine the percentage sulfur in these ores, results obtained were always high. No previous investigation has been made regarding the reason for the errors in this method.

Therefore, the object of the present work is to investigate the present method of gravimetric determination of the percentage sulfur in iron ores in order to find what variables in technique and treatment will cause variations in results.

HISTORICAL

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Several methods have been used for the determination of the amount of sulfur in iron ores. Kolthoff and Sandell[1] suggest the use of the following methods:

1. Evolution and measurement of H_2S.
2. Benzedine sulfate precipitation.
3. Volumetric methods usually involving a back-titration of excess $BaCl_2$ with sulfate solutions of known strength.
4. Precipitation of barium chromate.
5. Presipitation of barium sulfate.

Of these methods, the precipitation methods are the simpler and easier. As barium sulfate is somewhat less soluble than barium chromate, the percentage sulfur in a sample is usually determined by oxidation of the sulfur to the $SO_4^{=}$ ion and then precipitation using excess Ba ions.

However, even this method of sulfur determination is subject to many errors. The author found references in the library regarding these errors as follows:

1. Willard and Furman[2] found that an oxidizing agent must be used that will oxidize the sulfur completely to the $SO_4^{=}$ ion. This oxidation must not involve strong acids that could cause a loss

of sulfur as H_2S gas. Potassium permanganate or bromine solutions with later addition of HNO_3 are often used for this oxidation. A typical equation for this type of reaction is

$$FeS + 3HNO_3 + 3\,HCl = FeCl_3 + H_2SO_4 + 3NO + 2H_2O$$

2. Although Marjanovic[3] stated that Na, K, Mg, Fe, Cu, Al, and NH_4 ions do not affect the accuracy of gravimetric determinations, work done by Kolthoff and Vogelgang[8] indicated that almost all anions and cations are coprecipitated to some extent with the barium sulfate. They also showed that the coprecipitated ions are chemically combined with the barium sulfate. Ferric ions coprecipitate very readily and must either be removed or reduced to the ferrous state. Either powdered aluminum or powdered zinc may be used to accomplish this reduction according to Willard and Furman[2]. Work done by Germuth[4] indicated that the amount of coprecipitation was reduced sharply if the solution from which the barium sulfate was precipitated was cold.

3. Chatterjee[5] showed that an excess of acid in the precipitating solution causes error because the barium sulfate is more soluble in acid than in water. The volume of HCl should be kept down to less than 0.1% of the solution.

4. Willard and Diehl[6] found that if the barium sulfate crystals were not allowed to grow for at least 24 hours, some of the crystals might be so small as to pass through ordinary filtering mediums.

5. Research by Kolthoff and Vogelgang[8] showed that ignition might reduce the barium sulfate. Schleicher[7] showed that if the barium sulfate is collected on filter paper, the filter paper might absorb ions, especially barium and chloride ions, and cause results to be high.

PROCEDURE

PROCEDURE

The following procedure was used to determine the percentage sulfur in an iron ore sample:

1. A weighed sample of 0.5495 gm. of the ore is place in a 600cc beaker and treated with 10cc of Br-KBr solution*. This solution is allowed to stand for 15 minutes with occasional shaking.

2. To this solution 10cc of concentrated HNO_3 is now added and the solution is again allowed to stand for fifteen minutes with occasional shaking. (A large portion of the excess bromine is expelled here.)

3. Keeping the temperature below 100°C the mixture is evaporated to dryness.

4. Next 10cc of HCl is added and the solution is again taken to dryness. The residue is then heated at 100°C for thirty minutes and cooled.

5. The residue is moistened with 5cc of HCl and allowed to stand for five minutes. Then 50cc of hot water is added. Low heat is applied until all the ferric salts are dissolved. (This leaves a white powder of silica or its compounds undissolved.)Cool.

*The Br-KBr solution is composed of 320gm KBr plus 200cc liquid bromine in 200cc of aqueous solution.

6. Ferric salts are reduced by the addition of 0.1gm of powdered aluminum.

7. As soon as the ferric salts are reduced (indicated by a colorless solution) and there is no further misting, the solution is filtered into a 1000cc beaker. The residue is washed free of chlorides. This requires 7 to 10 washings.

8. The solution is treated with 5cc of 1-1 HCl.

9. A precipitating solution of 500cc of water and 50cc of 6% $BaCl_2$ is added and the mixture is allowed to stand overnight.

10. The solution is filtered through a weighed gooch crucible and the precipitate is washed free of chlorides. This usually requires 7 to 10 washings.

11. The crucible is dried for two hours at 105°C and weighed. The weight of the precipitate times 25 equals percent sulfur.

EXPERIMENTAL

EXPERIMENTAL

The author made two runs of 2 samples each using the standard procedure to familiarize himself with the technique required. Then fourteen samples (five runs) were run and an average %S was calculated. The %S according to this procedure was 20.02. The results of the individual samples are found on page 10 in Table I.

The author then ran a series of samples in which the amount of Br-KBr solution was varied. The remainder of the procedure was not changed. When no Br-KBr solution was used, the sulfur content appeared to be 26.59%. As previously stated, standard procedure using 10cc of Br-KBr solution indicates a sulfur content of 29.02%. When 15cc of Br-KBr was used, the sulfur content appeared to be 29.72%. When 20cc of Br-KBr solution was used, the sulfur content appeared to be 29.70%. A tabulation of the results obtained for each sample in this series may be found on page 10 in Table II.

To obtain some indication of the effect of the KBr on the results, five samples were treated with 10cc of a solution of 10cc of bromine in enough CCl to make 100cc of solution. The tabulated results from these samples may be found on page 11 in Table III. The average %S was 28.34.

A series of 5 samples was run in which the amount of HCl added in step 5 was varied. The results of the various samples checked fairly closely although there was some indication that an excess of HCl would cause lower results. A tabulation of the results for these samples may be found on page 11 in Table IV.

In order that the effect of excess acid during precipitation might be checked, another run was made in which the amound of 1-1 HCl added in step 8 was varied. From the results of this run, it appears that excess acid will cause low results. A tabulation of the results of this run may be found on page 11 in Table V.

Several mechanical difficulties were encountered in the procedure used. It was necessary to do all evaporation at a temperature below 100°C as higher temperatures caused sputtering. The reduction of ferric ions was often very time consuming. The precipitate of barium sulfate forms a film on the sides of the beaker that may be removed only by careful policing.

DATA AND RESULTS

DATA AND RESULTS

Table I

Sample	%S	Sample	%S
1	29.43	8	28.94
2	28.57	9	29.02
3	28.91	10	29.14
4	28.47	11	29.11
5	28.71	12	29.38
6	28.83	13	29.40
7	29.00	14	29.35

Average %S in a standard run 29.02

Table II

Results obtained when the amound of Br-KBr was varied.

Sample	cc Br-KBr	Precipitate Weight	%S
1	0	1.0052	25.13
2	0	1.0697	26.74
3	0	1.0181	25.45
4	0	1.0260	25.65
Average %S			26.59
5	5	1.0936	27.34
6	5	1.0741	26.85
7	5	1.0430	26.08
8	5	1.0564	26.41
9	5	1.0710	26.59
According to standard procedure using 10 cc, %S=29.02. See Table I.			
Average %S			26.69
10	15	1.1855	29.64
11	15	1.1891	29.76
12	15	1.1907	29.80
Average %S			29.72
13	20	1.1853	29.63
14	20	1.1904	29.76
15	20	1.1898	29.74
Average %S			29.71

Table III

Results obtained using Br-CCl_4 instead of Br-HBr solution.

Sample	cc Br-CCl_4	Precipitate Weight	%S
1	10	1.1291gm	28.23
2	10	1.1582	28.82
3	10	1.1286	28.22
4	10	1.1179	28.00
5	10	1.1360	28.40
Average %S			28.34

Table IV

Results obtained using various amounts of HCl in the reduction of ferric ions.

Sample	cc HCl	Precipitate Weight	%S
1	3	1.1699gm	29.25
2	3	1.1733	29.33
Average			29.28
3	5	1.1662	29.16
4	5	1.1616	29.04
Average			29.10
5	10	1.1510	28.78

Table V

Results obtained varying HCl in the precipitating solution.

Sample	cc- 1-1 HCl	Precipitate Weight	%S
1	0	1.1776gm	29.44
2	0	1.1933	29.83
Average			29.64
Standard procedure uses 5cc of 1-1 HCl gives %S=29.02.			
3	10	1.1217	28.06
4	10	1.1199	27.95
Average			27.99
5	20	1.0835	27.09
6	20	1.0786	26.96
Average			27.03

DISCUSSION

DISCUSSION

It was very difficult to get results that checked within the desired degree of accuracy. Therefore, a large number of samples were run and an average taken to get the actual concentration of sulfur in the sample. The sample used was found to contain 29.02%S.

When less than the standard amount of Br-KBr solution was used, results were always low. An excess of Br-KBr solution caused the results to be slightly high although an excess of 10cc extra had only the same effect as an excess of 5cc. The use of a solution containing no KBr showed that the KBr has a marked effect on the final results obtained.

The samples tested using various amounts of HCl to dissolve the salts before reducing the ferric salts to ferrous indicated that an excess of HCl at this point could cause lower results. However, the differences between samples using 3cc and 10cc of HCl was small. This was probably due to the fact that any large excess of HCl would react with the powdered aluminum added in the next step.

Results obtained when the amount of HCl added to the precipitating solution was varied were to be expected as Willard and Furman[1] had already stated that the barium sulfate is soluble in acid solutions. It was found that an increase of the amount of HCl added caused results to be low.

SUMMARY

SUMMARY

The work done by the author indicates that when %S is determined by gravimetric methods as indicated the volume and concentration of reagents used is very important.

It appears that an excess of KBr solution will cause results to be high. An excess of acid in the precipitating solution will cause results to be low.

FOOTNOTES

(1) Kolthoff, I. M. & Sandell Textbook of Quantitative Inorganic Chemistry, p. 309.

(2) Willard, H. H. & Furman, N. H. Elementary Quantitative Analysis, 3rd Edition, pp 323-327.

(3) Marjanovic, V. "Arhiv Hemiju" 1, 5-18 (1927), Chemical Abstracts 22:1928.

(4) Germuth, F. G. "The American Journal of Pharmacy" 99, 271-274 (1927).

(5) Chatterjee, K. P. "Z. Anovg. Allgem. Chem." - 121, 128-134, (1922) Chemical Abstracts 16:2821.

(6) Willard, H. H. and Diehl, H. Advanced Quantitative Analysis, pp. 188-296.

(7) Schleicher, A. "Z. Anal. Chem." 121, 90-2 (1942). Chemical Abstracts 37:6589.

(8) Kolthoff, I. M. & Vogelgang, E. H. "Pharm. Weekblad" 56, 122-42 (1949). Chemical Abstracts - 13:944.

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(1) Kolthoff, I. M. & Sandell Textbook of Quantitative Inorganic Chemistry, p. 309.

(2) Willard, H. H. & Furman, N. H. Elementary Quantitative Analysis, 3rd Edition, pp 323-327.

(3) Marjanovic, V. "Arhiv Hemiju" 1, 5-18 (1927), Chemical Abstracts 22:1928.

(4) Germuth, F. G. "The American Journal of Pharmacy" 99, 271-274, (1927).

(5) Chatterjee, K. P. "Z. Anorg. Allgem. Chem." - 121,128-134, (1922) Chemical Abstracts 16: 2821.

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(8) Kolthoff, I. M. & Vögelgang, E. H. "Pharm. Weekblad" 56, 122-42 (1949). Chemical Abstracts - 13:944.