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A STUDY OF THE DETERMINATION OF SILICA IN
THE PRESENCE OF FLUORINE ²⁶³⁹₂

BY

WILLIAM HARLAN ODE

A

THESIS

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in partial fulfilment of the work required for the

Degree of

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Approved by W.T. Schrenk.

Associate Professor of Chemistry

FOREWORD

The author wishes to express appreciation to Dr. W.T. Schrenk for the suggestion of this research and for the valuable advice and suggestions given while the work was in progress.

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A STUDY OF THE DETERMINATION OF SILICA IN
THE PRESENCE OF FLUORINE

INTRODUCTION

The determination of silica in the presence of fluorine has always been accomplished either by difficult and complex analytical procedures or by rapid arbitrary control methods of doubtful precision. Berzelius, Jannasch, Seeman, and Sisco are chemists who have developed methods for this determination. The method suggested by each in order are as follows: fusion with alkali carbonate followed by precipitation with ammonium carbonate-zinc oxide; fusion with lead oxide; fusion with alkali carbonate followed by precipitation with mercury-ammonium carbonate; extraction of the ore with acetic acid.

A. Stadeler¹ studied five methods for the determination of silica in the presence of fluorine and found only one, the method of Berzelius, to give reliable results if the fluorine content was above one percent. Hence, a resumé of Berzelius's method will be given.

The ore is fused with alkali carbonate, and the melt is extracted with hot water and filtered from the insoluble residue. To the filtrate four grams of solid ammonium carbonate is added, heated for some time at 40 C^o, and

¹ A. Stadeler. Stahl u. Eisen 47, 662-4 (1927)

then allowed to stand over night. The precipitate is filtered off and washed with water containing a little ammonium carbonate. The silica thus obtained is saved. To recover the silica still remaining in the filtrate, one or two cubic centimeters of ammonical zinc oxide is added to the solution, boiled until all of the ammonia is expelled, and the precipitate of zinc silicate filtered off. The zinc silicate precipitate is treated with hydrochloric acid and the solution evaporated to dryness. The silica thus obtained is filtered off and saved. The insoluble part of the melt may contain silica, and this is obtained by treatment with hydrochloric acid and subsequent evaporation. Finally, the three precipitates are ignited and weighed together. This procedure shows that the method of Berzelius is difficult and complex even though accurate.

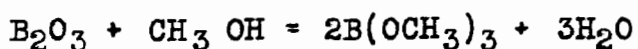
Hence, this study was undertaken in order to determine whether a more simple method might be found for the determination of silica in the presence of fluorine.

In looking about for some suggestion that might be helpful in finding a new method, it was found that Jannasch and Weber² in 1899, reported that when silicates

²P. Jannasch and H. Weber. -----
Berichte der Deutschen
Chemischen Gesellschaft 32, 1670-5 (1899)

containing fluorine or mixed with fluorides had been fused with boric oxide over an oxygen blast flame, the fluorine seemed to be wholly expelled as boric fluoride without loss of silica. The writer has found no confirmation of this observation in the literature up to the present time.

Jannasch and Weber used the following method in determining silica in the presence of fluorine. A half gram sample of the ore was fused with boric oxide in a platinum crucible until all visible action had ceased. The crucible and contents were then quickly cooled in cold water and put in a porcelain dish, to which, after covering with a watch glass, a saturated solution of hydrochloric acid in methyl alcohol was added. When the solution had been completed, the crucible was removed and the liquid slowly evaporated to dryness. The alcoholic solution of hydrochloric acid caused the volatilization of the excess boric acid as methyl borate according to the following equation.



To insure complete removal of the excess boric acid, the residue was digested with repeated treatment of small amounts of methyl alcohol-hydrochloric acid solution followed by subsequent evaporation. The heating should

be carried out in a separate hood as the boric ether driven off, decomposed in contact with moisture forming large deposits of boric acid. Finally the residue was moistened with 1:3 hydrochloric acid, evaporated to dryness, and baked for one hour at 110° C. The residue was taken up in dilute hydrochloric acid and boiled to effect the solution of all soluble salts. The solution was filtered, the precipitate washed five or six times with hot three percent hydrochloric acid and finally with hot water. The precipitate was transferred to a platinum crucible, the filter paper ashed, treated with one or two drops of sulfuric acid, and finally ignited to constant weight. The silica was determined by volatilization with hydrofluoric acid and sulfuric acid.

EXPERIMENTAL

It was thought that the method of Jannasch and Weber might be suitable for determining the silica in fluorspar. Accordingly, a sample of fluorspar whose percentage composition had been determined by the method of Bidtel, was analyzed using the method of Jannasch and Weber. The fluorspar taken for this analysis had the following composition: silica 11.05-11.10%; calcium carbonate 3.60-5.60%; calcium fluoride 76.68-76.81%. The results of the analysis by the Jannasch-Weber method are tabulated in Table 1.

Table 1.

| Weight of Sample | Weight of Silica Determined | Percent of Silica |
|------------------|-----------------------------|-------------------|
| .4802 | .0544 | 11.33 |
| .4711 | .0280 | 6.16 |
| .4997 | .0469 | 9.36 |
| .4994 | .0376 | 7.53 |
| .4999 | .0221 | 4.42 |
| .5001 | .0241 | 4.82 |

The results are exceedingly variable and show that this method is unsatisfactory for materials high in calcium fluoride content. In fusing, the blast lamp was not used, and the temperature may not have been great enough to volatilize the fluorine as boro-fluoride.

A modification of the Jannasch-Weber method was then used. This method differed from the previous one in that the methyl alcohol-hydrochloric acid treatment was omitted. The fusion was dissolved in hydrochloric acid, evaporated to dryness, and finally baked for one hour at 110°C: to completely dehydrate the silica. From this point the analysis was identical to that recorded in the previous section. The results are listed in Table 11.

Table 11.

| Weight of Sample | Weight of Silica Determined | Percent of Silica |
|------------------|-----------------------------|-------------------|
| .5000 | .0713 | 14.26 |
| .5000 | .0841 | 16.82 |
| .5000 | .0830 | 16.60 |

The results obtained by this method are apparently better than the previous one, although the results are still unsatisfactory.

A series of determinations were then made by decomposing the fluoride material by fusion using sodium Borax. The melt was dissolved in 1:3 hydrochloric acid, evaporated to dryness, and baked for one hour at 110°C. The residue was taken up in dilute hydrochloric acid, digested, filtered, and the precipitate washed with hot dilute hydrochloric acid followed by hot distilled water. The filter paper was ashed, two drops of sulfuric acid added, and the residue ignited to constant weight. The silica was determined in the usual manner using hydrofluoric acid. The results using this method are listed in Table 111.

Table 111.

| Weight of Sample | Weight of Silica Determined | Percent of Silica |
|------------------|-----------------------------|-------------------|
| .5000 | .0701 | 14.02 |
| .4998 | .0665 | 13.30 |
| .4998 | .0655 | 13.10 |
| .4997 | .0701 | 14.03 |
| .4998 | .0682 | 13.65 |
| .5002 | .0694 | 13.87 |
| .4997 | .0732 | 14.65 |
| .4997 | .0727 | 14.55 |
| .4999 | .0718 | 14.36 |
| .5002 | .0681 | 13.61 |
| .5003 | .0718 | 14.35 |
| .5002 | .0696 | 13.91 |
| .4999 | .0706 | 14.12 |
| .5000 | .0708 | 14.16 |

The above results show that the borax fusion method is superior to the Jannasch-Weber method. The results

are higher and check fairly closely. Any particular samples determined at the same time check more closely than those determined at another time.

The examination of the filtrate from this fusion showed that some of the silica was carried into the filtrate.

The determination of silica in the presence of fluorine was rather encouraging although not as accurate as desired, and it was decided to determine the silica in this sample by decomposing the ore with sulfuric acid in the presence of an excess of boric acid. The following method was used for this determination. A half gram sample of the fluorspar was mixed intimately with two grams of boric acid. To this mixture twenty-five cubic centimeters of 1-2 sulfuric acid saturated with boric acid was added. The ore was digested with this solution until fumes of sulfuric acid came off. The residue was then dissolved in five percent hydrochloric acid so far as possible, the silica and insoluble material filtered off, washed with hot dilute hydrochloric acid and finally with hot water until free from calcium salts as tested with ammonium oxalate. The filter paper containing the silica was ashed, two drops of sulfuric acid added, and the residue ignited to constant weight. The silica was determined in the usual manner by treatment with hydrofluoric acid. The results obtained by this method are tabulated in Table IV.

Table 1V

| Weight of Sample | Weight of Silica Determined | Percent of Silica |
|------------------|--------------------------------|-------------------|
| .5000 | .0732 | 14.64 |
| .5002 | .0728 | 14.55 |
| .5001 | .0725 | 14.50 |
| .5000 | .0727 | 14.54 |
| .5000 | .0732 | 14.64 |
| .5001 | .0730 | 14.60 |
| .5001 | .0729 | 14.58 |
| .4998 | .0723 | 14.47 |
| .5001 | .0715 | 14.30 |
| .5000 | .0732 | 14.64 |
| .5000 | .0718 | 14.36 |
| .5000 | .0727 | 14.54 |

This method gives exceedingly consistent results for the determination of silica in fluorspar. With the exception of two results in a series of twelve determinations, the maximum deviation is .17 percent. The results, however, indicate a higher silica content than that found by use of the Bidtel method.

In order to determine whether there was a possibility of losing silica by the previous method, a synthetic sample of a fluorspar was made by mixing quartz and calcium fluoride in such a proportion that the percent of silica was 12.60. This sample was analyzed by means of the sulfuric-boric acid treatment. The results obtained are tabulated in Table V.

Table V.

| Weight of Sample | Weight of Silica Determined | Percent of Silica |
|------------------|-----------------------------|-------------------|
| .5000 | .0586 | 11.48 |
| .5000 | .0503 | 10.06 |
| .5003 | .0526 | 10.51 |
| .5003 | .0559 | 11.17 |

As Table V shows, the method in this case was entirely unsatisfactory. The results would indicate that the decomposition is accompanied by slight loss of silica. This may be due to the fact that the silica present here is in a different form than that present in the natural ore.

The method of determining the silica in the fluorspar was changed by using perchloric acid instead of sulfuric acid for decomposition. A solution of five percent perchloric acid saturated with boric acid at room temperature was used, and the procedure followed was exactly like that used in the sulfuric boric acid decomposition. Tests were made on both the synthetic sample containing 12.60 percent silica and the natural fluorspar containing 11.05-11.10 percent silica as determined by the method of Bidtel. The results obtained for the natural fluorspar are listed in Table VI and those for the synthetic sample in Table VII.

Table VI.

| Weight of Sample | Weight of Silica Determined | Percent of Silica |
|------------------|-----------------------------|-------------------|
| .5003 | .0727 | 14.53 |
| .5003 | .0728 | 14.55 |

Table VII.

| Weight of Sample | Weight of Silica Determined | Percent of Silica |
|------------------|-----------------------------|-------------------|
| .5000 | .0630 | 12.60 |
| .5000 | .0623 | 12.46 |
| .5000 | .0626 | 12.52 |
| .5000 | .0637 | 12.74 |
| .5000 | .0629 | 12.58 |
| .5000 | .0634 | 12.68 |

The results in Table VI show that the treatment of the natural fluorspar by means of the perchloric acid-boric acid treatment gives consistent results and compares favorably with the method using sulfuric acid and boric acid. See Table IV for comparison of results.

The results in Table VII gives very conclusive evidence that the perchloric acid-boric acid treatment gives a method which is accurate for determining silica in the presence of calcium fluoride. Much better results are obtained than when using sulfuric acid and boric acid in decomposing this synthetic fluorspar as is shown when comparing Table VII and Table V.

The determination of silica in the synthetic sample gave such accurate results when using the perchloric-boric acid method that it was decided to analyze samples containing varying amounts of silica and calcium fluoride in order to determine the limits of applicability of the method. The results of this set of analyses are listed in Table VIII.

Table VIII.

| Weight of Calcium Fluoride | Weight of Silica in the Sample | Weight of Silica Determined | Grams Error |
|----------------------------|--------------------------------|-----------------------------|-------------|
| .5000 | .0100 | .0102 | +.0002 |
| .5000 | .0100 | .0099 | -.0001 |
| .5000 | .0199 | .0196 | -.0003 |
| .5000 | .0200 | .0198 | -.0002 |
| .5000 | .0349 | .0347 | -.0002 |
| .5000 | .0350 | .0347 | -.0003 |
| .5000 | .0498 | .0495 | -.0003 |
| .5000 | .0498 | .0494 | -.0004 |
| .5000 | .0998 | .0994 | -.0004 |
| .5000 | .0998 | .0994 | -.0004 |

These results show that the silica content of a synthetic fluorspar can be determined with considerable accuracy, the method being applicable to mixtures containing as high as one tenth gram of silica in the presence of one half gram of calcium fluoride.

SUMMARY

Several methods for the determination of silica in the presence of fluorine have been tested.

The method of Jannasch and Weber is not suitable without modification for the determination of silica in the presence of fluorine.

Decomposition of the fluorspar by means of the borax fusion gives fairly consistent results but are not entirely satisfactory.

The decomposition of the natural fluorspar by means of a mixture of sulfuric acid and boric acid gives consistent results for the determination of silica in a natural ore.

The decomposition with a mixture of perchloric and boric acids also gives excellent results. Synthetic mixtures of quartz and calcium fluoride analyzed by this method shows that the silica content can be determined with considerable accuracy, the method being applicable to mixtures containing as high as one tenth gram of silica in the presence of one half gram of calcium fluoride. The maximum deviation found was four tenths of a milligram.

CONCLUSION

A satisfactory method for the determination of silica in the presence of fluorine has been studied. Tests show that silica varying in amounts from one hundredth of a gram to one tenth of a gram in the presence of a half a gram of calcium fluoride can be accurately determined. The method is rapid.

In the light of these facts set forth, further studies should be made in the analysis of fluorspar which should entirely revise the modern methods of fluorspar analyses.

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