October 15, 1929

and in the other as SiO₂. This table indicates that calculating silica as silicate alters the hypotheticals very little.

Table IV-Comparison of Calculated and Determined Values for

		By DIFFERENCE					
SAMPLE	DETD.	Without SiO ₃	With SiO ₃				
	P. p. m.	P. p. m.	P. p. m.				
63.154	56.6	45.2	57.3				
63,279	18.7	5.9	19.3				
63,280	20.3	10.5	23.4				
63,282	43.8	36.6	53.4				
63,293	59.9	51.1	65.9				
62,780	83.7	77.4	87.3				
63,008	11.1	1.0	21.5				
62.779	107.9	103.6	112.4				

Table V--Comparison of Values for Residue and Sum of Hypothetical Combinations

		SUM OF HYPOTHETICAL	COMBINATIONS
SAMPLE	RESIDUE (BY	Silica as	Silica as
SAMPLE	P, h, m	$P_{1} h_{1} m_{2}$	P. p. m.
63,154	566	556.3	555.9
63,279	381	377.2	368.1
63,280	352	377.2	378.5 566.9
63,293	877	827.3	825.8
62,780	822	741.2	740.6
63,008	409	426.3	425.9 666 4
u ,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	001	000.0	00012

In soft waters of comparatively low mineral content, more commonly in surface waters, we have often found that our boiler water analysis shows the presence of no sodium. Repeated checks on the determinations made have shown them to be correct and only by the inclusion of silica as the silicate ion is the presence of sodium shown. In one case the inclusion of silica as the silicate ion made the analysis show the presence of 3 p. p. m. of sodium. (Of course this figure represents sodium and potassium combined.) By actual determination 6 p. p. m. of sodium and potassium combined were shown to be present.

In harder waters of comparatively high mineral content, and in waters where the silica is quite small in amount, the inclusion of the silicate ion is probably not so important. While, strictly speaking, we believe it should always be included, yet for practical purposes its inclusion may be limited. We suggest that where the silicate amounts to half the error between the positive and negative ions it should be included. Otherwise it need not be included.

Literature Cited

(1) Winkler, Z. anal. Chem., 54, 365 (1914).

Note—The silica determinations for the boiler water analyses of Samples 60,206 and 63,413 were made colorimetrically. The silica determinations in the mineral analyses were all made gravimetrically except No. 63,282. This sample had a rather high turbidity, so a colorimetric determination was made on a filtered sample.

The analyses used in the above tables were picked at random from the files of the State Water Survey. All samples were collected in bottles of resistant glass and analyses were made soon after collection. See Collins and Riffenburg, IND. ENG. CHEM., **15**, 48 (1923).

Determination of Silica in the Presence of Fluorspar¹

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THE determination of silica in the presence of fluorspar has always been accomplished either by difficult and complex analytical procedures or by rapid arbitrary control methods of doubtful precision. The method is usually one of the following types: fusion with alkali carbonate followed by extraction with water and treatment of the filtrate with either ammonium carbonate-zinc oxide or mercury-ammonium carbonate; fusion with lead oxide; extraction of the ore with acetic acid. Stadeler (3) studied five methods for the determination of silica in the presence of fluorine and found only one, that of Berzelius, to give reliable results if the fluorine content was above one per cent. The method of Berzelius, however, is long and tedious, even though accurate. The present study was undertaken to determine whether a more simple method could be found for the determination of silica in the presence of fluorspar.

Jannasch and Weber (1) in 1899 reported that there was no loss of silica when a silicate containing a fluoride was fused with boric oxide over an oxygen blast lamp. The fluorine was expelled as boron trifluoride. Meulen (2) in 1923 proved that calcium fluoride could be decomposed by sulfuric acid in the presence of boric acid without etching glass. This was confirmed in the following experiments. The hydrofluoric acid liberated by the acid treatment immediately reacts with the boric acid to form boron trifluoride, which does not attack glass. In all the experiments performed, Pyrex beakers were used and in no case was there the slightest evidence of etching from repeated determinations in the same beakers. The fluorspar was decomposed with an acid in the presence of an excess of boric acid. Hydrochloric, sulfuric, and perchloric

¹ Presented before the Division of Industrial and Engineering Chemistry at the 77th Meeting of the American Chemical Society, Columbus, Ohio, April 29 to May 3, 1929. acids were each separately used for the decomposition. Preliminary results showed that the perchloric-boric acid decomposition gave the most satisfactory results. That the perchloric acid was more satisfactory was due to the fact that calcium perchlorate is very soluble and can be more easily removed from the residue than calcium sulfate.

The following procedure was used in all of the subsequent determinations of silica: A 0.5-gram sample of the finely ground fluorspar was treated with 15 ml. of 20 per cent perchloric acid saturated with boric acid at 50° C. The ore was digested with this solution in a Pyrex beaker until fumes of perchloric acid had come off for 4 to 5 minutes. A few milliliters of water were then added, and the fuming repeated for 4 to 5 minutes. The residue was then diluted to 50-75 ml., the solution heated, and the silica and insoluble material filtered off. The filter paper was washed first with a dilute solution of perchloric acid and finally with hot water until free of calcium salts as shown by tests with ammonium oxalate. The filter paper containing the silica was ashed in a platinum crucible, two drops of concentrated sulfuric acid added, and the residue ignited to constant weight. The silica in the residue was determined in the usual manner by volatilization with hydrofluoric acid. An examination of the residue with a microscope before volatilization with hydrofluoric acid showed that there was no undecomposed calcium fluoride.

A sample of c. p. calcium fluoride which was analyzed for silica and found free of this substance was used in making the following tests. A very pure specimen of quartz was used as a source of the silica. The analysis of the quartz showed that it contained 99.92 per cent silica.

Constant weights of the powdered calcium fluoride were mixed with varying amounts of pulverized quartz and the silica was determined by decomposition with the perchloricboric acid mixture. These results show that the silica content of a calcium fluoride-quartz mixture can be determined very accurately. Tests were made on mixtures containing 0.5 gram of calcium fluoride and from 0.01 to 0.1 gram of quartz. The method is no doubt applicable to samples containing larger amounts of quartz. The results are listed in Table I.

Table I—Determination of Silica in Fluorspar-Quartz Mixture (Weight of CaFt, 0.5000 gram)

3102			S1U2		
CONTAINED	SiO ₂ Detd.	ERROR	CONTAINED	SiO ₂ Detd.	Error
Gram	Gram	Gram	Gram	Gram	Gram
0.0100	0.0102	+0.0002	0.0498	0.0495	-0.0003
0.0100	0.0099	-0.0001	0.0498	0.0494	-0.0004
0.0199	0.0196	-0.0003	0.0511	0.0511	0,0000
0.0200	0.0198	-0.0002	0.0527	0.0527	0.0000
0.0200	0.0199	-0.0001	0.0987	0.0988	+0.0001
0.0217	0.0217	0.0000	0.0987	0.0987	0.0000
0.0349	0.0347	-0.0002	0.0998	0.0994	-0.0004
0.0350	0.0347	-0.0003	0.0998	0.0994	-0,0004
0.0475	0.0477	+0.0002			

A synthetic sample containing 12.60 per cent silica was prepared from a sample of fluorspar and quartz. The results of a series of analyses on this sample are given in Table II.

In order to test further the accuracy of the perchloric-boric method, a Bureau of Standards sample of fluorspar No. 79 was obtained. The silica content as determined by the Bureau of Standards was 1.89 per cent with a maximum deviation of ± 0.15 per cent. The results of a series of determinations made in this laboratory using the perchloric-boric acid method of decomposition was 1.87 per cent silica, the maximum deviation in results being ± 0.05 per cent.

Table	II-Det	ermination	of	Silica	in	Synthetic	Sample
		(Weight of s	amp	le, 0.50	00 gi	ram)	
S	iO2	SiO ₂					

CONTAINED	FOUND	DEVIATION	SiO ₂
Gram	Gram	Gram	Per cent
0.0630	0.0626	-0.0004	12.52
0.0630	0.0630	0.0000	12.60
0.0630	0.0629	-0.0001	12.58
0.0630	0.0634	+0.0004	12.68

Tests were also made to determine whether perchloric acid could be used alone for decomposition without losing silica. The analysis of synthetic samples and the Bureau of Standards sample for silica gave low results.

Conclusions

(1) Fluorspar can be decomposed by treatment with a mixture of perchloric and boric acids without an appreciable loss of silica.

(2) The method is rapid and is capable of a high degree of precision.

(3) Decomposition of the fluorspar with perchloric acid alone gives low results.

Literature Cited

(1) Jannasch and Weber, Ber., 32, 1670 (1899).

(2) Meulen, Chem. Weekblad, 20, 59 (1923).

(3) Stadeler, Stahl Eisen, 47, 662 (1927).

Determination of Total Carbon in Soils¹

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THE great diversity of the soil carbon compounds introduces certain difficulties into the determination of total carbon that are not encountered in ordinary analyses. The wet combustion method (3) commonly employed has two major disadvantages—an elaborate train to remove the large quantities of sulfur dioxide and sulfur trioxide fumes, and the inconvenience of handling boiling sulfuric acid. Further, there is the possibility that inert portions of the organic matter may not be completely oxidized by this method, especially in heavy soils, because of the relatively low temperature of the reaction, approximately 400° C. The difficulty of destroying the carbon that often collects on the sides of the flask in Kjeldahl digestions points strongly to the possibility of such an error.

These objections are not found in the dry combustion method described by Salter (1). It seemed to give promise of being a more convenient method and at the same time of yielding more accurate results than the wet combustion method, and therefore an investigation of its suitability for making a large number of total carbon determinations in soils was undertaken.

The great "dilution" of the soil organic matter by inert mineral material suggested the possibility of dispensing with the usual two-unit furnace for organic work and of inserting the loaded boat immediately into the hot unit containing the copper spiral, thus avoiding the loss of time occasioned by heating the charge gradually. The mineral portion of the soil, usually exceeding 95 per cent, is relied on to retard volatilization sufficiently to permit complete oxidation. If the volatile compounds are driven off too rapidly to be fully oxidized, the results will be low and the method unsatisfactory. No reference was found in the literature concerning this

¹ Received April 5, 1929.

point, and therefore it was thought necessary to give it some attention.

Samples whose carbon content had been determined by the wet combustion method were available. It was assumed that, should the dry combustion figures check with the above and in addition be consistently reproducible, the method could be called satisfactory.

Preliminary work indicated that the dry combustion results were too low, as is shown in Table I. In addition to the possibility of too rapid volatilization, it seemed likely that the oxygen might not readily penetrate through the charge to react with the more inert carbon compounds. Both of these difficulties should be overcome by a suitable oxidizing agent in the bottom of the boat. Manganese dioxide was chosen because of its infusibility and the high temperature at which it releases oxygen, 570° C.

Table I—Comparison of Methods						
(Grams of CO_2)						
Soil	Dry Combustion with MnO ₂	DRY Combustion without MnO ₂	Wet Combustion			
	Gram	Gram	Gram			
234 236 238 244 250 251 256 267 249 270 273	$\begin{array}{c} 0.0840\\ 0.0545\\ 0.0550\\ 0.0550\\ 0.0510^a\\ 0.0518\\ 0.0420\\ 0.0525\\ 0.0525^a\\ 0.0826\\ 0.0885\\ 0.0680\\ 0.0080\end{array}$	0.0550 0.0550	$\begin{array}{c} 0.0820\\ 0.0528\\ 0.0536\\ 0.0526\\ 0.0480^a\\ 0.0500\\ 0.0439\\ 0.0535\\ 0.0490^a\\ 0.0535\\ 0.0490^a\\ 0.0980\\ 0.0635\\ 0.0993\end{array}$			

^a Difference exceeds experimental error.

With this modification the agreement between the two methods is good, in general, as indicated in Table I. The dif-