DETERMINATION OF SILICA IN FILTERED SEA-WATER[1]

BY ROGER C. WELLS

Received July 5, 1922

Introduction and Conclusions.—One would suppose that the many papers which have appeared on the determination of silica, especially the important papers of Hillebrand,[2] and of Lenher and Truog,[3] must have exhausted this subject. The writer concludes, however, that an effective way to remove small amounts of silica from a solution, such as sea-water, is to add an aluminum salt (unless one is already present) and precipitate with a definite excess of ammonia, say enough to produce a pink with rosolic acid; the silica carried down in the ammonia precipitate is then recovered and determined in the usual way. Incidentally, it follows that in ordinary analysis, when dehydrating silica with acids, a double evaporation and filtration is unnecessary, provided the residual silica carried down in the ammonia precipitate is also determined.

Object of the Investigation.—At the request of Dr. H. F. Moore of the U. S. Bureau of Fisheries some determinations of the soluble silica in sea-water were attempted in the chemical laboratory of the U. S. Geological Survey which is equipped with platinum ware indispensable in researches of this nature. The samples were collected under the direction of Dr. H. B. Bigelow, of the Museum of Comparative Zoölogy of Harvard University, who is engaged in studying certain biologic features of the Gulf of Maine. The silica content is of interest in connection with the growth of siliceous organisms, such as diatoms and the phytoplankton, which in turn serve directly or indirectly as food for fish.

Previous Determinations.—Murray and Irvine[4] in an important paper published in 1891 point out that the results for the silica content of sea-water obtained by early investigators are mostly very high, and that if the soluble silica alone is desired it is necessary to filter off the suspended algae and diatoms. Their determinations show from 2 to 5 mg. of soluble silica per liter, but the analytical procedure was admittedly somewhat lacking in refinement.

The problem was again taken up by Raben[5] in 1905, whose method is as follows.

> The water is first filtered through a hardened filter paper using zinc vessels. Three liters is then evaporated in platinum on the steam-bath, after the addition of a little hydrochloric acid. The residue is broken up with a platinum spatula, moistened with hydrochloric acid, again dried and this procedure carried out three times altogether. The final residue is heated for 1 hour at 120°. It is then moist-

---

[1] Published by permission of the Director of the U. S. Geological Survey.

[2] Hillebrand, THIS JOURNAL, **24,** 362 (1902).

[3] Lenher and Truog, *ibid.*, **38,** 1050 (1916).

[4] Murray and Irvine, *Proc. Roy. Soc. Edinburgh,* **18,** 229 (1891).

[5] Raben, *Wissensch. Meeresuntersuch.*, **8,** *Abt. Kiel,* 99, 277 (1905).

ened with hydrochloric acid for 20 minutes, dissolved in warm water, and the solution warmed on the steam-bath until any basic salts are dissolved. The insoluble matter is collected on a small filter and washed until silver nitrate no longer indicates chlorides. The residue is ignited, finally blasted for 10 minutes and weighed. If the residue is not perfectly white the correct weight of silica is obtained by treatment with sulfuric and hydrofluoric acids. Final traces of sulfur trioxide are expelled by moistening the ignited and cooled residue with ammonium carbonate and again igniting. The silica is then obtained from the loss of weight.

In this way Raben found from 0.4 to 1.5 mg. per liter in the water of the North Sea and Baltic Sea. The average result was about 0.9 mg. It seems probable that the "soluble silica" must vary somewhat with the efficiency of the filter used to remove "suspended matter" but this question is beyond the scope of this paper.

Removal of Silica with Acids

The various methods that have been proposed to render silica insoluble and effect its complete removal from solution are discussed by Hillebrand.[6] It is now recognized that successive evaporations with fresh portions of hydrochloric acid without intervening filtration help but little; that dehydration at 110° or 120° effects a more complete dehydration of the silica than evaporation on the steam-bath; but that a small quantity of silica, possibly 1 or 2 mg., is generally found in wash solutions containing hydrochloric acid, sodium chloride, or sulfuric acid, whatever the previous treatment. In view of these facts it appears that any silica obtained from sea-water by evaporation with hydrochloric acid must be considered a minimum figure for that actually present. Evaporation with sulfuric acid to the formation of white fumes is the best method of dehydrating silica.

In attempting to lessen the loss of silica, by reducing the quantity of acid and water used for washing, a new source of error in the opposite direction was discovered in dealing with sea-water, caused by the behavior of calcium sulfate, which generally accompanies the silica under these

TABLE I

BEHAVIOR OF CALCIUM SULFATE WITH HYDROFLUORIC ACID

Treatment	Weight G.	Remarks
Crucible	27.8538	
Plus 1 g. of pure gypsum	28.8538	
Ignition, very dull red	28.6439	loss, 0.2099; calc., 0.2094
" red, 15 minutes	28.6437	loss, 0.2101
H_2SO_4, evaporated, dull red	28.6437	no acid salt formed
H_2SO_4, HF, evaporated, etc.	28.6213	considerable fluoride formed
H_2SO_4, 4 drops + water, etc.	28.6317	sulfate not all regenerated
" "	28.6336	
5 cc. conc. H_2SO_4, etc.	28.6397	
" "	28.6411	

---

[6] Hillebrand, *U. S. Geol. Survey Bull.*, **1919**, 700.

circumstances. It was found that during volatilization with hydrofluoric acid a portion of the calcium sulfate is converted into fluoride and cannot be completely reconverted into sulfate even by several evaporations with sulfuric acid.[7] This behavior makes it impossible to correct for small quantities of silica in calcium sulfate by means of hydrofluoric acid. It is equally out of the question to determine the silica in sea-water by evaporation to fumes with sulfuric acid. The behavior of calcium sulfate with hydrochloric acid is shown in Table I.

Removal of Silica in the Ammonia Precipitate

Hillebrand leaves the efficiency of the removal of silica in the ammonia precipitate in some doubt.[8] In 7 trials he found an average of 1.4 mg. remaining unprecipitated, in 1 case none, in the highest 2.1 mg.[9] Lindo's belief was that silica can be completely removed in this way.[10] In the hope of gaining further light on this question the behavior of silica in the precipitation of aluminum hydroxide was studied. Aluminum was chosen on account of its extensive use in water purification, but most of the conclusions would doubtless apply equally well to ferric hydroxide. The problem was investigated from two points of view especially,—the excess of aluminum oxide required to give the most complete removal of silica, and the best hydrogen-ion concentration. In regard to the first point, Table II shows the percentage of silica removed at 4 different molecular ratios of alumina to silica, namely, $^1/_2$, 1, 2, and 10 of the first to 2 of the second. The second ratio is that of kaolin. The method was as follows.

To 100 cc. of filtered sea-water was added a little macerated filter paper, 1 g. of ammonium chloride, 0.0106 g. of silica in the form of a very dilute water-glass solution, a measured quantity of a dilute solution of alum, and sufficient ammonia to give a yellow color with methyl red. The solution was heated to boiling, boiled for 2 minutes, and filtered through a quantitative[11] paper. The solution usually turned slightly pink. The precipitate was washed with hot water, dried by suction, ignited and the silica determined with hydrofluoric acid as usual, after fusing with sodium hydrogen sulfate, evaporating the solution to fumes, etc.

TABLE II

SILICA RECOVERED WITH DIFFERENT PROPORTIONS OF ALUMINUM SALT PRESENT AT PRECIPITATION

Expt.	Wt. Al_2O_3 taken G.	Wt. SiO_2 taken G.	Wt. SiO_2 found G.	SiO_2 recovered %
10	0.0045	0.0106	0.0064	60
11	0.0090	0.0106	0.0068	64
12	0.0180	0.0106	0.0087	82
13	0.0900	0.0106	0.0083	78

---

[7] Mr. E. P. Henderson of the U. S. Geological Survey kindly assisted in checking this behavior of $CaSO_4$.

[8] Ref. 6, p. 118.

[9] Ref. 2, p. 362.

[10] Lindo, *Chem. News*, **60,** 14 (1889).

[11] Schleicher and Schüll, No. 589.

It is evident that at least 2 parts of alumina to one part of silica are necessary for the most complete removal of the silica. A small part of the silica was not recovered, but as shown later the results would have been a little better if more ammonia had been used or if a trace of silica in the wash waters had been allowed for.

The experiments in which the hydrogen-ion concentration was determined are shown in Table III. The results are arranged in order of Sörensen values of ($P_H = -\log [H^+]$). Expt. 9, which was made according to Blum's directions for precipitating Al_2O_3,[12] as were all the precipitations in Table II, was the first in the table in which all of the alumina present was precipitated. The procedure was as follows.

To 100 cc. of filtered sea-water was added a little macerated filter paper, 1 g. of ammonium chloride, 0.0106 g. of silica in the form of a dilute water-glass solution, 5.0 cc. of alum solution equivalent to 0.0363 g. of alumina and the stated quantity of a dil. ammonia solution (approximately 1.13 *N*). The solution was brought to boiling, boiled for 2 minutes and filtered through quantitative paper. The undiluted filtrate was cooled to 25° and tested for its alkalinity at once in a Clark cell with the usual apparatus.[13] The precipitate was washed with hot water, finally dried by suction, ignited, and the silica determined by fusing with sodium hydrogen sulfate in the usual way.[14]

TABLE III

SILICA PRECIPITATED AS RELATED TO THE FINAL HYDROGEN-ION CONCENTRATION AT PRECIPITATION

Expt.	SiO_2 taken G.	NH_4OH Cc.	P_H mother liquor	SiO_2 found G.
6	0.0106	None	4.09	0.0039
3	0.0106	1.0	4.15	0.0074
7	0.0106	1.2	4.41	0.0077
5	0.0106	1.5	6.34	0.0061
9	0.0106	1.66	6.68	0.0098
2	0.0106	2.0	7.02	0.0100
8	0.0106	3.5	7.74	0.0101
1	0.0106	...	8.52	0.0092
4	0.0106	40.0	9.20	0.0109

In order to test every possible way in which silica might escape determination, the wash waters in Expts. 1, 2, 3 and 4 were evaporated with sulfuric acid to the formation of white fumes and the silica found amounted to 0.4, 0.4, 0.1 and 0.2 mg.; mean 0.3 mg. Thus, the silica which is not recovered is about equally divided between the mother liquor and the wash waters. But the total amount unrecovered under the best conditions appears to be less than 1.0 mg. This slight improvement over the results found by Hillebrand may be dependent on the presence of additional salts or of macerated filter paper.

---

[12] Blum, THIS JOURNAL, **38,** 1282 (1916).

[13] Wells, *ibid.*, **42,** 2160 (1920).

[14] Ref. 6, p. 116.

It is of course possible to interpret the results of Table III as showing that sufficient alumina must be precipitated to carry down the silica. It appears, however, that an excess of ammonia is somewhat advantageous as far as the precipitation of silica is concerned. A large excess apparently does not dissolve any silica under the conditions in these experiments.

In applying these conclusions to rock analysis it seems logical to suggest that the alkalinity proposed by Blum for the precipitation of alumina be extended very slightly for the reason that the quantity of alumina dissolved will be practically negligible, whereas the probability of getting all the silica will be strengthened. Accordingly, the permissible Sörensen value would be from 7 to 8, at least, corresponding to a pink with rosolic acid.

In 20 complete rock analyses recently made by the writer, in which only one evaporation with hydrochloric acid was made and silica was determined in the ammonia precipitate, the average quantity of silica recovered from the ammonia precipitate was 0.0070 g., highest 0.0135, lowest 0.0037. The average summation was 100.00, highest 100.40, lowest 99.69. These results point clearly to the conclusion that a double evaporation for silica is unnecessary when the residual silica is to be recovered in the ammonia precipitate. The trace of silica not recovered seems to have been just about balanced by that which is generally acquired in the operations of a complete analysis. The silica from the hydrochloric acid evaporation in these analyses was filtered off on a rapid quantitative paper[15] to expedite the procedure.

Results with Sea-water

The procedure finally adopted is as follows.

About 3 liters of filtered sea-water is evaporated to approximately 200 cc. For each liter is added 10 cc. of hydrochloric acid and a quantity of alum solution equivalent to 0.04 g. of alumina, then some macerated filter paper, rosolic acid or phenolphthalein, and finally ammonia to the formation of a pink color. The solution is boiled for 2 minutes and filtered. The precipitate is ignited, fused with about 4 g. of sodium hydrogen sulfate until clear, and the melt dissolved in water containing about 15 cc. of 1-1 sulfuric acid. The solution is evaporated to the formation of white fumes, cooled, diluted with water and filtered at once through a small filter. The silica is ignited strongly, weighed, evaporated with hydrofluoric and sulfuric acids, again ignited and the silica computed from the loss on volatilization.

The results with sea-water are shown in Table IV. Three samples (7, 8, and 9) were investigated by the combined methods of evaporation with hydrochloric acid and precipitation of alumina with ammonia, the single exception to Raben's procedure being that only one evaporation with acid was employed.

The quantities of silica obtained with the acid treatment were insignificant although in 1 sample (9) the same was true of both treatments.

---

[15] Schleicher and Schüll No. 589.

All of the samples were collected about 1 mile south of Eastern Point Light, Gloucester, Massachusetts, and had been filtered and shipped to Washington in 2-gallon tinned-iron cans. The iron was somewhat attacked in several of the cans, but careful analysis of the sediment showed practically no silica in most cases. The iron of the cans was also analyzed and the silicon content found not to correspond to more than 0.0002 g. of silica per gram of iron. Assuming that all of the silica in the sediment came from the water it would not have amounted to more than 0.1 mg. of silica per liter in most of the samples. There was 0.0115 g. or 0.0015 g. of silica per liter, found in Sample 1, which may represent an accidental impurity. The results in Table IV have not been corrected for the trace of silica presumably washed out of the ammonia precipitate in the wash waters.

TABLE IV

SOLUBLE SILICA IN SEA-WATER

No.	Date of collection 1921	SiO_2 G. per liter	
1	Dec. 28[a]	0.0015	From sediment only
2	Jan. 26	0.0025	
3	Received in Washington, Mar. 2	0.0029	
4	Mar. 25	0.0014	
5	Apr. 25	0.0003	
6	May 26	0.0004	
7	June 27	0.0019 0.0009	
8	July 27	0.0006	
9	Aug. 26	0.0003	
10	Sept. 26	....	Container leaked
11	Oct. 26	0.0004 0.0007	

[a] 1920.

Owing to the fact that for various reasons duplicate determinations could not be made, the results are not wholly conclusive with regard to a seasonal variation of the silica content, although such a variation is strongly suggested.

Summary

1. A method is outlined and some results are given for the determination of the soluble silica in sea-water.

2. Silica cannot be determined from the loss on evaporation with hydrofluoric acid in the presence of calcium sulfate, but calcium sulfate is not ordinarily contained in the silica obtained in rock analysis.

3. The co-precipitation of small amounts of silica with aluminum hydroxide by ammonia has been studied.

4. An excess of at least 2 parts of aluminum oxide to 1 of silica is essential for the complete inclusion of silica in the ammonia precipitate.

5. An excess of ammonia favors the inclusion of silica in the ammonia precipitate, but this has a slightly solvent action on the aluminum hydroxide.
6. A Sörensen value of from 7 to 8, as shown by a pink color with rosolic acid, is advised in making the ammonia precipitation.
7. A very small quantity of silica, roughly 0.3 mg., escapes precipitation, and an equal quantity is generally found in the wash waters from the ammonia precipitate.
8. In rock analysis a single evaporation with hydrochloric acid is sufficient, provided silica is also determined in the ammonia precipitate.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

A STUDY OF THE VELOCITY OF HYDROLYSIS OF ETHYL ACETATE

BY HERBERT S. HARNED AND ROBERT PFANSTIEL[1]

Received July 11, 1922

From various considerations regarding the independent character of the ions in dilute solutions, MacInnes[2] has assumed that, in dilute solutions of the same molality of hydrochloric acid and potassium chloride, the chloride ion has the same activity. Further, he assumed that in a solution of potassium chloride of a given strength, the activities of the potassium and chloride ions are the same. Harned[3] found evidence from electromotive-force data for the validity of these assumptions in conc. solutions and calculated the individual activity coefficients of the ions of these electrolytes. If these assumptions are correct, it follows from these calculations that the activity coefficient of the hydrogen ion in solutions of hydrochloric acid decreases with increasing concentration until a concentration of 0.15 M is reached, and then increases.

In many recent studies,[4] the contention has been made that the velocities of homogeneous reactions catalyzed by ions are a function of the ion activities and not the ionic concentrations. It has been pointed out by Jones and Lewis that other causes such as "the water displacement effect" may also influence the reaction velocity. From this point of view,

---

[1] Presented to the Faculty of the Graduate School of the University of Pennsylvania by Robert Pfanstiel in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] MacInnes, THIS JOURNAL, **41**, 1086 (1919).

[3] Harned, *ibid.*, **42**, 1808 (1920).

[4] (a) Harned, *ibid.*, **40**, 1461 (1918). (b) Jones and Lewis, *J. Chem. Soc.*, **117**, 1120 (1920). (c) Scatchard, THIS JOURNAL, **43**, 2387 (1921). (d) Akerlöf, *Z. physik. Chem.*, **98**, 260 (1921). (e) Harned and Seltz, THIS JOURNAL, **44**, 1475 (1922); etc.