the membrane, and to the magnitude of the difference of potential which exists between the solutions bathing the two faces of the membrane. In most cases the orientation of the membrane is that which would be expected from the difference in migration velocities of the ions without considering the membrane, but in a few cases the orientation is the reverse.

6. In all cases of the monobasic salts studied, the greater the rate of diffusion of salt through the membrane of the cells the greater the positive osmose. This rate of diffusion is always closely related to the magnitude of cell potential.

7. The facts brought out seem to indicate that the osmose of these solutions of electrolytes is primarily due to an electrical effect, and is analogous to electric osmose. The explanation which seems most reasonable is that the osmose is due to the passage of a charged liquid layer along the capillary tubes of the membrane under the driving force of a difference of potential which acts as though it were set up between the two faces of the membrane. The charge of the movable liquid layer is determined by the charge which the porcelain assumes when immersed in water, but this charge may be altered by selective adsorption of ions when the membrane is brought in contact with solutions of electrolytes; and other ions than H and OH may effect the charge on the membrane. The polarization of the membrane is probably determined by the relative rates of diffusion of the ions through the membrane, but may be altered by such factors as ionic adsorption.

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THE QUANTITATIVE DETERMINATION OF SILICA.

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The conventional method of attack of silicates in general consists in the sodium carbonate fusion, the treatment of this fusion with hydrochloric acid for the purpose of separating out the silicic acid, and the subsequent evaporation for the purpose of dehydrating this silicic acid and rendering the silica insoluble in water and in dilute hydrochloric acid. This method of separating silica from the bases has received a great deal of study, yet the results obtained are not all that might be desired. There is considerable uncertainty regarding the necessary length of time and temperature of dehydration, the need of repeated evaporation, the solubility of silica in acids and in the wash solutions used, and the presence of ferric oxide, alumina, lime, magnesia, potash and soda in the nonvolatile residue which remains when the weight of the silica is obtained by its loss when treated with hydrofluoric and sulfuric acids. The present investigation was undertaken for the purpose of studying the various errors in the determination of silica with the view of making the determination more accurate and if possible more expeditious.

Fresenius[1] states that direct heating over the lamp is not advisable as in the most strongly heated parts the silicic acid is liable to unite again with the separated bases to form compounds which are not decomposed, or only imperfectly by hydrochloric acid.

Gilbert[2] investigated the effect of different temperatures of dehydration, and the presence of considerable calcium and magnesium on the solubility and contamination of the silica. He worked with several furnaces lags and orthoclase feldspar. His conclusion may be summarized as follows: Temperatures of dehydration above that of the water bath do not give much higher results for silica, but may increase the impurities in the silica considerably. These impurities cannot be removed by digestion for one hour with strong acid. Calcium and aluminum have no tendency to form silicates even at temperatures up to 280°. When magnesia is present, the best results are obtained by dehydrating at 120°. Higher temperatures may cause the formation of partially soluble magnesium silicate.

Hillebrand[3] furnishes data showing that the silica recovered with alumina and other oxides may again be partially lost, due to its increased solubility after the pyrosulfate fusion. This, he states, is an added argument in favor of recovering all of the silica at the outset, since the expectation of recovering all of what remains is based on an erroneous assumption. Because of this he states that Gilbert's results lose much of their value. If this criticism be accepted, Gilbert's results still show that high temperatures of dehydration increase the impurities in the silica, and that the presence of considerable magnesia tends much more than lime and alumina to still further increase the impurities, besides causing more silica to go into solution.

Bloor,[4] in the analyses of clays, made special note of the residues left after volatilization of the silica, and found lime and magnesia present in amounts ranging from practically nothing to about two milligrams of each. The dehydration was made on a water bath. The total residues averaged about 1% of the separated silica. When the dehydration temperature was raised to 125° the residues were greater, due largely to an increase of lime and magnesia. As possible reasons for the presence of lime and magnesia in the residues, Bloor gives as the causes of

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[1] Fresenius, *Quant. Chem. Anal.*, 1, 510 (1904).

[2] *Tech. Quart.*, 3, 61 (1890).

[3] THIS JOURNAL, 24, 362 (1902).

[4] *Ibid.*, 29, 1603 (1907).

error insufficient washing, incomplete decomposition at the outset, contamination from porcelain, and different deportment of clay and rock powder in the fusion.

Hillebrand[1] states that he has tested the residues carefully for lime and magnesia, and finds none of the former present and from nothing to 0.2–0.3 mg. of the latter.

Gooch,[2] Reckert and Kuzirian indicate that the main source of trouble in bringing precipitated silica to constant weight is not due to the presence of water, but to impurities which are partially volatile. They also indicate that the impurities may consist in part of sodium chloride, which on heating with the blast lamp, gradually loses chlorine and produces sodium silicate.

Bauer[3] states that silica may hold hydrochloric acid so strongly that a blast flame will not drive it off. He does not state whether the silica used was free from bases or salts, and hence the presence of chlorides is not precluded and his contention correspondingly loses weight.

Wunder[4] and Suleimann present results which show that the solubility of precipitated silica increases with the strength of hydrochloric acid used and also with the temperature of digestion.

Hillebrand[5] states that hydrochloric acid has a marked solvent action on the silica that is obtained in the usual analysis. He states that the use of dilute hydrochloric acid in place of water for washing gave unfavorable results.

Experimental.

Temperature of Dehydration.—Undoubtedly the more complete the dehydration the more insoluble does the silica become to the subsequent acid treatment. The completeness of dehydration is, however, limited by the temperature at which the silica reacts with the chlorides and the time which is permissible to use. The writers have been unable to find in the literature any report of a systematic investigation regarding this reversion temperature at which the bases, especially magnesia, start to combine with silica to a material degree. For the purpose of determining this, the following experiments were carried out in which only materials of known composition and high state of purity were used in order that the conditions could be controlled properly.

Materials Used.—Practically all of the silica on the market contains various bases as impurities. Therefore, silica of a high degree of purity was prepared as follows: Silicon tetrafluoride was evolved by the action of sulfuric acid on a mixture of powdered quartz and calcium fluoride.

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[1] U. S. Geol. Survey, *Bull.* 422, 97 (1910).

[2] *Am. J. Sci.*, 186, 598 (1913).

[3] *Tonind. Ztg.*, 37, 89 (1913).

[4] *Ann. chim. anal.*, 19, 45 (1914).

[5] U. S. Geol. Survey, *Bull.* 422, 92 (1910).

From the generating flask the gas was conducted through a rubber funnel into water contained in a paraffined beaker. The gelatinous silica which separated out was filtered off, and after thorough washing was heated in a platinum dish with sulfuric acid until copious fumes of sulfur trioxide came off for ten minutes. This was done to drive out the last traces of hydrofluoric acid from the silica. The silica was then washed with pure water and strongly ignited. A 0.5 g. sample of this silica left no weighable residue when treated with hydrofluoric and sulfuric acids and evaporated; hence was considered pure.

A second preparation was made as follows: Pure silicon tetrachloride was dropped into water. After evaporating to dryness, which converted the gelatinous silica which had separated out to the granular form, the material was powdered and treated with sulfuric acid and thoroughly washed in the same way as the silica obtained by decomposing the fluoride. On evaporating a 0.5 g. sample with hydrofluoric and sulfuric acids, a residue of 0.05 mg. was obtained, which is within the limits of error of working. This silica was, therefore, as pure as that prepared from the tetrafluoride. When the silica from the tetrachloride was not treated with sulfuric acid, it contained more impurities. Iron appeared to be the main impurity, and the conversion to the sulfate made its removal by washing possible.

Silica prepared from the tetrafluoride is very light and voluminous, making it difficult to handle and weigh. That prepared from the tetrachloride is more like ground quartz and hence is readily handled.

The hydrofluoric acid used was prepared by redistilling pure commercial acid in a platinum still. A 50 g. sample left no weighable residue on evaporation and ignition.

The supply of sulfuric acid on hand gave on evaporation and ignition a residue of 0.0002%, and hence was sufficiently pure.

The hydrochloric acid used was prepared both by redistilling pure acid, in which case the first and last portions were discarded, and by the action of sulfuric acid on sodium chloride, using appropriate wash bottles.

The other chemicals employed showed by blank tests or otherwise that they were sufficiently pure for the purposes intended.

Analytical Methods.—In our experiments 0.5 g. samples of silica were always used. To the weighed sample were added the various amounts of calcium, magnesium or ferric oxides and from four to six parts of sodium carbonate. The amount of sodium carbonate used was regulated according to the amount of basic oxide added. The materials were mixed in a platinum crucible and heated by means of a burner until the fusion was quiet. The fused mass was then transferred to a platinum dish and treated with an excess of dilute hydrochloric acid (sp. gr. 1.05). After all but the silica had dissolved, the solution was evaporated to dryness on the water bath and the residue further heated for two hours at the temperature indicated in each series of experiments. After dehydration, the mass was treated with 25 cc. of hydrochloric acid (sp. gr. 1.1). The dish was covered and digested on the water bath for 10 to 20 minutes. Any lumps appearing were broken up, and after diluting with water, the solution was filtered. The silica was washed with water till the runnings no longer gave a turbidity with silver nitrate. This gave a filtrate of 200 to 300 cc. The silicate was volatilized in a weighed platinum crucible, after the addition of a few drops of sulfuric acid and about 3 cc. of hydrofluoric acid. The residue was ignited and the crucible and contents weighed.

Two double walled drying ovens, one of copper and one of sheet iron, were first used in the dehydrations. They were heated by two Bunsen burners. On testing these ovens carefully, it was found that under the best conditions the temperature at various points on the same shelf in the oven varied as much as 10° and sometimes even more. The ovens were in good condition and the burners were carefully regulated. With less care and the use of two shelves, thermometers variously placed would show a difference if as much as 20° in different parts of the same oven. The experiments with lime and with magnesia given in Table I were carried out in these ovens. In all of the other experiments, except when a temperature higher than 120° was required, an automatic electric oven

TABLE I.

Nonvolatile Residues Using Various Amounts of Basic Oxides.

Dehydration Temperature 110°.

SiO_2, g.	Na_2CO_3, g.	CaO, g.	N. V. R., g.	SiO_2, g.	Na_2CO_3. g.	MgO, g.	N. V. R., g.
0.5000	2	0.0000	+0.0001	0.5000	2	0.0010	−0.0001
0.5000	2	0.0000	−0.0001	0.5000	2	0.0010	....
0.5000	2	0.0010	−0.0001	0.5000	2	0.0100	....
0.5000	2	0.0010	−0.0001	0.5000	2	0.0100	....
0.5000	2	0.0100	+0.0001	0.5000	2	0.5000	+0.0002
0.5000	2	0.0100	+0.0001	0.5000	2	0.5000	+0.0002
0.5000	2	0.0500	+0.0001	0.5000	2	0.1000	+0.0005
0.5000	2	0.0500	..	0.5000	2	0.1000	+0.0001
0.5000	2	0.1000	+0.0001	0.5000	4	0.2000	+0.0003
0.5000	2	0.1000	+0.0001	0.5000	4	0.2000	+0.0002
0.5000	4	0.2000	+0.0002	0.5000	6	0.5000	+0.0003
0.5000	4	0.2000	..	0.5000	6	0.5000	+0.0001
0.5000	6	0.5000	..	0.5000	2.5	0.0100	+0.0009
0.5000	6	0.5000	−0.0003	0.5000	2.5	0.0100	+0.0005
				0.5000	2.5	0.0500	+0.0021
				0.5000	2.5	0.0500	+0.0028
				0.5000	2.5	0.2000	+0.0005
				0.5000	2.5	0.2000	+0.0019
				0.5000	5.0	0.5000	+0.0012
				0.5000	5.0	0.5000	+0.0009

was used, which made it possible to control the temperature to which the dishes were heated to within one degree.

In Table I are given the results when various amounts of calcium, magnesium and ferric oxides were fused with silica and sodium carbonate and where a dehydration temperature of 110° was used. From these data it is evident that lime does not seriously contaminate the silica at this temperature. With the large amounts of magnesia there are indications of contamination, but this is undoubtedly due to the poor regulation of temperature secured with the gas heated oven, as already explained. The results with magnesia given in Table II entirely confirm this probability. The ferric oxide contaminated the silica in all cases in an irregular way.

TABLE II.

Nonvolatile Residues under Different Temperatures of Dehydration.

Temperature.	SiO_2, g.	Na_2CO_3, g.	CaO, g.	N. V. R., g.	Temperature.	SiO_2, g.	Na_2CO_3, g.	MgO, g.	N. V. R., g.
110°	0.5000	2	0.1000	+0.0001	105°	0.5000	2.5	0.1000	+0.0001
110	0.5000	2	0.1000	+0.0001	110	0.5000	2.5	0.1000	+0.0001
115	0.5000	2	0.1000	..	110	0.5000	2.5	0.1000	+0.0001
115	0.5000	2	0.1000	..	115	0.5000	2.5	0.1000	+0.0002
120	0.5000	2.5	0.1000	+0.0002	115	0.5000	2.5	0.1000	+0.0006
120	0.5000	2.5	0.1000	+0.0002	120	0.5000	2.5	0.1000	+0.0010
150	0.5000	2	0.1000	+0.0003	120	0.5000	2.5	0.1000	+0.0012
150	0.5000	2	0.1000	+0.0004	150	0.5000	2.5	0.1000	+0.0008
175	0.5000	2.5	0.1000	+0.0003	150	0.5000	2.5	0.1000	+0.0018
175	0.5000	2.5	0.1000	+0.0004	175	0.5000	2.5	0.1000	+0.0007
			Fe_2O_3.		175	0.5000	2.5	0.1000	+0.0011
110	0.5000	2.5	0.0500	+0.0021	Free flame	0.5000	2.5	0.1000	+0.0008
110	0.5000	2.5	0.0500	+0.0028	Free flame	0.5000	2.5	0.1000	+0.0016
120	0.5000	2.5	0.0500	+0.0004					
120	0.5000	2.5	0.0500	+0.0004					
150	0.5000	2.5	0.0500	+0.0015					
150	0.5000	2.5	0.0500	+0.0013					

Table II shows the results obtained when the amount of basic oxide added was constant (0.1 g.), and the temperature of dehydration varied. From these data it is evident that lime does not seriously contaminate the silica, unless the temperature of dehydration is at least over 115°. With magnesia the point at which the silica becomes contaminated with magnesia is reached at 115°. At 110° there is no appreciable contamination, which shows that the slight contamination of magnesia reported in Table I was probably due to the poor regulation of temperature secured with the gas heated ovens.

Ferric oxide contaminates the silica in an entirely irregular way at all temperatures, which suggests that it may be due to physical causes. Undoubtedly on evaporation and dehydration the ferric chloride by hydrolysis changes partly to oxide and oxychloride, which, because of their lesser solubility, are not as readily removed from the interior of the dried silica as calcium chloride.

Potash and soda have been repeatedly tested for in many experiments, but in our work have never been detected in the nonvolatile residue. This is in accord with the work of Hillebrand[1] but not with the observations of Kuzirian.[2]

The general knowledge of the contamination of silica by the bases has been emphasized by those who have studied in detail the silica determination. It has been assumed by some that actual reversion to silicate takes place. It is not possible at the present time to state definitely just how these bases are retained by the silica. Hydrolysis alone will not account for the retention of lime or magnesia, since the products of the hydrolysis of calcium or magnesium chlorides are readily soluble in even dilute hydrochloric acid. The subsequent extraction with dilute acid should, therefore, remove the lime or magnesia, but such is not the case. In the case of contamination of the silica by iron, hydrolysis probably can be assumed to be at least one cause.

Adsorption might be advanced as a possible explanation, but would hardly seem plausible. As a matter of fact, the contamination is a very real thing, and in the analysis of silicates always takes place. In the silica from basic rocks the nonvolatile residue is usually very much higher than from those of acidic character.

It should be emphasized at this point that in the regular procedure of a silicate analysis, if the dehydrated silica and chlorides are treated first with water, insoluble basic chloride of iron is formed which will not completely dissolve in hydrochloric acid of any strength in any reasonable length of time. This is especially true when hot water is used. Sufficient hydrochloric acid, therefore, must be added to prevent this decomposition. On the other hand, large excess of hydrochloric acid must be avoided on account of its solvent action on the silica.

Solubility of Silica in Hydrochloric Acid and in Wash Solutions.—In order to determine what effect the concentration of the hydrochloric acid used in taking up the dehydrated silica has on the amount of silica which passes into solution and is recovered in the subsequent dehydration, the following experiments were carried out:

One-half gram of pure silica was fused with 2.5 g. of sodium carbonate, treated with hydrochloric acid, evaporated, dehydrated at 110° for 2 hours and then taken up with hydrochloric acid of different strengths, as indicated in Table III. After filtering and washing to a volume of about 250 cc. the silica in the filtrate was determined by evaporation, dehydration and filtration in the usual way. The results are given in the first three columns

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[1] This Journal, **24**, 373 (1902).

[2] *Am. J. Sci.*, **37**, 61 (1914).

of Table III. The main bulk of silica filtered off after the first dehydration was further treated with acid in order to determine if more silica would go into solution. The silica was transferred from the filter papers to platinum dishes. One series was treated with hydrochloric acid in exactly the same way as before and the dissolved silica determined. The other series were treated similarly with an equivalent amount of sulfuric acid. The results are given in the last two columns of Table III.

TABLE III.

Solubility of Dehydrated Silica in Acid Treatments Indicated.

Grams of SiO_2 Dissolved.

	First treatment with HCl.			Second treatment with	
Method of treating dehydrated silica.	a.	b.	av.	HCl.	H_2SO_4.[1]
12.5 cc. con. HCl (sp. gr. 1.2) digested 15 min. Dil. to 25 cc. and digested 15 min. Dil. to 50 cc. and filtered	0.00251	0.00251	0.00251	0.00068	0.00103
25 cc. HCl (sp. gr. 1.1) digested 30 min. Dil. to 50 cc. and filtered	0.00230	0.00212	0.00221	0.00048	0.00136
50 cc. HCl (sp. gr. 1.05) digested 30 min. and filtered	0.00410	0.00402	0.00407	0.00286	0.00279

The data in Table III indicate that digestion with concentrated hydrochloric acid or with a considerable volume of dilute acid are both to be avoided. Hydrochloric acid (sp. gr. 1.1) appears to be about the right concentration for the first moistening of dehydrated silica. The amount used and time of digestion should be the minimum.

A comparison of the data in Table III shows that less silica goes into solution in the second treatment. The results corroborate the work of Hillebrand,[2] who has shown that hydrochloric acid has a distinct solvent action on the silica. Completeness of dehydration is not the only factor that must be considered in accounting for the silica found in the filtrate after the first dehydration. Dilute sulfuric acid has about the same solvent action as dilute hydrochloric acid, while somewhat stronger sulfuric acid has a more marked action.

Although the amount of silica dissolved in the second treatment as given in Table III is less than that dissolved in the first treatment, yet it cannot be concluded from this that there is a definite amount of silica present after dehydration which is more soluble than the rest. In the first extraction with hydrochloric acid there was a considerable amount of sodium chloride present, which, as following results show, has a considerable solvent action on the silica.

Solubility of Silica in Different Wash Solutions.—In order to determine what kind of a washing solution would have the least solvent action on the silica, the following experiments were made. The silica on the filter

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[1] The H_2SO_4 was used in amounts equivalent to the HCl.

[2] THIS JOURNAL, **24**, 368 (1902).

papers from the previous work was thoroughly washed with water and then washed with 300 cc. of the respective wash solutions indicated in Table IV. The filtrates were evaporated and the silica determined in each case. The silica in 300 cc. of original wash solution was also determined in each case:

TABLE IV.

Solubility of Silica in Wash Solutions. Results in Grams.

Washed solution used.	SiO_2 in 300 cc. of blank.	SiO_2 in 300 cc. after washing.	SiO_2 dissolved by wash sol.
Distilled water	0.00040	0.00106	0.00066
1% HCl	0.00050	0.00138	0.00088
1% NaCl	0.00016	0.00243	0.00227
1% NH_4Cl	0.00094	0.00586	0.00492

The data in Table IV indicate that distilled water has the least solvent action of any of the washing solutions used. Solutions of sodium and ammonium chloride have a distinct solvent action. All things considered, a wash solution of distilled water just acidified with hydrochloric is perhaps the most desirable. The presence of a very small amount of hydrochloric acid has no marked solvent effect on the silica, but does have the advantage of helping to remove occluded bases in the silica and preventing the silica from going into a colloidal condition, in which condition it will pass through the filter paper to a considerable extent. A wash solution, consisting of 1 cc. concentrated hydrochloric acid in 100 cc. water, appears quite desirable, and this was later used with good results.

Solubility of Silica as Influenced by Extent and Nature of Dehydration.—It was thought that perhaps if the period of dehydration at 110° was increased over two hours, the silica would be made more insoluble in the subsequent acid treatment. Dehydration at one-fourth atmospheric pressure was also tried. For this purpose a vacuum desiccator attached to a filter pump was placed in the drying oven. Two samples of material, a silicate rock and a clay loam soil, were fused with sodium carbonate and the fusion was treated with hydrochloric acid. The results are given in Table V.

TABLE V.

Solubility of Silica as Influenced by Nature and Extent of Dehydration.

		Grams SiO_2 recovered in successive dehydrations.				
Nature and extent of dehydration.	Material.	1st dehydr.	2nd dehydr.	3rd dehydr.	4th dehydr.	Total first two dehydr.
4 hr. at 110°, $^1/_4$ atm.	Blank	0.0008	0.0002	0.0002	0.0001	0.0010
2 hr. at 110°	Soil	0.7878	0.0016	0.0003	0.0004	0.7894
4 hr. at 110°	Soil	0.7887	0.0019	0.0002	0.0004	0.7906
2 hr. at 110°, $^1/_4$ atm.	Soil	0.7873	0.0014	0.0003	0.0003	0.7887
4 hr. at 110°, $^1/_4$ atm.	Soil	0.7876	0.0016	0.0002	0.0004	0.7892
2 hr. at 110°	Silicate	0.6491	0.0014	0.0006	0.0003	0.6505
4 hr. at 110°	Silicate	0.6511	0.0015	0.0007	0.0003	0.6526
2 hr. at 110°, $^1/_4$ atm.	Silicate	0.6506	0.0014	0.0007	0.0002	0.6520
4 hr. at 110°, $^1/_4$ atm.	Silicate	0.6490	0.0016	0.0005	0.0003	0.6506

The results in Table V indicate that there is no advantage in dehydrating more than two hours, or in carrying out the dehydration under reduced pressure. This indicates that the failure to recover all the silica in one dehydration is not due to insufficient dehydration, but to the great opportunity afforded by the large mass of silica for its direct solution during the acid treatment. From this it may be concluded that the dehydrated mass should be taken up with as little acid as possible, and that this acid should be allowed to act only until the bases are in solution and then filtration proceeded with immediately.

In a further experiment the period of dehydration at 110° was extended to 24 hours. In this case the total amount of silica recovered in all of the dehydrations was less by several milligrams than when a 2-hour period of dehydration was used. This indicates that continued dehydration for a long period, at even 110°, may cause the silica to become contaminated with sufficient magnesia to seriously affect the results. It seems that when magnesia thus contaminates silica it is practically impossible by subsequent evaporations with acid and dehydration to render the silica free from magnesia.

Adopted Procedure for the Determination of Silica.

After a careful study of the results thus far reported, the following procedure was adopted:

A one-half to one gram sample of silicate is intimately mixed with 5 g. of sodium carbonate and fused in a platinum crucible. In the case of a limestone, as suggested by Hillebrand,[1] much less flux is required. The cold fusion is treated with 60 cc. of hydrochloric acid (sp. gr. 1.07). After all carbonates are decomposed and the lumps are broken up, evaporation on steam or water bath is proceeded with until the residue begins to powder or crumble. Further evaporation should be avoided. Breaking up of lumps and crusts greatly expedites the evaporation near the end. The residue is treated with 15 cc. of hydrochloric acid (sp. gr. 1.1) covered and heated on the water bath for 10 minutes. After diluting with 10 cc. of water, filtration is proceeded with immediately, and the silica is washed with a hot solution consisting of 5 cc. of hydrochloric acid (sp. gr. 1.2) to 95 cc. of water. This filtration is preferably performed with suction. The filtrate is evaporated to dryness and until the smell of acid has practically disappeared. The residue is dehydrated at 110° for 2 hours, taken up with 8 cc. of hydrochloric acid (sp. gr. 1.1), covered and heated on the water bath five to ten minutes, diluted to about 50 cc. and filtered immediately. This filtration is performed without suction and the washing is done with cold water containing 1 cc. concentrated hydrochloric

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[1] THIS JOURNAL, 25, 1202 (1903).

acid to 99 cc. water.[1] The paper and silica from the second dehydration are placed in a platinum crucible and the paper burned. The paper containing the silica from the first dehydration is then added to the crucible and the silica is ignited to constant weight. Great care should be exercised in burning the paper, as the current of air produced by a rapidly burning filter paper is sufficient to carry finely divided silica out of the crucible. Loss in this way is more serious when the amounts of silica are quite large, in which case a platinum crucible of at least 30 cc. capacity should be used. Ignition for about 30 minutes with a Mèker burner is usually sufficient to produce constant weight. If the amount of silica is low, less time may be required. Breaking up of crumbs and lumps with a stiff platinum wire aids greatly in burning the last traces of carbon and reducing to constant weight. The silica is then determined by loss, volatilizing in the usual way with hydrofluoric acid after the addition of a few drops of sulfuric acid. The nonvolatile residue is then fused with four times its weight of sodium carbonate and after acidifying with dilute hydrochloric acid is added to the filtrate from the silica which is examined in the usual way for the bases.

Table VI shows the results of analyses by the method given of two silicates, one of which was a feldspar, and two limestones, one of which was dolomitic. The results of a third dehydration are also given. As indicated in the table, porcelain casseroles were used in one set and platinum dishes in the other.

TABLE VI.

Silica Determinations with Adopted Procedure.

		Grams SiO_2 and nonvolatile residue recovered in successive dehydrations.						
		First recovery.		Second recovery.		Total first two.		Third recovery.
Material.	Evaporation in	SiO_2.	N. V. R.	SiO_2.	N. V. R.	SiO_2.	N. V. R.	SiO_2.
Blank	Plat.	0.0008	0.0003	0.0002	..	0.0010	..	0.0002
Silicate 8	Plat.	0.4372	0.0008	0.0030	0.0004	0.4402	0.0012	0.0003
	Porc.	0.4329	0.0003	0.0072	0.0005	0.4401	0.0008	0.0010
Silicate 20	Plat.	0.6935	0.0011	0.0033	0.0001	0.6968	0.0012	0.0003
	Porc.	0.6804	0.0004	0.0166	0.0003	0.6970	0.0007	0.0012
Limestone 12	Plat.	0.0547	0.0003	0.0020	0.0004	0.0567	0.0007	0.0002
	Porc.	0.0551	0.0003	0.0017	0.0007	0.0568	0.0010	0.0001
Dolomitic limestone 13	Plat.	0.1889	0.0004	0.0022	0.0003	0.1911	0.0007	0.0001
	Porc.	0.1880	0.0015	0.0029	0.0001	0.1909	0.0016	0.0001

The data in Table VI indicate that the method outlined gives very satisfactory results. The duplicates agreed to within 0.1 or 0.2 mg., which is much better than the previous results in Table V. Two evapora-

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[1] Often a little silica sticks so tenaciously to the sides of the dish that washing fails to remove it, and in such cases it is best removed with a little piece of ashless filter paper which is subsequently burned with the main precipitate of silica.

tions conducted as stated are sufficient to recover the silica when the acid treatment is performed as outlined. The silica recovered in a third evaporation, when platinum dishes are used, ranges from 0.1 to 0.3 mg. These amounts are of the same order as those obtained in blank determinations or when a fourth evaporation is made, and are to be regarded as due to contamination from the glass beakers, funnels, wash water and acid used. Hillebrand[1] states that from 2–4 mg. of silica remain in the solution after the second evaporation and filtration. The presence of such large amounts has been entirely prevented by the method outlined. The results when porcelain casseroles are used have been favorable. The results of the third evaporation indicate that in certain cases there may be contamination from the porcelain.

In other methods of procedure the nonvolatile residue frequently ranges from 2 to 6 mg. or even much more in basic rocks. In the method outlined this has been reduced with the materials with which we worked to about 1 mg., on the average, for both recoveries of silica. Prevention of excessive drying in the first evaporation and the use of a hot acidified wash solution has made this possible. This is a very desirable feature, as it greatly reduces the time necessary to ignite the silica to constant weight and hence reduces errors incident to long continued heating of platinum and also those which may arise in the correction for impurities which have been suggested by previous workers.

Summary.

The investigation reported was undertaken for the purpose of making the determination of silica more accurate and expeditious. Certain causes of error were first investigated and later remedies worked out and applied. The errors and corrections may be summarized as follows:

Dehydration above 110° leads to erroneous results. Long-continued baking of a *large mass* of silica at 110° is objectionable, since the result is to greatly increase the nonvolatile residue. When natural silicates are analyzed, as is well known, it is impossible to recover all the silica in one dehydration, no matter how complete the dehydration may be. This is due to the fact that silica has a distinct solubility in hydrochloric acid, the extent of which is dependent on the strength and volume of acid used, and time of contact. The presence of considerable impurities in the silica is objectionable, since it greatly increases the time necessary for ignition to constant weight, and may also cause an error in the correction of silica for impurities.

The difficulties just stated are overcome by the modified procedure outlined, the essential features of which are as follows: The main mass of silica is removed after simple evaporation on the water or steam bath till the material begins to get granular but still contains considerable

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[1] U. S. Geol. Survey, *Bull.* **422**, 94 (1910).

acid and water. In this way opportunity for the contamination of the silica is greatly lessened as is also the amount of nonvolatile residue, which is further decreased by the use of the wash solution recommended. A dehydration temperature of more than 110° should never be used. After the second dehydration, the solution of appreciable amounts of silica is prevented by limiting the amount and strength of acid used and also the period of its contact.

Our experience as well as our students' experience with this procedure as outlined has given more accurate silica results than any other procedure, and with the purpose of calling to the attention of the analyst some of the pitfalls in the determination of silica and in the subsequent determination of the bases, the following observations are appended, all of which our laboratory experience has induced us to emphasize, though some have been repeatedly pointed out:

1. In the sodium carbonate fusion method with silicates, there is always a nonvolatile residue when the silica is volatilized with hydrofluoric and sulfuric acids.

2. The nonvolatile residue contains the various bases, and should be fused with sodium carbonate and added to the filtrate from the silica when the bases are to be determined.

3. In the dehydration of the silica from the hydrochloric acid treatment of the fusion, the temperature should never be allowed to go above 110°.

4. Dehydrated silica is appreciably soluble in hydrochloric acid of all strengths. With the dilute acid used, this error is almost negligible.

5. Dehydrated silica is slightly soluble in solutions of the alkaline chlorides. As sodium chloride is always present from the sodium carbonate fusion, an inherent error is obviously thus introduced.

6. The dehydrated silica along with the mass of anhydrous chlorides must not be treated first with water, since hydrolysis causes the formation of insoluble basic chlorides of iron and aluminum, which do not dissolve completely in hydrochloric acid.

7. Hydrochloric acid (sp. gr. 1.1) in minimum amount should be used first to wet the dehydrated chlorides and should be followed by water to bring the volume to about 50 cc., after which the silica should be filtered off as quickly as possible.

8. Pure silica comes quickly to constant weight on ignition. Slightly impure silica frequently requires long heating with the blast flame in order to attain constant weight, and is then commonly hydroscopic.

9. Evaporations of the acidulated fusion in porcelain give practically as good results as when platinum is used.

10. Filtration of the main bulk of the silica after one evaporation is desirable, inasmuch as the silica is removed at once from the solutions which act as solvents.

11. Dehydration of the silica under reduced pressure has no advantages over the common evaporation at ordinary atmospheric pressure.

12. Excessive time of dehydration, *viz.*, 4 hours, possesses no advantages.

13. Excessive amounts of sodium carbonate should be avoided, since the sodium chloride subsequently formed exerts a solvent action on the silica. The best proportions are 4-5 parts sodium carbonate to 1 of silicate. Less than 4 parts of sodium carbonate is frequently insufficient to completely decompose many silicates.

14. The nonvolatile residue has been found to be invariably free from sodium. Pure silica, on fusion with sodium carbonate, subsequently gives no nonvolatile residue.

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NOTE.

A Simple Device for Regulating the Pump Used in Exhausting a Vacuum Oven.—When operating a vacuum oven it is customary to keep the pump running continuously, since the best ovens on the market will not hold a vacuum more than a few hours, especially at elevated temperatures. With a good pump the initial exhaustion of the oven can be accomplished in a very few minutes. The subsequent leakage of air is, however, so slow that the continuous operation of the pump for days at a time seems a waste of power. The simple device described in this paper can be so adjusted as to start and stop the motor automatically for any desired range of vacuum, thus effecting a considerable saving of power. The materials of which it is constructed are to be found in any chemical laboratory, and very little mechanical skill is required to assemble them.

The oven to which this device was attached is a Freas' Electrically Heated Vacuum Oven connected to a Crowell's Pressure and Vacuum Pump, the latter operated by a one-horse-power motor. When the oven is maintained at 100° temperature and 20 to 60 mm. pressure, the apparatus described below starts the motor 18 to 20 times per hour, allowing it to run about 30 seconds each time. Thus at an average pressure of 40 mm. the pump runs only one-sixth of the time. As stated above, the apparatus may be adjusted for any desired range of pressure, the motor starting at the maximum and stopping at the minimum pressure.

Referring to the diagram, *A* is the tube leading to the vacuum pump. The bottle *B* serves as a trap to catch any mercury that may be drawn out of *D*. The bottle *D* contains mercury, Tube *E* (6 mm. inside diameter) which is about 80 cm. long, projects 1 cm. into the mercury in *D*. When the pump stops, the atmospheric pressure raises the mercury in *E* corresponding to the vacuum, thus closing the chamber. When the pump is running, the air is required to bubble through only 1 cm. of mer-