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## The Determination of Silica

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## THE DETERMINATION OF SILICA.

BY NICHOLAS KNIGHT.

The method of procedure depends upon the amount in the substance under investigation and also upon the condition of the silica, whether in the form of sand, or as a soluble or an insoluble silicate. The determination is beset with difficulties, but these are by no means insurmountable. It has been the object of much careful study and investigation and very accurate results are attainable even by persons who have not had much experience in quantitative analysis.

There are two classes of minerals and rocks in which the analyst may be called upon to determine the amount of silica: In silicates proper, in which the percentage of silica is relatively large; and in rocks and minerals like limestone, dolomite, phosphorite, and the various ores of iron and manganese, where the silica content may be quite small.

In the important and growing Portland cement industry, there is often a call for the determination of the silica, as well as for complete analyses of the substances that enter into the cement.

### THE PREPARATION OF THE SPECIMEN.

It is very desirable that the substance to be analyzed should be in a very finely divided state. It is usually reduced to a coarse powder with an ore crusher, or with a mortar and pestle of iron or steel. It is afterwards finely pulverized with an agate mortar and pestle. The whole must be thoroughly mixed before beginning the analysis to secure perfect homogeneity. The fine material should be sifted through a piece of fine, clean linen cloth, and the coarser particles should not be discarded, but should be rendered as fine as possible and added to the other portion. To keep only that which is more easily powdered, and to throw away the rest would result in not having a fair sample for the analysis.

W. Hempel<sup>1</sup> has studied the abrading effect of pulverizing hard substances with mortars of iron, glass, agate, and hardened steel. He finds that for grinding hard substances like glass, hardened

1. *Zeits, Angew, Chemie* 1901, page 843.

steel is much superior to agate, and even green bottle glass is abraded less than agate. In finely pulverizing 10 grams of glass, an agate mortar and pestle 416 grams in weight lost 0.052 grams or 5.2 milligrams for each gram of the glass which was powdered. A hardened steel mortar and pestle of the same weight lost only one-tenth of that amount. It might often be desirable to grind one portion with steel apparatus for the silica determination and another portion with agate for the iron and other determinations.

#### SILICA IN LIMESTONE AND DOLOMITE.

These rocks for the most part are deep sea deposits and the amount of silica they contain is frequently very small. In some of the layers of the Niagara dolomites of Eastern Iowa, there is less than a half per cent of silica. The silica originated in the wearing away of older rock formations, igneous and metamorphic, as well as from non-metamorphic rocks, by the waves of the ancient seas, or it might have come from the marine fauna and flora. If from the older rocks, the silica can exist in a great variety of forms. It can be grains of pure sand, or small quartz crystals, or any of the numerous kinds of silicates. Ordinary acids would have little or no effect in decomposing most of the silicates. If the silica originated from non-metamorphic rocks, it is usually sand or clay, the hydrated aluminum silicate.

For determining the silica in dolomites and limestones, fusion with sodium carbonate in a platinum crucible is recommended by some authorities, contrary to the practice of many chemists. This does not require as much alkali as does the decomposition of a silicate,  $\frac{1}{4}$  to  $\frac{1}{2}$  a gram of alkali for each gram of substance being sufficient.<sup>1</sup> After the fusion the substance is transferred to a platinum or porcelain evaporating dish by the use of water and hydrochloric acid. It is evaporated to dryness, stirring to a fine powder. Heating above the temperature of the steam bath accomplishes nothing except where much magnesium is present. Then 120° has been found to be the most favorable<sup>2</sup> temperature. Above 120°, the magnesium and silica will recombine, and the silica will again go into solution with hydrochloric acid. The dry and fine powder is moistened with concentrated hydrochloric acid, then with dilute hydrochloric acid and water, and after standing some time, the silica is filtered off. Two or three evaporations and treatment

1. P. W. Shimer in Meade the Chemists Pocket Manual, page 162.

2. J. P. Gilbert in Tech. Quarterly, Vol. 3, 1890, page 61.

with acids may sometimes be necessary to remove all the silica. The different portions are transferred with the filter ash to a weighed platinum crucible, and heated with a Bunsen burner and finally with a blast lamp for ten minutes, when it is cooled and weighed. The purity of the silica may be tested with a few drops of dilute sulphuric acid and 10 cc. to 15 cc. of dilute hydrofluoric acid, and evaporating to dryness by which the silica is volatilized. Quartz is especially hard to volatilize and several additions of hydrofluoric acid may be necessary.<sup>1</sup>

Instead of the fusion with sodium carbonate, the fine rock powder can be dissolved in a porcelain evaporating dish, covered with a watch glass and evaporated to a fine dry powder by constant stirring with a glass rod flattened on one end. The powder is moistened with concentrated hydrochloric acid, left on the water bath for a few moments and dilute hydrochloric acid and water are added. The insoluble residue is usually silica or clay, and the purity should be tested with sulphuric and hydrofluoric acids. The purity test may also be made by digesting the insoluble residue for one hour in a platinum dish on the water bath with a moderately concentrated solution of sodium carbonate.

By simply dissolving the rock powder in pure dilute hydrochloric acid and filtering off the insoluble residue, without evaporating the substance to dryness, the silica is often very satisfactorily determined as will be shown later. Kortright<sup>2</sup> calls attention to the adhering of silica to the surface of a porcelain dish, when it has been used to evaporate the substance to dryness, causing a rough coating on the glaze. This can not be removed even by a "police-man" but may be recovered by warming the dish on the steam bath with ammonium hydrate. This phenomenon had been noted by Hillebrand<sup>3</sup> and also by Morse.<sup>4</sup> To obviate this difficulty, it is recommended that platinum evaporating dishes be used instead of porcelain. In a large number of silica determinations made with evaporating dishes of porcelain, we have failed to notice the adherence referred to.

#### SILICA IN A SILICATE.

In the treatment of a silicate six or eight times as much sodium carbonate must be used as of the rock powder taken. All is thor-

1. Hillebrand Bulletin 305 U. S. Geol. Surv., page 174.
2. Chem. News 95.9, Jan. 4, 1907.
3. Journal Am. Chem. Soc. 25, 1192.
4. Exercises in Quant. Analy., page 311.

oughly mixed with a platinum spatula. The covered crucible, always of platinum, is heated for twelve to fifteen minutes with a Bunsen flame, and for about the same length of time with a blast lamp until there is no further escape of carbon dioxide, and the substance is in a state of quiet fusion. The flame should be directed obliquely against the sides of the crucible. This is a necessary precaution as it makes possible the oxidation of the substances rather than the reduction. The crucible containing the substance in a state of fusion is seized with the tongs and given a rotary motion to distribute the contents against the walls by which the melted mass is more easily removed. The mass is extracted with hot water, and hydrochloric acid is added, and the substance is evaporated, stirring until a fine, dry powder results. To hasten the removal of the fused mass from the crucible, hydrochloric acid can be added to it directly. If the fused mass is green it denotes the presence of manganese, and hydrochloric acid would liberate chlorine which would attack the crucible. Under such conditions, nitric acid can be used instead of hydrochloric acid.

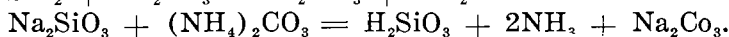
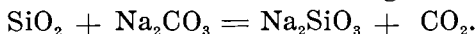
Many of the authorities suggest equal weights or molecular weights of sodium and potassium carbonates as the flux by which fusion takes place at a much lower temperature. Hillebrand<sup>1</sup> says, "There is no advantage in using the much recommended, because more fusible, double carbonate of sodium and potassium, or the equi-molecular mixture of the normal carbonates or of sodium carbonate and potassium bicarbonate. As Dittrich<sup>2</sup> says potassium salts are more prone to pass into precipitates than sodium salts and it may be that the higher melting point of sodium carbonate is a distinct advantage. Certainly, for effective decomposition of some rock constituents, a far higher temperature than that of the double salt is required."

Substances which contain a considerable quantity of fluorine can not be treated with hydrochloric acid, as silicon tetrafluoride would be volatilized. Substantially the old method of Berzelius is employed. After the fusion with sodium carbonate, the mass is extracted with water, the residue pulverized as finely as possible, filtered, and the greater part of the silica in the filtrate is removed by precipitation with ammonium carbonate. The precipitate is filtered off, ignited and weighed. The silicic acid which remains in the filtrate is precipitated by ammoniacal zinc sulphate. The

1. Bulletin 305, U. S. Geol. Surv., page 72.

2. Anleitung Zur Gesteinsanalyse 1905, page 5.

silica is obtained from this precipitate by treating it with hydrochloric acid, and evaporating as usual to a dry powder. The portion of the original fused mass that is insoluble in water may also contain silica, and this must be removed by evaporation with hydrochloric acid. The equations that express the principal reactions involved are the following:



But as the  $\text{SiO}_2$  is not completely precipitated the ammoniacal zinc sulphate is added:



In all these fusions, the difficulty of securing pure sodium carbonate can not escape attention. The purest specimens on the market usually or frequently contain silica, iron and other impurities, often in considerable quantities. To secure a proper degree of accuracy, the commercial article should be dissolved in pure distilled water, filtered, and allowed to crystallize in a platinum or porcelain dish. If the pure sodium carbonate is not obtainable, its use in an analysis should be avoided whenever possible.

#### SILICA BY THE LEAD OXIDE AND BORIC OXIDE METHOD OF JANNASCH.<sup>1</sup>

This is worthy of consideration, as it renders possible the determination of silica and the alkalies in the same sample. The lead oxide of commerce so frequently contains impurities that the substance can better be prepared for the analysis by the ignition of pure lead carbonate. The carbonate is prepared by adding the equivalent amount of ammonium carbonate to a boiling solution of lead acetate. The precipitated lead carbonate is thoroughly washed and afterwards dried on the water bath.

With a gram of silicate, 10 to 12 grams of lead carbonate are used, after mixing thoroughly with a platinum spatula. The crucible is gently heated at first with a small flame, and finally the heat is increased until fusion is complete. The substance after fusion is treated in the usual way, using nitric acid instead of hydrochloric acid. It is evaporated on the water bath to a fine dry powder, moistened with nitric acid, and once more evaporated to a fine powder. It is finally treated with concentrated nitric acid and water when the silica is filtered off.

Jannasch also maintains that a silicate can be decomposed with pure alkali free boric oxide. The oxide to be previously fused and

1. Chem. News, Aug. 2, 1895.

finely pulverized. After dissolving the fused mass, the boric oxide is completely volatilized with methyl chloride. An advantage of this and the lead oxide method is that they do not introduce alkalies into the substance to be analyzed.

FUSION WITH BISMUTH SUBNITRATE.

Hempel and Koch have obtained satisfactory results by fusing with bismuth subnitrate. A half gram of the powdered silicate is fused with ten grams of the subnitrate. On diluting the filtrate from the  $\text{SiO}_2$  with water, a greater part of the bismuth is precipitated as oxychloride, and the remainder is afterwards removed with sulphuretted hydrogen. A silicate can also be fused with borax. It must, nevertheless, be said that the different fluxes mentioned, with the exception of the alkaline carbonates, will answer in certain cases, but they are not of universal application.

SOME EXPERIMENTS IN ESTIMATING SILICA.

1. The Niagara dolomites of Eastern Iowa.

The silica was determined by two methods:

(a) A gram of the finely powdered rock was placed in a small beaker, and covered with a watch glass, a small quantity of hydrochloric acid was added, and the carbonates were dissolved by carefully heating to the boiling point. The insoluble portion was filtered off and its weight determined.

(b) A gram of the powder was dissolved in a porcelain evaporating dish, evaporated and stirred to a fine powder, and treated with hydrochloric acid and water in the usual way. The insoluble residue was finally filtered and weighed. The results of the two methods are as follows:

(a) .78% $\text{SiO}_2$	(b) .75%
.76% $\text{SiO}_2$	I .73%
.81% $\text{SiO}_2$	.85%
.87% $\text{SiO}_2$	.87%

The residues were tested with sulphuric and hydrochloric acids and found to be practically pure silica. Most of the layers of this rock in the vicinity of Mount Vernon will leave a residue on treatment with the sulphuric and hydrochloric acids. The insoluble residue from hydrochloric acid in this particular layer must have been grains of fine, pure sand, or pure quartz crystals.

In the various layers of the rock which we have studied, whether the insoluble residue is pure silica or not, the treatment described

under (a) is equally satisfactory with that under (b). Treatment (a) requires much less time and labor than (b).

An analysis of this layer of rock resulted as follows:

CaCO <sub>3</sub> .....	53.62%
MgCO <sub>3</sub> .....	44.96%
SiO <sub>2</sub> .....	0.83%
Al <sub>2</sub> O <sub>3</sub> .....	0.25%
Fe <sub>2</sub> O <sub>3</sub> .....	0.34%
	<hr/>
	100.00%

The rock is essentially a true dolomite.

## 2. Silica in the Bedford Limestone.

The specimen was obtained from a quarry near Bedford, Indiana. It is a light-colored rock, fine-grained in texture, and it is widely used and favorably regarded as a building material. It is subcarboniferous limestone. The fine powder was treated as described under (a) and (b) in the foregoing. The following results were obtained: (a) 0.54%; (b) 0.55%. The same results could be obtained whether one gram, three grams, or ten grams were used. The residue in the crucible after treatment with sulphuric and hydrofluoric acids was .13%. This was found to be:

Aluminum and Iron Sulphate .....	0.08 %
Calcium Sulphate .....	0.058 %
	<hr/>
	0.138 %

To compare these results with those from an alkaline fusion. A gram of the fine powder was thoroughly mixed with seven grams of purified sodium carbonate, and fused in the usual way. The insoluble residue was found to be .53%. On treating this with sulphuric and hydrofluoric acids, the residue in the crucible amounted to 0.16%. Nothing seemed to be gained by this method.

The first filtrates from the silica were frequently evaporated a second time, but no trace of residue was found.

The analysis of the Bedford limestone resulted as follows:

CaCO <sub>3</sub> .....	93.55 %
MgCO <sub>3</sub> .....	5.42 %
Fe <sub>2</sub> O <sub>3</sub> and Al <sub>2</sub> O <sub>3</sub> .....	0.50 %
Insoluble residue mainly SiO <sub>2</sub> .....	0.55 %
	<hr/>
	100.02 %

The concordant results obtained by methods (a) and (b) show that the silica is of the insoluble kind.



When the specimen of argillaceous limestone was first sent out for the co-operative analysis, about two and one-half years ago, we experienced no difficulty in obtaining<sup>1</sup> 18% of silica, all that it contains, by a single evaporation. The specimen seems to have undergone a change and in recent months it has been impossible to secure all the silica even by two or three evaporations. We have been obliged to follow the method of Hillebrand<sup>2</sup> and seek for three or four per cent of the silica in the iron and aluminum precipitates. These are fused with acid potassium sulphate, and afterwards digested with sulphuric acid and heated until fumes are given off. When the silica in the specimen amounts to only a few per cent, the portion that persists in solution is necessarily small. It is usually greater when the silica is determined by an alkaline fusion.

#### THE EFFECT OF DIFFERENT ACIDS AS SOLVENTS.

Dolomite rock, and ores of iron and manganese were treated with different acids as solvents and the resulting insoluble residue was investigated. In some cases the nature of the residue other than the silica was examined. Each specimen studied was finely ground with agate mortar and pestle until the powder did not feel gritty when placed between the teeth, and it was then thoroughly mixed. About one gram of the powder was used in each determination.

#### SIDERITE.

(a) A gram of the powder was dissolved in pure dilute hydrochloric acid, and the insoluble residue at once filtered off. This was found to be 6.06%. When treated in the platinum crucible with sulphuric and hydrofluoric acids, the loss of weight representing the silica was 1.44%. A blank test was made of the sulphuric and hydrofluoric acids and no residue was left on their evaporation. No residue was obtained by evaporating the filtrate from the insoluble residue.

(b) A portion of the powder evaporated in a porcelain dish on the water bath and stirred to a fine, dry powder gave an insoluble residue of 6.07%. The treatment of this with hydrofluoric and sulphuric acids showed that 1.45% of silica was present. The residue in the crucible which had the appearance of iron was dis-

1. Chem. News 92, 61, Aug. 11, 1905.

2. Journ. Am. Chem. Soc., Nov 1903.

solved in concentrated hydrochloric acid and the iron precipitated with ammonia. There was obtained 4.64% of ferric oxide. The comparatively large amount of insoluble residue, practically the same by both tests, was something of a surprise. The amounts of the ferric oxide and silica are not in proportion to form a silicate, or at best only a portion is silicate. The remainder seems to be iron oxide in such a condition as not to be acted upon readily by hydrochloric acid. The next two experiments tend to confirm this view.

(c) Method (a) was repeated except dilute nitric acid (equal parts nitric acid of a specific gravity of 1.42 and water) was substituted for the hydrochloric acid. This leaves a smaller and lighter colored residue than the hydrochloric acid. The insoluble residue was 1.34%, which proved to be 1.30% silica. On evaporating the filtrate to dryness, a second portion of insoluble residue was not obtained.

(d) Method (b) was repeated, using dilute nitric acid. The insoluble residue was 1.30%, the silica 1.28%. No residue appeared on second evaporation.

The experiments were repeated, using dilute sulphuric acid. The results were unsatisfactory, as the residues obtained were abnormally large, confirming the well-known fact that the ores of iron are not easily soluble in sulphuric acid. A complete analysis of the specimen of ore resulted as follows:

FeO.....	52.59
Fe <sub>2</sub> O <sub>3</sub> .....	4.20
MnO.....	3.30
MgO.....	2.68
CaO.....	0.82
SiO <sub>2</sub> .....	1.45
CO <sub>2</sub> .....	35.00
	100.04

2. Another specimen of siderite was examined, and treated by each of the four different methods described in the foregoing. The following figures were obtained:

	a	b	c	d
Residue, per cent.....	1.33	1.26	0.85	0.94
SiO <sub>2</sub> , per cent.....	0.91	0.86	0.80	0.85

No residue was obtained on evaporating the filtrates in the foregoing experiments.

A third specimen of siderite was available for examination, and it was subjected to the same treatment as before, with the following results:

	a	b	c	d
Insoluble residue, per cent.....	0.40	0.36	0.40	0.38
SiO <sub>2</sub> , per cent.....	0.36	0.31	0.35	0.32

DOLOMITE.

Specimens from Mount Vernon, Iowa:

	a	b	c	d
1. Insoluble residue, per cent.....	0.83	0.89	0.88	0.83
SiO <sub>2</sub> , per cent.....	0.50	0.64	0.62	0.60
2. Insoluble residue, per cent.....	0.54	0.53	0.58	0.56
SiO <sub>2</sub> , per cent.....	0.41	0.42	0.41	0.41

When the dolomites are treated with nitric acid, it is impossible to stir the substance to a dry powder at the temperature of the water bath, the large amounts of calcium and magnesium nitrates seriously interfering with the drying.

In the following determinations, a second portion of residue was obtained in nearly every case. It was found impossible to dissolve the substances in nitric acid, and aqua regia was substituted. The results from the different methods are not all concordant.

HAEMATITE

	a	b	c
			Aqua Regia
Residue, per cent.....	2.26	2.52	3.19
Residue from filtrate, per cent.....	0.71	0.22	0.00
Silica from first residue, per cent.....	1.94	2.23	
Silica from second residue, per cent.....	0.65	0.22	
Total silica obtained, per cent.....	2.59	2.45	2.90

MAGNETITE

Residue, per cent.....	5.76	6.47	11.69
Residue from filtrate, per cent.....	0.96	0.30	0.30
Silica from first residue, per cent.....	1.44	2.53	3.09
Silica from second residue, per cent.....	0.96	0.80	0.30
Total silica, per cent.....	2.40	2.83	3.39

## LIMONITE

	a	b
Residue, per cent.....	2.25	3.68
Residue from filtrate, per cent.....	1.60	0.12
Silica from first residue, per cent.....	2.12	3.52
Silica from second residue, per cent.....	1.40	0.12
Total silica, per cent.....	3.52	3.64

## A SPECIMEN OF COMMERCIAL MANGANESE DIOXIDE

Residue, per cent.....	12.76	13.95
Residue from filtrate, per cent.....	1.32	0.12
Silica from first residue, per cent.....	7.56	7.81
Silica from second residue, per cent.....	0.42	0.12
Total silica, per cent.....	7.98	7.93

## A SPECIMEN OF PYROLUSITE

	a	b
Residue, per cent.....	12.79	14.79
Residue from filtrate, per cent.....	1.60	0.19
Silica from first residue, per cent.....	7.92	7.92
Silica from second residue, per cent.....	0.28	0.19
Total silica, per cent.....	8.20	8.11

In the case of the siderites and dolomites studied, the simpler method gives results fairly concordant with the more complicated method, and the former is therefore to be preferred. A second evaporation and stirring to a dry powder gave no residue and added nothing to the value of the results. Nitric acid as a solvent of the siderites gave smaller residues than hydrochloric acid. With the ores of iron other than siderite that were studied, as well as the specimens of manganese dioxide, the shorter method, simply dissolving in hydrochloric acid, gave generally as satisfactory results as the longer method.

Among the works consulted or referred to in this paper may be mentioned Bulletin 305 of the United States Geological Survey (Hillebrand); The Chemical Analysis of Rocks, Washington; Miller-Kiliani Analytische Chemie; Treadwell-Hall Quantitative Analysis; Talbot's Quantitative Chemical Analysis; Fresenius' Quantitative Analysis; Cairn's Quantitative Analysis; Clowes and Coleman Quantitative Analysis; Crooke's Select Methods; Morse, Exercises in Quantitative Analysis.