

A Combined Gravimetric and Photometric Procedure for Determining Silica in Silicate Rocks and Minerals*

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A method is described for determining silica in rocks and minerals. Most of the silica is removed by evaporation with hydrochloric acid and volatilisation with hydrofluoric acid; the remaining traces are determined in the filtrate photometrically by a molybdenum-blue method. Interference by minor amounts of iron does not occur at the wavelength chosen for the photometric measurement. When present in the amounts usually encountered in silicate rocks, neither titanium nor phosphorus interferes with the determination. The photometric determination, however, cannot be made if either of these elements or iron is present in quantity. Modified procedures are described in which cations are removed from the solution before colour formation.

THE classical method for determining silica in silicate rocks and minerals¹ is long and tedious; it involves two or three evaporations of the rock solution to dryness with hydrochloric acid. Silica in the filtrate from the second or third dehydration is recovered, together with iron, aluminium, titanium and other elements of this group, by precipitation with ammonia. The agreement that can be expected between duplicate results obtained by this method is about 0.1 to 0.2 per cent. of the rock.

Some photometric procedures for determining silica have been applied to silicate rocks and minerals.^{2,3,4,5,6} These are based on formation of a yellow molybdosilicate complex or its subsequent reduction with a suitable reagent to molybdenum blue. As silica is the major constituent of silicate rocks, generally exceeding 50 per cent. and commonly 60 to 75 per cent., great care must be taken to avoid serious error. The precision is not high. Riley,⁴ for example, recommends determination in quadruplicate as a means of increasing the precision and the accuracy.

In the method described below, most of the silica is recovered by a single evaporation with hydrochloric acid, and the small amount remaining in the filtrate from these operations is determined photometrically. This permits an accurate gravimetric determination to be

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made of the major fraction, and, as the amount of silica in the filtrate is only about 2 to 8 mg, it can also be determined accurately. The procedure is more precise than are direct photometric methods and is more rapid and more precise than the classical gravimetric method. Moreover, the separation from iron and alumina commonly used to determine the "silica traces" is not necessary.

EXPERIMENTAL

The recovery of silica from silicate rocks and minerals by fusion with sodium carbonate and then evaporation with hydrochloric acid is well established.¹ It was considered that attempts to recover the maximum amount of silica by this method would not be justified. Accordingly, in the procedure adopted, only one evaporation is made, and the dehydration of the silica is continued until the dark yellow colour of the moist residue has only just given place to the pale yellow colour of the completely dry residue. At this stage, 10 ml of concentrated hydrochloric acid are added, and the separated silica is recovered and determined by volatilisation with hydrofluoric acid in the usual way. The filtrate from the separated silica is collected in a 200-ml calibrated flask and is diluted to the mark. This solution, containing 2 to 8 mg of silica, is approximately 0.5 *N* in hydrochloric acid and is used for the photometric determination.

As well as a few milligrams of silica, the filtrate contains all or almost all of the iron, titanium, phosphorus and other elements present in the rock, with the possible exception of barium, which, when the rock contains sulphur, may be largely associated with the major part of the silica. Of the two general methods available for determining silica photometrically, attention was first paid to the molybdosilicate method, in which the yellow molybdosilicate colour given by silica with ammonium molybdate in acid solution is measured photometrically. Under the conditions used, any phosphorus present will form the analogous molybdophosphate complex. When the molybdosilicate method is applied directly to solutions prepared by alkali fusion of the silicate material, unless phosphorus is present in more than the usual amounts, interference from the molybdophosphate complex is small and can be neglected; for more precise work a correction may be applied (*e.g.*, as described by Ringbom, Ahlers and Siitonen⁶). In the filtrate from the separated silica, however, the concentration of phosphorus is enhanced, and interference by the yellow molybdophosphate complex cannot be neglected; it may be too great for the application of corrections. Further, the colour is unstable and does not obey the Beer - Lambert law.

For these reasons the molybdosilicate method was abandoned in favour of a method based on molybdenum blue, in which the yellow molybdosilicate complex is reduced to give a stable blue solution that obeys the Beer - Lambert law and has a maximum absorption at about 810 μ . The conditions under which iron and phosphorus do not interfere with the determination of silica by measuring the blue colour have been investigated by Mullin and Riley,⁷ Greenfield⁸ and Bunting⁹ following Schwartz.¹⁰

TABLE I
FORMATION OF YELLOW MOLYBDOSILICATE COMPLEX

Volume of 2 <i>N</i> hydrochloric acid added, ml	Time for maximum optical density of yellow solution, minutes	pH	Optical density of molybdenum blue solution at dilution of 100 ml
<i>Complex formed at dilution of 15 ml—</i>			
2	24	0.8	0.347
1	3	1.1	0.342
0.5	2	1.5	0.342
0.25	2	2.2	0.321
0.125	3	2.8	0.300
<i>Complex formed at dilution of 60 ml—</i>			
4	36	1.1	0.340
2	4.5	1.4	0.342
1	2	1.7	0.342
0.5	5	2.0	0.330
0.25	5.5	2.4	0.312
0.125	12	3.2	0.286

FORMATION OF MOLYBDOSILICATE COMPLEX—

Conditions for the quantitative formation of the yellow molybdosilicate complex were first investigated. In each test 125- μ g portions of silica were taken, and 1 ml of neutral 10 per cent. w/v aqueous ammonium molybdate solution was added. The formation of the yellow molybdosilicate complex was followed by measuring the optical densities of the solutions at 400 m μ , and the times taken to attain maximum values were noted. When fully formed, the yellow molybdosilicate was reduced to molybdenum blue by adding 5 ml of 10 per cent. w/v aqueous oxalic acid and 2 ml of reducing solution. The volumes were then adjusted to 100 ml, and the solutions were set aside before measurement of the optical densities at 650 m μ . The pH measurements were recorded to one decimal place with a Pye pH meter. The results are shown in Table I. It was confirmed that the pH necessary for quantitative formation of this complex^{11,12,13} lies in the range 0.8 to 1.7; the time required, however, was found to be longer under the more acid conditions. The concentrations of ammonium molybdate solution and of hydrochloric acid appreciably affect the formation of the complex, and care must be taken to ensure that at this stage the pH of the rock solution is within the range stated.

REDUCTION OF MOLYBDOSILICATE COMPLEX—

Conditions used for the reduction of the molybdosilicate complex were similar to those described by Shapiro and Brannock³ and Bunting.⁹ The reagent for the reduction, introduced by Lindsay and Bielenberg,¹² contains alkali sulphite and 1-amino-2-naphthol-4-sulphonic acid. Bunting used tartaric acid to prevent reduction of the excess of molybdate and to suppress interference from phosphate; he stated that citric, oxalic or phosphoric acid was equally effective. Tartaric, oxalic and citric acids also prevent interference by small amounts of ferric iron, but for larger amounts, as, for example, in basic rocks, such as basalt or dolerite, it is necessary to reduce the iron to the ferrous state before adding the ammonium molybdate solution. The use of hydroxylamine hydrochloride for this purpose has been described by Riley.⁴

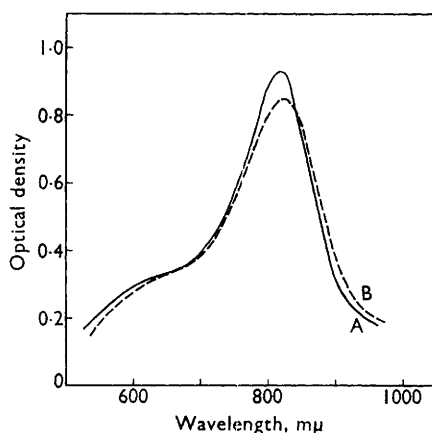


Fig. 1. Absorption spectra of molybdenum blue solutions: curve A, 125 μ g of silica; curve B, 125 μ g of silica to which 5 mg of Fe_2O_3 , as ammonium ferric sulphate, had been added. For both curves oxalic acid was used to prevent reduction of the excess of molybdate reagent

In the filtrate from the separated silica, the concentration of iron has been considerably enhanced, and it has therefore been necessary to pay particular attention to the interference by iron. Interference may arise by precipitation of the molybdate reagent. This could be prevented by prior reduction to the ferrous state by hydroxylamine hydrochloride.⁴ We have found, however, that the addition of this reagent reduces any molybdophosphate complex formed when the rock sample contains phosphorus; it also reduces slightly the optical densities of the molybdenum blue solutions, even in the absence of iron.

In addition to interference resulting from the precipitation of ferric molybdate, ferric iron also interferes in the reduction of the yellow molybdosilicate complex. It was found

that the addition of a solution containing ferric ions to a molybdenum blue solution restored the yellow colour previously given by the molybdosilicate complex and that subsequent addition of oxalic acid reversed this reaction.

The presence of more than a trace of iron has also been found to affect the absorption spectrum of the reduced molybdosilicate solution, even when oxalic acid is present (see Fig. 1). The addition of iron reduces the optical-density values of the molybdenum blue solutions over the wavelength range in which maximum optical density occurs. At about $650\text{ m}\mu$, however, the two curves were found to coincide, and optical-density measurements at this wavelength were therefore not subject to interference from iron.

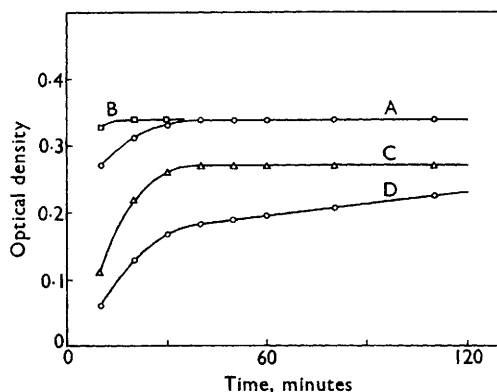


Fig. 2. Increase in optical density at $650\text{ m}\mu$ of molybdenum blue solution with time, different reagents being used to prevent reduction of the excess of molybdate reagent: curves A and B, oxalic acid; curve C, tartaric acid; curve D, sulphuric acid. Curves A, C and D were recorded in presence of 5 mg of Fe_2O_3 , as ammonium ferric sulphate; curve B in absence of iron

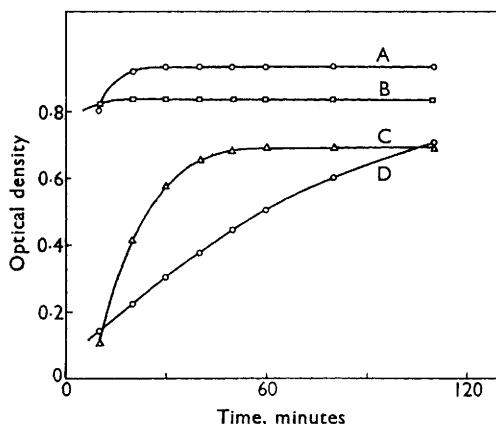


Fig. 3. Increase in optical density at $810\text{ m}\mu$ of molybdenum blue solution with time (curves lettered as for Fig. 2)

In the absence of iron, tartaric, citric or sulphuric acid can also be used to prevent reduction of the excess of molybdate reagent during reduction of the yellow molybdosilicate complex; the absorption spectra of the molybdenum blue solutions were similar to that shown in Fig. 1, curve A (when oxalic acid was used for this purpose). In the presence of iron and tartaric, citric or sulphuric acid, however, lower optical densities were recorded over the complete wavelength range, and the time necessary for complete reduction of the yellow complex was considerably increased. This increase in time is shown for tartaric and

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sulphuric acids in Figs. 2 and 3, at 650 and 810 $m\mu$, respectively. Measurements at both wavelengths show that the reduction of the molybdosilicate complex in the presence of iron and oxalic acid is more rapid than in the absence of iron, although, as noted above, the maximum optical-density values are the same at the shorter wavelength only. When the oxalic acid was replaced by citric acid, a curve similar to that shown for tartaric acid was obtained.

INTERFERENCE FROM OTHER ELEMENTS—

As the titanium ion, Ti^{4+} , forms a precipitate with ammonium molybdate under the acid conditions prescribed in the proposed method, possible interference was investigated by adding solutions of pure titanium to the silicate solution before adding ammonium molybdate reagent solution. The results are shown in Table II.

TABLE II
INTERFERENCE BY TITANIUM

In each test, 125- μg portions of silica were used with 5 ml of oxalic acid solution and 2 ml of reducing solution, as described in the proposed method. The reduced solutions were diluted to 100 ml before colour measurement

Titania added—		Optical density at 650 $m\mu$
mg	rock equivalent, %	
0	0	0.340
0.25	1	0.342
0.5	2	0.340
1.25	5	0.335
2.5	10	0.313

It can be seen that, although interference from titanium does occur, it is not necessary to introduce modifications to the method unless, as rarely happens, the titanium content of the sample greatly exceeds 5 per cent. of the rock, when it can be removed from the solution with iron, as is described below.

Phosphorus present in solution forms a molybdophosphate complex on the addition of the molybdate reagent, but it is decomposed by oxalic acid within a few seconds of the addition of the reagent and does not interfere. The possibility of interference by competition for the molybdate reagent remains; it has been investigated by applying the photometric procedure to standard silica solutions to which various amounts of phosphate had been added.

TABLE III
INTERFERENCE BY PHOSPHORUS

In each test, 125-mg portions of silica were used with 5 ml of oxalic acid solution and 2 ml of reducing solution. The solutions were diluted to 100 ml before colour measurement

P_2O_5 added—		Optical density at 650 $m\mu$
mg	rock equivalent, %	
0	0	0.340
0.5	2	0.343
1.25	5	0.342
2.5	10	0.339
4	16	Yellow precipitate formed
8	32	No colour or precipitate formed

As shown by the figures in Table III, interference by phosphorus does not occur at concentrations up to the equivalent of 10 per cent. of P_2O_5 , but above this concentration the interference rapidly becomes complete, first by precipitation of the molybdate reagent and then by complete suppression of molybdosilicate and molybdophosphate complexes. When the phosphate content of the rock exceeds 10 per cent. it is not possible to determine the silica by the photometric method described.

When present in more than trace amounts, fluorine interferes with the determination by removing some of the silica as the volatile silicon tetrafluoride during the initial evaporation

of the rock solution. No other element commonly present in silicate rocks interferes with the determination by the proposed method. The small amounts of platinum introduced during fusion and evaporation in platinum vessels do not interfere with the determination. The amount of silica introduced as an impurity with the reagents should be determined and a correction applied to the amount of silica found. With micro-analytical-reagent grade sodium carbonate (M.A.R. grade, obtained from the British Drug Houses Ltd.), a reagent blank value equivalent to 0.03 per cent. of the rock was obtained. Silica from the reagents similarly introduced into the standard silica solutions can be neglected.

REMOVAL OF IRON AND TITANIUM—

As noted above, it is possible to avoid interference by titanium when present in more than usual amounts by removing it from the solution; interference by iron can be avoided similarly. Removal of these elements is recommended when a large amount of either is present. Two procedures have been devised for this purpose, *viz.*, extraction with a solution of cupferron in chloroform and alkaline fusion.

Cupferron extraction procedure—To test this procedure, aliquots containing 125 μg of silica in 0.5 *N* hydrochloric acid were used, to which had been added a solution containing 20 mg of ferric oxide (equivalent to 80 per cent. of the rock) and a solution containing 2.5 mg of titania (equivalent to 10 per cent. of the rock). The cations were extracted by shaking with a 1 per cent. solution of cupferron in chloroform, as described by Milner and Woodhead.¹⁴ After shaking with pure chloroform to remove the excess of reagent, the solution was finally shaken with 20 ml of *n*-hexane and rinsed into a 100-ml flask; the silica present was then determined as described below. In three such experiments, optical densities of 0.328, 0.330 and 0.335 were recorded for the molybdenum blue solutions at 650 $\text{m}\mu$, which indicates that only a little of the silica had been lost from the aqueous solution and that iron and titanium could be separated from silica in this way.

Alkaline fusion procedure—To test this procedure, aliquots of the silicate solution containing 125 μg of silica to which solutions of iron and titanium had been added were evaporated to dryness in platinum crucibles, and the solid residues were fused with a little sodium carbonate or hydroxide. The fused melts were extracted with water, and the residues, consisting of oxides of iron and titanium, were collected on small filters. The combined filtrates and washings were acidified and used for the determination of silica by the method described.

TABLE IV
RECOVERY OF SILICA AFTER ALKALINE FUSION

Ferric oxide added—		Titania added—		Optical density at 650 mμ*
mg	rock equivalent, %	mg	rock equivalent, %	
<i>Fusion with sodium carbonate—</i>				
5	20	1.25	5	0.337
10	40	2.5	10	0.341
<i>Fusion with sodium hydroxide—</i>				
5	20	1.25	5	0.340
10	40	2.5	10	0.335

* Corrected for silica in the reagents.

From Table IV it can be seen that silica can be determined in the filtrate obtained after extraction of the alkaline melt with water. Silica was, however, found as an impurity in all the specimens of sodium carbonate and sodium hydroxide examined, and a reagent blank correction had to be applied.

The proposed method has been used for determining silica in a number of rocks, and the results obtained have been compared with results for the same rocks by the classical or other procedures (see Table V).

TABLE V
COMPARISON OF RESULTS BY DIFFERENT METHODS

Rock material	Silica found by—	
	proposed method, %	other method, %
1734. Hornblende-biotite granodiorite, Allt Buidhe Mòr, Morvern, Argyllshire	61.98	61.97*
1735. Biotite granite, Allt Buidhe Mòr, Morvern, Argyllshire ..	70.55	70.46*
1747. Ferruginous limestone (20 per cent. Fe_2O_3), Warlingham, Surrey	4.01	3.99*
1383. Quartz from quartz vein, Daluhinnie, Inverness-shire ..	99.70	99.81†
	99.69	
G1, granite Westerly, Rhode Island, U.S.A.	72.60	72.86‡
	72.66	72.66§
W1, diabase (dolerite), Centerville, Virginia, U.S.A.	52.63	52.69‡
	52.67	52.74§

* Classical procedure.¹

† Loss on evaporation with hydrofluoric and sulphuric acids.

‡ "Preferred values" (Fairbairn¹⁵).

§ "Revised values" (Jeffery¹⁶).

METHOD

REAGENTS—

Ammonium molybdate solution—A 10 per cent. w/v solution in *N* aqueous ammonia.

Oxalic acid solution—A 10 per cent. w/v aqueous solution.

Reducing solution—Dissolve 0.15 g of 1-amino-2-naphthol-4-sulphonic acid, 0.7 g of anhydrous sodium sulphite and 9 g of sodium metabisulphite in 100 ml of water. This solution should be freshly prepared each month, as it slowly deteriorates on standing.

PROCEDURE—

The separation and collection of silica from silicate rocks and minerals by fusion with sodium carbonate and dehydration in the presence of hydrochloric acid is a well known procedure; it will not be described in detail here.

Fuse 1 g of the rock powder ground to --70 mesh with 5 g of sodium carbonate in a platinum crucible, and digest the melt with water. Acidify with concentrated hydrochloric acid, adding approximately 10 ml in excess, and evaporate to dryness in a large platinum vessel. When completely dry add a further 10 ml of concentrated hydrochloric acid and sufficient water to dissolve all soluble material. Collect the precipitated silica on a small filter, and wash well with hot water. Determine the silica in the residue by ignition and loss in weight after evaporation with hydrofluoric and sulphuric acids in the usual way. Collect the filtrate and washings from the silica residue in a 200-ml calibrated flask, and dilute the solution to the mark. Determine the minor portion of silica present in this solution as described below.

Transfer by pipette 5 ml of this solution to a 100-ml calibrated flask, and dilute to 15 ml with water. Add 1 ml of ammonium molybdate solution, and set aside for 10 minutes to complete the formation of the molybdosilicate complex. After exactly 10 minutes, add 5 ml of oxalic acid solution, gently swirl the flask to mix the contents, and then add 2 ml of reducing solution. The addition of reducing agent should not be delayed. Dilute the solution to 100 ml, and set aside for at least 30 minutes, but preferably for 1 hour, and then measure the optical density of the solution in 2-cm cells on a spectrophotometer at 650 m μ .

If the rock material under examination contains excessive amounts of iron or titanium, the cupferron-extraction technique or the alkaline-fusion procedure described above (see p. 483) can be used to remove them.

For the preparation of standard silica solutions a sample of quartz was used containing 99.8 per cent. of silica. The solutions were prepared as described below. Fuse 1 g of the quartz with 5 g of sodium carbonate in a platinum crucible, and extract the melt with water. Filter the alkaline solution into a 1000-ml calibrated flask, rinse the small amount of residue with 2 per cent. w/v aqueous sodium carbonate solution, add the washings to the contents of the flask, and dilute the solution to 1000 ml. This stock solution contains approximately 1 mg of silica per ml. Prepare the working solution by transferring 5 ml of this solution to a 200-ml calibrated flask, adding 10 ml of concentrated hydrochloric acid, and diluting

to the mark. If required, a calibration curve for silica can be prepared by using aliquots of this solution, but, as the optical densities of the blue reduced solutions obey the Beer-Lambert law, it is sufficient to carry out the procedure described below on a single aliquot of the standard silica solution.

Transfer a 5-ml aliquot of the working silica solution to a 100-ml calibrated flask, add 1 ml of ammonium molybdate solution, and, after 10 minutes, 5 ml of oxalic acid solution and 2 ml of reducing solution. Measure the optical density of the blue solution as described above. This optical density corresponds to 125 μg of silica.

CONCLUSIONS

A method for the determination of silica in silicate rocks and minerals has been described. The classical gravimetric procedure is used for determining the major part of the silica present, and a molybdenum-blue photometric procedure to determine the few milligrams of silica not rendered insoluble by one dehydration in the presence of hydrochloric acid. The method developed is quicker in operation and more direct than the classical procedure and is at least as reliable and as accurate. It has been shown that iron, titanium and phosphorus do not interfere provided that the concentrations of these elements in the original material do not exceed 20 per cent. of Fe_2O_3 , 8 per cent. of TiO_2 and 10 per cent. of P_2O_5 , respectively. Methods for removing iron and titanium from the solution before the colorimetric stage of the determination have been described and are applicable to all silicate rocks and minerals, with the exception of phosphate rock and phosphate minerals containing more than 10 per cent. of P_2O_5 .

Good agreement has been obtained by comparing the method described with the classical and other procedures. When discrepancies have arisen, the higher values obtained by the new method were preferred, as the classical method tends to give low results. For a statistical treatment of this problem see, for example, Fairbairn.¹⁵

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DISCUSSION

DR. H. J. CLULEY expressed surprise at the amount of silica (2 to 8 mg) that was stated to escape precipitation. Experience, particularly with glass analysis, showed that the amount of silica escaping precipitation could be reduced to negligible proportions by effecting the classical separation of silica under more efficient conditions. For instance, in the so-called "sinter" method (see, e.g., *J. Soc. Glass Tech.*, 1950, **34**, 257r), the sample was decomposed by fusion or sintering with only a small proportion of flux, and the fusion, extraction of the melt, and the evaporation and dehydration of the silica were all effected in a 3-inch platinum dish. These conditions promoted more efficient dehydration and separation of the silica, so that recovery of silica was essentially complete after the customary two evaporations with hydrochloric acid; the amount of silica subsequently found in the R_2O_3 precipitate was negligible.

DR. JEFFREY said in reply that this amount of silica (2 to 8 mg) had been found in the filtrate after a single evaporation with hydrochloric acid, and that the amount of silica depended to some extent upon the magnesium content of the rock.

MR. P. J. MOORE said that a number of workers had observed that the addition of tartaric acid to suppress the formation of the yellow molybdophosphoric acid complex resulted in a fading of the yellow colour of the molybdosilicic acid complex. He asked if the authors had observed this effect in their use of oxalic acid to suppress interference from phosphorus, or if it had some advantage over tartaric acid in this respect.

MR. WILSON replied that the fading of the yellow colour of the molybdosilicate complex was also observed when oxalic acid was added to solutions prepared from pure silica. With silicate rocks, as a result of the presence of iron, the reduction of molybdenum blue began as soon as oxalic acid was added and it was not possible to observe fading of the yellow colour.