

Photometric Determination of Silica in the Presence of Phosphates

M. C. SCHWARTZ, Louisiana State University and Gulf States Utilities Co., Baton Rouge, La.

THE determination of silica in the presence of phosphates is of importance in phosphate-treated boiler waters and in hot-process phosphate softeners where special attention is being given to silica removal.

The most widely used colorimetric method for silica depends upon the formation of a colored silicomolybdic acid (5, 7-9, 11-13, 17, 18, 21-24, 27, 29, 32, 36-39; for a comprehensive survey of the literature up to 1938 see reference 29). Since phosphate ions react similarly, special attention must be given to the determination of silica in the presence of phosphates. The interference of phosphates has been removed by precipitation prior to colorimetric determination: King (14) used magnesia mixture; Thayer (33) used calcium chloride; Liebknecht, Gerb, and Bauer (20) used calcium chloride and calcium carbonate; King and Stantial (16) used calcium chloride and ammonium hydroxide; Schwartz (28) used calcium chloride and a sodium borate-sodium hydroxide buffer solution.

TABLE I. EFFECT OF OXALIC ACID

PO ₄ P. p. m.	Oxalic Acid ^a Ml.	Transmittance ^b %
5	0	69
	1	70
	2	88
	3	94
	4	94
25	0	28
	1	33
	2	79
	3	94
	4	94
50	0	15
	1	21
	2	79
	3	94
	4	94

^a 100 grams of (COOH)₂·2H₂O per liter.

^b Filter photometer, filter No. 511, 3 mm.; 50-mm. liquid depth.

Precipitation methods for removal of interfering phosphate are, at best, time-consuming. Another method for avoiding phosphate interference depends upon the effect of pH upon the reduction of the phospho- and silicomolybdic acid complexes; with proper pH adjustment the silicomolybdic acid complex alone is reduced. A recent paper illustrating this method is by Kahler (12).

However, the interference of phosphates is most simply avoided by destroying the phosphomolybdic acid complex with various acids and some of their salts—e. g., oxalic, tartaric, citric, and phosphoric (1, 4, 6, 19, 25, 26, 34, 35, 39). On the basis of this fundamental information and further experimental work a procedure has been developed for determining silica in the presence of phosphates, using oxalic acid for destroying the interfering colored phosphomolybdic acid. Although it is known that oxalic acid reduces any interfering effect from the presence of tannins, consideration of interference from tannin compounds has been omitted from this paper because of the varying nature of commercial tannin compounds.

Apparatus and Reagents

A filter photometer (30) and a Coleman double monochromator spectrophotometer were used for colorimetric analyses of silicate and phosphate concentrations.

Ammonium molybdate solution, 10.0 grams of ammonium molybdate tetrahydrate per 100 ml. of distilled water.

Hydrochloric acid solution, one volume of concentrated acid to one volume of distilled water, 1 to 1.

Oxalic acid solution, 10.0 grams of oxalic acid dihydrate per 100 ml. of distilled water.

Sodium silicate solution. Fuse 3.0 grams of sodium carbonate with 0.200 gram of pure, dry silica. Dissolve in 200 ml. of distilled water. Dilute tenfold if desirable.

Potassium dihydrogen phosphate standard solution, 1.4328 grams of potassium dihydrogen phosphate per liter of distilled water.

The ammonium molybdate, hydrochloric acid, and oxalic acid solutions are kept in Pyrex bottles. The sodium silicate solution is stored in a hard-rubber bottle.

Procedure

Based partly on previous work (3, 28) and the existing literature and the remainder on material developed in this paper, the following procedure is recommended.

Filter the sample if necessary, and dilute with distilled water to suit the range of the measuring instrument (filter photometer, spectrophotometer, etc.). Add and mix 4 ml. of ammonium molybdate solution and 2 ml. of 1 to 1 hydrochloric acid solution in rapid succession to a 100-ml. sample. Wait 5 to 10 minutes for full color development, then add and mix 3 ml. of oxalic acid solution. Determine silica color intensity with suitable instrument.

The reagents may be suitably proportioned to the size of sample used and their strengths may be changed to give equivalent values when using different volumes of reagents other than those given. A blank correction should be made to correct for silica in the reagents and water, if necessary.

Experimental

The color developed by various concentrations of phosphate ion after adding ammonium molybdate and hydrochloric acid solutions was destroyed by addition of oxalic acid. The data of Table I show that 300 mg. of oxalic acid dihydrate are sufficient to destroy the phosphomolybdic acid complex formed. Tschopp and Tschopp (34) indicate the reaction to be in the proportion of 1 MoO₃ to 1 (COOH)₂. Since the phosphomolybdic acid complex is formed in the proportion of 12 MoO₃ to 1 PO₄, it will be seen that 284 mg. of oxalic acid are sufficient to destroy all the molybdate added. This amount of molybdate is equivalent to approximately 180 p. p. m. of PO₄. The residual absorption of 6 per cent shown in the table is the blank correction with the filter combination used.

TABLE II. EFFECT OF OXALIC ACID

Original SiO ₂ P. p. m.	PO ₄ Added P. p. m.	Transmittance ^a	
		Before adding oxalic acid %	After adding oxalic acid %
5	0	80.5	80.5
5	5	75	80.5
5	25	58	80.5
5	50	46.5	80.5
10	0	67	67
10	5	63	67
10	50	42	67
20	0	52.5	52.5
20	5	50	52.5
20	50	37	52.5
50	0	32	32
50	5	31	32
50	50	27	33

^a Filter photometer, filter No. 511, 1 mm., and No. 038, 2 mm.; 50-mm. liquid depth, silica as sodium silicate.

The data of Table II serve to show that, for the range of silicate- and phosphate-ion concentrations employed, oxalic acid completely destroys the interference of phosphate without affecting the color due to the silicomolybdic acid. If appreciably higher concentrations are encountered, the amount of the oxalic acid may have to be increased proportionally.

The method, as described above, was tried out and compared with the author's earlier method (28) on phosphate-conditioned boiler water at the Louisiana Station power plant of the Gulf States Utilities Co. The tests were carried out on a routine basis, by two different men and using a different photoelectric photometer from the one described in this article. The data of Table III indicate satisfactory agreement under the conditions described.

TABLE III. BOILER WATER SILICA^a

(P. p. m. of silica)	
CaCl ₂ -Borate Buffer Method	Oxalic Acid Method
25.8	25.7
33.0	33.9
31.2	30.8
24.0	24.7
27.0	26.8
31.2	31.9

^a Phosphate-conditioned boiler water, Gulf States Utilities Co.

Silica Standards

The preparation of silica standards from silicon compounds has been troublesome because of the apparent lack of stability of such solutions. Previous unpublished work, which has been substantiated during the course of this research, has shown that sodium silicate solutions, as prepared in this paper and also from sodium silicate nonahydrate, are surprisingly stable in hard rubber bottles. The data are presented in Table IV.

The use of liquid standards—e. g., potassium chromate and picric acid—as silica standards is in a somewhat confused state.

In 1914 Winkler (40) proposed, for the first time, the use of potassium chromate. He stated that 1 ml. of a solution containing 0.530 gram per 100 ml. was equivalent to 1 mg. of silica. His procedure was to add to a 100-ml. sample 1 gram of solid ammonium molybdate and 5 ml. of 10 per cent hydrochloric acid. He then took 105 ml. of distilled water and added potassiumchromate solution until a color match was obtained. The number of milliliters used times 10 equaled p. p. m. of silica.

In 1923 Dienert and Wandenbulcke (10) proposed the use of picric acid, stating that a solution containing 36.9 mg. per

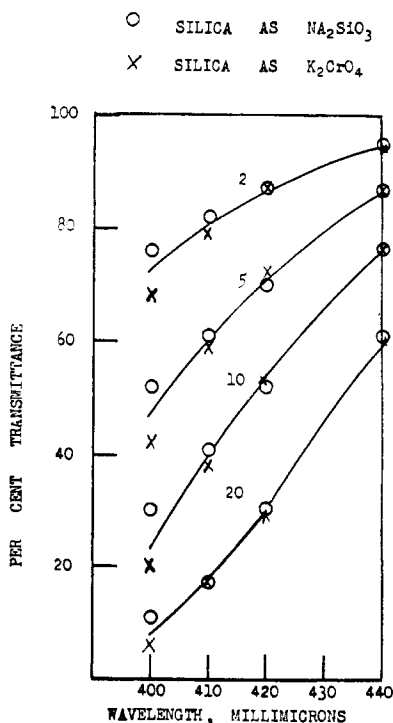


FIGURE 1

TABLE IV. STABILITY OF SODIUM SILICATE SOLUTION^a

Time Days	SiO ₂ ^b Gram
0	0.1057
8	0.1061
35	0.1047
65	0.1054

^a Stored in hard-rubber bottle.

^b Silica gravimetrically determined by J. L. Matherne.

liter was equivalent to 50 p. p. m. of silica. Their procedure was to add to a 50-ml. sample 2 ml. of 10 per cent ammonium molybdate solution and 4 drops (less than 0.5 ml.) of 50 per cent ("au 1/2") sulfuric acid. Comparison was made with picric acid solutions.

In 1928 King and Lucas (15), using the same procedure as Dienert and Wandenbulcke, found that purification and vacuum-drying of picric acid changed its relationship as a standard, so that a solution containing 25.6 mg. per liter was now equivalent to 50 p. p. m. of silica.

In 1933 the American Public Health Association (2) adopted the Winkler potassium chromate standard but used a different procedure, calling for the use of a 50-ml. sample to which was added 5 ml. of a solution containing 200 ml. of 1 to 1 by volume hydrochloric acid, 30 grams of ammonium molybdate, and 400 ml. of distilled water. One milliliter of potassium chromate solution, containing 0.530 gram per 100 ml. diluted to 55 ml., was considered equivalent to 20 p. p. m. of silica when a 50-ml. sample was tested as described.

In 1934 Swank and Mellon (31), comparing picric acid and potassium chromate spectrophotometrically with sodium silicate solutions, proposed the use of buffered potassium chromate solutions as a standard. Using 5 ml. of the A. P. H. A. reagent, described above, and a 50-ml. sample, they proposed a standard containing 0.630 gram of potassium chromate per 100 ml. of water. One milliliter of this solution diluted to 55 ml. is considered equivalent to 20 p. p. m. of silica. In diluting the chromate solution to a final volume of 55 ml., one uses 25 ml. of a 1 per cent solution of borax plus distilled water. As Swank and Mellon pointed out, variations in the volume of sample and reagents, or a change in the concentration of the reagents, may require a different concentration of potassium chromate standard.

As a result the author deemed it advisable to check the Swank and Mellon buffered chromate standards (31) against silica standards whose color is developed with the reagents given in this paper. The buffered potassium chromate solutions were prepared from a solution containing 0.63 gram of potassium chromate per liter. One milliliter of solution, diluted with 25 ml. of a 1 per cent solution of sodium tetraborate, made up to 50 ml. with distilled water, plus 3 ml. of water to make a total of 53 ml., is assumed equivalent to 2 p. p. m. of silica.

The data in Figure 1 and Table V, obtained with the Coleman spectrophotometer show, that under the conditions described, the potassium chromate standards are good color matches for silicomolybdic solutions at wave lengths at or above 410 millimicrons, in which range of the spectrum Beer's law is followed. Using the filter combinations Corning No. 511, 4-mm., No. 038, 2-mm., with the filter photometer, the chromate and silicate standards check well.

TABLE V. LIQUID STANDARDS

Concentration P. p. m. SiO ₂	Per Cent Transmittance ^a Wave Length, Millimicrons				
	400	410	420	440	470
2	68	79	87	94	98.5
5	42	59	72	87	98
10	20	38	53	77	95.5
20	6	17	29	59	91.5
	As SiO ₂		Per Cent Transmittance ^b As K ₂ CrO ₄ (buffered)		
	2	5	10	15	20
	83.5	64.5	44	31	24
			19		18

^a Coleman double monochromator spectrophotometer, 19-mm. liquid depth. SiO₂ as buffered K₂CrO₄.

^b Filter photometer, filters No. 511, 4 mm., and No. 038, 2 mm.; 50-mm. liquid depth.

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Spectrophotometric Determination of Magnesium by Titan Yellow

E. E. LUDWIG AND C. R. JOHNSON, University of Texas, Austin, Texas

FOLLOWING Kolthoff's (6) introduction of Titan yellow as a reagent for magnesium, his method has been adapted to various determinations of this element (7). A limited amount of spectrophotometric data is available (10). The method has been recommended for the colorimetric determination of magnesium in water (6, 8, 9, 10), but there has been no attempt to develop a standard spectrophotometric procedure and to compare it with the official gravimetric method. The present research was undertaken for this purpose, since it seemed likely that there could be worked out a rapid spectrophotometric procedure, comparing favorably in accuracy with the official gravimetric method, and less subject to uncertainties than standard volumetric methods. The increasing availability of fine yet comparatively inexpensive spectrophotometers also made this work seem worth while.

Principle of the Method

When magnesium hydroxide is precipitated in the presence of Titan yellow by sodium hydroxide the yellow color of the reagent changes to red or orange-red. With dilute magnesium solutions the lake which is formed remains dispersed for rather long periods, particularly in the presence of protective colloids such as starch, agar, or dextrin, and the suspension appears clear to the eye. In the presence of calcium ion the red color is deeper, and the suspension has a minimum trans-

mittance at a wave length of 525 millimicrons when compared spectrophotometrically with a suitable blank. Transmittance readings are highly reproducible and sufficiently constant to allow ample time for precise observation. The lake is apparently kept in suspension by electrostatic forces created by the calcium salt and the protective colloid, since suspensions prepared without either calcium sulfate or starch, or similar materials, flocculate readily or give transmittance readings which are not reproducible. Statements made in this connection by Hirschfelder and Serles (5) in criticizing Becka's (2) procedure should not be interpreted as meaning that accurate analyses cannot be made in the presence of excess calcium.

Apparatus and Reagents

A Coleman 10-S-30 spectrophotometer was used to measure transmittances. Matched square cuvettes 1.308 cm. in depth were used to hold the blanks and test solutions. Measurements were made at temperatures from 25° to 29° C.

Several sets of reagents were prepared during the work. The chromogenic agent was a 0.05 per cent solution of Eastman's Titan yellow. Calcium sulfate solution was made by stirring 5 grams of reagent grade calcium sulfate in contact with 1 liter of distilled water for about 4 hours and filtering the liquid. One per cent starch solution was prepared every few days from soluble starch. Normal sulfuric acid and 2 N sodium hydroxide were prepared in the usual manner.