

Application Bulletin



Of interest for:
Soft drinks industry, spas, water-analysis laboratories,
laboratories for monitoring boiler-feed waters

No. 45/1 e

Colorimetric determination of silicic acid

Summary

The determination of silicic acid is important for both mineral waters (spa waters) and normal water supplies (percolating ground-waters). The content of silicic acid is particularly important for steam-raising plants, in which a maximum silica content in boiler-feed waters must not be exceeded owing to the volatility of this impurity.

The classical gravimetric method of analysis is time-wasting, and requires a sample of several litres. The method given in the "Deutschen Einheitsverfahren" enables colloidal silicic acid to be disaggregated by sodium carbonate. Fresenius and Schneider have published a method in which a hydrofluoric/perchloric acid mixture reacts in the cold with quantities of silicic acid which will not react with ammonium molybdate after sodium carbonate treatment.

1. Determination of silicic acid by the "Deutschen Einheitsverfahren" method

Reagents

- ▶ Dilute hydrochloric acid (420 mL conc. HCl + 260 mL distilled water)
 - ▶ 10% oxalic acid solution
 - ▶ 10% ammonium molybdate solution
 - ▶ 0.25 mol/L sodium carbonate solution
 - ▶ Standard silica solution:
fuse 100 mg SiO₂ in a platinum crucible with 2 g soda ash (anhydrous Na₂CO₃) and then dissolve the fused mass in water. Make the solution up to 1 litre in a graduated flask.
1 mL of the solution contains 100 µg SiO₂.
- All reagent solutions should be stored in plastic bottles.

Apparatus

2.662.0010 Photometer with 6.1108.010 light guide

Method

- ▶ Decompose 50 mL sample in a Nessler cylinder by the successive addition of 2.5 mL ammonium molybdate solution, 1 mL dilute HCl, and 1 mL oxalic acid solution, mixing thoroughly after each addition.
 - ▶ After 15 min, measure the extinction at 400 nm with the 662 Photometer.
- The law of Lambert and Beer hold good for quantities of 0 ... 10 mg/L SiO₂.

Calculation

The results are evaluated by drawing a calibration curve.

Limit of determination

0.5 mg/L SiO₂

Remarks

- ▶ Only dissolved silicic acid can be determined by this method. Should some of the silice be present in the form of colloidal silicic acid, the following method is indicated:
Decompose a 50 mL sample with 10 mL 0.25 mol/L sodium carbonate and evaporate down to half the original volume over a water-bath in a platinum dish. After cooling, make up to 50 mL again with distilled water and then proceed as mentioned above.
- ▶ Samples containing more than 10 mg/L SiO₂ should be correspondingly diluted.
- ▶ The results should be quoted to the nearest 0.1 mg.

Colorimetric determination of silicic acid

2. Determination of silicic acid by Fresenius' and Schneider's method

Reagents	<ul style="list-style-type: none"> ▶ Hydrofluoric/perchloric acid mixture: 45 mL 40% HF + 45 mL 70% HClO₄ + 10 mL distilled water ▶ 10% ammoniummolybdate solution (adjust the pH of this solution to 8.2 with sodium hydroxide) ▶ 20% sodium hydroxide solution ▶ Boric acid (solid) ▶ Nitric acid (diluted 1:1) ▶ Sodium acetate solution 1 mol/L ▶ Standard silica solution: fuse 100 mg SiO₂ in a platinum crucible with 2 g soda ash (anhydrous Na₂CO₃) and then dissolve the fused mass in water. Make the solution up to 1 litre in a graduated flask. 1 mL of the solution contains 100 µg SiO₂.
Apparatus	2.662.0010 Photometer with 6.1108.010 light guide
Method	<ul style="list-style-type: none"> ▶ Decompose a 50 mL sample on the spot in a plastic vessel with 2 mL of the acid mixture. ▶ Take 10 mL of the resulting solution and mix it thoroughly with 2 mL NaOH and 1 g boric acid in a polyethylene beaker. ▶ After 15 min add 5 mL HNO₃ + 5 mL CH₃COONa. The pH of the solution should now be around 1 ... 1.2. ▶ Add 10 mL ammonium molybdate solution, place the sample in a Nessler cylinder, and make it up to 50 mL with distilled water. ▶ Wait another 15 min, and then measure the extinction at 400 nm with the 662 Photometer. <p>The law of Lambert and Beer holds good for quantities of 1 ... 10 mg/L SiO₂.</p>
Calculatiuon	The results are evaluated by drawing a calibration curve.
Limit of determination	1.0 mg/L SiO ₂
Remarks	<ul style="list-style-type: none"> ▶ Samples containing less than 1 mg/L SiO₂ should be concentrated by evaporation, while those with more than 10 mg/L SiO₂ should be correspondingly diluted.
Sources of error	<p>Both methods are liable to be upset by the presence of phosphates in quantities > 1 mg/L phosphorus. Phosphates can be removed by the following method:</p> <p>The samples are decomposed and mixed with reagents as described under "Method". The mixture is now pipetted into a separating funnel containing 25 mL of 1:1 benzene/isopropanol alcohol mixture. After shaking vigorously for 1 min, the phosphatemolybdate complex passes into the organic (non-aqueous phase). After leaving 10 min for the two phases to separate, the aqueous phase is run off and analysed colorimetrically, not forgetting to make the sample up to 50 mL first if Method 2 is being used.</p>
Literature	<ul style="list-style-type: none"> ▶ <i>Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung</i> 3. Auflage, Verlag Chemie GmbH, Weinheim ▶ W. Fresenius, W. Schneider Fresenius, Z. Anal. Chem. 207, 16 (1965) ▶ W. Geilmann, G. Tölg Glastech. Ber. 33, 245 (1960)