# Silicon in Waters and Effluents 1980

**Methods for the Examination of Waters and Associated Materials**

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# Silicon in Waters and Effluents, 1980

## Methods for the Examination of Waters and Associated Materials

This booklet describes two spectrophotometric methods for the determination of both monomeric and dimeric soluble silicon by reaction with ammonium molybdate and contains three appendices describing pretreatments to enable total and total soluble silicon to be determined.

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# Warning to Users

The analytical procedures given in this booklet should only be carried out by competent trained persons, with adequate supervision when necessary. Local Safety Regulations must be observed. Laboratory procedures should be carried out only in properly equipped laboratories. Field operations should be conducted with due regard to possible local hazards, and portable safety equipment should be carried. Care should be taken against creating hazards. Lone working, whether in the laboratory or field, should be discouraged. Reagents of adequate purity must be used, along with properly maintained apparatus and equipment of correct specifications. Specifications for reagents, apparatus and equipment are given in manufacturers' catalogues and various published standards. If contamination is suspected, reagent purity should be checked before use.

There are numerous handbooks on first aid and laboratory safety. Among such publications are: 'Code of Practice for Chemical Laboratories' and 'Hazards in the Chemical Laboratory' issued by the Royal Society of Chemistry, London; and 'Safety in Biological Laboratories' (Editors Hartree and Booth), Biochemical Society Special Publication No 5, The Biochemical Society, London, which includes biological hazards.

Where the Committees have considered that a special unusual hazard exists, attention has been drawn to this in the text so that additional care might be taken beyond that which should be exercised at all times when carrying out analytical procedures. It cannot be too strongly emphasised that prompt first aid, decontamination, or administration of the correct antidote can save life; but that incorrect treatment can make matters worse. It is suggested that both supervisors and operators be familiar with emergency procedures before starting even a slightly hazardous operation, and that doctors consulted after any accident involving chemical contamination, ingestion, or inhalation, be made familiar with the chemical nature of the injury, as some chemical injuries require specialist treatment not normally encountered by most doctors. Similar warning should be given if a biological or radio-chemical injury is suspected. Some very unusual parasites, viruses and other micro-organisms are occasionally encountered in samples and when sampling in the field. In the latter case, all equipment including footwear should be disinfected by appropriate methods if contamination is suspected.

The best safeguard is a thorough consideration of hazards and the consequent safety precautions and remedies well in advance. Without intending to give a complete checklist, points that experience has shown are often forgotten include: laboratory tidiness, stray radiation leaks (including ultra violet), use of correct protective clothing and goggles, removal of toxic fumes and wastes, containment in the event of breakage, access to taps, escape routes, and the accessibility of the correct and properly maintained first-aid, fire-fighting, and rescue equipment. If in doubt, it is safer to assume that the hazard may exist and take reasonable precautions, rather than to assume that no hazard exists until proved otherwise.


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# About this series

This booklet is part of a series intended to provide recommended methods for the determination of water quality. In addition, the series contains short reviews of the more important analytical techniques of interest to the water and sewage industries. In the past, the Department of the Environment and its predecessors, in collaboration with various learned societies, have issued volumes of methods for the analysis of water and sewage culminating in 'Analysis of Raw, Potable and Waste Waters'. These volumes inevitably took some years to prepare, so that they were often partially out of date before they appeared in print. The present series will be published as individual methods, thus allowing for the replacement or addition of methods as quickly as possible without need of waiting for the next edition. The rate of publication will also be related to the urgency of requirement for that particular method, tentative methods being issued when necessary. The aim is to provide as complete and up to date a collection of methods and reviews as is practicable, which will, as far as possible, take into account the analytical facilities available in different parts of the Kingdom, and the quality criteria of interest to those responsible for the various aspects of the water cycle. Because both needs and equipment vary widely, where necessary, a selection of methods may be recommended for a single determinand. It will be the responsibility of the users – the senior analytical chemist, biologist, bacteriologist etc, to decide which of these methods to use for the determination in hand. Whilst attention of the user is drawn to any special known hazards which may occur with the use of any particular method, responsibility for proper supervision and the provision of safe working conditions must remain with the user.

The preparation of this series and its continuous revision is the responsibility of the Standing Committee of Analysts (to review Standard Methods for Quality Control of the Water Cycle). The Standing Committee of Analysts is one of the joint technical committees of the Department of the Environment and the National Water Council. It has nine Working Groups, each responsible for one section or aspect of water cycle quality analysis. They are as follows:

1.0 General principles of sampling and accuracy of results
2.0 Instrumentation and on-line analysis
3.0 Empirical and physical methods
4.0 Metals and metalloids
5.0 General non-metallic substances
6.0 Organic impurities
7.0 Biological methods
8.0 Sludge and other solids analysis
9.0 Radiochemical methods.

The actual methods etc are produced by smaller panels of experts in the appropriate field, under the overall supervision of the appropriate working group and the main committee. The names of those associated with this method are listed inside the back cover.

Publication of new or revised methods will be notified to the technical press, whilst a list of Methods in Print is given in the current HMSO Sectional Publication List No 5, and the current status of publication and revision will be given in the biennial reports of the Standing Committee of Analysts.

Whilst an effort is made to prevent errors from occurring in the published text, a few errors have been found in booklets in this series. Correction notes for booklets in this series are given in the Reports of The Standing Committee of Analysts, published by the Department of the Environment but sold by the National Water Council, 1 Queen Anne's Gate, London SW1H 9BT. Should an error be found affecting the operation of a method, the true sense not being obvious, or an error in the printed text be discovered prior to sale, a separate correction note will be issued for inclusion in the booklet.

TA DICK
*Chairman*

LR PITTWELL
*Secretary*

*4 December 1980*

# Introduction

0.1 Silicon may be present in water, effluents and sewage in a variety of forms. For example it may be present in true solution as monomeric and dimeric forms, it may also be present in solution in a polymeric form, or it may be present as insoluble silica which can be retained on a filter. Silicon present as sub micron particles of 'colloidal silica' is difficult to define and may fall somewhere between the polymeric form in solution and the insoluble form.

Arbitrary distinctions on the basis of particle size distribution are commonly used. In this booklet soluble silicon is defined as that which passes a 0.45 $\mu$m filter although in some instances a 0.1 $\mu$m filter may be considered more appropriate.

0.2 Often for natural waters (fresh and saline) and waste waters (sewages and effluents) it is sufficient to determine the soluble monomeric and dimeric forms. The spectrophotometric methods described in sections A and B of this booklet, based on the formation of a molybdenum blue complex will determine both these forms.

0.3 Section A describes a relatively new tentative method based on the use of ascorbic acid to achieve the reduction step. The spectrophotometric measurement is made at 700 nm in 10 mm cells, which makes it particularly suitable for a wide range of silicon concentrations up to 100 mg/l, although it can easily be modified to increase or decrease the sensitivity.

0.4 Section B describes an established method based on the use of 1-amino-2 naphthol-4 sulphonic acid *(ANSA)* to achieve the reduction step, and is intended for the analysis of clean waters, especially those with low silicon content.

0.5 Limited testing has shown that with slight adaptation, both methods are interchangeable. Analysts wishing to do this are advised to recheck the performance characteristics of their variant.

0.6 Occasionally it may be necessary to determine monomeric, dimeric and polymeric forms of silicon or total silicon. For these purposes a series of pretreatments are described in a series of appendices. Silicones are unlikely to occur. If their presence is suspected consult reference 1.

0.7 Silicon is, by convention, normally reported as Silica ($SiO_2$) in water analysis, this procedure has been adopted throughout this booklet.

# A. Spectrophotometric Determination of Molybdate Reactive Silicon Ascorbic Acid Reduction Method

## A1. Performance Characteristics of the Method (a)

(For further information on the determination and definition of performance characteristics see General Principles of Sampling and Accuracy of Results, also published in this series).

| | | |
|---|---|---|
| A1.1 | Substance determined | Molybdate reactive silicon – mainly monomeric and dimeric silicic acids and silicate. |
| A1.2 | Type of sample | All types of water and effluents, and also solutions from pretreatments (see appendices). |
| A1.3 | Basis of method | Reaction with ammonium molybdate under controlled acid conditions to form yellow molybdosilicic acid that is reduced in situ with ascorbic acid to yield a silicomolybdenum blue complex which is measured spectrophotometrically. |
| A1.4 | Range of Application (b) | Up to 10 mg/l as $SiO_2$. (Range may be extended by dilution or by the use of smaller aliquots, see section A10). |
| A1.5 | Calibration curve (b) | Linear to 10 mg/l $SiO_2$. |
| A1.6 | Total standard deviation | Type of sample: Standard solution (d); " ; " ; " <br> $SiO_2$, concentration (mg/l): 0; 2.0; 8.0; 50.0 <br> Total standard deviation (mg/l): 0.01; 0.05; 0.10; 0.32 (e) <br> each estimate has 19 degrees of freedom. |
| A1.7 | Limit of detection | 0.03 mg/l (10 degrees of freedom). |
| A1.8 | Sensitivity (b) | 10 mg/l $SiO_2$ gives an absorbance of approximately 0.84 in a 10 mm cell (based on a sample volume of 50 ml). |
| A1.9 | Bias (c) | In saline waters the slope of the calibration curve is changed (see section A11.5). |
| A1.10 | Interferences (b) | See section A.3. |
| A1.11 | Time required for analysis | Typical times for 12 samples are 1.5 hr operator time, 3 hr total time. |

(a) Data obtained by Imperial Chemical Industries Limited, Mond Division, Winnington Laboratories.
(b) Confirmed by Southern Water Authority, Sussex River and Water Division, including the pretreatment in Appendix III.
(c) Confirmed by Imperial Chemical Industries Ltd Brixham Laboratory.
(d) Distilled water spiked with the stated concentration of silicon.
(e) Using a 5.0 ml aliquot. Other data obtained using 50.0 ml aliquots.

## A2. Principle

A2.1 The method is based on work carried out at Imperial Chemical Industries, Mond Division, Winnington Laboratories.

A2.2 Monomeric and dimeric silicon in acid solution below pH 2 reacts with molybdate ions to form a yellow $\beta$-silicomolybdate which is reduced in situ with ascorbic acid to a blue silicomolybdate complex.

A2.3 When it is required to determine total silicon and forms of molybdate unreactive silicon the sample requires pretreatments to convert the unreactive species to a form capable of reacting with molybdate reagent (see appendices).

## A3. Interferences (2)

A3.1 There is no detailed information concerning the effect of interfering substances on the method described. Generally no important interference problems are likely with unpolluted fresh waters, but the effect of interferences should be considered particularly in polluted samples. The most likely sources of interference are listed below.

A3.2 **Phosphorus**

Initially phosphorus and silicon compete for the molybdate reagent to form their respective complexes, but the phosphate complex is decomposed under the strong acid conditions that prevail at a later stage of the method.

Up to 10 mg/l of silicon (as $SiO_2$) can be determined in the presence of 60 mg/l of phosphorus (as P) without interference exceeding 0.01 mg/l (as $SiO_2$). Higher levels of phosphorus may prevent complete formation of the silicomolybdate complex and also cause a precipitate to form which persists throughout the procedure and interferes with spectrophotometric measurements.

A3.3 **Arsenic** (a)

Although arsenic V is known to form an arsenomolybdate complex it has been shown that under the conditions of this method no significant interference takes place until the arsenic V concentration exceeds 400 mg/l (as As).

A3.4 **Germanium**

Germanates interfere by forming a germanomolybdate complex.

A3.5 **Nitrite** (a)

The effect of nitrite is both complex and variable. At concentrations greater than 0.5mg/l (as N) nitrite appears to catalyse the formation of silicomolybdenum blue. However, where levels exceed 2mg/l (as N) colour bleaching may subsequently occur and this appears to be related to the degree of exposure to air.

(a) Based on tests carried out at Southern Water Authority, Sussex River and Water Division.

## A4. Hazards

Only normal laboratory hazards are known to occur with this method.

## A5. Reagents

Analytical reagent grade chemicals are suitable.

A5.1 **Water**

The water used for blank determinations, preparing standard and reagent solutions, and for dilution purposes, should have a silicon content that is negligible compared with the smallest concentration to be determined in samples.

Distilled water is preferred. Deionized water may be suitable if the water supplied to the ion-exchange unit has a negligible silicon content (see section A11.2).

### A5.2 **10% m/V Ammonium molybdate solution**

Dissolve 25 ± 0.2 g of finely powdered ammonium molybdate $(NH_4)_6\ Mo_7O_{24}4H_2O$ in about 200 ml water and dilute with water to 250 ml in a measuring cylinder. Store in a polyethylene bottle. Discard if a precipitate forms.

### A5.3 **25% V/V Sulphuric acid solution**

Add slowly and cautiously with stirring 200 ± 2 ml of sulphuric acid ($d_{20}$ 1.84) to 600 ± 10 ml of water in a 2 litre beaker immersed in cold water, allow to cool. Store in a glass or polyethylene bottle.

### A5.4 **Ascorbic acid**

0.2g of powder is normally used for each determination of silicon. Alternatively use an equivalent weight of ascorbic acid in the form of tablets or a freshly prepared 10% aqueous solution.

### A5.5 **Methyl orange indicator solution (0.05% m/V)**

Dissolve 0.05 ± 0.01 g of methyl orange in about 100 ml of water.

### A5.6 **Hydrochloric acid solution (1.00N)**

Dilute 90 ± 1 ml of hydrochloric acid ($d_{20}$ 1.18) with water to 1 litre in a calibrated flask.

Standardize this solution as follows:—

Dry 5 ± 1g of sodium carbonate, anhydrous at 260 ± 10° C for 2 ± 0.25 hours. Allow to cool in a desiccator.

Weigh out accurately 1.330 ± 0.001g of this dried material into a 250 ml conical flask. Let this mass be Wg. Add 50 ± 5 ml of water and swirl to dissolve. Add 2 drops of methyl orange indicator solution and titrate with hydrochloric acid solution just to the appearance of a permanent red colour. Let the titre obtained by $T_1$ ml.

Then the normality of the hydrochloric acid solution = $\frac{W \times 18.87}{T_1}$

If necessary adjust the concentration of hydrochloric acid so that the normality falls within the range 1.000 ± 0.005.

Alternatively use commercially prepared hydrochloric acid solution (N).

### A5.7 **Sodium hydroxide solution (1.00N)**

Dissolve 40.8 ± 0.3 g of sodium hydroxide in about 800 ml of water in a plastic beaker, cool and dilute with water to 1 litre in a calibrated flask. Store in a polyethylene bottle. Standardize this solution as follows.

Pipette 25.00 ± 0.05 ml of sodium hydroxide solution into a 250 ml conical flask. Add 2 drops of methyl orange indicator solution and titrate with hydrochloric acid solution (1.00N) just to the appearance of a permanent red colour. Let this titre be $T_2$ ml.

Then the normality of the sodium hydroxide solution = $\frac{T_2 \times N_1}{25.00}$

where $N_1$ is the normality of the hydrochloric acid solution (1.00N)

If necessary adjust the concentration of the sodium hydroxide solution so that the normality falls within the range 1.000 ± 0.005. Alternatively use commercially prepared sodium hydroxide solution (N).

### A5.8 **Standard silica solutions**

A5.8.1 *Solution A* 1 ml is equivalent to 1000 $\mu$g $SiO_2$

Weigh 1.000 g ± 0.001 g of finely powdered silica, spectrographic grade, into a clean silver

or platinum crucible, add 5 ± 0.1 g of anhydrous sodium carbonate and mix intimately with a thin nickel spatula, cover the crucible with a platinum lid. Heat the crucible to red heat until the mixture begins to fuse, careful control of the heating will be required to avoid losses due to the spitting as the melt bubbles. When bubbling has subsided heat the crucible strongly until a clear transparent melt is obtained. Allow the crucible to cool, place it on its side in a 250 ml polyethylene beaker and place the lid in the beaker. Add 150 ± 10 ml of boiling water to the beaker and place it on a steam bath until the melt has dissolved. After rinsing the crucible and lid, remove from the beaker and cool the solution. Transfer the contents of the beaker with washings to a 1 l calibrated flask and dilute to the mark with water, mix well, and transfer the solution to a clean, dry polyethylene bottle.

The solution is stable for at least 1 year.

NB. The method described above is recommended. Alternatively transparent Spectrosil rod, 3mm diameter, may be used to prepare the solution.

As supplied by Thermal Syndicate Limited the impurity content is less than 1 ppm and the rod does not require to be heated or ignited before use as it is not appreciably hydroscopic. 300 mm of rod weigh about 5 g. A solution of sodium fluorosilicate containing the appropriate concentration of silicon may be used provided the reagent is of suitable quality and that the solution prepared is free from undissolved particles. Silicon standards are available commercially, but may contain polymeric silicates and may therefore be unsuitable.

A5.8.2 *Solution B* 1 ml is equivalent to 50 $\mu$g $SiO_2$

Dilute 25.00 ± 0.05 ml of solution A to 500 ml with water in a calibrated flask.

Store in a polyethylene bottle. This solution is stable for at least one week.

## A6. Apparatus

A6.1 **Spectrophotometer**

A spectrophotometer for use at 700 nm and at 810 nm capable of accepting 10 mm cells is suitable. If greater sensitivity is required 40 mm cells may be used.

(See Section A10).

A filter photometer may be used, but a difference in sensitivity may occur and the results may be less reliable.

A6.2 **10 mm optically matched cells**

Both sample and reference cells must be kept scrupulously clean. The same cells should be used for sample and reference solutions. They should always be placed in the same position in the holder with the same face towards the light source.

A6.3 **Plastic* vacuum filtration unit with 0.45 $\mu$m membrane filters**

A water pump or hand operated piston device is usually satisfactory.

A6.4 **Plastic* beakers 100 ml capacity, plastic* graduated pipettes and plastic* stirring rods**

* eg Polyethylene, polypropylene, polycarbonate or PTFE.

## A7. Sample Collection and Preservation

Collect a representative sample in a polyethylene or similar plastic bottle and analyse as soon as possible. If storage is unavoidable maintain the sample at 4 ± 1°C.

If microbiological activity within the sample is suspected, or is of special interest eg in eutrophication studies, it may be desirable to filter the sample on site at the time of collection, and also to consider whether either a 0.45 $\mu$m or a 0.1 $\mu$m membrane should be used. Silicon can occur as a vital natural or impurity constituent in many forms of living

matter. Knowledge of the forms in which silicon can occur may be of interest for biological and medical studies (see Appendix I).

## A8. Analytical Procedure

| Step | Procedure | Notes |
|---|---|---|
| | Analysis of sample | |
| A8.1 | Filter a sufficient quantity of sample through a 0.45 $\mu$m membrane filter to obtain a clear solution (note a). | a. This step may be omitted if the analyst, due to his experience, judges it to be unnecessary. |
| A8.2 | Using a plastic pipette transfer a suitable volume V (not exceeding 50 ml) of the sample, filtered if necessary, to a 100 ml plastic beaker (note b). | b. See section A10 for suitable sample volumes. |
| A8.3 | Add a second Vml of (filtered) sample to a 250 ml conical flask. Add 2 drops of methyl orange indicator and as appropriate titrate with either hydrochloric acid solution (1.00N) or with sodium hydroxide solution (1.00N) to the indicator end point. Note the titre and discard this second sample. Let the titre of hydrochloric acid solution (1.00N) obtained be x ml. | |
| or | Let the titre of sodium hydroxide solution (1.00N) obtained be y ml. | |
| | If the sample is neutral proceed to step A8.4a. | |
| | If the sample is alkaline proceed to step A8.4b. | |
| | If the sample is acid proceed to step A8.4c. | |
| A8.4 | *a. Sample neutral:* Add 10.00 $\pm$0.05 ml of hydrochloric acid solution (1.00N) to the filtered sample in the polyethylene beaker and stir. | |
| | *b. Sample alkaline:* Add (10 + x) $\pm$ 0.05 ml of hydrochloric acid solution (1.00N) to the (filtered) sample in the polyethylene beaker and stir. | |
| | *c. Sample acid:* Add (10.00 – y) $\pm$ 0.05 ml of hydrochloric acid solution (1.00N) to the (filtered) sample in the polyethylene beaker and stir. | |
| A8.5 | Add 5.0 $\pm$ 0.2 ml of 10% m/V ammonium molybdate solution stir and allow to stand for 12 $\pm$ 2 minutes. | |
| A8.6 | Add 20 $\pm$ 0.5 ml of 25% V/V sulphuric acid solution stir and allow to stand for 1 to 1.5 minutes. | |
| A8.7 | Add 0.2 $\pm$ 0.01 g of ascorbic acid and stir to dissolve. | |

| Step | Procedure | Notes |
|---|---|---|
| A8.8 | Transfer the solution quantitatively to a 100 ml calibrated flask and dilute with water to the mark. Stopper the flask and mix well and allow to stand for 60 ± 10 minutes away from bright sunlight, preferably in the dark. | |
| A8.9 | Meanwhile set up the spectrophotometer according to the manufacturers instructions. Adjust the zero of the instrument with water in the reference cell. | |
| A8.10 | Measure the absorbance of the solution at 700 nm using 10 mm cells, against water in the reference cell. Let the absorbance of the sample be $A_s$. | |
| | Blank determination (note c) | |
| A8.11 | A blank must be included with each batch of determinations using the same batch of reagents as for samples. Carry out steps A8.2 to A8.10 using 50 ml water in place of the sample. Let the absorbance of the blank be $A_b$. | c. The blank may be water if no other pretreatment was required, or the blank solution from a pretreatment described in the appendices. |
| | Calculation | |
| A8.12 | The absorbance due to silicon in the sample is given by $A_p = A_s - A_b$ For coloured or turbid samples see also section A11.4. | |
| | Determine the mass M (in $\mu$g $SiO_2$) of silicon in the processed sample, from the value of $A_p$ and the calibration curve (see Section A9). | |
| | Calculate the silicon concentration of the original sample (in mg/l $SiO_2$) C from $C = \frac{M}{V}$ | |

## A9. Preparation of calibration curve

The procedure given in this section must be carried out on at least two independent occasions before the application of this method to any samples and regularly thereafter. Any significant departure from linearity indicates that the technique is suspect at some stage.

To a series of 100 ml plastic beakers add 0.00, 2.00, 4.00, 6.00, 8.00 and 10.00 ml of standard silicon solution B. The beakers now contain 0, 100, 200, 300, 400 and 500 $\mu$g of $SiO_2$. Dilute each solution to 50 ± 5 ml with water and mix well. Proceed as described in section A8 steps A8.5 to A8.10. Plot the results for ($A_s$ - $A_b$) against $\mu$g $SiO_2$. The calibration graph is linear to at least 500 ug $SiO_2$.

## A10. Concentration ranges of the method

A10.1 Suitable volumes of sample to be used may be estimated from the following table:

Table 1

| Expected concentration (mg/l $SiO_2$) | Aliquot to be used (ml) |
|---|---|
| <10 | 50 |
| 10 – 20 | 25 |
| 20 – 50 | 10 |
| 40 – 100 | 5 |

When higher concentrations of silicon are likely to be encountered, it is recommended that the samples are diluted to an appropriate concentration and a corresponding multiplication factor incorporated in the calculation of the results.

A10.2 If greater sensitivity is required measure the absorbance at 700 nm using 40 mm cells.

A10.3 If even greater sensitivity is required measure the absorbance at 810 nm in either 10 mm or 40 mm cells.

(At 810 nm a 40 mm cell offers a sensitivity about 10 times that of absorbance measured at 700 nm in a 10 mm cell). When using these modifications appropriate calibration graphs must be prepared, and the linear range checked.

## A11. Sources of error

The attention which it is necessary to pay to sources of error depends on the accuracy required of the analytical results. The following sub sections summarize the main sources of error.

### A11.1 Contamination

Silicates are ubiquitous. The technique and working conditions should be critically examined and any sources of contamination eliminated or minimised. It is advisable to carry out a preliminary series of blank determinations before analysing any samples. This will ensure that any unduly high and/or variable blank values are detected so that steps can be taken to eliminate the problem.

### A11.2 Silicon content of the water used for blank determinations

If the water used for the determinations contains silicon compounds the results for samples will be falsely low. Clearly the importance of this error depends on the silicon content of the water and the concentrations of interest in the samples. Experience has shown that with good quality reagents blank values should not exceed 0.02 absorbance units. Ideally the silicon content of the water should be less than 10$\mu$g/l and tests should be made to verify this (see section B10.2). If this concentration is likely to lead to unacceptable bias in the sample results then method B should be used together with suitably purified water. When preparing deionized water care should be taken not to run the ion exchange beds too near to exhaustion as "silica breakthrough" could produce very high silicon concentrations without any conductivity increase in advance of the appearance of major anions. Such breakthrough is a potential source of blank bias.

### A11.3 Interfering substances

See section 3.

### A11.4 Colour and Turbidity

Coloured and/or turbid samples may interfere in the spectrophotometric measurement of the silico-molybdenum blue complex.

It may be possible to compensate for such interference by taking the same volume of sample through the colorimetric procedure except that step A8.5, the addition of ammonium molybdate, is omitted and replaced by an equal volume of water.

Note the absorbance due to this solution, let it be $A_c$

Then $A_p = A_s - A_b - A_c$ and this value of $A_p$ should be used in the calculation step.

### A11.5 **Saline Waters**

Calibration curves in saline waters and distilled water are linear, but differ significantly in slope (eg sea water of salinity 35 g/l, 10 mg/l $SiO_2$ = 0.79 absorbance units in a 10 mm cell). Saline samples determined using a calibration curve prepared with distilled water may be negatively biased. Such saline samples should be analysed by a standard addition procedure, with a distilled water reagent blank.

# B. Determination of Molybdate Reactive Silicon, 1 - amino - 2 - naphthol - 4 - sulphonic acid (ANSA) Reagent Reduction Method

**B1. Performance Characteristics of the Method (a)**
(For further information on the determination and definition of performance characteristics see General Principles of Sampling and Accuracy of Results, also published in this series).

| | | |
|---|---|---|
| B1.1 | Substance determined | Molybdate reactive silicon – mainly monomeric and dimeric silicic acids and silicate. |
| B1.2 | Type of sample | Clean waters. |
| B1.3 | Basis of method | Reaction with ammonium molybdate under controlled acid conditions to form yellow molybdosilicic acid which is reduced in situ with ANSA to yield a heteropoly molybdenum blue complex which is measured spectrophotometrically. The corresponding phosphate complex is destroyed using tartaric acid prior to reduction. |
| B1.4 | Range of application | Up to 500 $\mu$g/l $SiO_2$. |
| B1.5 | Calibration curve | Linear to at least 500 $\mu$g/l $SiO_2$, for a 100 ml sample volume. |
| B1.6 | Total standard deviation | Type of sample / $SiO_2$, concentration ($\mu$g/l) / Total standard deviation ($\mu$g/l)<br>standard solutions (b): 10 – 0.5; 200 – 0.8; 500 – 1.3<br>distilled water plus 50 mg/l $PO_4^{3-}$ (b): 10 – 1.1; 200 – 1.1; 500 – 2.0<br>boiler water (c): 4800 – 18<br>each estimate has 19 degrees of freedom. |
| B1.7 | Limit of detection | 2 $\mu$g/l $SiO_2$, when $PO_4^{3-}$ absent.<br>4 $\mu$g/l $SiO_2$, when 50 mg/l $PO_4^{3-}$ present both estimated with 10 degrees of freedom. |
| B1.8 | Sensitivity | 100 $\mu$g/l $SiO_2$, gives an absorbance of approximately 0.13 in 40 mm cell at 810 nm, for a 100 ml sample volume. |
| B1.9 | Bias | In fresh water no bias greater than 2% detected except when interference occurs. |
| B1.10 | Interferences | Phosphate, arsenate, and germanium may interfere slightly. Ferrous iron, hydrazine and sulphite may also interfere slightly in the presence of phosphate. All these effects will normally be inappreciable but for full details and the effects of other substances see Section B.3. |

| | |
|---|---|
| B1.11 Time required for analysis | The total analytical and operator times are the same. Typical times for 1 and 10 samples are 40 and 60 minutes respectively excluding any pre-treatment. |

(a) These data are from results obtained at the Central Electricity Research Laboratories.
(b) 100 ml sample volume.
(b) 10 ml sample volume.

## B2. Principle

B2.1 The method is based on the work of Webber and Wilson(3) and experimental work by Central Electricity Research Laboratories, Leatherhead. (4,5,6)

B2.2 Reactive forms of silicon are treated with ammonium molybdate under acid conditions, molybdophosphoric acid, which is formed in the presence of phosphates, is destroyed by addition of tartaric acid. The yellow $\beta$-molybdosilicic acid is reduced by means of 1-amino-2-naphthol-4-sulphonic acid to the heteropolymolybdenum blue complex.

B2.3 The method determines only "molybdate reactive" silicon compounds and certain silicon containing species may not react with molybdate even though they pass through filters and produce no noticeable turbidity in solution. The extent to which these forms of silicon exist varies with the type of water and the analyst should decide whether pretreatment(6) by fusing or heating with alkali is required (see appendices).

## B3. Interferences

If the pH of the sample falls outside the range 2-10 units and the sample is heavily buffered the required silico-molybdate complex may not be formed under the conditions of this method. Neutralization of the sample to a methyl orange indicator end point may be effective in eliminating this source of interference.

Phosphate may interfere slightly but in a complex way(3). Ferrous iron, hydrazine and sulphite may also interfere slightly in the presence of phosphate; although these effects will normally be minimal, details are given in Table 2.

Table 2

| Other ion or substance | Concentration of other substances (mg/l) (in order given in first column if two impurities) | Effect in $\mu$g/l $SiO_2$, of other substances at silicon concentrations of $\mu$g/l $SiO_2$ (d) | | |
|---|---|---|---|---|
| | | 0 | 100 | 500 |
| Iron III | 5.0 | <1 | | −2 |
| Chromium III | 5.0 | <1 | | <1 |
| Aluminium III | 5.0 | <1 | | −1 |
| Copper II | 5.0 | 3 | | −3 |
| Nickel II | 5.0 | <1 | | −2 |
| Zinc II | 5.0 | <1 | | <1 |
| Calcium | 100 | <1 | | −2 |
| Magnesium | 100 | <1 | | −5 |
| Potassium | 100 | <1 | | −2 |
| Sodium | 100 | <1 | | −3 |
| Manganese II | 0.1) | | | |
| Cobalt II | 0.1) | | | |
| Tin II | 0.1) | | | |
| Molybdate VI | 0.1) | <1 | | 2 |
| Vanadate V | 0.1) | | | |
| Titanium IV | 0.1) | | | |
| Tungstate VI | 0.1) | | | |
| Fluoride | 10 | <1 | | <1 |
| Cyclohexylamine | 10 | <1 | | <1 |
| Morpholine | 10 | <1 | | <1 |
| Octadecylamine | 1.0 | 1 | | <1 |

Table 2 (continued)

| Other ion or substance | Concentration of other substances (mg/l) (in order given in first column if two impurities) | Effect in $\mu g/l\ SiO_2$, of other substances at silicon concentrations of $\mu g/l\ SiO_2$ (d) 0 | 100 | 500 |
|---|---|---|---|---|
| Alkyl-aryl-sulphonate | 5.0 | 2 | | 2 |
| Fluorescein | 5.0 | 1 | | 2 |
| Orthophosphate | 0.1 | 3 | 2 | 0 |
| | 5.0 | 3 | 3 | 1 |
| | 25.0 | 4 | 3 | −1 |
| | 50.0 | 5 | 2 | −7 |
| Sulphite + Orthophosphate | 50 + 0 | <1 | | <1 |
| | 50 + 5 | 3 | | 2 |
| | 50 + 50 | 4 | | <1 |
| Iron II + Orthophosphate | 0.1 + 0 | <1 | | |
| | 0.1 + 0.2 | 7 | | |
| | 0.1 + 1.0 | 7 | | |
| | 0.1 + 5.0 | 7 | | |
| | 0.1 + 25 | 5 | | |
| | 0.1 + 50 | 5 | | |
| | 0.3 + 0 | <1 | | |
| | 0.3 + 0.2 | 14 | | |
| | 0.3 + 1.0 | 15 | | |
| | 0.3 + 5.0 | 11 | | |
| | 0.3 + 25 | 9 | | |
| | 0.3 + 50 | 7 | | |
| | 1.0 + 0 | <1 | <1 | <1 |
| | 1.0 + 0.2 | 17 | <1 | |
| | 1.0 + 1.0 | 37 | 12 | |
| | 1.0 + 5.0 | 35 | 11 | <1 |
| | 1.0 + 25 | 20 | 9 | |
| | 1.0 + 50 | 15 | 8 | <1 |
| Hydrazine + Orthophosphate | 0.2 + 50 | 5 | | −6 |
| | 1.0 + 0 | <1 | | −3 |
| | 1.0 + 5 | 6 | | 3 |
| | 1.0 + 50 | 14 | | 4 |

If the other substances did not interfere, the effect would be expected (95% confidence) to lie within the following ranges:

$0 \pm 7$ for $0\ \mu g/l\ SiO_2$
$500 \pm 3$ for $500\ \mu g/l\ SiO_2$

## B4. Hazards

Some aromatic amino compounds can cause health problems. No data is available on ANSA (Reagent 5.4 below) but no hazard has so far been reported from its industrial use. It is recommended that it be handled with care to avoid skin contact, inhalation, ingestion or spillage.

## B5. Reagents

Analytical reagent grade chemicals are suitable unless otherwise specified.

### B5.1 Water

Prepare and store in a polythene bottle, a large batch of water containing not more than 5 $\mu g/l\ SiO_2$. Determine the "reactive" silicon content of this water by treating it as a sample and analysing it as described in section B8 (ie taking 100 ml aliquot at step B8.1). The

result obtained will be 5% low because of the 5 ml water used initially in the blank determination but this small error may usually be ignored. Use this water to prepare reagent and standard solutions and for diluting samples.

Distilled water from a still that has been flushed out with fresh water, and water that has been passed through a laboratory-scale mixed-bed de-ionization unit have been found to be adequately pure. Precautions should be taken against silica elution from the resin bed. (See Section A11.2).

B5.2 **Ammonium molybdate — sulphuric acid reagent**

Dissolve 89 ± 1 g of finely ground ammonium molybdate, $(NH)_4)_6Mo_70_{24}4H_20$ in about 800 ml of water at room temperature.

Add slowly and cautiously with stirring, 63 ± 0.5 ml of sulphuric acid ($d_{20}$ 1.84) to about 100 ml of water in a beaker immersed in cold water, allow to cool. Add the acid solution to the molybdate solution with stirring. Cool and dilute with water to 1000 ± 10 ml. Store in a polyethylene bottle.

This solution is stable for at least 6 months.

If a blue colour appears in the solution it need not be discarded until the absorbance of the blank determination exceeds 0.02 units.

B5.3 **28% m/V Tartaric acid solution**

Dissolve 280 ± 3 g of tartaric acid, in about 800 ml of water and dilute with water to 1000 ± 10 ml. Store in a polyethylene bottle.

This solution is stable for at least 6 months.

B5.4 **0.2% m/V 1-Amino-2-naphthol-4-sulphonic acid*** *(ANSA)* solution

Dissolve 2.4 ± 0.1 g of sodium sulphite, $Na_2SO_37H_20$, in about 10 ml of water. Add 0.2 ± 0.002 g of 1-amino-2-naphthol-4-sulphonic acid, $NH_2C_{10}H_50H.SO_3H$ (purest grade available) and stir to dissolve. Dilute the solution to about 90 ml with water and add 14 ± 0.7 g of potassium metabisulphite $K_2S_20_5$. Stir to dissolve and dilute the solution with water to 100 ± 1 ml.

Store in a polyethylene bottle in the dark. Prepare this solution freshly each week.

*also known as 4-amino-3-hydroxy naphthalene-1-sulphonic acid

B5.5 **Standard silicon solutions** (see Section A5.8)

B5.5.1 *Solution A.* (See section A5.8.1). 1 ml equivalent to 1000 $\mu$g $Si0_2$

B5.5.2 *Solution C.* 1 ml equivalent to 5 $\mu$g $Si0_2$

Dilute 5.00 ± .02 ml of solution A with water to 1 litre in a calibrated flask.

Transfer to a dry polyethylene bottle.

This solution must be freshly prepared on the day of use.

## B6. Apparatus

B6.1 **Plastic bottles,** 125 or 250 ml capacity, eg polyethylene, polypropylene, polycarbonate, or PTFE.

Clean new bottles by washing thoroughly with water.

Before using new bottles check that the effect of contamination is negligible. When bottles have been shown to be satisfactory they should be reserved for silicon determinations only.

### B6.2 Spectrophotometer

A spectrophotometer for use at 810 nm capable of accepting 40 mm cells is suitable. A wavelength of 670 nm may be used or a filter photometer with a suitable filter may be used but a loss of sensitivity will occur and the results will be less reliable.

### B6.3 40 mm optically matched cells

Use as described for 10 mm cells in section A6.2.

## B7. Sample Collection and Preservation

See Section A7.

## B8. Analytical Procedure

| Step | Procedure | Notes |
|---|---|---|
| | Analysis of sample | |
| B8.1 | Add (100 – V) ml (± 0.5 ml) of water to a clean plastic bottle. Add V ml (± 0.005 V ml) of sample at a temperature not below 15°C (notes a, b) and mix by swirling gently. | a. The Volume of sample taken (Vml) should not contain more than 50 $\mu$g silicon (as $SiO_2$), and not more than 800 $\mu$g of phosphorus (as P). If this sample volume is not 100 ml see also note (g) at step B8.8.<br>b. If the sample is coloured or if it contains suspended matter, carry out section B10.1 using a separate sample. |
| B8.2 | Add 2.5 ± 0.1 ml of ammonium molybdate – sulphuric acid reagent. Note the time and immediately mix the contents of the bottle by swirling (note c). | c. To ensure rapid delivery of reagents the use of a syringe type pipette is desirable. |
| B8.3 | 10 ± 1 minute after step B8.2 add 2.5 ± 0.1 ml of 28% m/V tartaric acid solution. Note the time and swirl the bottle to mix the solution (note c). | |
| B8.4 | 5 ± 1 minute after step B8.3 add 2.0 ± 0.1 ml of 0.2% m/V *ANSA* solution. Note the time and again mix the contents of the bottle by swirling (note c). | |
| B8.5 | Meanwhile set up the spectrophotometer (see section B6.2) according to the manufacturers instructions. Adjust the zero of the instrument with water in the reference cell. | |
| B8.6 | 40 ± 20 minutes following step B8.4 measure the absorbance of the solution in a 40 mm cell at a wavelength of 810 nm against water in the reference cell. Let the absorbance of the sample be $A_T$. | |

| Step | Procedure | Notes |
|---|---|---|
| | Blank determination | |
| B8.7 | A blank must be included with each batch of determinations using the same batch of reagents as for samples. (See Section B10.2). | |
| | Add (100-V) ± 0.5 ml of water at a temperature not below 15°C to a plastic bottle (notes d, e). | d. Strictly, a blank should be analysed for each different sample dilution that is used in the batch of analyses but see Section B10.2. |
| | Proceed as described above in steps B8.2 to B8.6 except that V ± 0.5 ml of water is added to the bottle after the addition of tartaric acid (note f). Let the absorbance of the blank be $A_O$. | e. If V = 100 ml, add 5 ml of water.<br>f. When V = 100 ml, add 95 ml of water. |
| | Calculation of results (note g) | |
| B8.8 | The absorbance due to silicon in the processed sample is given by:– $A_T - A_O$. | g. If the volume of initial sample (Vml) taken at step B8.1 was not 100 ml, correct for the initial dilution:– |
| | Determine the concentration of silicon in $\mu$g/l $SiO_2$ in the processed sample from the calibration graph (see section B9). | $\frac{(\mu g/l\ SiO_2\ found) \times 100}{V} = true\ \mu g/l\ SiO_2$ |

**B9. Preparation of Calibration Curve.**

The calibration curve is linear to about 500 $\mu$g/l $Si0_2$ but at 810 nm the slope of the calibration graph decreases by about 0.25% for an increase in temperature of 1°C.

Any significant departure from linearity indicates that the technique is suspect at some stage.

Add 100, 98, 96, 94, 92 and 90 ml (all to ± 0.3 ml) of water to a series of plastic bottles.

Add 0.00, 2.00, 4.00, 6.00, 8.00 and 10.00 ml respectively of standard silicon solution C and swirl to mix. The bottles now contain standard solutions representing 0, 100, 200, 300, 400 and 500 $\mu$g/l $Si0_2$ respectively. Subject the solutions to the procedure given in section B8 steps 2 to 6.

Plot the results for $(A_T - A_0)$ against $\mu$g/l $Si0_2$

**B10. Sources of error**

See also Section All.

B10.1 **Turbidity and/or Colour Correction**

If the sample is coloured or turbid, carry out the blank procedure in step B8.7 replacing the final addition of Vml of water by the same amount of sample. If V is 100, add the full amount (instead of the 95 mls of note B8.7f) and multiply the absorbance $A_E$ by $\frac{112}{107}$ to correct for the difference in total volume.

Note the absorbance due to this solution. Let this be $A_E$.

Then for such samples $A_R = A_T - A_0 - A_E$.

B10.2 **Silicon Content of the Water used for Blank Determinations**

The presence of silicon in the water used for blank determinations could lead to an unacceptable bias in results close to the limit of detection. There should be no cause for

concern provided the criteria set out in Section B5.1 are satisfied and if, when a number of samples requiring different dilutions are analysed, a blank is analysed for each different dilution as described in Section B8.7. When suitably prepared water (B5.1) is used for sample and blank analyses, the differences between the different blanks will be small and the error introduced by using a blank at only one dilution may be tolerable – this is for the analyst to decide upon.

The blank for a 100 ml sample is also slightly in error because of the silicon contained in the 5 ml of water initially added to the blank. The error is equivalent to 5% of the concentration of silicon in the water and may thus be ignored for most purposes.

### B10.3 **Effect of Temperature**

The temperature of the sample should not be less than 15° C during the determination or the formation of the molybdosilicic acid may be incomplete.

# C. Automated Procedures

Either method may be readily automated using a continuous flow analyzer, (7,8) or a discrete analysis system (9).

Manufacturers of automatic equipment may provide data sheets for the determination of silicon in water. Note however that some automated procedures for the analysis of silicon are based upon the formation of an $\alpha$-silicomolybdate complex rather than the $\beta$-form. Some methods may not be strictly comparable with methods A and B.

# D. Estimation of the Validity of Analytical Results

The analyst should establish an analytical quality control procedure to check the validity of results obtained. Because of the complex nature of silicon in water analysis in respect of the form of silicon to be determined and the wide range of concentration likely to be encountered, it is beyond the scope of this booklet to present a scheme that satisfactorily covers all possible parameters. The Analyst should follow the guidelines and statistical practices recommended by the Water Research Centre (10) and another publication in this series (11). Controls should be selected appropriate to the range and conditions that prevail in the chosen overall analytical procedure.

# Appendices

# Pretreatment Methods to Convert Other Forms of Silicon to Soluble Molybdate Reactive Silicon

As several variations in pretreatment are possible, the analyst is rccommended to try out the proposed procedures prior to analysing samples. As given, the pretreatment procedures are written for use with method A; but see Section 0.5. After neutralization it is often possible to use method B with treated samples.

## Appendix I

## General Information

### I.1. Forms of Silicon

Silicon occurs in natural (including saline) and waste waters in one or more of the following three principal forms (see Figure 1 which summarizes the pretreatment options):—

a. Silicon compounds present in true solution in monomeric and dimeric forms. These are the forms that react with ammonium molybdate.

b. Silicon compounds present in solution in a polymeric form, ie. may be present in a filtered sample, but do not react with ammonium molybdate unless converted to the reactive form by suitable pretreatment.

c. Insoluble silica that can be retained on a filter. This form can be converted to the soluble molybdate reactive form by suitable pretreatment.

Silicon present as sub micron particles of "colloidal silica" is difficult to define and may fall somewhere between the b. and c. forms listed above.

Arbitrary distinctions on the basis of particle size distribution are commonly used. In this booklet soluble silicon is defined as that which passes a 0.45 $\mu$m filter. In some instances a 0.1 $\mu$m filter may be more appropriate.

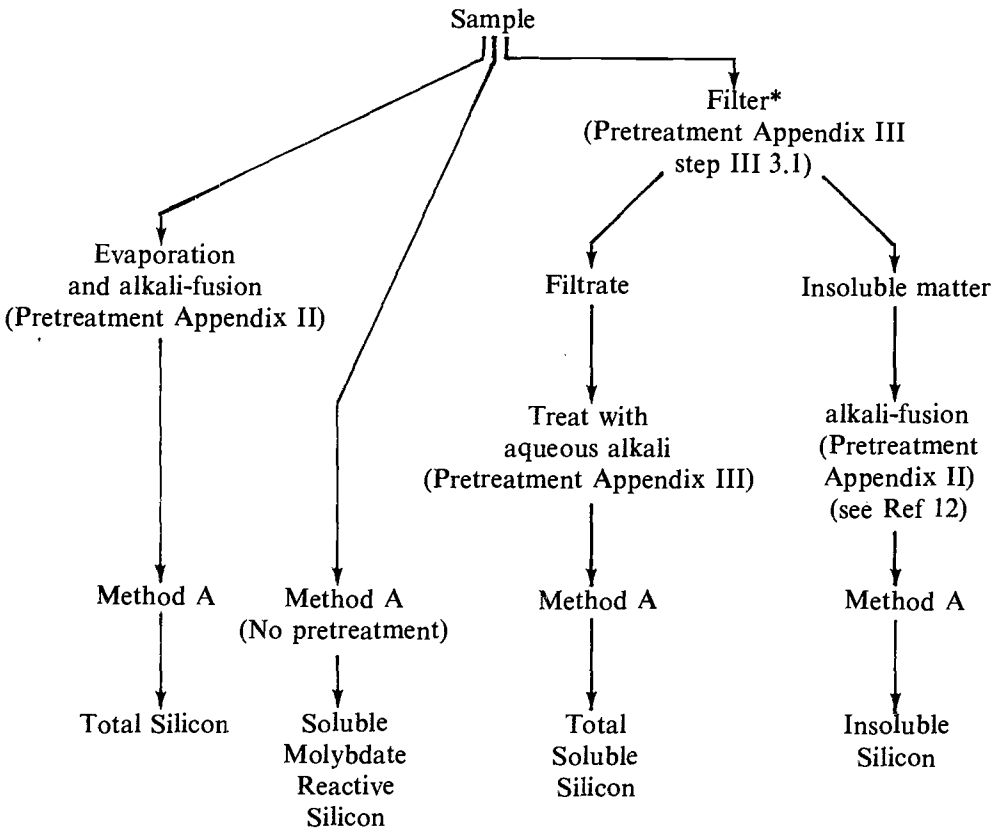
Insoluble silica cannot always be determined directly since it may not be possible to wash matter retained by a filter without altering its character. Therefore insoluble silica is determined as the difference between total silicon and total soluble silicon. When this difference is very small, at high total silicon contents, this procedure could lead to unacceptably large errors and it may then be preferable to determine the insoluble silica retained on the filter (12).

Figure 1 below illustrates this information.

**I.2. Sample Collection and Preservation** See Section A7.

Figure 1

Forms of Silicon obtained using Various Pretreatment in Combination with Method A.




*For clean waters, in the absence of suspended matter, filtration of the sample is not necessary and total soluble silicon will also be the total silicon.

Polymeric silicon = Total soluble silicon - soluble molybdate reactive silicon.

Insoluble silicon = Total silicon - total soluble silicon.

## Appendix II

## Sample Pretreatment for Converting Total Silicon to Molybdate Reactive Silicon

To determine total silicon it is necessary to pretreat a sample without filtration. Full blank determinations should be carried out before the routine use of pretreatment procedures and also alongside sample analyses. (See also section A11.4).

**II.1. Hazards** Only normal hazards, especially those associated with strong acids and with alkali fusions are known to occur with this method.

**II.2. Reagents** Analytical reagent grade chemicals are suitable.

In addition to the reagents described in section A5, the following will be required.

II.2.1 **20% m/V Sodium carbonate solution**

Using plastic apparatus, dissolve 20.0 ± 0.1 g of sodium carbonate anhydrous in about 80 ml of water, dilute to 100 ± 1 ml. Filter and store in a polyethylene bottle.

## II.3. Apparatus

In addition to the apparatus described in section A6 the following will be required.

II.3.1 **Platinum or silver crucibles** of about 30 ml capacity fitted with a lid.

*The usual laboratory precautions for the care of platinum apparatus must be observed, for instance, fusions must not be carried out in the presence of peroxides or hydroxides of the alkali and alkaline earth metals.*

*Never allow red-hot platinum crucibles to come into contact with base metals and handle crucibles only with platinum tipped tongs. Always use an oxidizing flame when gas burners are the source of heat since reducing flames, particularly smoky flames, will seriously damage platinum ware.*

*Crucibles may be cleaned by adding a small quantity of potassium hydrogen sulphate and heating to fusion. Ensure that the molten salt comes into contact with the entire inner surface of the crucible. Cool, dissolve the melt with water and rinse thoroughly with water.*

*In addition to the above treatment carry out the sodium carbonate fusion procedure given below in steps II4.3-5. Leach the crucible with hot water and rinse thoroughly with water. Dry the crucible in a dust free electric oven at 105°C and store protected from dust.*

II.3.2 **Plastic beakers** 250ml, eg polyethylene, polypropylene, polycarbonate, or PTFE.

III.3.3 **Muffle furnace** capable of heating a platinum crucible to a temperature sufficient to fuse sodium carbonate (ie intense red heat ca 850° C).

Alternatively a suitable gas burner may be used.

## II.4. Pretreatment procedure

| Step | Procedure | Notes |
|---|---|---|
| | Pretreatment of sample | |
| II.4.1 | Transfer a suitable volume of homogenous sample to a platinum crucible (note a). Let this volume be $V_1$ ml. | a. Select the volume of sample as shown in section II.5 of this appendix. If the volume $V_1$ exceeds 30 ml add sample in small portions and carry out step 2 until a total of $V_1$ ml has been evaporated. |
| II.4.2 | Evaporate the sample to dryness on a steam bath or by using a radiant heater taking care to avoid spattering (note b). | b. Take care to avoid loss of contents of spattering and/or frothing. Also see section II.3 concerning the care of platinum apparatus. |
| II.4.3 | Add 10.0 ± 0.1 ml of 20% m/V sodium carbonate solution ensuring that the entire residue is moistened. | |
| II.4.4 | Cover the crucible with a lid, evaporate to dryness then heat gently over a low flame until the contents become quiescent (note b). Transfer the crucible to the muffle furnace and continue this heating until the entire contents appear as a transparent glassy melt. | |

| Step | Procedure | Notes |
|---|---|---|
| | Allow the crucible to cool to room temperature in a dust-free atmosphere (note c). | c. The exterior surface of the crucible must be kept scrupulously clean to minimise contamination. |
| II.4.5 | Place the crucible on its side together with the lid in a 250 ml plastic beaker.<br>Add 150 ± 10 ml of boiling water and place on a steam bath until the melt has dissolved.<br>Remove the crucible and lid from the beaker using platinum tipped tongs, and rinsing with water so that the washings are collected in the beaker, allow the solution to cool to room temperature. | |
| II.4.6 | Cautiously add 50 ± 1 ml of hydrochloric acid solution (1.00N) (note d). Mix, allow to cool and transfer the solution to a 250 ml calibrated flask, dilute with water to the mark, stopper and mix well. | d. The acid must be added slowly to prevent frothing and loss of solution. |
| II.4.7 | Reserve this solution for the determination of molybdate reactive silicon as described in section A steps A8.2 to A8.10 inclusive (note e). | e. This solution is used in place of the sample. The volume (Vml) to use is given in section II.5 of this appendix. Pay particular attention to the neutralisation steps given in section A8 step A8.3 and note c. |
| | Blank determination (note f) | |
| II.4.8 | Add 10.0 ± 0.1 ml of sodium carbonate solution to a platinum crucible.<br>Proceed as described from step II.4.4 to step II.4.7.<br>Reserve this solution for the blank determination as described in section A8 step A8.11 (note g). | f. Carry out a blank determination with each set of sample determinations.<br>g. This solution is used in place of water. The volume to use will be the same as was used for the sample solution. Pay particular attention to the neutralisation steps given in section A8 step A8.3 and note c. |
| | Calculation of results | |
| II.4.9 | The adsorbance due to total silicon in the processed sample is given by $A_p = A_s - A_b$.<br>Determine the mass $M_1$ (in $\mu$g $SiO_2$) of total silicon in the processed sample from the value of $A_p$ and the calibration curve.<br>Calculate the total silicon concentration in the original sample (in mg/l $SiO_2$) from<br>$C_T = \frac{M_1}{V} \times \frac{250}{V_1}$ | |

**II.5. Suitable Sample Volumes**

**Suitable volumes of sample to be used may be estimated from the following table:**

Table 3

| Expected Total silicon content of the sample (mg/l $SiO_2$) | Aliquots to be used for pretreatment stage $V_1$ ml | for colorimetric stage Vml |
|---|---|---|
| 10 | 100 | 50 |
| 10 – 20 | 50 | 50 |
| 20 – 80 | 25 | 50 |
| 80 – 200 | 10 | 50 |
| 200 – 400 | 5 | 50 |
| 400 – 1000 | 5 | 20 |
| 1000 – 2000 | 5 | 10 |
| 2000 – 4000 | 5 | 5 |

## Appendix III

## Sample Pretreatment for Converting Total Soluble Silicon to Molybdate Reactive Silicon

To determine total soluble solutions it is necessary to pretreat a filtered sample.

**III.1. Reagents**

As described in section A5.

**III.2. Apparatus**

As described in section A6.

**III.3. Pretreatment procedure (see also II.1).**

| Step | Procedure | Notes |
|---|---|---|
| | Pretreatment of sample | |
| III.3.1 | Filter about 100 ml of homogenous sample through a 0.45 $\mu$m membrane filter to obtain a clear solution (notes a and b). | a. This step may be omitted if the analyst, due to his experience judges it to be unnecessary.<br><br>b. For some purposes 0.1$\mu$m membrane may be more suitable. |
| III.3.2 | Using a plastic pipette transfer a suitable volume V (not exceeding 50 ml) of the filtrate to a 100 ml plastic beaker (note c). | c. See section A10.1 for suitable volumes. A polyethlene bottle may be used instead of the beaker, in order to reduce the risk of contamination. |
| III.3.3 | Neutralize with sodium hydroxide solution (1.00N) or hydrochloric acid solution (1.00N) if necessary (note d) and add sufficient water to produce a volume of 50 ± 5 ml if necessary. | d. The quantity of sodium hydroxide solution (1.00N) or hydrochloric acid solution (1.00N) to be added to neutralise V ml of sample to methyl orange indicator should be determined on a separate V ml portion of the (filtered) sample. |

| Step | Procedure | Notes |
|---|---|---|
| III.3.4 | Add 5.0 ± 0.1 ml of sodium hydroxide solution (1.00N) and mix well. | |
| III.3.5 | Heat the solution on a steam bath for 30 ± 5 minutes.<br><br>Allow the solution to cool to room temperature. | |
| III.3.6 | Pipette 15.0 ± 0.1 ml of hydrochloric acid solution (1.00N) into the beaker and mix well. | |
| III.3.7 | Reserve this solution for the determination of silicon as described in section A8 commencing at step A8.5. | |
| | Blank determination (note e) | |
| III.3.8 | Transfer 50 ± 5 ml water to a 100 ml plastic beaker.<br><br>Proceed as described in steps III.3.4–6 of this Appendix Reserve this solution for the blank determination described in section A8 step A8.11 but omitting steps A8.2 to A8.4. | e. Carry out a blank determination with each set of sample determinations. |
| | Calculation | |
| III.3.9 | The absorbance due to total soluble silicon in the processed sample is given by<br><br>$A_p = A_s - A_b$<br><br>Determine the mass $M_2$ (in $\mu$g $SiO_2$) of total soluble silicon in the processed sample from the value of $A_p$ and the calibrated curve.<br><br>Calculate the total soluble silicon concentration in the original sample (in mg/l $SiO_2$) $C_S$ from<br><br>$C_S = \frac{M_2}{V}$ | |

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## Address for Correspondence

No method is perfect for all samples. The experience of users may be of use to others. Laboratories wishing so to do may send results of controlled tests to the Secretary of the Standing Committee of Analysts whose address is given below. Furthermore, however thoroughly a method may be tested, there is always the possibility of a user discovering a hitherto unknown problem. Users with information on this method are requested to write to:


The Secretary
Standing Committee of Analysts
Department of the Environment
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LONDON SW1P 3EB
England.



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