Method 9.7 – Boiler water: silica

1.

This applicable to boiler water and determines the soluble silica present in the sample litre.

2. Principle

A standard graph of silica concentration *versus* absorbance is plotted. The sample is treated with oxalic acid to mask interference from any phosphates present. The treated sample is reacted with ammonium molybdate. The absorbance of the colour of the resulting molybdenum blue complex is determined at 700 nm and the phosphate concentration is calculated from the standard graph.

3. Apparatus

3.1   **Spectrophotometer** operating at 700 nm

3.2   **Optical glass cell**: 10 mm

3.3   **Pipettes** with pipette stand: 5, 10, 20, 25 and 50 cm^3

3.4   **Volumetric flasks**: 7×100, 2×500, 1 000 and 2 000 cm^3

3.5   **Stopwatch**

3.6   **Conical flask**

3.7   **Measuring cylinder**: 500 cm^3

3.8   **Analytical balance** readable to 0.0001 g

3.9   **Top pan balance** readable to 0.01 g

3.10   **Funnel**: 50-60 mm ϕ

3.11   **Glass wool** or Whatman No. 91 filter paper or equivalent

3.12   **Platinum crucible**

3.13   **Muffle furnace** operating at 900°C

3.14   **Polyethylene bottle**: 500 cm^3

3.15   **Beaker**: 1 litre

4. Reagents

4.1   **Sodium carbonate** (Na_2CO_3)

4.2   Silica standard solution (200 mg/kg)

Weight 0.100 g silica and 1.00 g sodium carbonate into a platinum crucible. Fuse by heating in a muffle furnace at 900°C for 30 minutes. Cool and dissolve the melt in 100 cm^3 distilled water (heat gently to aid dissolution). Transfer quantitatively to a 500 cm^3 volumetric flask and make to the mark with distilled water.

Store in a polyethylene bottle.

4.3   Hydrochloric acid (concentrated, 32%)

Hydrochloric acid (HCl) is a corrosive acid and should be handled with gloves in a fume cupboard while wearing safety glasses.

4.4   Ammonium molybdate solution (1.5% m/m)

Ammonium molybdate tetrahydrate [$(NH_4)_2MoO_4 \cdot 4H_2O$] is an irritant and skin contact, inhalation and swallowing must be avoided. Work in a fume cupboard while wearing gloves and safety glasses.

Dissolve 15.0 g powered ammonium molybdate tetrahydrate in 300 cm^3 distilled water at 50°C in a 1 litre beaker and cool. Carefully add 310 cm^3 concentrated hydrochloric acid. This dilution is exothermic and the solution will heat. Cool to room temperature and transfer to a 1 000 cm^3 volumetric flask and make to the mark.

4.5   Hydrochloric acid (1:1)

Carefully add 500 cm^3 hydrochloric acid to 500 cm^3 water and mix. Always add the acid to the water and never the other way around. The dilution is exothermic and the solution will therefore heat.

4.6   Oxalic acid solution

Oxalic acid dihydrate [$(COOH)_2 \cdot 2H_2O$] is corrosive to the eyes, skin and respiratory tract. Work in a fume cupboard while wearing gloves and safety glasses.

Dissolve 10.0 g oxalic acid dihydrate in distilled water. Transfer to a 100 cm^3 volumetric flask and make to the mark with distilled water.

5. Procedure

5.1   Preparation of the standard graph

Measure 100 cm^3 of the standard 200 mg/litre silica solution and transfer to a 500 cm^3 volumetric flask. Make to the mark to prepare a 40 mg/litre silica solution.

Pipette aliquots of the 40 mg/litre silica solution into 100 cm^3 volumetric flasks according to the amounts indicated in Table 1. Add an empty volumetric flask to the series as a blank.

$$\text{Silica concentration (mg/litre)} = \frac{\text{aliquot} \times \text{concentration}}{\text{volume}} = \frac{\text{aliquot} \times 40\ \text{mg/litre}}{100\ \text{cm}^3}$$

Table 1: Calibration graph solutions

Flask no	Aliquot (cm³)	Silica concentration (mg/litre)
1	5	2
2	10	4
3	20	8
4	30	12
5	40	16
6	50	20

Add distilled water to the flasks to bring the total contents to about 85 cm³. To each flask add 1 cm³ of the 1:1 hydrochloric acid solution and 2 cm³ of the ammonium molybdate solution in rapid succession. Mix and allow the solutions to stand for 5 - 10 minutes.

Add 1.5 cm³ of the oxalic acid solution to the first flask and start the stopwatch. Quickly make to volume with distilled water and mix. Measure the absorbance after 2 minutes and before 15 minutes after addition of the oxalic acid solution at 410 nm in a 10 mm cell using distilled water as the reference. Plot a graph of absorbance (AU) against silica concentration (mg/litre).

5.2   Sample

Pipette 50 cm³ (aliquot) of the sample into two 100 cm³ volumetric flasks, one of which will be a blank. To the first flask, add enough distilled water to make the contents up to 85 cm³. Add 1 cm³ of the 1:1 hydrochloric acid solution and 2 cm³ of the ammonium molybdate solution in rapid succession. Mix well and allow the solution to stand for 5 - 10 minutes.

Add 1.5 cm³ of the oxalic acid solution and start the stopwatch. Quickly make to volume with distilled water and mix. Measure the absorbance after 2 minutes and before 15 minutes after addition of the oxalic acid solution at 410 nm in a 10 mm cell using distilled water as the reference.

Add 1 cm³ of the hydrochloric acid solution to the second flask and make to the mark with distilled water. This solution is the blank. Determine the absorbance of the blank at 700 nm in a 10 mm cell using water as a reference.

6. Expression of Results

Subtract the blank from the absorbance and read the corresponding silica concentration from the standard graph.

$$\text{Silica (mg/litre on sample)} \quad = \quad \text{silica concentration} \times \frac{\text{total volume}}{\text{aliquot}}$$

$$\text{silica concentration} \times \frac{100 \text{ cm}^3}{50 \text{ cm}^3}$$

where the silica concentration is obtained from the calibration graph

Report to the nearest unit in mg/litre on sample.

7. Example

7.1   Standard graph

Table 2: Example standard graph

Flask no	Aliquot (cm³)	Silica (mg/litre)	Absorbance (AU)
1	5	2.04	0.035
2	10	4.08	0.070
3	20	8.16	0.105
4	30	12.24	0.140
5	40	16.32	0.175
6	50	20.40	0.210

Actual mass silica weighed   =   0.1020 g
Actual concentration silica standard =   204 mg/litre
After dilution   =   40.8 mg/litre

$$\text{Silica concentration (mg/litre)} = \frac{\text{aliquot} \times 40.8 \text{ mg/litre}}{100 \text{ cm}^3}$$

$y = 0.0206x + 0.0193$
$R^2 = 0.995$
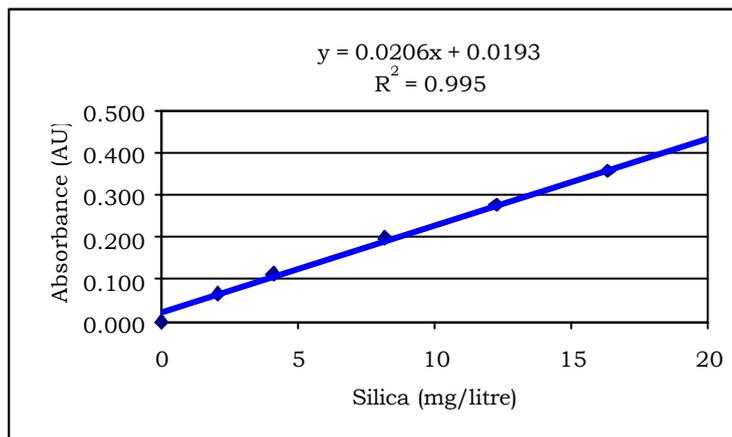
Figure 1: Silica standard graph

7.2   Sample

Absorbance of blank   =   0.026 AU
Absorbance of solution   =   0.256 AU
Absorbance of sample   =   (0.0256 - 0.026) AU
                            =   0.230 AU

Silica in solution   =   10.23 mg/litre
Silica in sample   =   20.46 mg/litre

Report as 21 mg/litre on sample

8. References

SASTA (1985). *Laboratory Manual for South African Sugar Factories.* 3rd Edition: 202 - 204, 355 - 356.