Method 9.6 – Boiler water: phosphates (P_2O_5)

1. Rationale

The method is applicable to boiler water and determines the soluble phosphates present in the sample in mg/litre P_2O_5. To obtain the total phosphates in the sample an ashing step may be included in the sample preparation.

2. Principle

A standard graph of phosphate concentration *versus* absorbance is plotted. The same standard graph may be used for raw sugar phosphates (Method 7.14) and juice phosphates (Method 3.8). The sample is reacted with ammonium molybdate and the absorbance of the colour of the resulting molybdenum blue complex is determined at 700 nm. The phosphate concentration is calculated from the standard graph.

3. Apparatus

3.1 **Spectrophotometer** with a wavelength of 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**: 100, 200, 1 000 and 2 000 cm^3

3.5 **Stopwatch**

3.6 **Analytical balance** readable to 0.0001 g

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

3.8 **Funnel**: 50-60 mm ϕ

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

3.10 **Beaker**: 1 litre

4. Reagents

4.1 **Sulphuric acid** (concentrated)

Sulphuric acid (H_2SO_4) is a corrosive acid and should only be handled with gloves while wearing safety glasses.

4.2 **Phosphate stock solution** (400 mg/litre P_2O_5)

Potassium dihydrogen orthophosphate (KH_2PO_4) is corrosive and should be handled with gloves to avoid skin contact and safety glasses. Avoid swallowing and inhalation of the fumes by working in a fume cupboard.

Dissolve 0.7668 g potassium dihydrogen orthophosphate in distilled water and transfer to a 1 000 cm^3 volumetric flask. Add 10 cm^3 concentrated sulphuric acid and dilute to volume to make a 400 mg/litre P_2O_5 solution. This standard will keep indefinitely.

4.3 Phosphate standard solution (10 mg/litre P_2O_5)

Dilute 25 cm^3 of the 400 mg/litre P_2O_5 standard to 1 000 cm^3 in a volumetric flask. This standard is used for the calibration graph.

4.4 Hydrochloric acid (concentrated, 32%)

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

4.5 Ammonium molybdate solution (1.5% m/m)

Ammonium molybdate tetrahydrate [$(NH_4)_2MoO_4 \cdot 4H_2O$] is an irritant and contact with the skin or through 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.

4.6 Reducing solution

Sodium metabisulphite ($Na_2S_2O_5$), sodium sulphite (Na_2SO_3) and 1-amino-2-naphthol-4-sulphonic acid ($C_6H_4C_4HNH_2OHSO_3H$) are irritants and contact with the skin, eyes and through swallowing should be avoided. Sodium metabisulphite is toxic to humans.

Solution A: dissolve 180.0 g sodium metabisulphite in 1 400 cm^3 distilled water.

Solution B dissolve 14.0 g anhydrous sodium sulphite and 3 g 1-amino-2-naphthol-4-sulphonic acid in 200 cm^3 distilled water.

Mix solutions A and B in a 2 000 cm^3 volumetric flask and make to the mark with distilled water. Stand overnight and filter through glass wool or a Whatman No. 91 filter paper or equivalent. Store in a dark bottle and in a refrigerator. This solution has a maximum shelf life of 2 months. Remove the required amount of reducing solution from the refrigerator about 1 hour before use and allow warming to room temperature.

5. Procedure

5.1 Preparation of a standard graph

Pipette volumes of the 10 mg/litre phosphate standard solution into 100 cm^3 volumetric flasks according to the amounts indicated in Table 1.

$$P_2O_5 \text{ concentration (mg/litre)} = \frac{\text{aliquot} \times \text{concentration}}{\text{volume}} = \frac{\text{aliquot} \times 10 \text{ mg/litre}}{100 \text{ cm}^3}$$

To each flask add 10 cm^3 of the ammonium molybdate solution and sufficient distilled water to bring the total volume in the flask to about 85 cm^3. Add 10 cm^3 reducing solution to the first flask and start the stopwatch. Quickly make to volume with distilled water and mix. Measure the absorbance exactly 10 minutes after addition of the reducing solution at 700 nm in a 10 mm cell using distilled water as the reference. Repeat these

steps for all the other flasks using distilled water as the blank. Plot a graph of absorbance (AU) against P_2O_5 concentration (mg/litre).

Table 1: Standard graph solutions

Flask no	Aliquot (cm^3)	P_2O_5 concentration (mg/litre)
1	5	0.5
2	10	1.0
3	15	1.5
4	20	2.0
5	25	2.5
6	30	3.0
7	35	3.5
8	40	4.0
9	45	4.5
10	50	5.0

5.2 Sample

The aliquot used will depend on the concentration of phosphates in the sample. As a guide boiler water contains about 70 - 110 mg/litre P_2O_5.

Therefore, pipette 5 cm^3 (aliquot) of the sample into two 100 cm^3 volumetric flasks, one of which will be a blank. To the first flask, add approximately 50 cm^3 water, 10 cm^3 of the ammonium molybdate solution and 10 cm^3 of the reducing solution. Start the stopwatch.

Mix by swirling and make to the mark with distilled water. Measure the absorbance exactly 10 minutes after addition of the reducing solution at 700 nm in a 10 mm cell using distilled water as the reference. Make the second flask to volume (blank) with distilled water. Determine the absorbance of the blank at 700 nm in a 10 mm cell using water as a reference.

6. Calculations

Subtract the blank from the absorbance and read the corresponding P_2O_5 concentration from the standard graph.

$$P_2O_5 \text{ (mg/litre on sample)} = P_2O_5 \text{ concentration} \times \frac{100\ cm^3}{\text{aliquot}}$$

where the P_2O_5 concentration is obtained from the calibration graph

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

7. Example

7.1 Standard graph

Actual mass KH_2PO_4 weighed = 0.7720 g
Actual concentration P_2O_5 standard = 10.07 mg/litre

$$P_2O_5 \text{ concentration (mg/litre)} = \frac{\text{aliquot} \times 10.07\ \text{mg/litre}}{100\ cm^3}$$

Table 2: Example standard graph

Flask no	Aliquot (cm^3)	P_2O_5 (mg/litre)	Absorbance (AU)
1	5	0.5	0.035
2	10	1.0	0.070
3	15	1.5	0.105
4	20	2.0	0.140
5	25	2.5	0.175
6	30	3.0	0.210
7	35	3.5	0.245
8	40	4.0	0.280
9	45	4.5	0.315
10	50	5.0	0.350

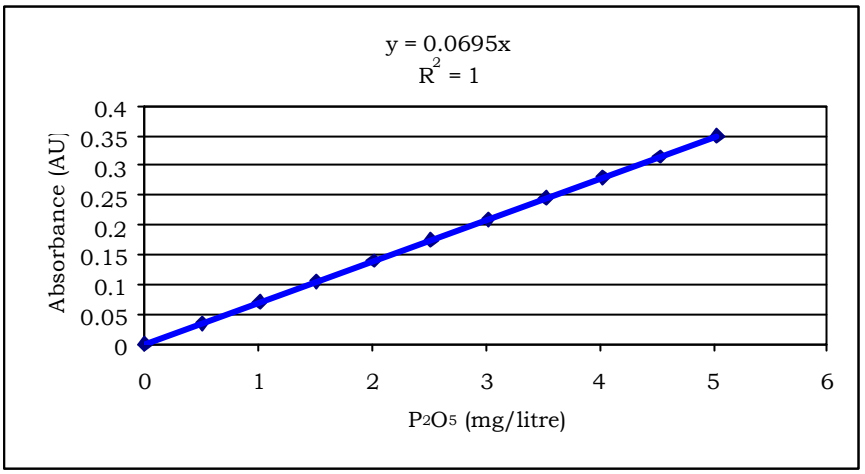

Figure 1: Phosphate standard graph

7.2 Sample

Absorbance of blank	=	0.046 AU
Absorbance of sample	=	0.256 AU
P_2O_5 in solution	=	3.02 mg/litre
P_2O_5 in sample	=	60.4 mg/litre

Report as 60 mg/litre on sample

8. References

SASTA (1985). *Laboratory Manual for South African Sugar Factories.* 3rd Edition: 191 - 192, 352.

SMRI (2004). Determination of the inorganic and total phosphate in raw sugar. *SMRI Test Methods*, TM041.