

Orthophosphate and Total P

- Orthophosphate reacts with ammoniummolybdate to a yellow-colored phosphoromolybdate acid, that is reduced with ascorbic acid in the presence of antimony to a strongly blue colored complex. This color is measured photometrically as described in Norwegian Standard (NS 4724).
- Determination of total phosphorous in water after digestion/dissolution of samples with potassium peroxodisulphate ($K_2S_2O_8$) as described in Norwegian Standard (NS 4725).

The method is applicable on freshwater and seawater samples, but is not applicable for water with high organic carbon content. Maximum P-concentration is $500 \mu\text{g P L}^{-1}$. Samples with higher concentrations have to be diluted. Detection limit: $1 \mu\text{g P L}^{-1}$. Silicon and arsenic in the form of arsenate can interfere with the analysis, as these compounds also create a blue complex with molybdate

PRINCIPLE

Orthophosphate: In a sulphuric acid solution ($\approx 0.1 \text{ mol L}^{-1}$) orthophosphate reacts with molybdate and antimony (Sb III) forming a yellow-colored molybdatephosphorous complex. By reducing this complex by ascorbic acid a bluecolored heteropolycomplex (molybdenum blue) is formed.

This coloured complex is determined spectrophotometrically at $OD_{880\text{nm}}$. Samples with high organic carbon content need a stronger oxidation procedure. Interference with free chlorine is eliminated by the ascorbic acid.

Total-P: Complex inorganic and organic P-compounds will be transformed to orthophosphate by addition of peroxodisulphate under acidic conditions by boiling the samples (in teflon-containers) in an autoclave.

REAGENTS

All chemicals should be of PA quality.

$K_2S_2O_8$, H_2SO_4 , $C_6H_8O_6$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, $K(SbO)C_4H_4O_6 \cdot 0.5H_2O$, $Na_2S_2O_3 \cdot 5H_2O$, Na_2CO_3 , KH_2PO_4 , HCl, NaOH.

- **4M Sulphuric acid**
222mL concentrated sulphuric acid (95-97%, density 1.84 g mL^{-1}) is carefully diluted to 5L with d.d.d. water. The solution is stored at room temperature for 1 week.
- **Washing water**
95mL of the 4M sulphuric acid is diluted to 5L with d.d.d. water. The solution may be stored at room temperature for 1 month.
- **Acid water**
To 1L d.d.d. water 10mL 4M sulphuric acid is added. The solution is stored at room temperature for 1 month.
- **Hydrochloric acid for cleaning (1M)**
80mL conc. Hydrochloric acid (HCl, 37%, density 1.19 g mL^{-1}) is diluted with d.d.d. to 1L. The solution is stored at room temperature for 1 year.
- **Ascorbic acid solution (reagent B)**
12,4g ascorbic acid ($C_6H_8O_6$) is dissolved in 1000mL d.d.d. water.

- Molybdate reagent (reagent A)
232mg potassiumantimon(III)oxidetartrate hemihydrate ($K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O$, 99.5%) is dissolved in 1600mL d.d.d. water. 38,8mL conc. Sulphuric acid is added while stirring and cooling. It is important that the solution is completely cooled. Then 6g ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$) is added before the solution is diluted to 2000mL. The solution is stored at room temperature for 2 months. The flask should be packed in Al-foil in order to prevent photo-degradation.
- Phosphate stock solution, 200mg P L⁻¹.
0,8780 ± 0,0002g dried (105°C for 2 hours) potassium dihydrogen phosphate (KH_2PO_4) is dissolved in d.d.d. water and diluted to 1000mL. The solution is stored at room temperature for 1 year.
- Phosphate working solution, 10 mg P L⁻¹.
50,00mL of the P stock solution and 1mL chloroform ($CHCl_3$) is diluted with d.d.d. water to 1000mL in a volumetric flask. The solution is stored at room temperature for 1 year.
- Phosphate working solution, 1 mg P L⁻¹.
50,00mL of the P working solution 10 mg P L⁻¹ is diluted with d.d.d. water to 500mL in a volumetric flask. The solution cannot be stored.
- Standard solutions

µg P L ⁻¹	mL	Conc. of working solution	Final volume, mL
2	2	1	1000
5	5	1	1000
10	10	1	1000
25	25	1	1000
50	50	1	1000
75	75	1	1000
100	10	10	1000
250	25	10	1000
350	35	10	1000
500	50	10	1000

The calibration solution are added 9mL sulphuric acid, 4M, prior to dilution and 10mL sulphuric acid, 4M, after dilution. The calibration solutions are not oxidised. The solutions are transferred to 1L plastic bottles. The solution is stored at room temperature for 6 months.

- Control solutions
Control stock solution, approx. 50 mg P L⁻¹
Dissolve 0,8059g disodium-adenosin-5-monophosphate with 6 crystal water ($C_{10}H_{12}N_5Na_2O_7P \cdot 6H_2O$) in d.d.d. water. Add 10mL sulphuric acid, 4M, and dilute with d.d.d. to 1L in volumetric flask. The solution is stored at room temperature for 1 year.
Control solutions
The control stock solution is diluted 1:10 and is used to make three control solutions.
100:1000mL that after addition of 10mL sulphuric acid gives 485 µg P L⁻¹.
10:1000mL that after addition of 10mL sulphuric acid gives 48,5 µg P L⁻¹.
1:1000mL that after addition of 10mL sulphuric acid gives 4,85 µg P L⁻¹.
The solution is stored at room temperature for 1 year.

Samples are conserved by adding 1mL 4M sulphuric acid to 100mL sample. The analysis should be performed within 3 months.

OXIDATION

Shake sample bottle before transferring 20mL sample to a 20mL scintillation vial. Add $0,20 \pm 0,04$ g potassiumperoxodisulphate. Include three blind samples. Transfer 20mL d.d.d. to the scintillation vials, add 0,20mL 4M sulphuric acid and $0,20 \pm 0,04$ g potassiumperoxodisulphate. The control samples with 4, 40 and $400 \mu\text{g P L}^{-1}$ are also oxidised.

DETERMINATION

P is determined in two calibration ranges: $0 - 100 \mu\text{g P L}^{-1}$ and $100 - 500 \mu\text{g P L}^{-1}$. The analysis start with the calibration solutions, then 2 acid waters, 3 blind samples, control samples. Then 10 and 10 samples are analysed separated by 2 acid waters. End the analysis with a set of calibration standards.

In the $0 - 100 \mu\text{g P L}^{-1}$ the 4 and $40 \mu\text{g P L}^{-1}$ control sample is used. In the $100 - 500 \mu\text{g P L}^{-1}$ the $400 \mu\text{g P L}^{-1}$ control sample is used.

The limits for acceptance of the results from the control samples are as follows:

$4 \mu\text{g P L}^{-1}$ control sample: $3.0 - 5.0 \mu\text{g P L}^{-1}$

$40 \mu\text{g P L}^{-1}$ control sample: $38,5 - 41,5 \mu\text{g P L}^{-1}$

$400 \mu\text{g P L}^{-1}$ control sample: $390 - 410 \mu\text{g P L}^{-1}$

44 measurements of a potassiumhydrogenphosphate solution of $4 \mu\text{g P L}^{-1}$ gave mean value: $3.86 \pm 0.17 \mu\text{g P L}^{-1}$ (1 SD). Correspondingly 40 measurements of standard solution of $40 \mu\text{g P L}^{-1}$ gave mean value: $400.3 \pm 2.9 \mu\text{g P L}^{-1}$ (1 SD).



Figure 1: Standard solutions with blue phosphate molybdate complex.