NITRITE (NO$_2^-$) and NITRATE (NO$_3^-$) MEASUREMENTS

1. OBJECTIVE AND IMPORTANCE OF EXPERIMENT

Nitrogen exists in four forms that are of interest in water resources. These are ammonia (NH$_4^+$), nitrite (NO$_2^-$), nitrate (NO$_3^-$), and organic nitrogen.

Chemists working with wastes and freshly polluted waters learned that most of the nitrogen is originally present in the form of organic (protein) nitrogen and ammonia. As time progresses, the organic nitrogen is gradually converted to ammonia nitrogen, and later on, if aerobic conditions are present, oxidation of ammonia to nitrite and nitrate occurs. Waters in which most of the nitrogen was in the form of nitrate were considered to have been polluted a long time previously and therefore offered a little threat to the public health.

In 1940, it was found that drinking waters with high nitrate content often caused methemoglobinemia in infants. For this reason, the U.S. E.P.A. has set a maximum contaminant level requiring that the nitrate-nitrogen concentration not exceed 10 mg/L and the nitrite-nitrogen concentration not exceed 1 mg/L in public water supplies.
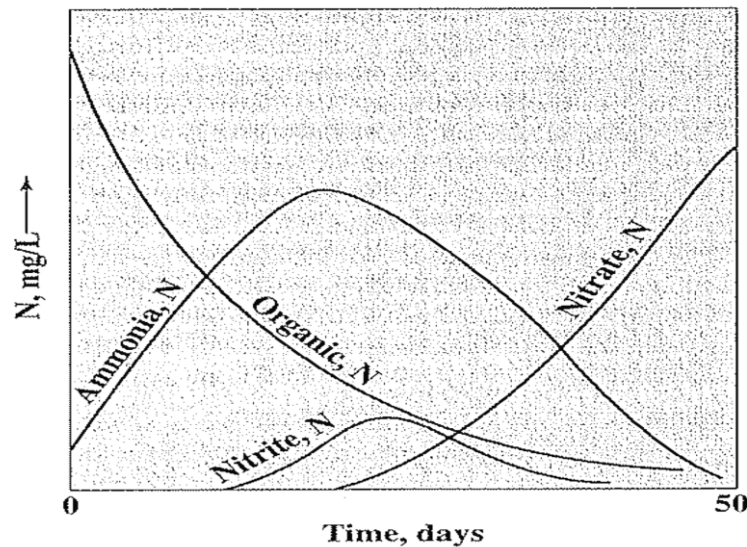

Figure 25.3
Changes occurring in forms of nitrogen present in polluted water under aerobic conditions.

1.1 Nitrite Nitrogen (NO$_2^-$–N)

Nitrite is determined through formation of a reddish purple azo dye produced at pH 2.0 to 2.5 by coupling diazotized sulfanilamide with *N*-(1-naphthyl)-ethyl-enediamine dihydrochloride (NED dihydrochloride).

The applicable range of the method for spectrophotometric measurements is 0,01 to 1 mg NO_2^-–N/L. Higher NO_2^- concentrations can be determined by diluting a sample.

Free chlorine, nitrogen trichloride (NCl_3), Sb^{3+}, Au^{3+}, Bi^{3+}, Fe^{3+}, Pb^{2+}, Hg^{2+}, Ag^+, chloroplatinate ($PtCl_6^{2-}$), and metal vanadate (VO_3^{2-}) interfere. Suspended solids must be removed by filtration.

To prevent bacterial conversation of NO_2^- to NO_3^- or NH_3, store at 4ºC.

1.1.1. EXPERIMENTAL PROCEDURE

1.1.1.1. Materials and Equipment

- Spectrophotometer (provides 540 nm wavelength and 1 cm light path or longer)
- 1 cm cuvette
- 50 mL volumetric flasks
- Pipette
- 0.45 μm filter paper (if necessary)
- Filtration tool
- Nitrite-free water (distilled water)
- 1 N HCl (if necessary)
- Color reagent
- Stock nitrite solution (dissolve 1.232 g $NaNO_2$ in water and dilute to 1000 mL = 250 mg N / L. Preserve with 1 mL $CHCl_3$ or prepare it daily)

1.1.1.2. Steps of the Experiment

➢ Take 50 mL sample and 50 mL nitrite free water for blank to the volumetric flasks.
➢ If sample contains suspended solids, filter through a 0.45μm filter paper.
➢ If sample pH is not between 5 and 9, adjust to that range with 1 N HCl or NH_4OH as required.
➢ Add 2 mL color reagent and mix.
➢ Between 10 min and 2 h after adding color reagent to samples and standards, measure absorbance at 543 nm.
➢ Pour blank into a cuvette and measure the absorbance.
➢ Repeat it for all samples and standards.
➢ Draw a calibration curve.

ABS	KONS (mg/L)
0.03	0.01
0.153	0.05
0.306	0.1
0.612	0.2
0.912	0.3
1.212	0.4
1.475	0.5

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$y = 0.3361x - 0.0028$
$R^2 = 0.9995$

KONS (mg/L) vs *ABS*
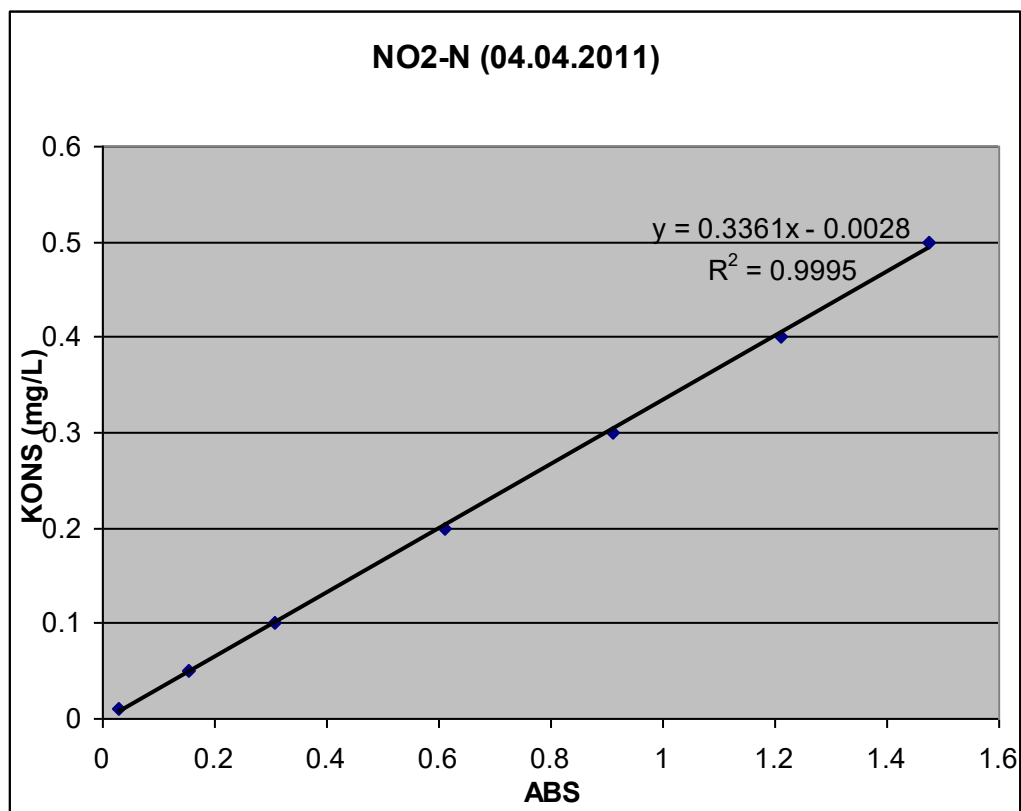
1.1.1.3. Calculations

Put the absorbance in the equation above. Calculate the concentration.

1.2. Nitrate Nitrogen (NO$_3^-$–N)

Measurement of UV absorption at 220 nm enables rapid determination of NO$_3^-$. Because dissolved organic matter also may absorb at 220 nm and NO$_3^-$ does not absorb at 275 nm, a second measurement made at 275 nm may be used to correct the NO$_3^-$ value. However, this

method is not recommended if a significant correction for organic matter absorbance is required.

Sample filtration is intended to remove possible interference from suspended particles. Acidification with 1 N HCl is designed to prevent interference from hydroxide or carbonate concentrations up to 1000 mg $CaCO_3$ / L. Chloride has no effect on the determination.

Dissolved organic matter, surfactants, NO_2^-, and Cr^{6+} interfere. Various inorganic ions not normally found in natural water, such as chlorite and chlorate, may interfere.

1.2.1. EXPERIMENTAL PROCEDURE

1.2.1.1. Materials and Equipment

- Spectrophotometer (for use at 220 nm and 275 nm wavelength and 1 cm light path or longer)
- 1 cm cuvette
- 50 mL volumetric flasks
- Pipette
- 0.45 μm filter paper (if necessary)
- Filtration tool
- Nitrite-free water (distilled water)
- 1 N HCl
- Stock nitrate solution (Dry potassium nitrate (KNO_3) in an oven at 105°C for 24 h. Dissolve 0.7218 g in water and dilute to 1000 mL = 100 mg NO_3^- - N / L. Preserve with 2 mL $CHCl_3$ / L. This solution is stable for at least 6 months.)

1.2.1.2. Steps of the Experiment

➢ Take 50 mL sample and 50 mL nitrite free water for blank to the volumetric flasks.
➢ If sample contains suspended solids, filter through a 0.45μm filter paper.
➢ Prepare a blank and NO_3^- calibration standards in the range 0 to 7 mg NO_3^- - N / L by diluting to 50 mL.
➢ Add 1 mL HCl solution and mix thoroughly.
➢ Pour blank into a cuvette and measure the absorbance.
➢ Repeat it for all samples and standards.
➢ Use a wavelength of 220 nm to obtain NO_3^- reading and a wavelength of 275 nm to determine interference due to dissolved organic matter.
➢ Draw a calibration curve.

1.2.1.3. Calculations

Subtract two times the absorbance reading at 275 nm from reading at 220 nm to obtain absorbance due to NO_3^-.

If correction value is more than 10% of the reading at 220 nm, do not use this method.

ABS	KONS. (mg/L)
0.028	0.1
0.05	0.2
0.105	0.4
0.211	0.8
0.362	1.4
0.517	2
1.425	6
1.619	7

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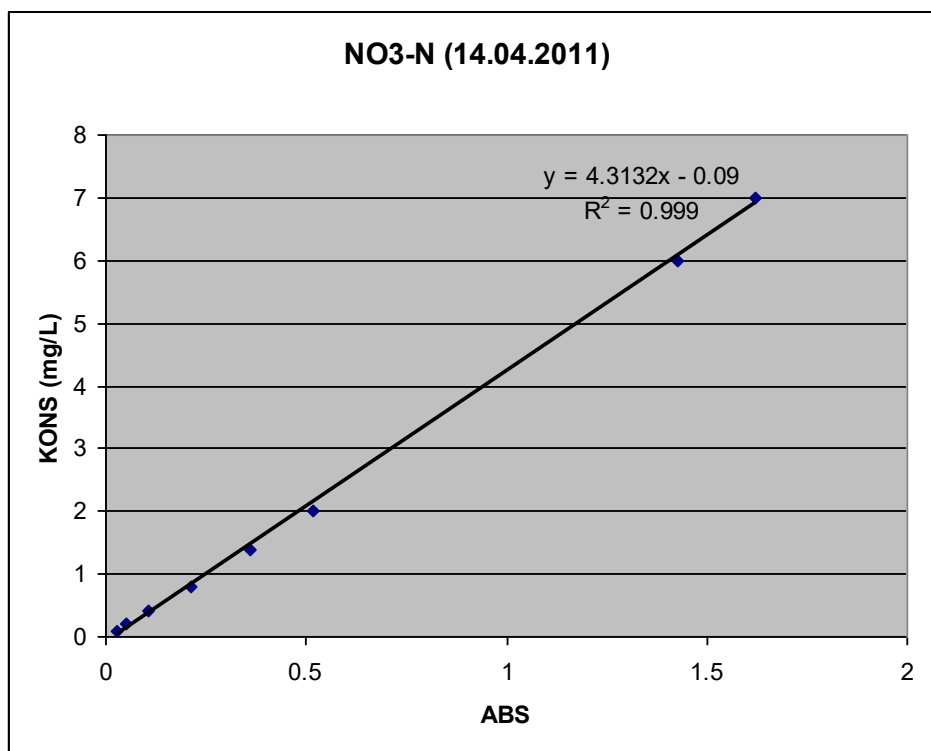
An example: Abs at 275 is 0.015 and abs at 220 nm is 0.98.

The real abs is = 0.98 – (0.015 x 2) = 0.98 – 0.03 = 0.95

0.03 is not more than 10% of 0.98 so this method is suitable for that sample.