




Universität Stuttgart

Methods for the determination of nitrate


Dr.-Ing. Michael Koch
Institut für Siedlungswasserbau, Wassergüte und Abfallwirtschaft
der Universität Stuttgart
Abteilung Hydrochemie
Bandtäle 2
D-70569 Stuttgart
Tel.: 0711 685 65444 / Fax: 0711 685 67809
E-Mail: Michael.Koch@iswa.uni-stuttgart.de



Universität Stuttgart

Applied methods

- **More than 10 different methods**
- Mostly ion chromatography and different spectrometric methods

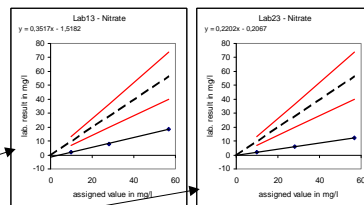
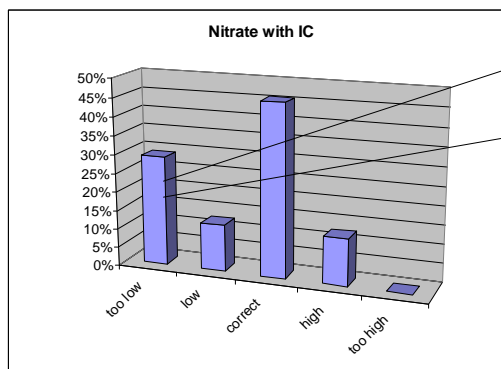


M. Koch – Methods for nitrate analysis – SACMET PT Workshop 2008 Kampala

Ion chromatography

- ISO 10304-1:1992
 - Water quality – Determination of dissolved fluoride, chloride, nitrite, orthophosphate, bromide, nitrate and sulfate ions – part 1: Method for water with low concentration
- Standard Methods (APHA/AWWA/WEF) – 4500-NO3-C
 - Determination of anions by ion chromatography
- Other IC method

Ion chromatography

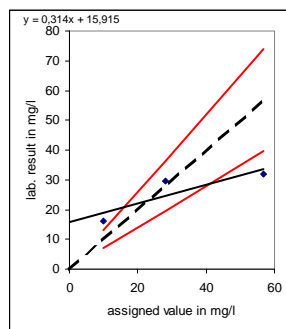


- Typical unit problem – nitrate-N instead of nitrate
- Otherwise almost all values would be within limits

Nitrate electrode

- Standard Methods (APHA/AWWA/WEF) – 4500-NO3-D
 - Principle: Selective sensor that develops a potential across a thin, porous, inert membrane holding an ion exchanger
 - Application range: 0,6 to 6200 mg/l NO_3^-
 - Interferences: Cl^- , if weight ratio $> 2,26$ ($\text{Cl}^- : \text{N} > 10:1$), removed by using a Ag_2SO_4 -containing buffer solution.
 - Precision: $\pm 2,5\%$ in concentration is expected (confidence level?)
 - Trueness: depending on correct calibration

Nitrate electrode

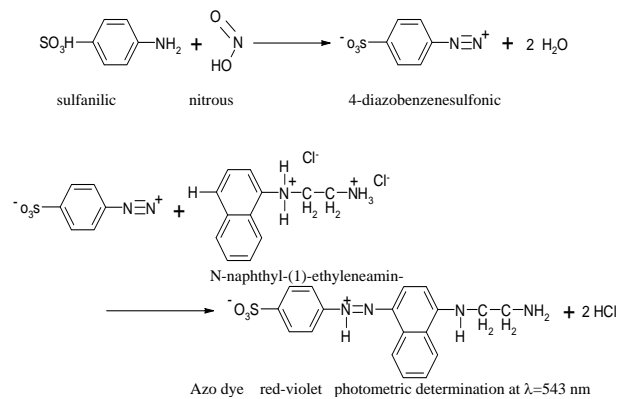


• ???

Cd reduction method

- Standard Methods (APHA/AWWA/WEF) – 4500-NO3-E
 - Nitrate is reduced to nitrite in the presence of Cd, The nitrite produced is determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride, followed by colorimetric measurement at 543 nm

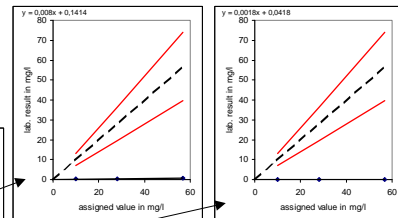
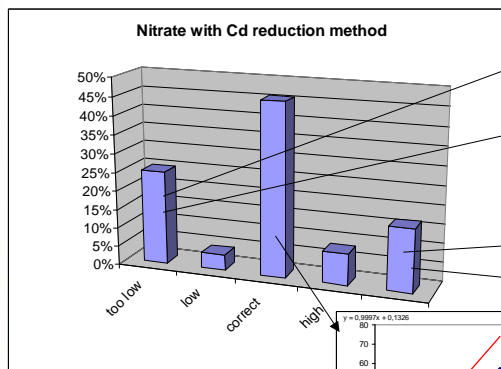
Cd reduction method



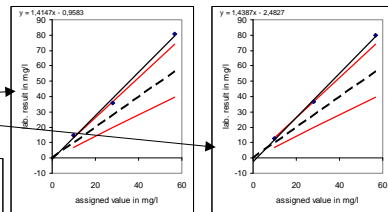
Cd reduction method

- Application range: 0.04 to 4.4 mg/l NO_3^-
- Interferences: Iron, copper and other metals above several milligrams per liter lower reduction efficiency. This interference is removed by adding EDTA
- Precision: $\pm 1\%$ in concentration was reported for a single lab at 4 mg/l Nitrate
- Trueness: depending on correct calibration; recovery was reported to 100%

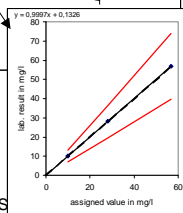
Cd reduction method



Gross errors – no reduction?



Most probably calibration errors

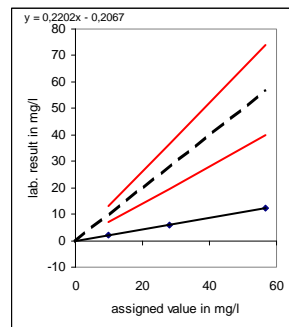


Cd reduction method – CFA/FIA

- ISO 13395:1996 - Water quality – Determination of nitrite nitrogen and nitrate nitrogen and the some of both by flow analysis (CFA and FIA) and spectrometric detection
 - Principle: Automated Cd reduction method
 - Application range: 0.9 to 88 mg/l NO_3^-
 - Interferences: pH has to be 6.5 to 7.5.
 - Precision: for drinking water: VC 2.6 to 6.3 %
 - Trueness: Recovery 102 – 104%

Cd reduction method – CFA/FIA

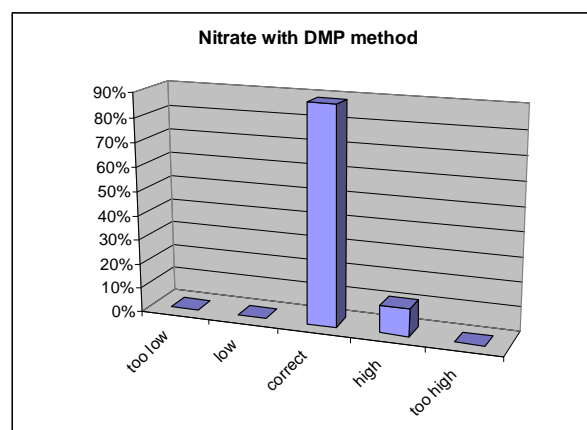
- Wrong unit



2,6 Dimethylphenol method

- ISO 7890-1:1986 (withdrawn 07/2005) / DIN 39405-9-2:1979 Water quality -- Determination of nitrate -- Part 1: 2,6-Dimethylphenol (2,6-xylenole)spectrometric method
 - Principle: Reaction of nitrate with 2,6-Dimethylphenol to 4-Nitro-2,6-dimethylphenol in acidic solution, followed by colorimetric determination at 324 nm
 - Application range: 2 to 110 mg/l NO_3^-
 - Interferences: Cl^- , if ratio > 2.3
- Also realized as Merck cuvette test

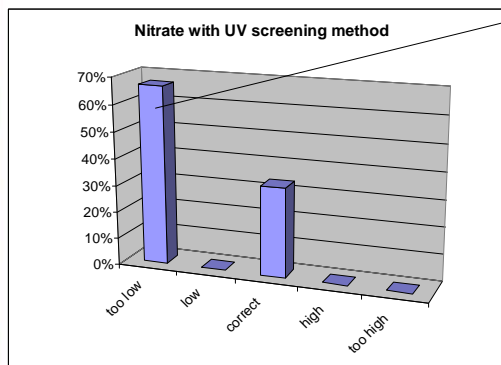
2,6 Dimethylphenol method



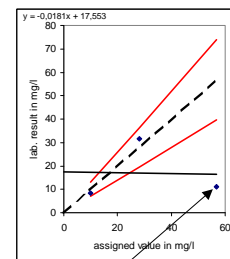
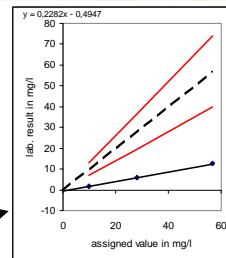
Direct UV screening method

- Standard Methods (APHA/AWWA/WEF) – 4500-NO₃-B
 - Principle: Direct UV extinction measurement at 220 nm
 - Application range: only for screening
 - Interferences: dissolved organic matter

Direct UV screening method



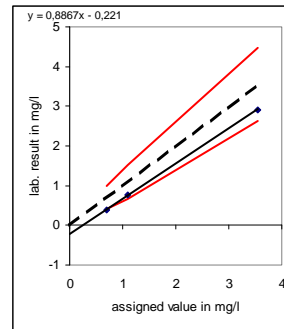
Wrong unit!



Gross error

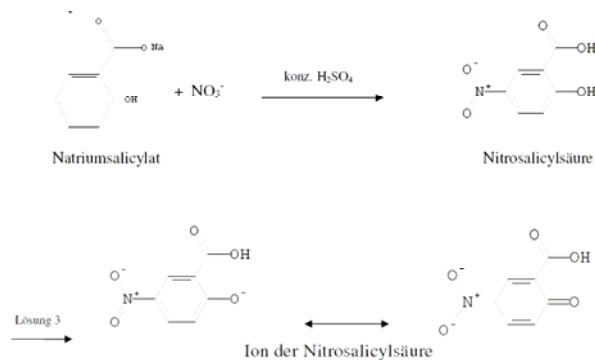
Phenol-2,4-disulfonic acid method

- Principle:
 - Reaction of nitrate with phenol-2,4-disulfonic acid to 6-nitro-2,4-disulfonic acid.
 - Reaction with ammonia to triammonium-nitro-phenol-disulfonate (yellow)

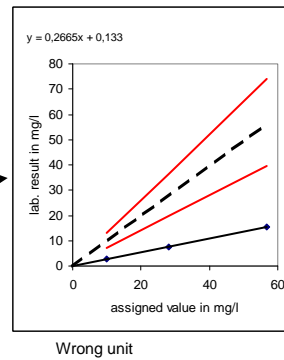
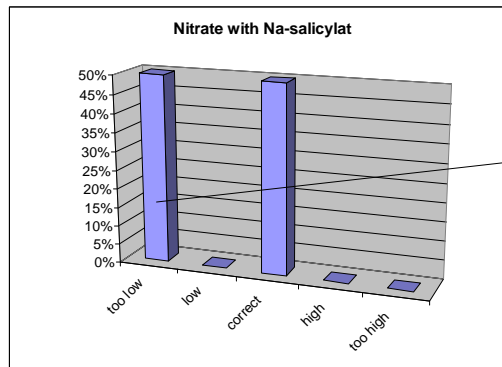


Na-salicylat method

- Reaction of nitrate with Na-salicylat, addition of sodium hydroxide and potassium sodium tartrate results in yellow coloured ion, colorimetric determination at 420 nm

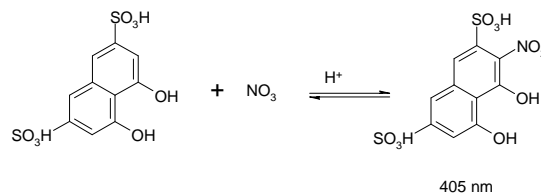


Na-salicylat method



Chromotropic acid method

- Principle: reaction of nitrate with chromotropic acid to the mononitro derivate



- Only one value report – that was much too high

Other methods

- SANS 5210:2006 →→↑
- Spectrophotometer ↑→→
- Lab SOP based on UV/VIS technique →→↓
- UV-VIS Spectrophotometric method (4x)
↓↓↓ ↑↑→ ↓↓↓ ↑↑↑
- Steam distillation ??? →→→
- Palintest photometric method →↓↓↓
- Colorimetric – Phenol derivation →→→

Conclusions

- The following methods seem to deliver reliable results
 - Ion chromatography
 - Cd reduction method
 - 2,6-Dimethylphenol method
 - Na-salicylat method
- Be aware of reporting in correct units
- Be careful with calibration



How to solve this lack of harmonization?

- Recommendation by SADCWATERLab?
- Standard procedure written by SADCWATERLab?
- What is your opinion?