מודוטק בע"מ

יום עיון מדידות אנליטיות – ISA ישראל

2/12/2009

מרצה: שמוליק אוסטר

אצלנו כל טיפה נחשבת

O_2 measurement

O_2 measurement

why measuring oxygen

oxygen plays a key role in many biological and chemical processes:

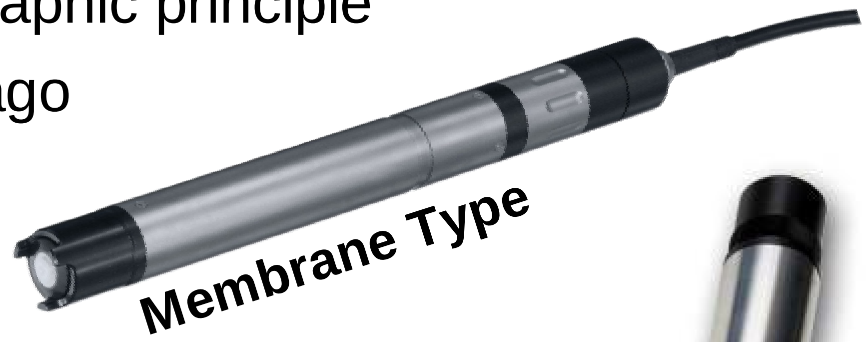
- waste water treatment
- fish-farming
- river/fresh water monitoring
- boiler feed water - corrosion

O_2 measurement

- electrochemical method

  Clarke type electrode, polarographic principle

  - developed approx. 60 years ago
  - **WTW: 20 years of field-use, more than 20.000 soled**



- optical method

  based on dynamic quenching of fluorescent light by oxygen, found by Kautsky in the 1930`s

  - since 1980`s medical application
  - since 1990`s marine applications
  - **relatively new in waste water applications**

electrochem. O_2 measurement

electrochemical detection of O_2

Membrane Type

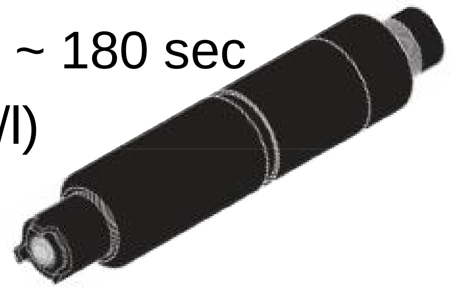
electrochem. O_2 measurement

sensor types

Membrane Type(also as sea-water version)

universal sensor, durable 50 µm membrane, response time ~ 180 sec

=> ideal for general oxygen control/measurement (0-60 mg/l)



Membrane Type for low levels

improved response time ~ 30 sec (25 µm membrane) and resolution

=> ideal for low level O_2 control e.g. denitrification process (0-20 mg/l)

Membrane Type for very low levels

similar performance as TriOxmatix 701, but for trace level O_2 concentration

=> ideal for boiler feed water, drinking water purification, ultra-pure water applications (0-2 mg/l)

electrochem. O_2 measurement

polarographic O_2 sensors:

- slow sensor drift **=> regular calibration** needed
- when changing membrane or electrolyte:
  - surfaces of the electrodes have to be polarized
  - a steady state has to be obtained (depletion of oxygen in electrolyte and membrane)
- self-diagnosis system: SensReg & SensLeck
- consumes oxygen => **flow needed**
- poisoned by **H_2S**

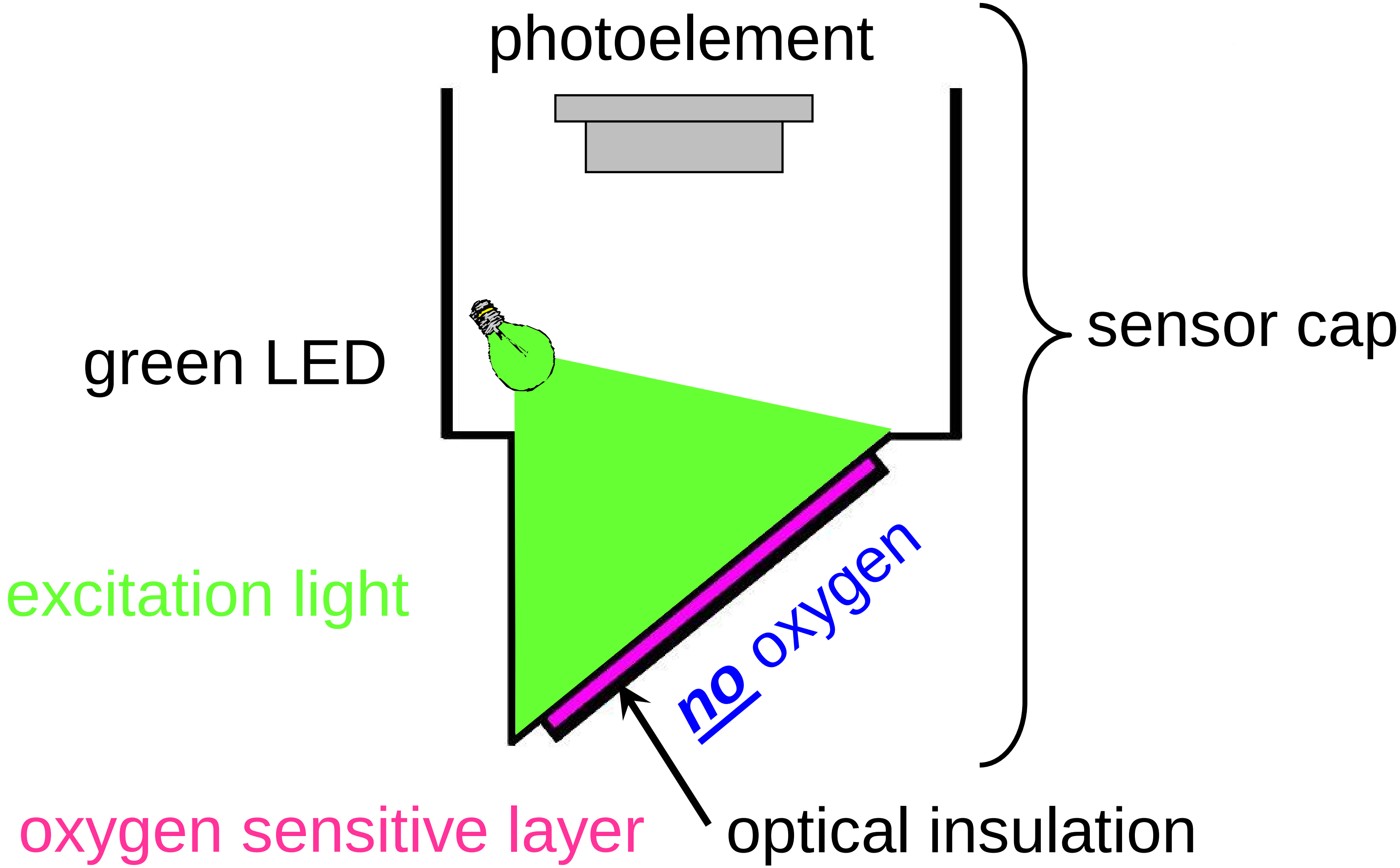
no problem in “normal” waste water applications optical O_2 measurement

optical detection of O_2

Optical Type

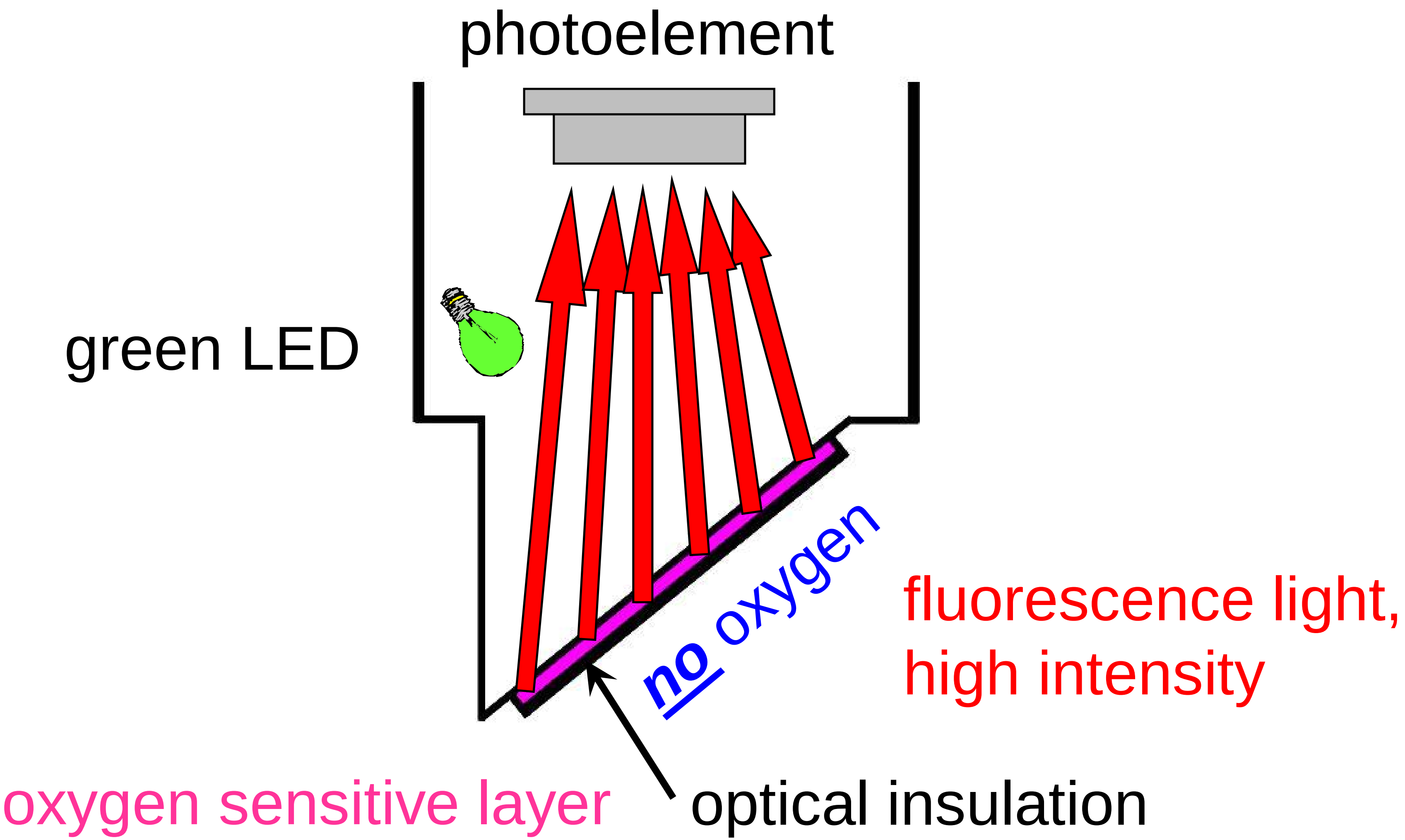
optical O_2 measurement

principle of optical O_2 sensor



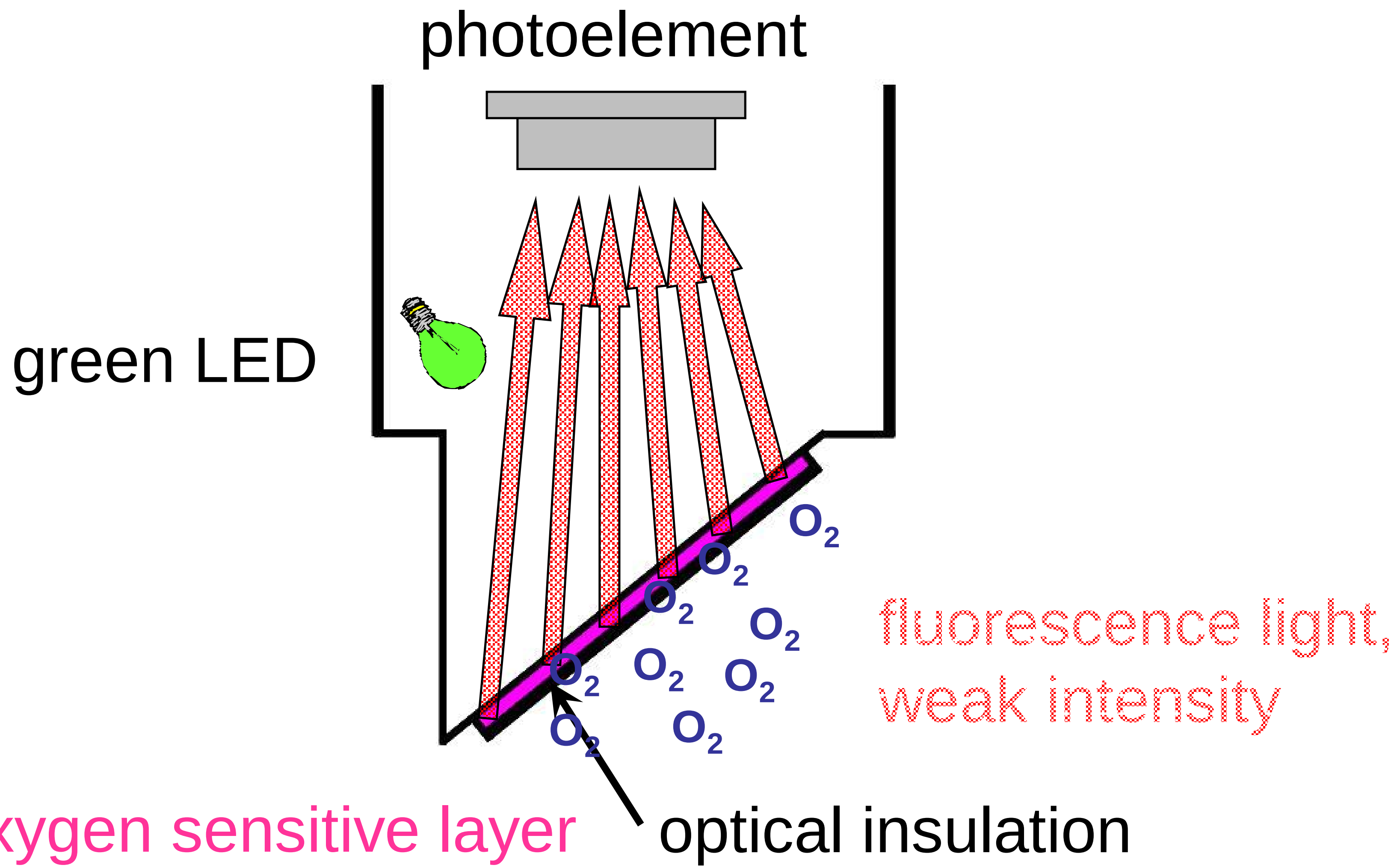
optical O_2 measurement

principle of optical O_2 sensor



optical O_2 measurement

principle of optical O_2 sensor



optical O_2 measurement

principle of optical O_2 sensor

no oxygen present:

high fluorescent light intensity

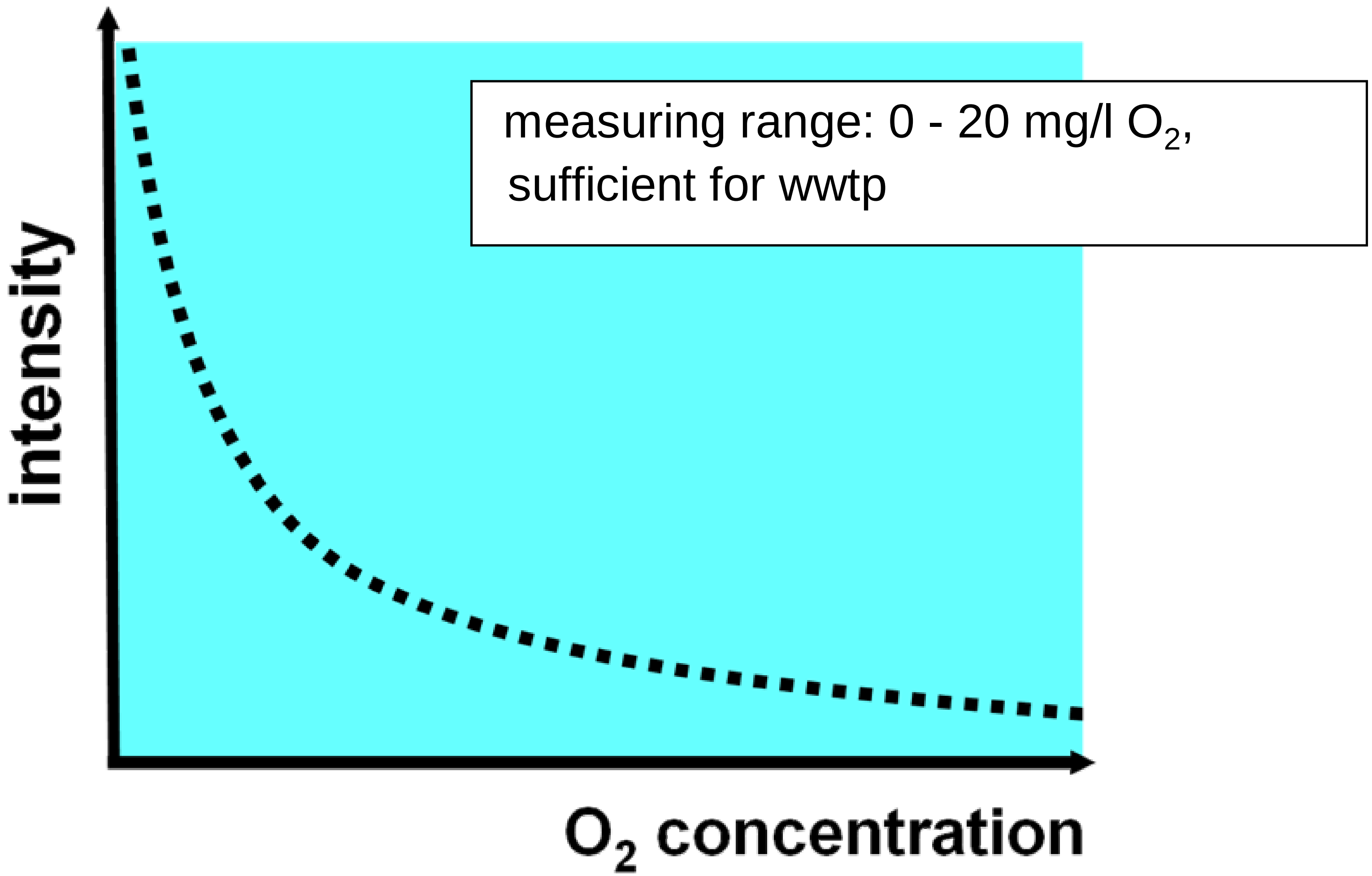
oxygen present:

weak fluorescent light intensity

optical O_2 measurement

principle of optical O_2 sensor

<u>nonlinear</u> dependence



optical O_2 measurement

new standard for optical O_2 measurement

- **high accuracy from the first moment**
- **high stability**
- **low maintenance**

optical O_2 measurement

high accuracy from the first moment

“intelligent membrane”:

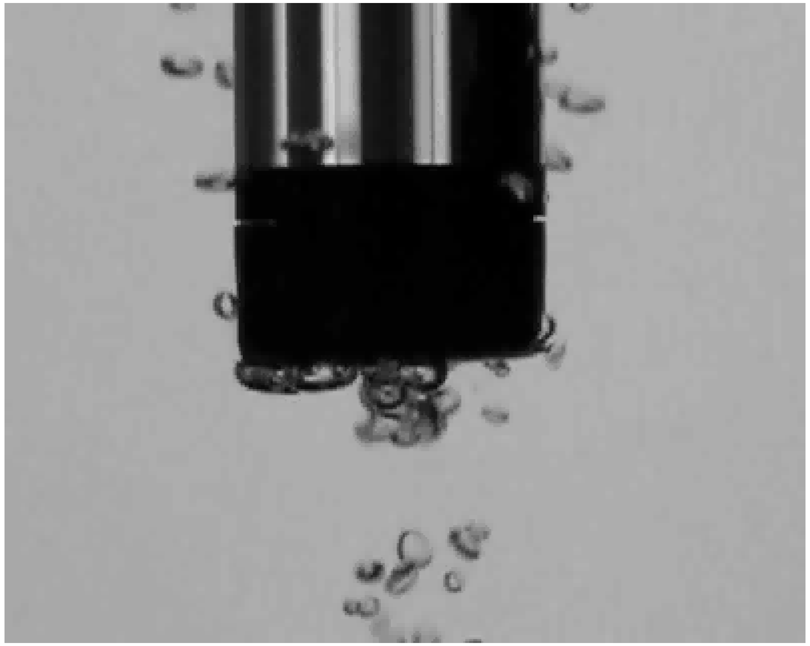
- each membrane cap is individually factory calibrated
- all data is stored in a memory chip in the cap
- data is automatically transmitted when the cap is attached to the sensor

=> plug and play

optical O_2 measurement

high accuracy from the first moment

“membrane angle of 45°”



conventional design:

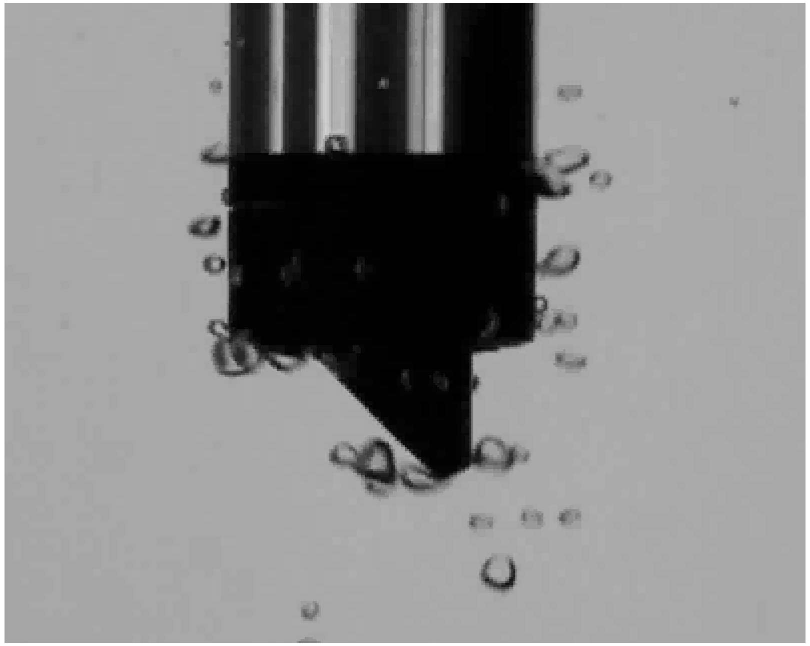
influence of air bubbles

=> can lead to O_2 overestimation

optical O_2 measurement

high accuracy from the first moment

"membrane angle of 45°"



45° angle design:

no influence of air bubbles

=> correct O_2 values, independent of mounting

optical O_2 measurement

high stability

"green light technology":

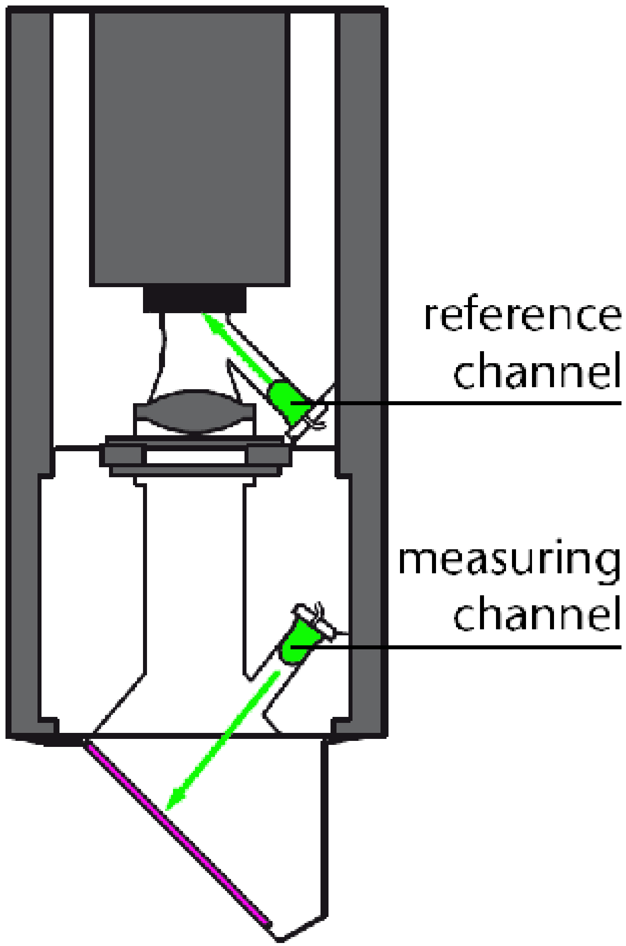
- "soft" excitation light compared to blue light
- prevents bleaching of sensing dye

=> stable dye, no drift

optical O_2 measurement

high stability

“equal path reference system”



- identical optical paths for measuring and reference channel
- identical components for measuring and reference channel

=> minimum of drift of the optical system

optical O_2 measurement

low maintenance

- changing sensor cap every 2 years
- no use of electrolyte
- no calibration
- no polarization time

=> low maintenance, low costs

optical O_2 measurement

sensor types

Optical Type Standard Condition

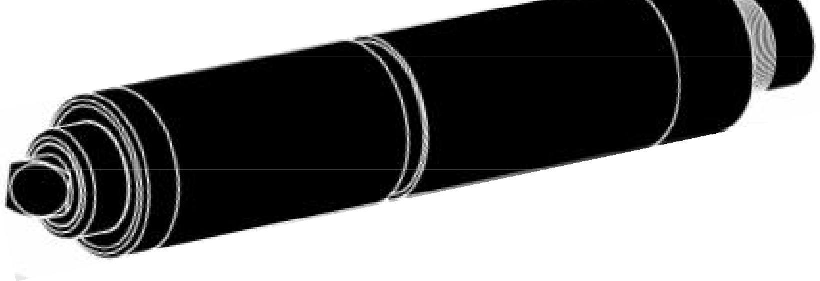
universal sensor, response time ~ 150 sec

=> ideal for general oxygen control/measurement (0-20 mg/l)

Sea water Version

sea water version, same performance as “normal” Optical Type

=> for fish-farming and applications with high chloride concentrations (0-20 mg/l)



optical O_2 measurement

advantages

- free of calibration, highly accurate
- stable signal over 2 years
- plug and play, no watering effect of membrane
- no influence of air bubbles
- no special mounting equipment needed

ISE measurements of

NH_4 & NO_3

ISE measurement

measuring systems for nitrogen parameters

in-situ ISE sensors

parameters: NH_4^+ & NO_3^-

AmmoLyt®Plus: NH_4^+

NitraLyt®Plus: NO_3^-

VARiON®Plus: NO_3^- & NH_4^+

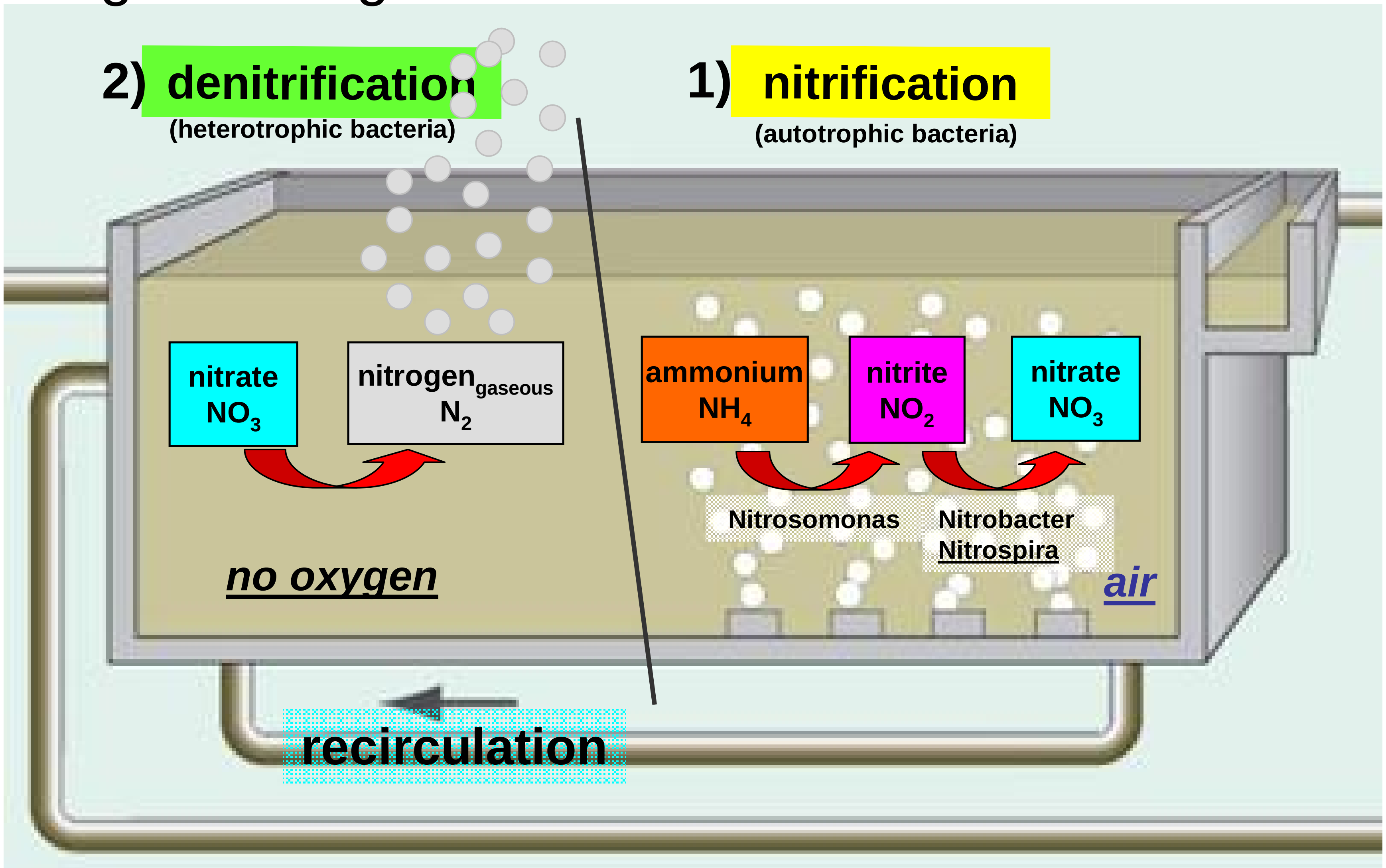
ISE measurement

reasons to measure ammonium- and nitrate

- **control/optimization of nitrification/denitrification**
- **load/peak load detection**
- **controlling discharge values**

ISE measurement

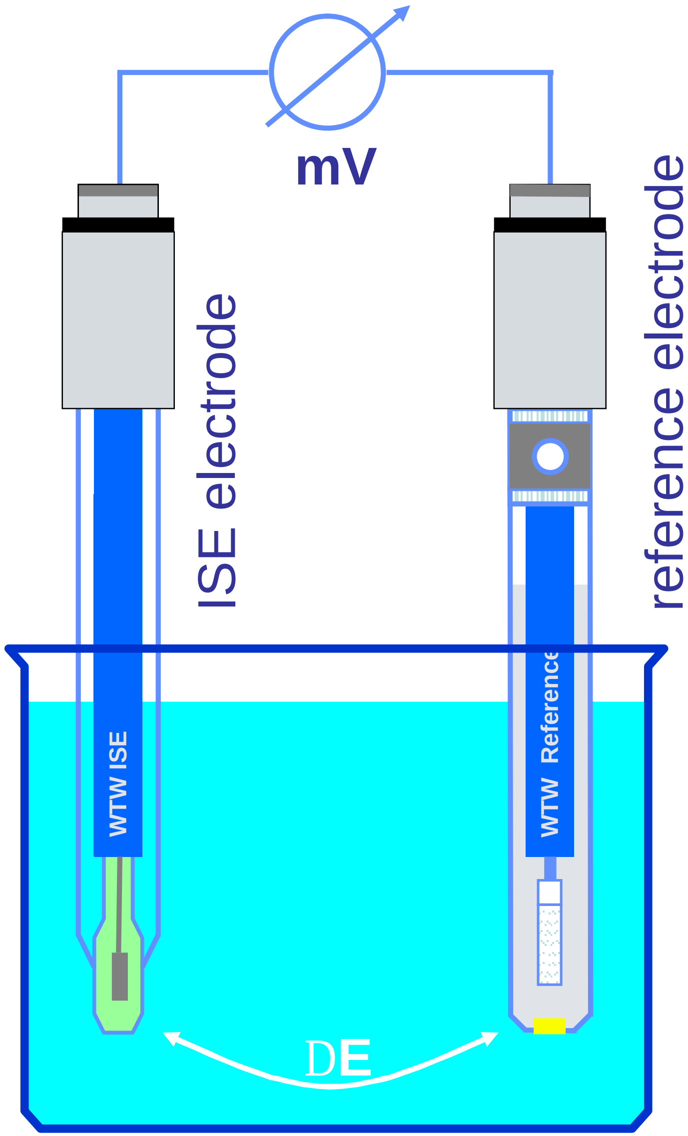
biological nitrogen elimination



ISE measurement

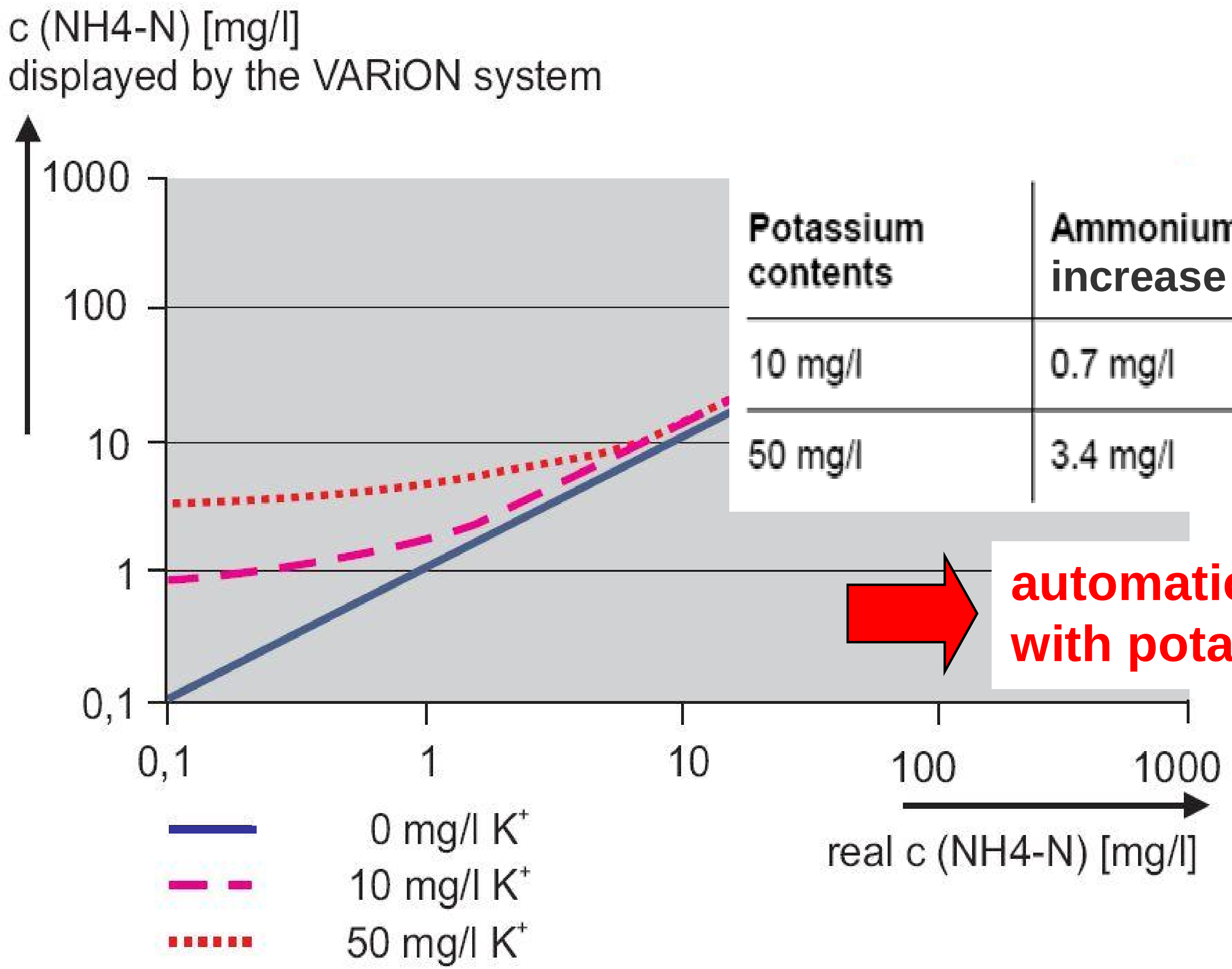
potentiometric principle

- sensor consists of ISE measuring electrode and reference electrode
- potential-difference of these electrodes is measured with a voltmeter
- potential difference is function of activity of the measured ion in the measuring solution



ISE measurement

NH_4: interference by potassium-ions

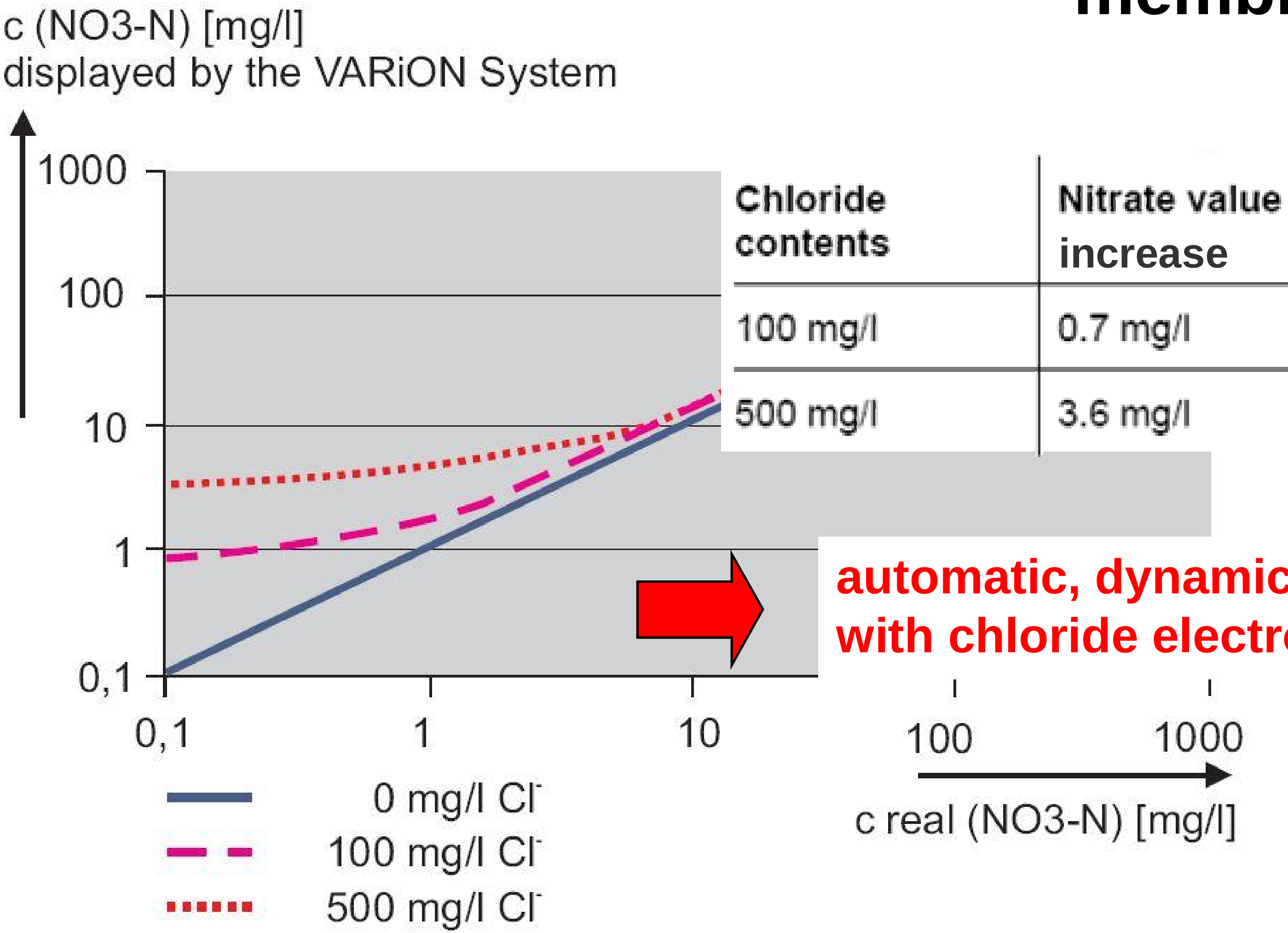


Potassium contents	Ammonium value increase
10 mg/l	0.7 mg/l
50 mg/l	3.4 mg/l

automatic compensation with potassium electrode

ISE measurement

NO_3: interference by chloride-ions: **normal nitrate membrane**



Chloride contents	Nitrate value increase
100 mg/l	0.7 mg/l
500 mg/l	3.6 mg/l

automatic, dynamic compensation with chloride electrode

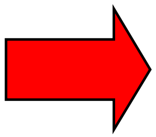
ISE measurement

NO_3: interference by chloride-ions

new high selectivity (hs) NO_3 membrane

interference reduced by factor of 4

Chloride contents	Nitrate value increase
100 mg/l	0.2 mg/l
500 mg/l	1.0 mg/l



no compensation needed for chloride range of 0-200 mg/l

ISE measurement

new high selectivity (hs) membrane

no compensation needed for chloride range of 0-200 mg/l

manual or automatic compensation with Cl-electrode when chloride > 200 mg/l

new display/output of potassium value

beside NH_4 and NO_3, also K can be used as value

ISE measurement
applications

influent (not always possible):

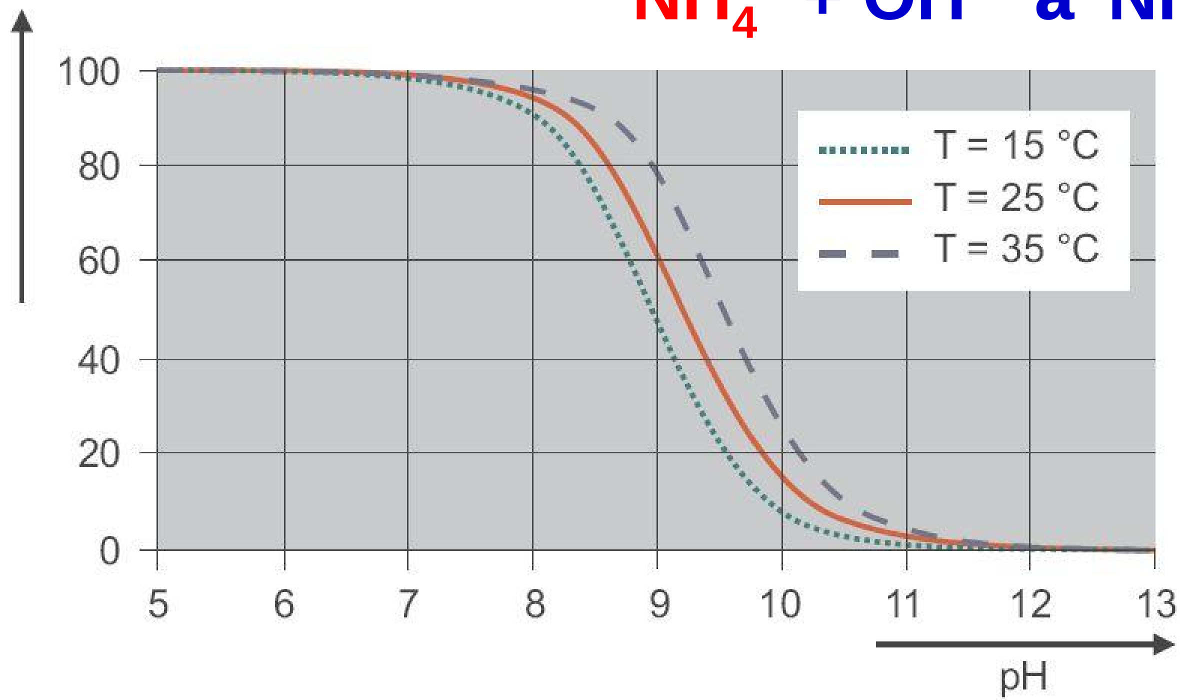
- load detection
- peak load detection
- inflow control

ISE measurement

influence of pH on ammonium measurement:

ammonium-ammonia-equilibrium

NH_4^+ + OH^- à NH_3 + H_2O



- **uncompensated NH_4^+ detection possible up to approx. pH 8,5**
- **pH values > 8,5 NH_4^+: detection requires pH compensation**

ISE measurement

applications

biological basins (main application)

- NH_4 measurement

  => control of aeration (energy optimization)

  => complement to O_2-measurement

- NO_3 measurement

  => control of recirculation to denitrification

  => process optimization

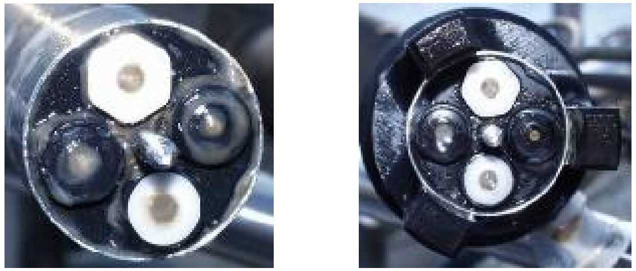
- **NH_4 & NO_3 also suitably for SBR reactors with high solid concentrations**

ISE measurement

air-pressure cleaning system

ISE measurement

no cleaning | **air-pressure cleaning**



after 5 weeks

after 8 weeks

after 10 weeks

no cleaning | **air-pressure cleaning**

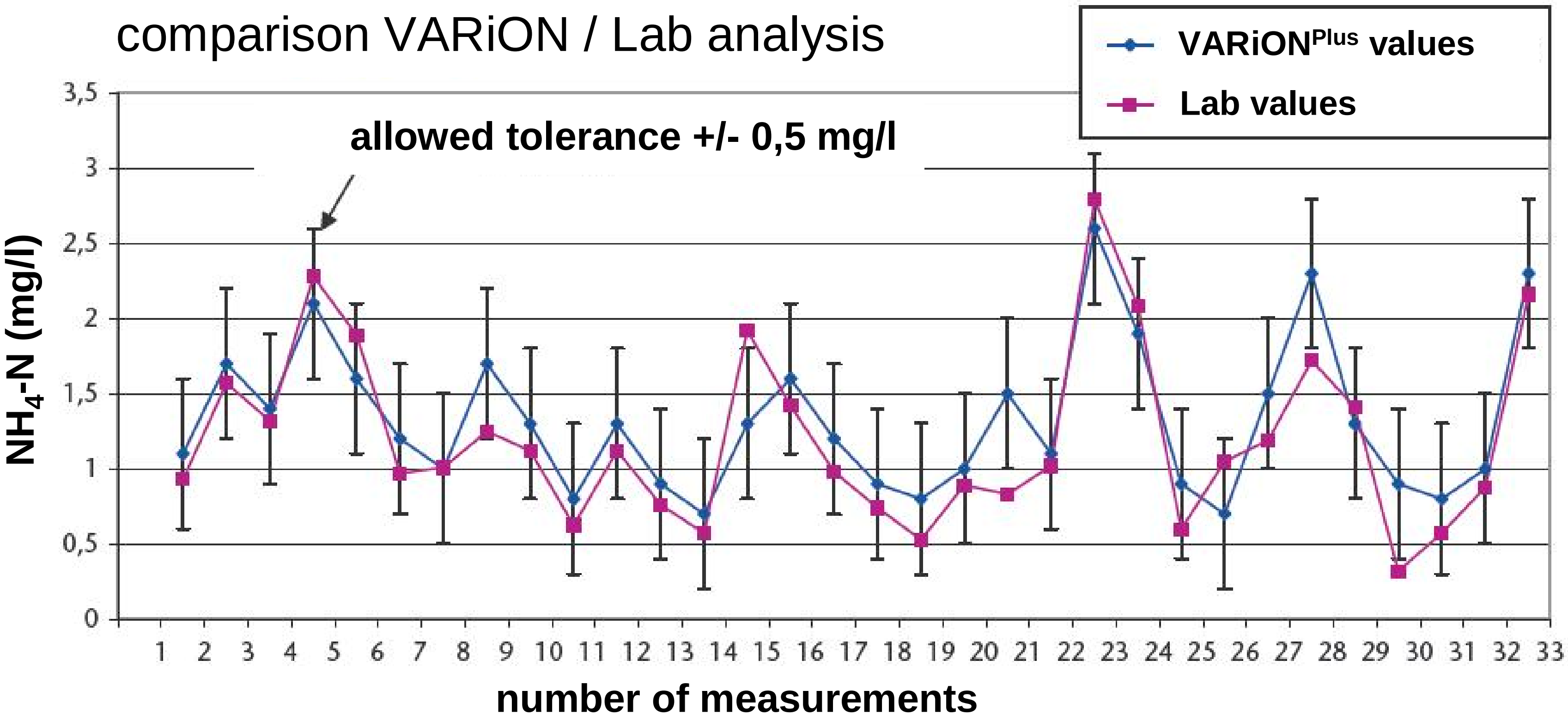
after 11 weeks

after 12 weeks

after 14 weeks

ISE measurement

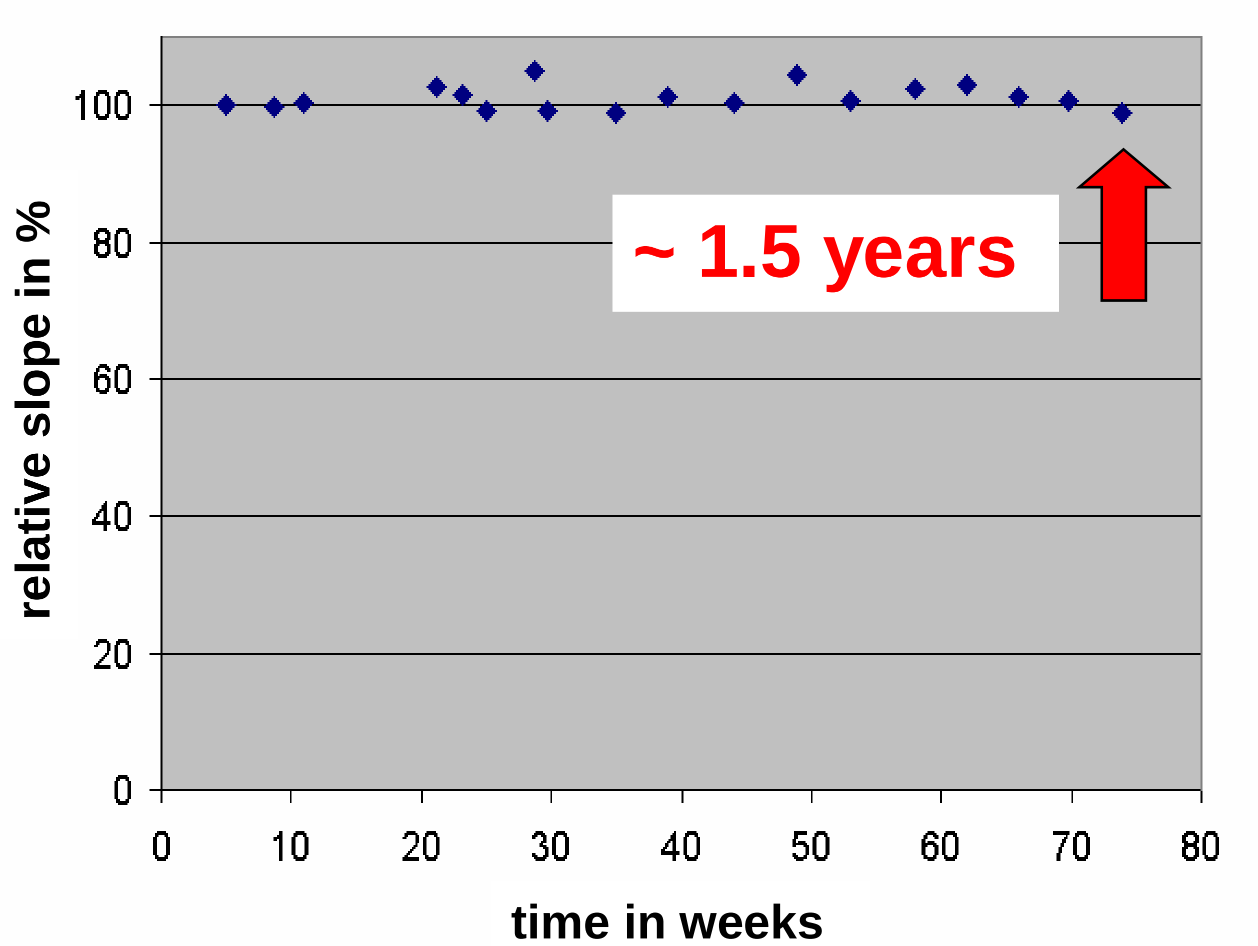
measurement accuracy



important: samples for Lab analysis have to be directly filtrated

ISE measurement

stability of the measuring signal



ISE measurement

technical data

Technical Data VARiON®*Plus*		
Maximum Configuration	Common reference electrode, two measuring electrodes, one compensation electrode	
	Ammonium Measurement	**Nitrate Measurement**
Integrable Electrodes: Reference Electrode Measuring Electrode Compensation Electrode	 VARiON®*Plus* Ref VARiON®*Plus* NH_4 VARiON®*Plus* K	 VARiON®*Plus* NO_3 or VARiON®*Plus* NO_3-HS VARiON®*Plus* Cl
Measuring Ranges / Resolution Compensation Ranges	NH_4-N: 1 ... 1,000 mg/l / 1 mg/l; 0.1 ... 100 mg/l / 0.1 mg/l NH_4^+: 1 ... 1,290 mg/l / 1 mg/l; 0.1 ... 129.0 mg/l / 0.1 mg/l K+: 1 ...1,000 mg/l / 1 mg/l	NO_3-N: 1 ... 1,000 mg/l / 1 mg/l; 0.1 ... 100 mg/l / 0.1 mg/l NO_3^-: 5 ... 4,500 mg/l / 1 mg/l; 0.5 ... 450.0 mg/l / 0.1 mg/l Cl^-: 1 ...1,000 mg/l / 1 mg/l
Temperature Measurement and Compensation	Integrated NTC thermistor, Range 32 °F ... 104 °F (0 °C ... +40 °C), Accuracy ±0.5 K, Resolution 0.1 K, t_{95} < 20 s	
Calibration Procedures	2-point-calibration with multiple standard solutions, calibration against any reference value	

ISE measurement

advantages

factory calibration

all electrodes are factory calibrated & long term stable

=> calibration possible, but not recommended

matrix adjustment

to ensure optimal functionality of ISE sensors
regular matrix adjustments are required

precise measurement

improved ISE membranes ensure high accuracy,
without any influence of color of the process water

robust electrodes

metal grid protect membranes => cleaning with brush possible

ISE measurement

ISE sensors Nitrate, Ammonia & VARiON

- full compensated VARiON possible with new NO_3-hs membrane
- automatic compensation of one interference ion
  => either potassium, or chloride
- factory calibrated, no calibra
- high accuracy (regular matrix
- lifetime of electroc
- all electrodes can
  individually, autom
- huge measuring range for NO_3^- & NH_4^+: 0 – 1000 mg