August 24th, 2022

Optical Reagent-Free Measurement

COD, Nitrate and Nitrite with photoLab® 7600 UV-VIS

WEBINAR //
SUSANNE GOLLOR & QUENTIN MIRABEL

Today's Topics

① Xylem Intro

② Basics of Opt-RF

③ Opt-RF Implementation

④ Question & Answer Session

House Keeping

- We are recording!
- A link to the recording & a pdf version of this presentation will be shared in a follow up email
- Ask your question at any time in the "question" section of your Zoom screen
- All questions will be answered at the end of the webinar

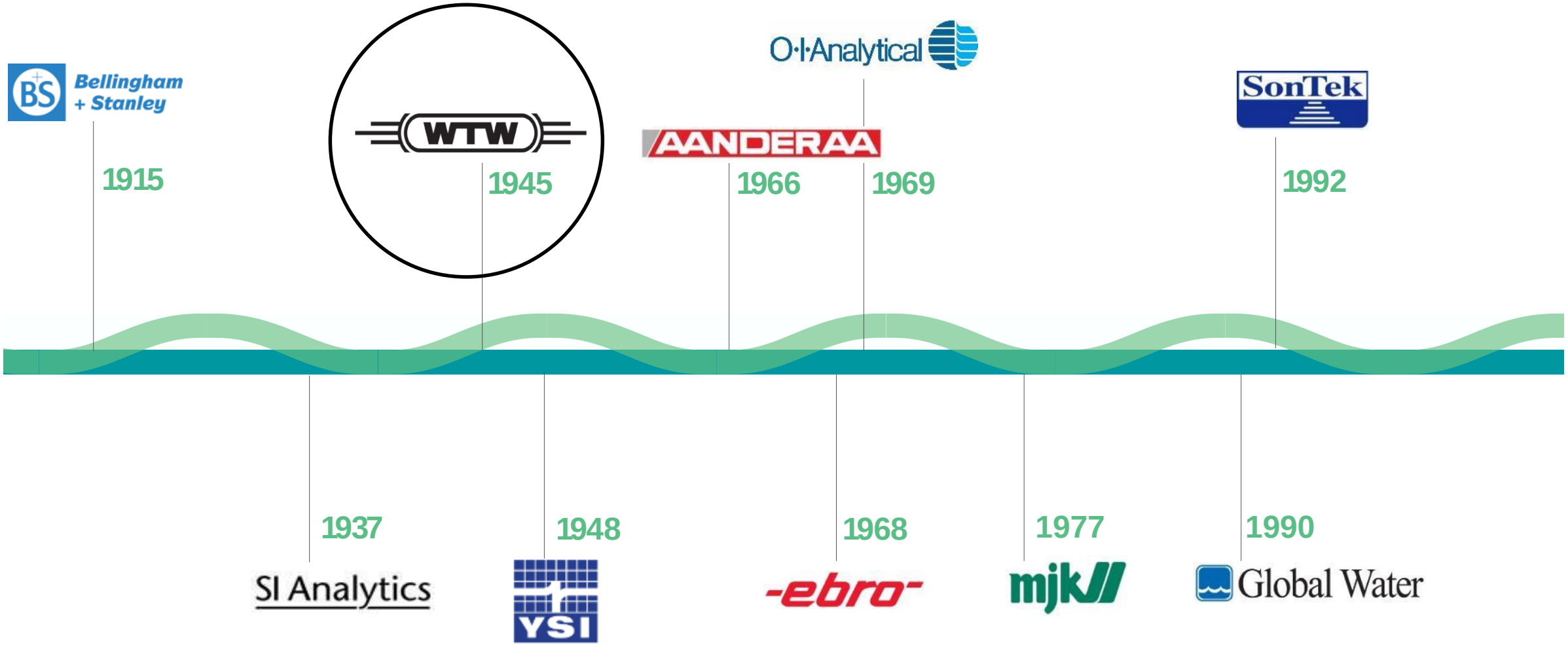
What is Xylem?

Xylem (XYL) is a leading

global water technology company committed to developing innovative technology solutions to the world's water challenges.

$5.2bn	**18,000**	**150**	**6**
Revenue	Employees	Countries	Continents

Bringing together the most progressive Analytics brands



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Factories & EM Regional Offices

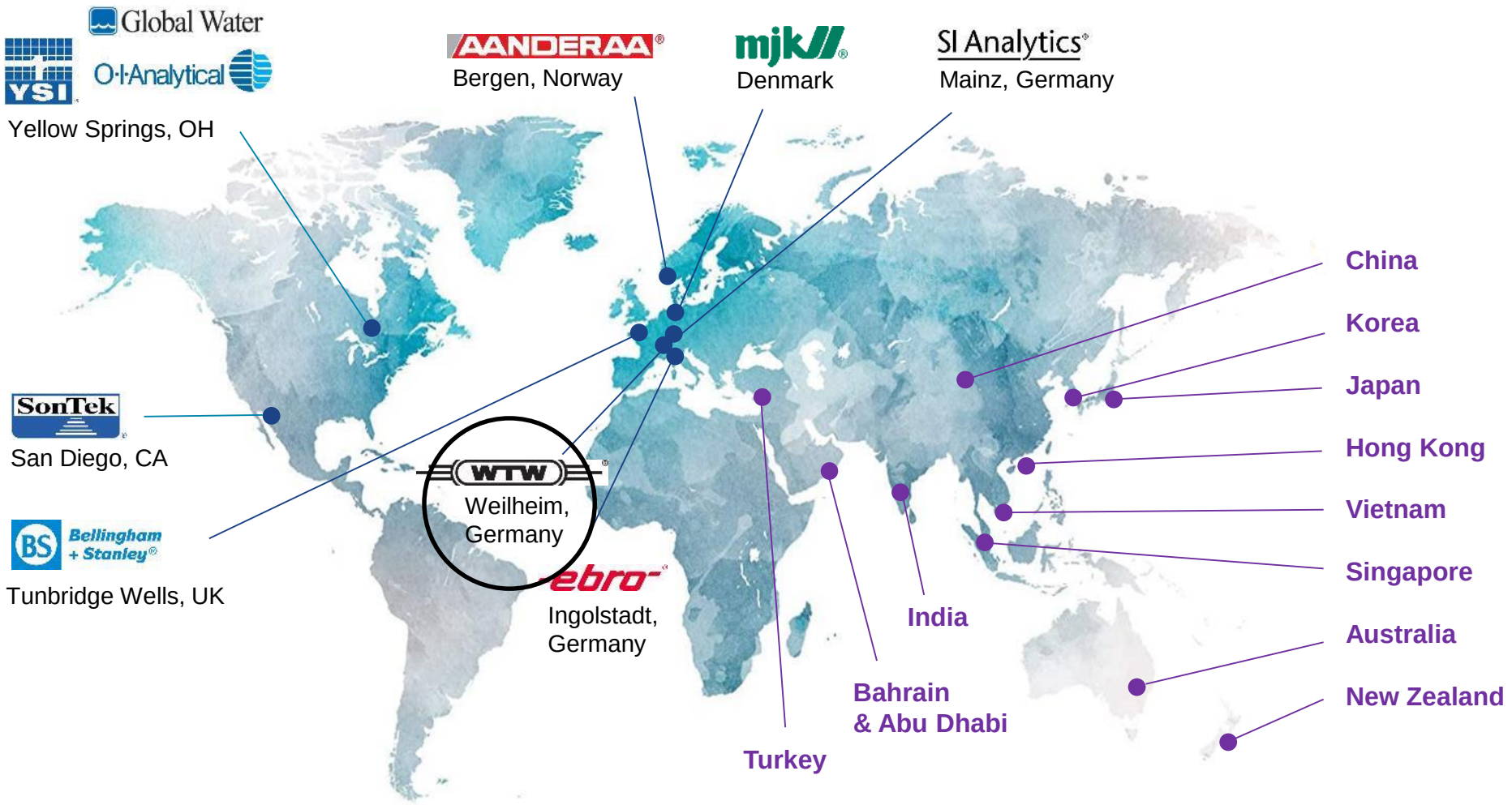
xylem
Let's Solve Water

Analytics:

60 Facilities

23 Companies

3300 employees



WTW
a xylem brand

Market Segments

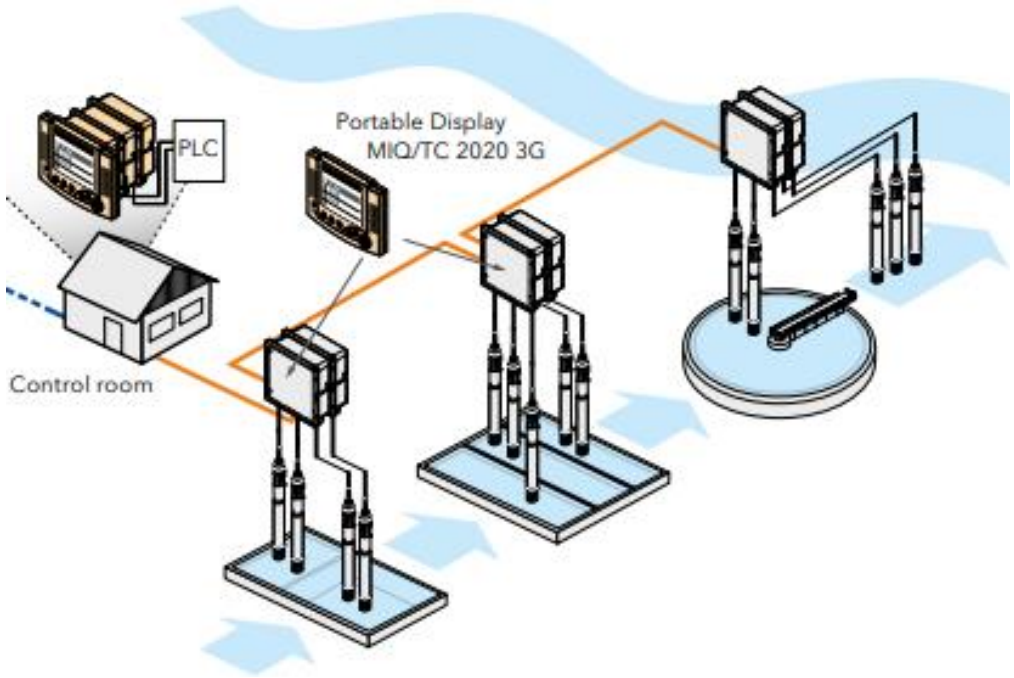
- Desalination plants
- Groundwater
- Surface water, rivers, lakes
- Aquaculture
- Ports & harbors

- QA & QC Lab
- Pharmaceuticals
- Industrial
- Food and beverage

- Drinking water
- Domestic wastewater
- Industrial wastewater

WTW - reliability, operational safety and versatility

Process / Online



Laboratory

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Spectrophotometer **photoLab® 7600 UV-VIS**

One for all – all in One

- **Routine analysis:**
  Test programs for all standard parameters

- **Pioneering:**
  Spectral analysis - **OptRF**
  Optical **R**eagent-**F**ree Measurement in the UV range for COD, Nitrate, Nitrite

- **Multistep measurement procedures**
  e.g. chlorophyll determination in water
  enzymatic test kit support, color for wine quality

- Comprehensive **color measurement**, CIE based & standard methods

The importance of COD measurement

Chemical oxygen demand (COD) :

COD is a sum parameter for determination of organic compound in waste water and is measured and determined as the equivalent of its oxidation in O_2 mg/l.
The oxygen required for its oxidation is provided by the agent (Potassium-Dichromate) within a 2 hrs. digestion process.

DIN 38409-41 standard method
Describes the procedure for its determination.

ISO 15705:2002
Specifies the procedure using the sealed test tube method allowing reduced reagent consumption!

The importance of COD measurement

Chemical oxygen demand (COD) :

- is the measure and the main parameter for successful waster water cleaning
- is the parameter to pay discharge fees
- underlies an additional self control
- is a time-consuming test following standard methods: 2hr digestion + cool down process

Optical reagent-free measurement of COD

- Constant optical reagent-free monitoring has been introduced with the WTW® IQ SENSORNET 2001, optical UV-VIS sensors 2004, improved 2012
- OptRF transferred to lab in the year 2015: Pioneering photoLab® 7600 UV-VIS offers reagentfree outlet test!

WTW – IQ SENSOR NET Highlights

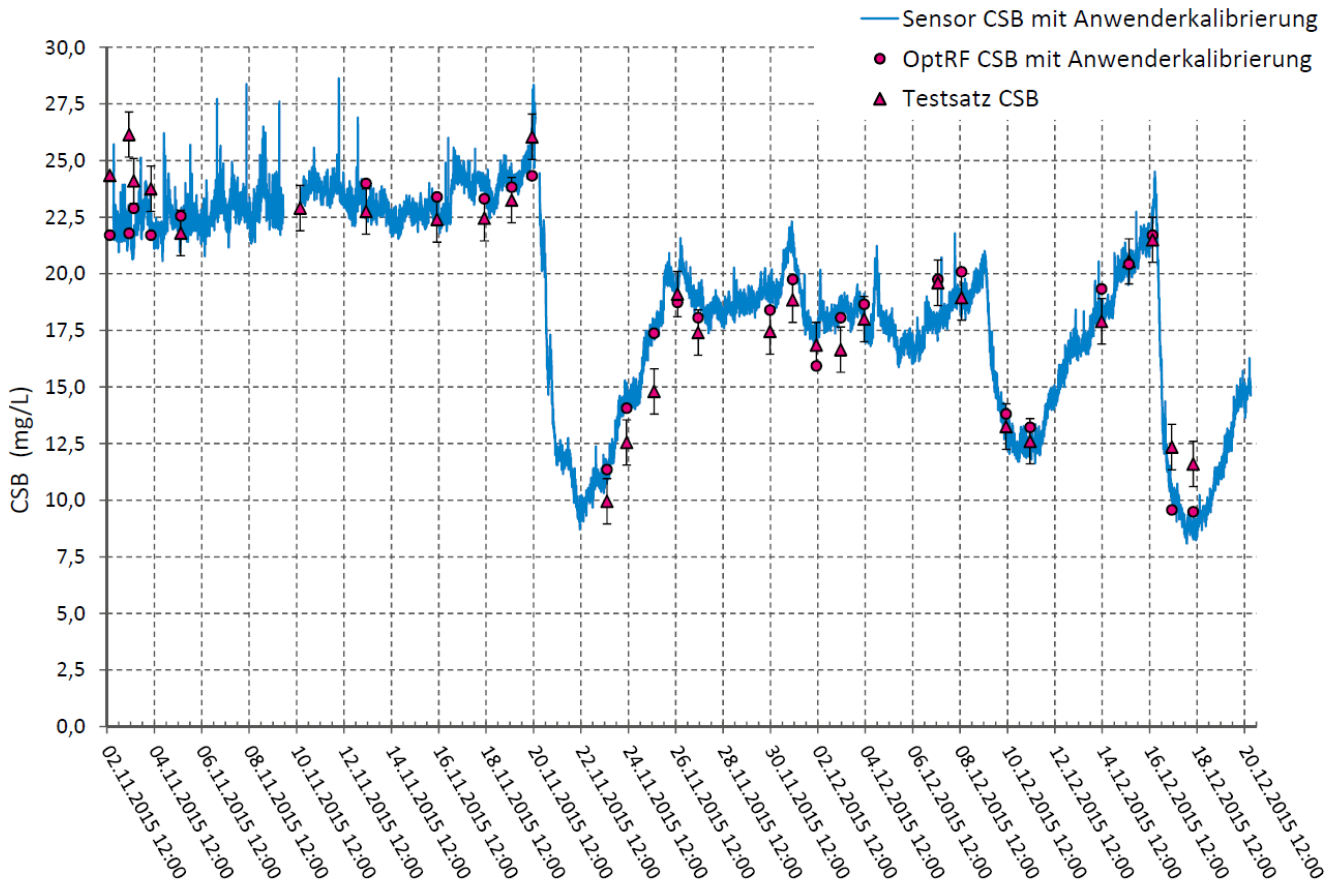
2001	**IQ SENSOR NET**	the multi-parameter measuring system offers unlimited possibilities for online measurements
2004	**NitraVis®, CarboVis® and NiCaVis®**	spectral "in-situ" Online sensors for Nitrate, Carbon and TSS measurement for wastewater control
2012	**UV-VIS sensors - Next generation**	CarboVis®, NitraVis® and NiCaVis® sensors with the optical design, integrated ultrasonic cleaning technology and high-tech materials

Process Measurement in Sewage Plants

Process Measurement with IQ SENSORNET

- Spectral probes for COD, NO3 and NO2: CarboVis, NitraVis, NiCaVis…
- Can monitor inlet, aeration and outlet

Many years of experience in optical reagent-free measurement => transfered to Lab

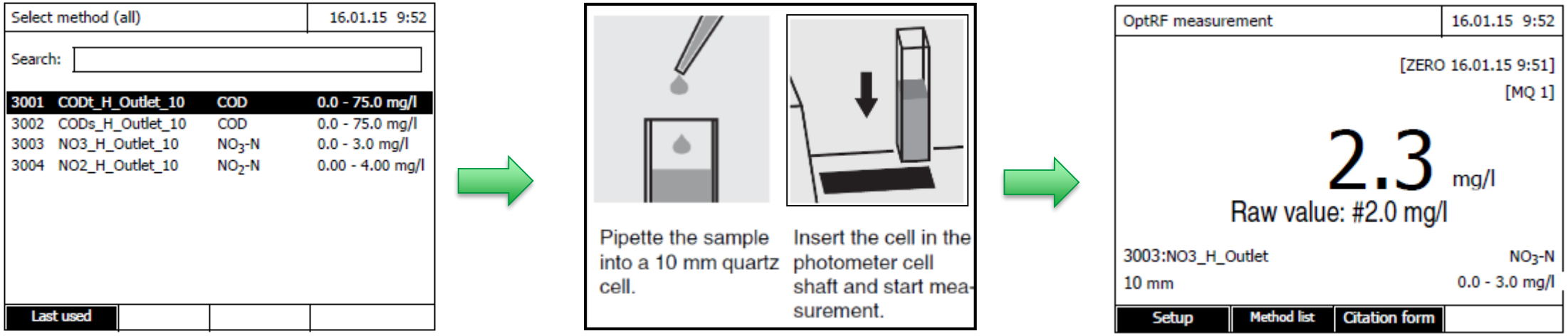


Pioneering Online procedures transferred to Lab!

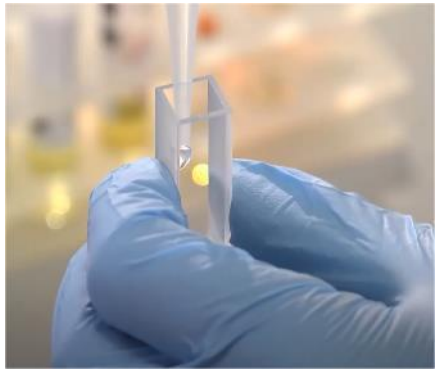
Optical Reagent-Free Measurement OptRF

for outlets of municipal waste water treatment plants (WWTP)
and in many surface waters applications with photoLab® 7600 UV-VIS

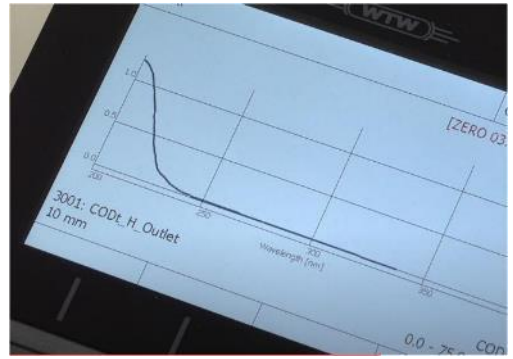
COD, NO_3, NO_2 - Just measure!



OptRF – The principle



- Direct absorbance measurement by **NO_3, NO_2** in UV range
- **COD = sum parameter** with absorbance „behaviour“ depending on sample matrix
- Pipette sample in 10 mm quartz cuvette (UV!)
- Spectral reading from 200-390 nm
- Evaluation of scan based on reference spectra by water matrix from many sewage plants: so based on real samples
- Instant value output on display



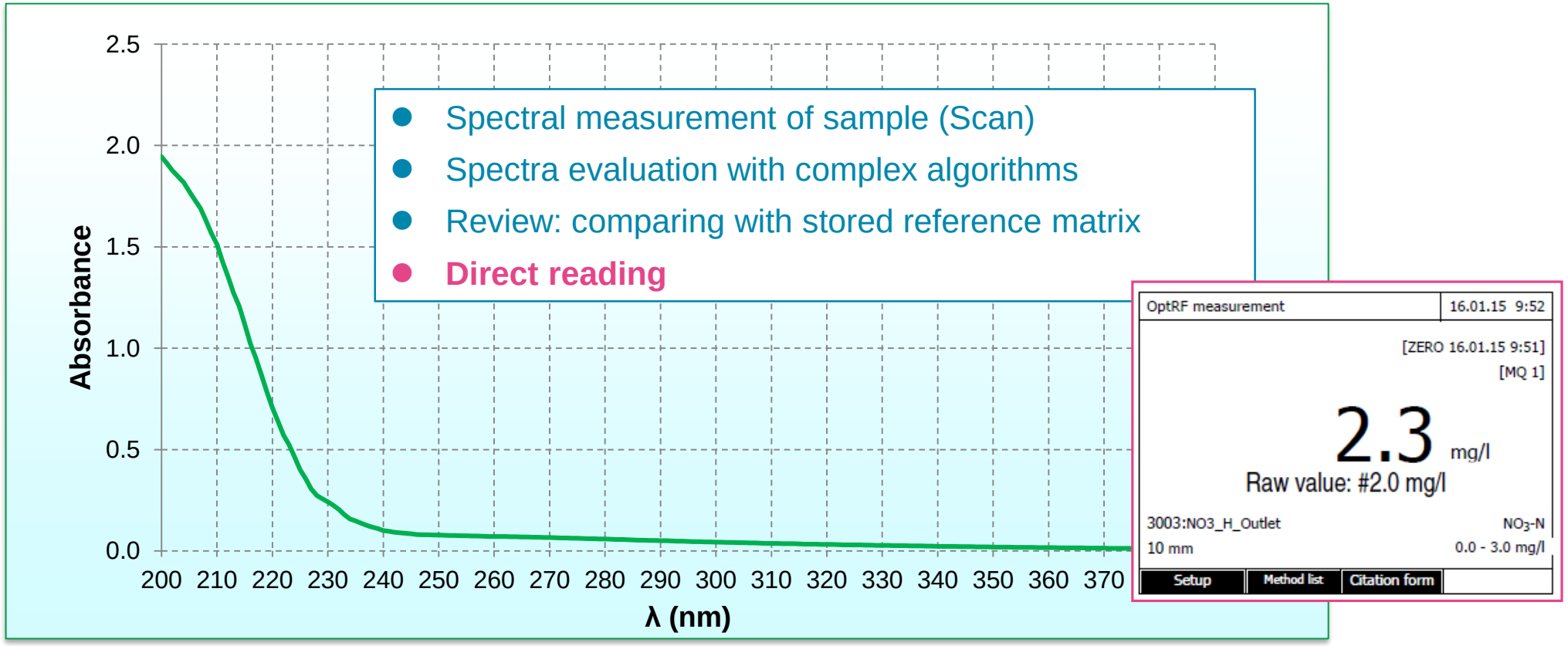
Methods designed for sewage plant outlets!

Not suitable for most of industrial waste water
since not all carbon sources (sugar/alcohol…) absorb in UV-range!

Turbidity effects are disturbing, no inlet method available actually.

OptRF – based on spectral measurement

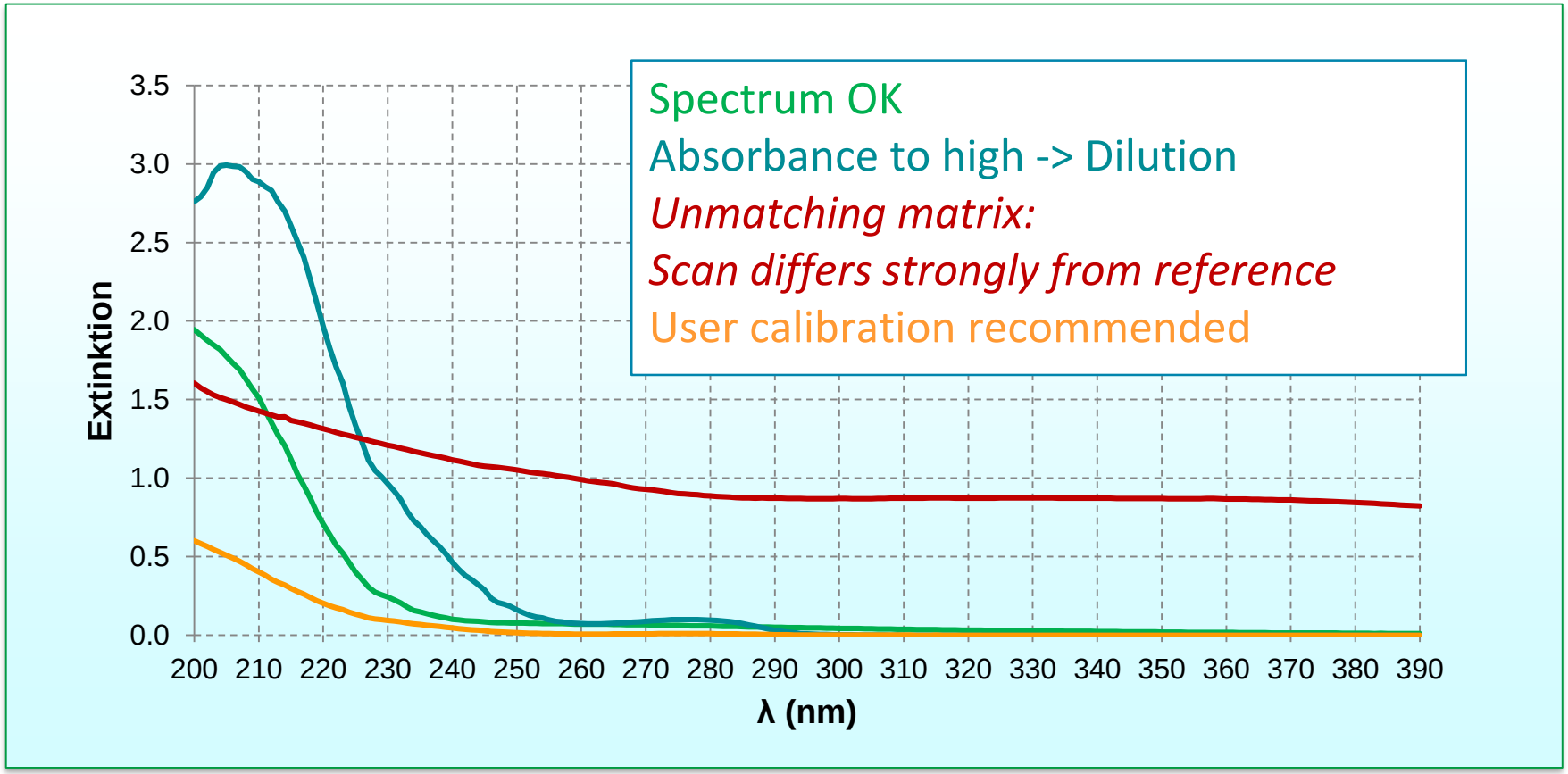
From spectral measurement to instant data output:



OptRF : menu-guided procedure

No water is alike = varying matrix!

Background evaluation and qualitative review of spectra



OptRF - Procedures

What is the measurement range?

based on standard solutions; for real samples they are matrix-dependent

COD	2.0 - 75.0 mg/l	
NO_3-N	0.1 - 3.00 mg/l	
NO_2-N	0.1 - 4.00 mg/l	depending on absolut NO_3/NO_2 conc.!

Is dilution possible?

Absorbance behaviour of the parameters and algorithms are different:
To measure all parameters in a sample, it might be necessary to dilute with different dilution factors per parameter: This changes the matrix of the water =>
Dilution as low as possible as much as needed!

OptRF can be used in surface water

Depending on environment and matrix, but frequently suitable: Verification with test kits ahead recommended, especially when high dynamics like heavy rain events etc.: method COD_s (dissolved)

Pioneering!

Optical Reagent-Free measurement

Many benefits:

- ✓ Faster than any digestion
  (1 min vs. COD standard method: 2.5 hrs min.)
- ✓ Cost free w/o need of chemicals
- ✓ Reduction of over-all costs
- ✓ Check of required measurement range
- ✓ Cost-free test of retainer samples
- ✓ Ecofriendly w/o potassium Dichromate, Hg…
- ✓ Non-hazardous, non carcinogenic

OptRF – Linking with IQ SENSORNET

- Fast check of abnormal events
- Onsite check for process sensors
- Matrix adjustment of process sensors

For both, process and OptRF measurement,

the lab testing is the reference!

POLL QUESTION #1

Q1 How many determinations per parameter do you usually perform for each sample?

1. Single determination (1 test)
2. Double determination (2 test)
3. Triple determination (3 tests)

OptRF - Higher Convenience

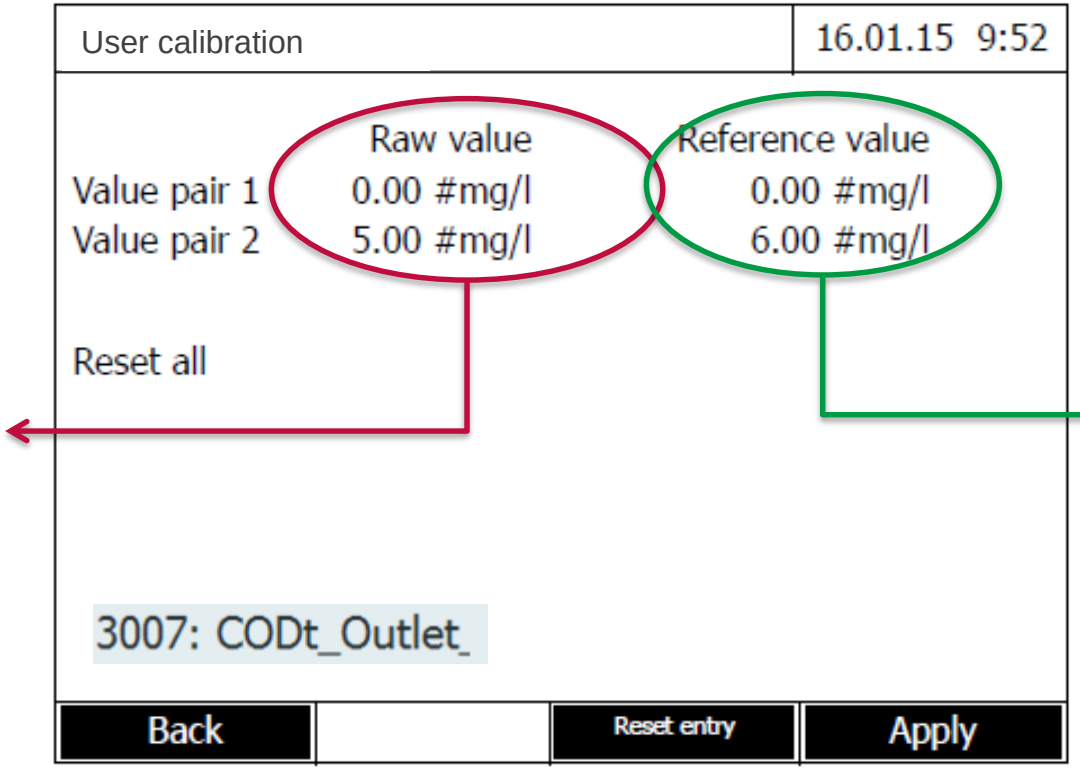
OptRF – even more comfortable in daily use

- ✓ Profiles can be saved as user calibrations for various locations
- ✓ ID for each actual user calibration (storing seasonal settings)
- ✓ AQA: Chosen profile is displayed and printed with ID and name
- ✓ Selection of the stored calibration settings comfortable via F1-Key
- ✓ Dilution setting can be kept for several measurement series

OptRF – User Calibration to match your site!

Optimization for the individual sewage plant or even basins:

Adjustment of characteristics via raw & reference value pairs

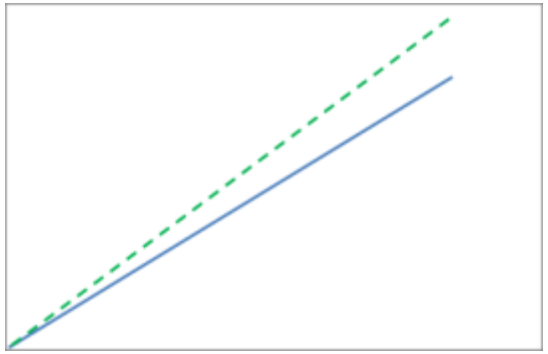


Directly measured sample (OptRF)
Negative raw values **must** be entered negatively!

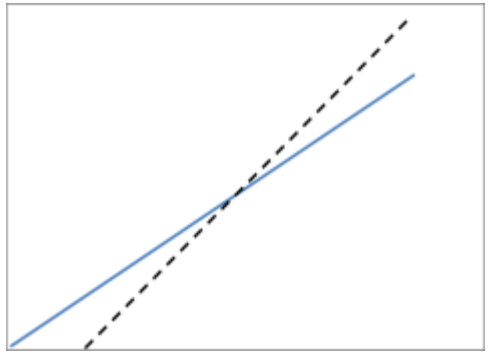
Concentration determination
with test kits or standard methods

OptRF – User Calibration

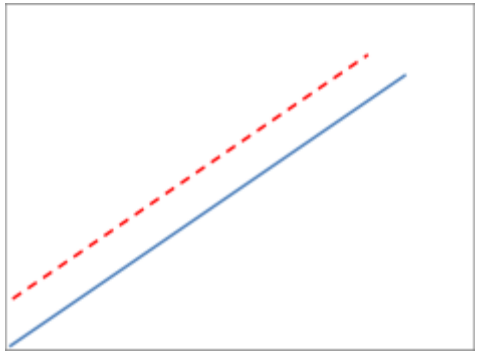
Adjustment of characteristics („calibration curve“) via reference measurements:



1-point calibration changing second pair at the end of measurement range:
Slope correction



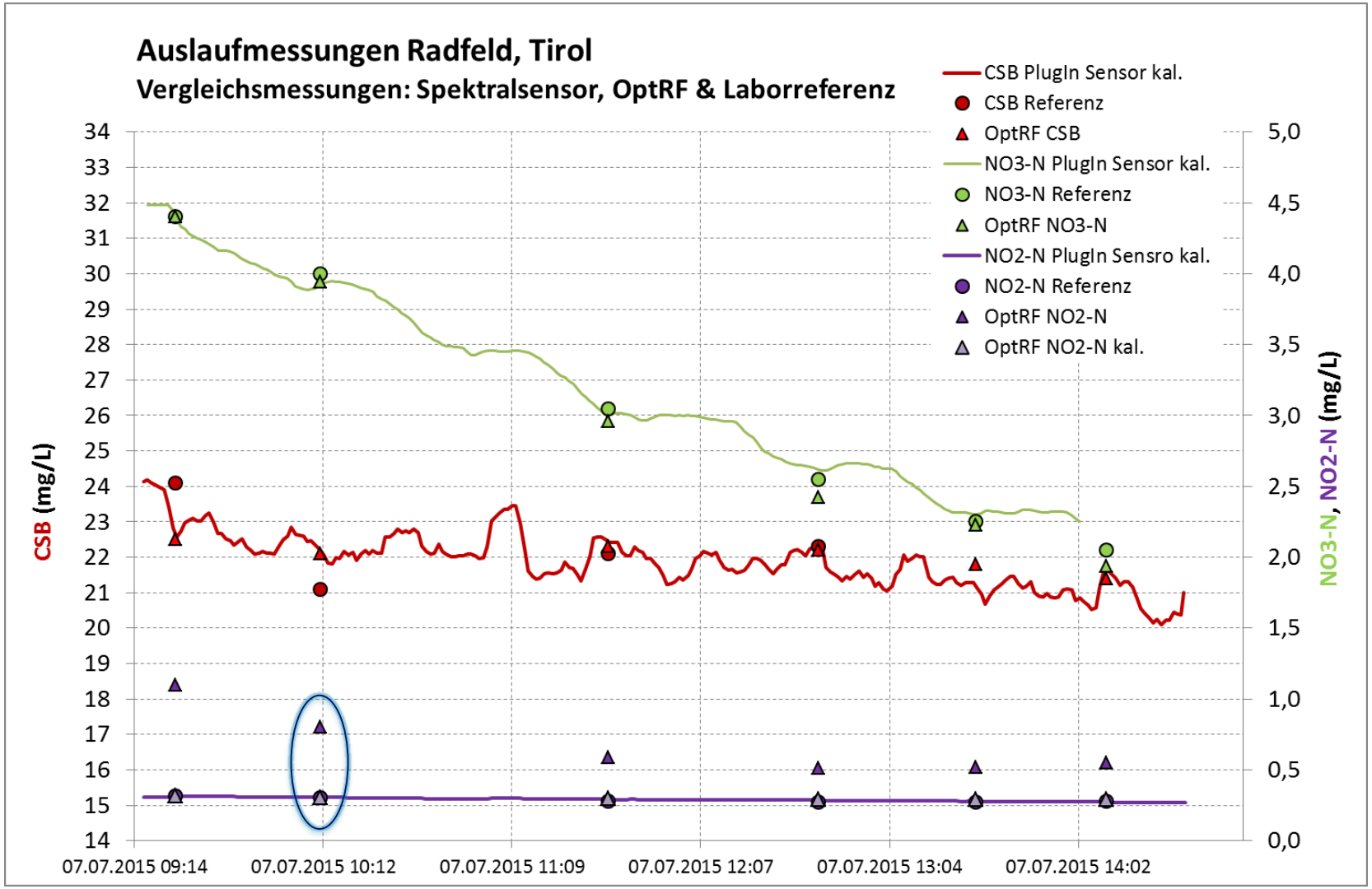
2-point calibration changing both pairs of variates:
slope correction



2-point calibration, change of both pairs of variates:
Offset-correction

- Periodical reference measurements:
  e.g. seasonal variations of NO_3 => seasonal optimization take place in Europe

Comparison of OptRF, WTW sensors and test kits



After user calibration for NO_2^-:

the values of
- the sensor,
- the lab test and
- the OptRF result

are matching as seen in violett curve

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Implementation Guide for OptRF:

How to Assure best results

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Implementing OptRF at Customer Sites (Sewage)

- The optical reagent-free (OptRF) measurement of COD and Nitrate can be a powerfull option for monitoring, self check and range detection.
  OptRF results are higly precise, when optimized.

- To achieve valuable and good results, there are some key facts to consider: lab skills & user calibration with matrix adjustment

- Read manual first, even for preparation and evaluation, if this methods can be performed at your site.

  A seperate operations manual OptRF tests can be downloaded from Xylem Analytics
  https://www.xylemanalytics.com/en/File%20Library/Resource%20Library/WTW/01%20Manuals/ba77167e03_PhotoLab_7600_OptRF_Tests.pdf

Our team and our partners consult and support the implementation!

Implementing OptRF at Customer Sites

Which sample/waters can be measured via OptRF?

(Testing and matrix adjustment period is useful respectively mandatory!)

1. Sewage plants – Outlets = based matrix of the OptRF algorithms (If industrial waste water does not exceed aprox. 30%, OptRF may work: trial period required)
2. River and Surface waters: are working mostly

Which sample/waters cannot be detected via OptRF

1. Industrial waste water: non-absorbing substances in UV such as sugars, alkohol, …
2. Samples with high turbidity or TSS due to high matrix variations
3. For photoLab® 7600 OptRF measurement cannot offer matrix models for inlets and biological tanks (due to scan speed/settlement, cuvette sizes etc.)

Q2 Do you have changing industrial compounds in waste water plants?

1. Yes
2. Less than 30%
3. No

OptRF Implementation - Overview

1. Make good handling skills sure: of sampling and data collection
2. Be aware of the difference in sample handling for OptRF measurement
3. Improve your lab skills, if necessary: this helps in daily routine too!
4. Be aware of negative OptRF # (raw) values
5. Perform a matrix adjustment / user calibration with the reference results for your site using our Xylem Analytics Excel sheet for OptRF implementation:

   This will caculate your entered data via linear regression to optimize the OptRF-testing procedure to your ambient condition.

Implementing OptRF: Sampling and preparation

- ✓ Grab sample at a good = matching spot:
  Representative sample showing the average,
  well mixed matrix

  For lab/matrix adjustment: near IQ SENSOR NET UV-VIS sensors

- ✓ Note time and date of sample (and IQ Sensor values)
- ✓ Do not filter samples for OptRF measurement
- ✓ => Fix only a part for the routine analysis of sample
  with lab methods: NO_3, NO_2 turn over quickly
  Method: Syringe Filter 45 µm or fixation with acid, cooling

Implementing OptRF: Referencing in the lab

Best lab performance required!

- ✓ Start with daily measuerment, evtl. drop down to 1-2 per week
- ✓ Best matching measurement range of reference kit
- ✓ GLP: double, better triple determinations per sample in the beginning, control standards help to check skills
- ✓ Lab measurement of filtered samples for NO_3, NO_2
- ✓ **COD: standard digestion method** (148° C, 2 hrs, slow cool down)

- Blank value per new box for optimum accuracy
- 10 min. after digestion end, swivel cuvette (hot!) to pick up condensation drops in the lid
- Let the kits cool down slowly to complete settlement of particles
  => no turbidity effects will disturb the readings!

Implementing OptRF: OptRf reading

The procedure differs from lab method

- ✓ No matter, what the standard regulation is for lab testing:
  do not filter the OptRF sample, since the models are based on IQ SENSOR NET sensors algorithms measuring original water matrix unfiltered in the outlet of sewage plants
- ✓ Easy method selection, settings and zeroing acc. to operations manual and menu guidance
- ✓ Pipette the sample directly in the 10 mm quartz cuvette
  NO single use UV-plastic cells – no transmission below 220 nm
- ✓ No bubbles, no condensation no finger prints in or on the cuvette
- ✓ Minimum sample dilution to keep original matrix unchanged as much as possible
- ✓ Note OptRF #value with date/time to match lab results

Implementing OptRF in surface water monitoring

- **Different water matrix in rivers, lakes..**
  => Check with reference measurements!
  => OptRF reading w/o filtering the sample !

- **COD method: dissolved COD for surface water**
  Difference to sewage water: COD results from sludge particles in the outlet surface and river waters carry sand and others instead with less organic load of bacteria:

  it is better to choose OptRF method for dissolved COD of the reagent-free measurement with the spectrophotometer photoLab® 7600 UV-VIS

Implementing OptRF at waste water treatment plants

Optimization = User calibration = Matrix Adjustment

Each matrix is different => Optimization for each location!

- ✓ Even for several basins in the same sewage plant
- ✓ Each location has an individual biology = bacteria mix
  due to sun, tree shade, adaption of bacteria to seasons or geographical regions, temperature … => also seasonal adjustment can be useful/needed
- ✓ Easy handling: Profiles and user calibration with ID
  for various locations can be stored (F1-key)
- ✓ **1** profile for Nitrate in sewage plants often matches many locations
  (experience in Denmark, Germany…..)
- ✓ Link the OptRF (raw) #values correctly to reference lab values!
  (Note date and time!) Enter negative #values being negative!

Implementing OptRF: User Calibration Process

The Linear Regression Tool from Xylem Analytics

- ✓ Making your life easy with our XLS Sheet
- ✓ Enter matching value pairs in the green fields for Lab and OptRF (#!) The more values over a 2-3 weeks period, the better the adjustment will be achieved, periods are depending on each site.
- ✓ For OptRF values enter the raw values (#) including negative values!
- ✓ Don‘t enter values into red fields: they are reserved for automatic calculation based on your entries
- ✓ 2-3 lab determinations per value:
  calculate the average value, eliminating outlier ins case of triple determinations, if usefull

enter Date and Time	enter measured # Sensor data mg/L	enter measured Lab data mg/l	corrected Sensor data calculated with slope & off-set from linear regression mg/L
27.01.2014 09:00	70,8	79,0	82,2
28.01.2014 09:15	50,3	60,0	66,1
29.01.2014 09:30	37,6	58,0	56,1
30.01.2014 09:45	37,1	57,0	55,7
31.01.2014 10:00	50,3	70,0	66,1
01.02.2014 10:15	62,7	74,0	75,9
02.02.2014 10:30	33,7	60,0	53,0
03.02.2014 10:45	35,9	59,0	54,7
04.02.2014 11:00	36,2	58,5	55,0
05.02.2014 11:15	29,2	49,5	49,5
06.02.2014 11:30	23,2	43,0	44,7
07.02.2014 11:45	21,8	42,5	43,6
08.02.2014 12:00	20,2	42,0	42,4
09.02.2014 12:15	20,0	41,0	42,2
10.02.2014 12:30	19,3	41,0	41,7
11.02.2014 12:45	25,0	47,0	46,1
12.02.2014 13:00	55,0	75,0	69,8
13.02.2014 13:15	60,0	75,0	73,7
14.02.2014 13:30	80,0	90,0	89,5
15.02.2014 13:45	85,0	95,0	93,4
16.02.2014 14:00	65,0	78,0	77,7
17.02.2014 14:15	45,0	60,0	61,9
18.02.2014 14:30	40,0	55,0	58,0
19.02.2014 14:45	37,0	50,0	55,6
20.02.2014 15:00	49,0	60,0	65,1
min values	19,3	41,0	
max values	85,0	95,0	

Calculation of value pairs for local COD Sensor Calibration		
	# Sensor data mg/L	calculated Lab data reference value calculated with slope & off-set from linear regression mg/L
value pair 1	5	30
Value pair 2	90	97

enter values only in green cells
do not change red cells

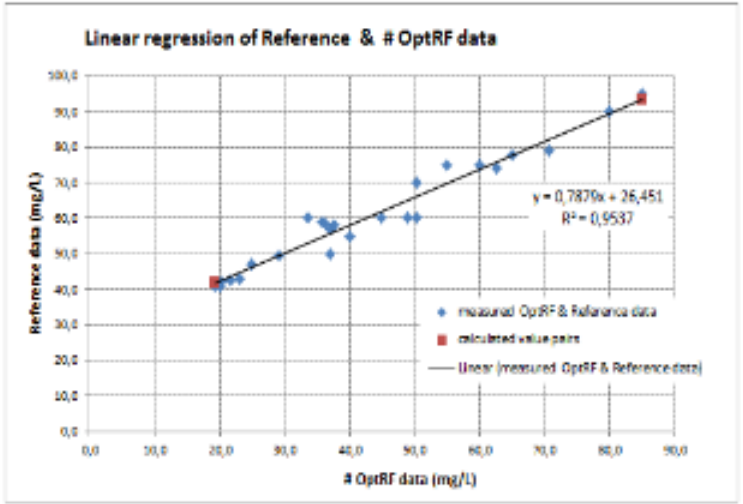
Optimized results with OptRF

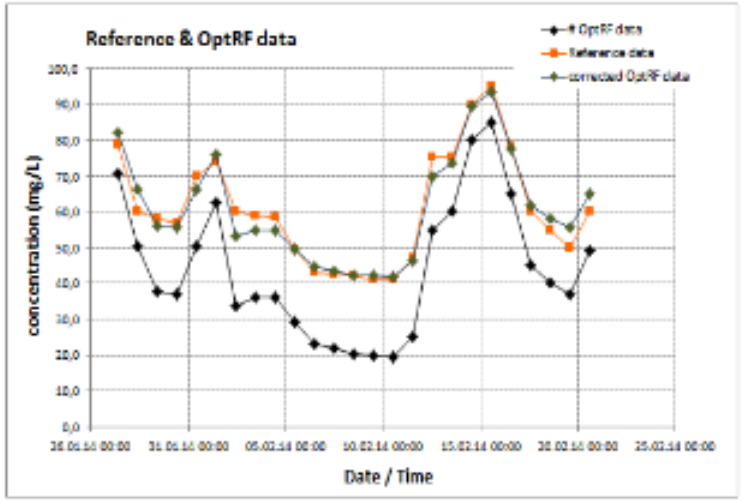
- ✓ Automatic calculation of the corrected value pairs for **2 point calibration:** red squares in graph 1

- ✓ Graph 2 shows OptRF #values before (black) and corrected OptRF values (green) via linear regression: it can be seen clearly, that the user calibration is almost 100% matching the reference lab values (orange).

- ✓ Finally: enter the calculated value pair in the respective OptRF user calibration menu of the spectrophotometer photoLab® 7600 UV VIS

Calculation of value pairs for local OptRF Calibration		
	# OptRF data mg/L	calculated reference value calculated with slope & off-set from linear regression mg/L
value pair 1	19,3	41,7
Value pair 2	85,0	93,4





This ensures the best and reliable matching results!

To Go - Get instant results – Routine and OptRF

Handy: Analysis-to-Go for onsite-testing

- Low weight, just 4.5 kg
- Power supply via standard car battery
- Standard cable for car batteries
- Onsite needs: weather protected location
  like a customer lab, a trunk, a van, a shed….
- Optional field case for transportation

Ideal for huge location, surface water monitoring and at multiple locations!

photoLab® 7000 Series Spectrophotometers

Well proven and reliable photometric analysis

Barcode for round and rectangular cells

- Advantage of cell tests: very fast & convenient
  - Reagent mix, lot certificated
  - method selecetion with all settings, fault-free
- Advantage of reagent test kits: fast & economic
- Unique with barcode support = method setting selection
- Offering lot certificated quality at cost level of powder pillows

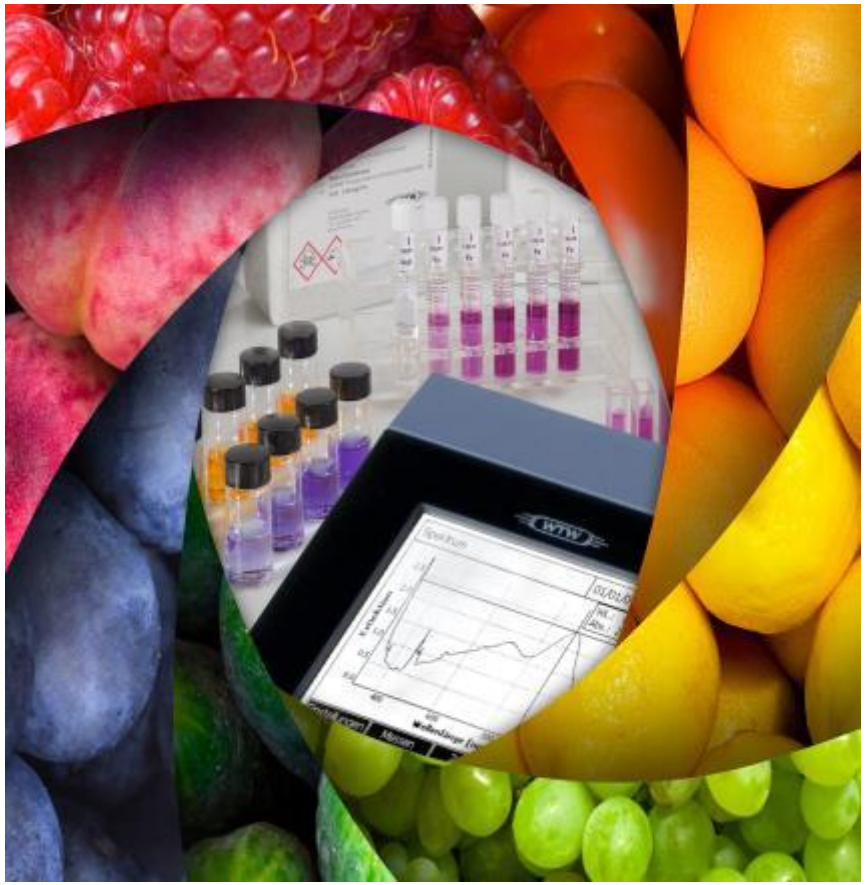
Automatic cell recognition for all cells without adapters

- Round and rectangular cell identification (10, 20, 50 mm)
- Automatic measurement range switch:
  corresponding range matching cell size

photoLab® 7000 Series Spectrophotometers

Application Overview

- Aquaculture
- General Labs
- Beverage Industry
- Education
- Fish Farming
- Food Industry
- Mining
- Petro Industry
- Pharma
- Research Labs
- Service labs
- Universities & schools
- **Water Analysis**
- Wine & Beer
- ……



Q3 Would you like a WTW Specialist to contact you with more information?

1. Yes, please
2. No, thanks.

Questions?

***An email will be sent out in the next few days that will include a link to the recording*

CONTACT US

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