# HACH's answers to wastewater challenges PART VIII : Self monitoring

# Disclaimer

Hach webinars are educational in nature and not an endorsement of other manufacturers' treatment technologies or processes.

# Speakers

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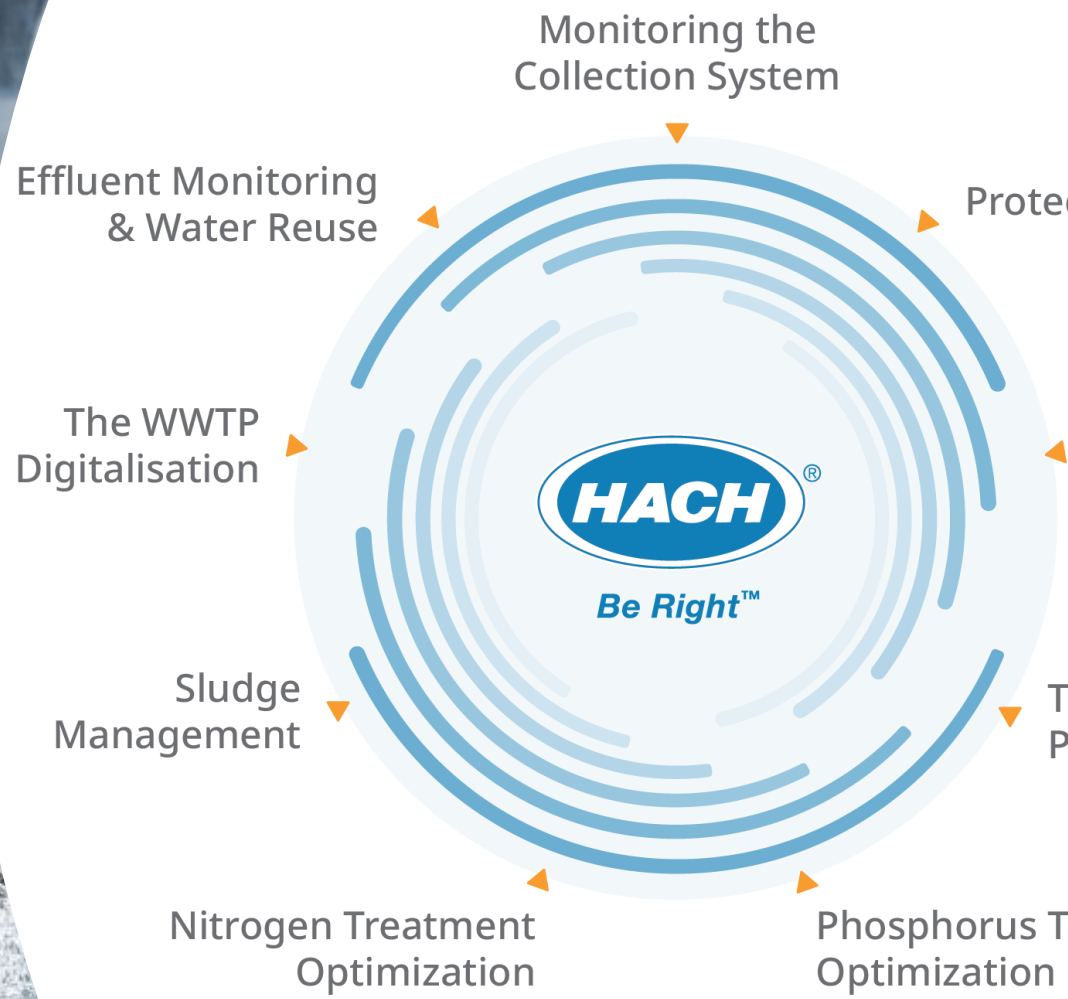
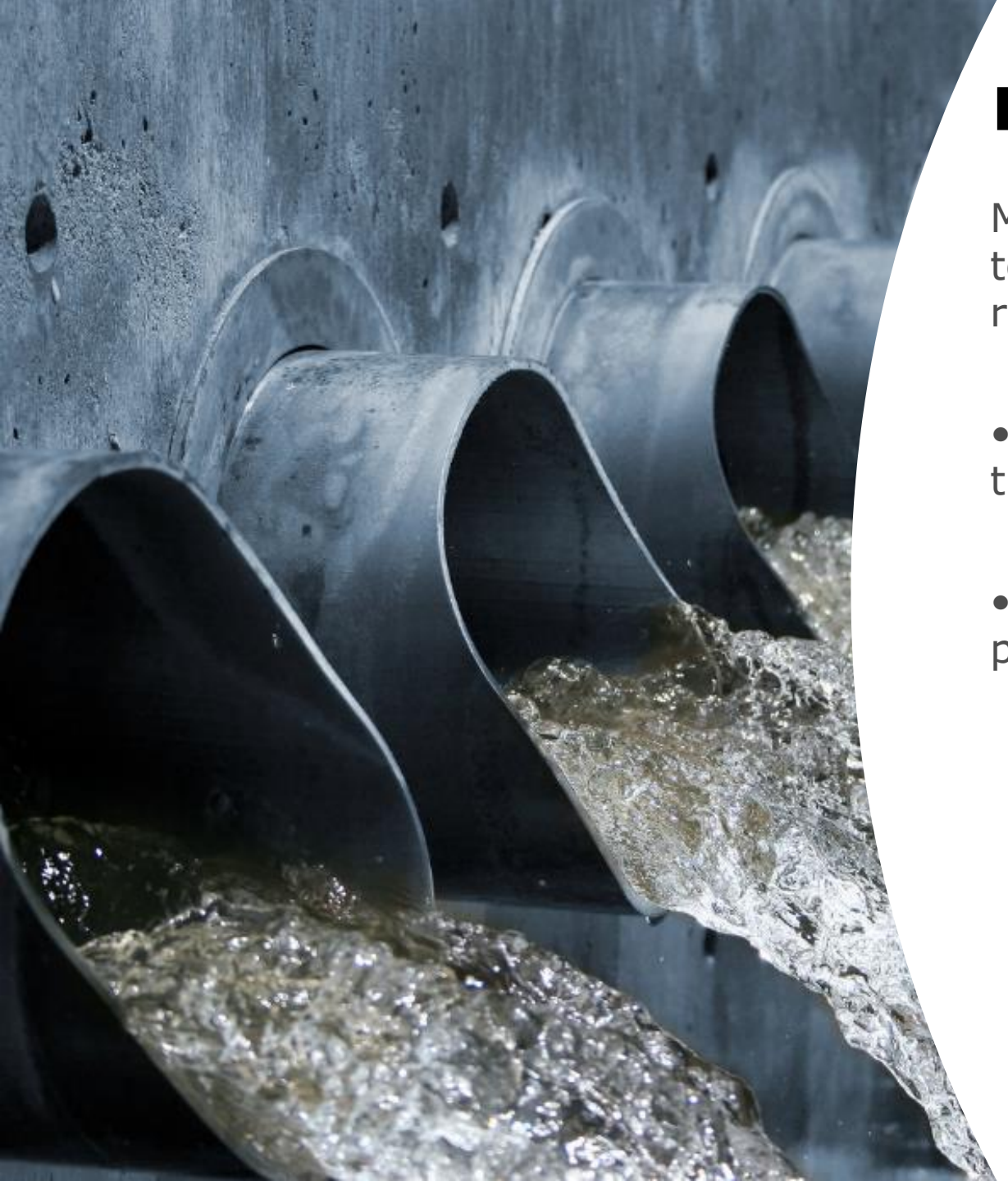
# WWTP monitoring
# Overview of Hach solutions



# Agenda

1. Laboratory measurements: Why?
2. Automatic water samplers
3. Laboratory: Instruments and analytical techniques
    - Spectrophotometry
    - Benefits of cuvette tests
    - COD
    - TOC
    - Phosphate
    - Nitrogen parameters



# Laboratory measurements: Why?

Main goal of Municipal plants is to correctly treat water to protect environment and meet regulatory requirements

- On-line instruments are used to monitor and optimize the efficiency of the process in real time

- Laboratory instruments are used to measure ponctually samples:
  - To monitor the process if there is not online instruments
  - To calibrate / check the online instruments
  - For self-monitoring in accordance with EU / Local regulation

**Only laboratory results are accepted by authorities to prove the proper functioning of the plant (self-monitoring)!**

# Self-monitoring process for Muni WW

## Urban Wastewater Treatment Directive 91/271/EEC (UWWTD) - 21/05/91

(Applicable for plants > 2000 PE)

**Defines…**

- The parameters to be monitored
  DBO5 / COD / TSS / TP / TN
- The anaytical technique (not mandatory)

**… And, depending on the plant size and on the aera type (sensible or not),…**

- The maximum limit for each parameters
- The frequency of self-measurements

**Local regulation can be stricter than EU recommendations**

**The UWWTD is under revision! New version will be more restrictive**

### Measurement frequency

Minimum number of samples to be taken at regular intervals over a full year and according to the size of the treatment plant:

- P.E. between 2,000 and 9,999:
  - 12 samples in the first year.
  - 4 samples in subsequent years if it can be demonstrated that the water complies with the provisions of this Directive in the first year; if any of the 4 samples do not meet the standards, 12 samples are taken the following year.
- P.E. between 10 000 and 49 999: 12 samples / year.
- P.E. of 50 000 or more: 24 samples / year.

*(PE: Organic load of DBO5 = 60 grs/day)*

# Laboratory analysis: 5 Steps

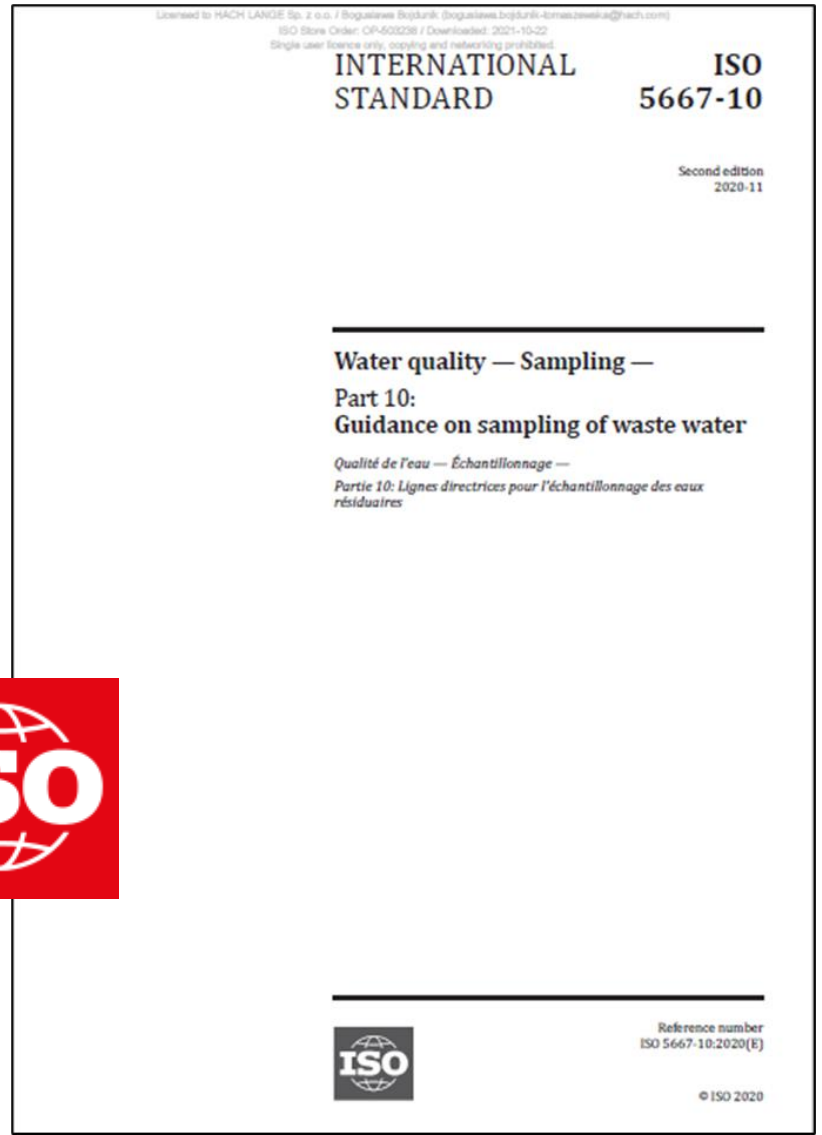
- Sampling
- Sample Preservation
- Sample Preparation
- Use of Standards (check and calibration)
- Analysis

The analysis is only as good as the sample!

# Automatic Water Samplers

# SAMPLING METHODS: How and when?

## HOW?: ISO Standard: **ISO 5667-10 :2020**





INTERNATIONAL STANDARD

ISO 5667-10

Second edition
2020-11

Water quality — Sampling —
Part 10:
Guidance on sampling of waste water

*Qualité de l'eau — Échantillonnage —*
*Partie 10: Lignes directrices pour l'échantillonnage des eaux résiduaires*

Reference number
ISO 5667-10:2020(E)



## WHEN?: Local regulation

*Ex: Fench water agencies*

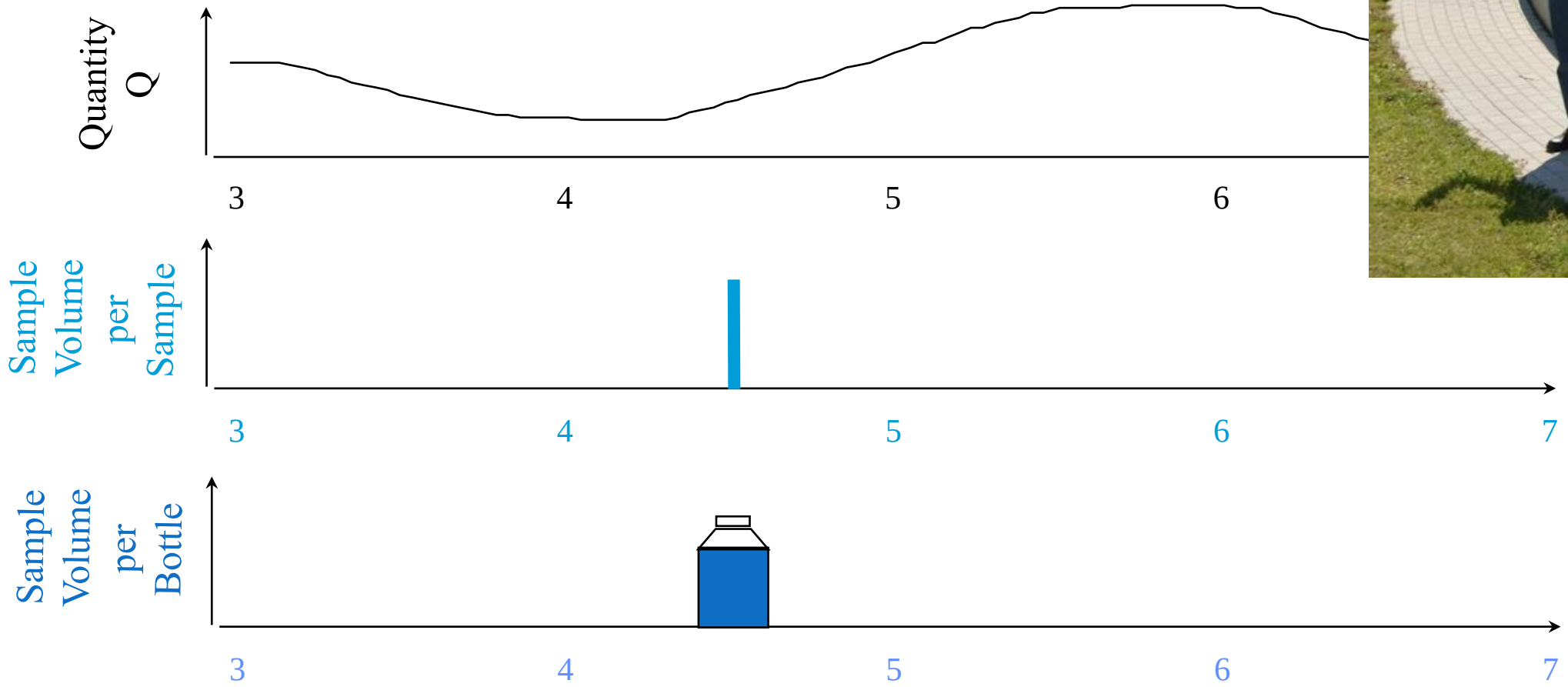
| **Critères de représentativité** *et valeur à respecter* | **Fréquence de vérification préconisée …** | **… en fonction de la fréquence d'utilisation du préleveur** |
|---|---|---|
| Vérification lors d'un bilan 24 h :<br>• **Volume unitaire d'un prélèvement (1)** *≥ 50 ml*<br>• **Répétabilité ou distribution des volumes (2)** *Ecart maximum toléré ≤ 5%*<br>• **Nombre de prélèvement en 24h** *≥ 100*<br>• **Volume total prélevé en 24h** *≥ 5 litres* | Mensuelle | 1 fois par jour |
| | Trimestrielle | Entre 1 fois par jour et 1 fois par mois |
| | Semestrielle | Moins d'1 fois par mois |
| Vérification lors d'un bilan 24 h :<br>• **Température de l'enceinte** *3°C± 2°C (NF ISO 5667-3)* ou *2°C± 2°C sans congélation (NF ISO 5667-10)* ou *4°C± 2°C (règles de l'art)* | Au moins 2 fois par an | Toutes fréquences confondues |
| • **Vitesse d'aspiration** *≥ 0,5 m/s* | | |

# SAMPLING METHODS

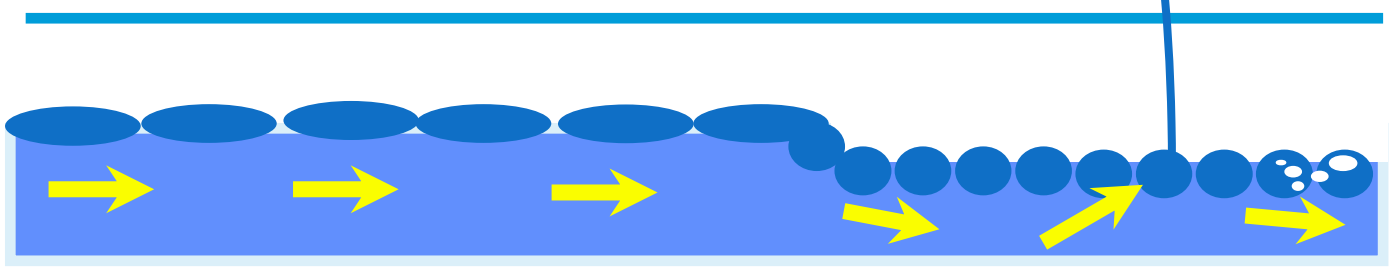
- **Manual Sampling**

- **Automatic Sampling**

# Manual sample: SPOT CHECK



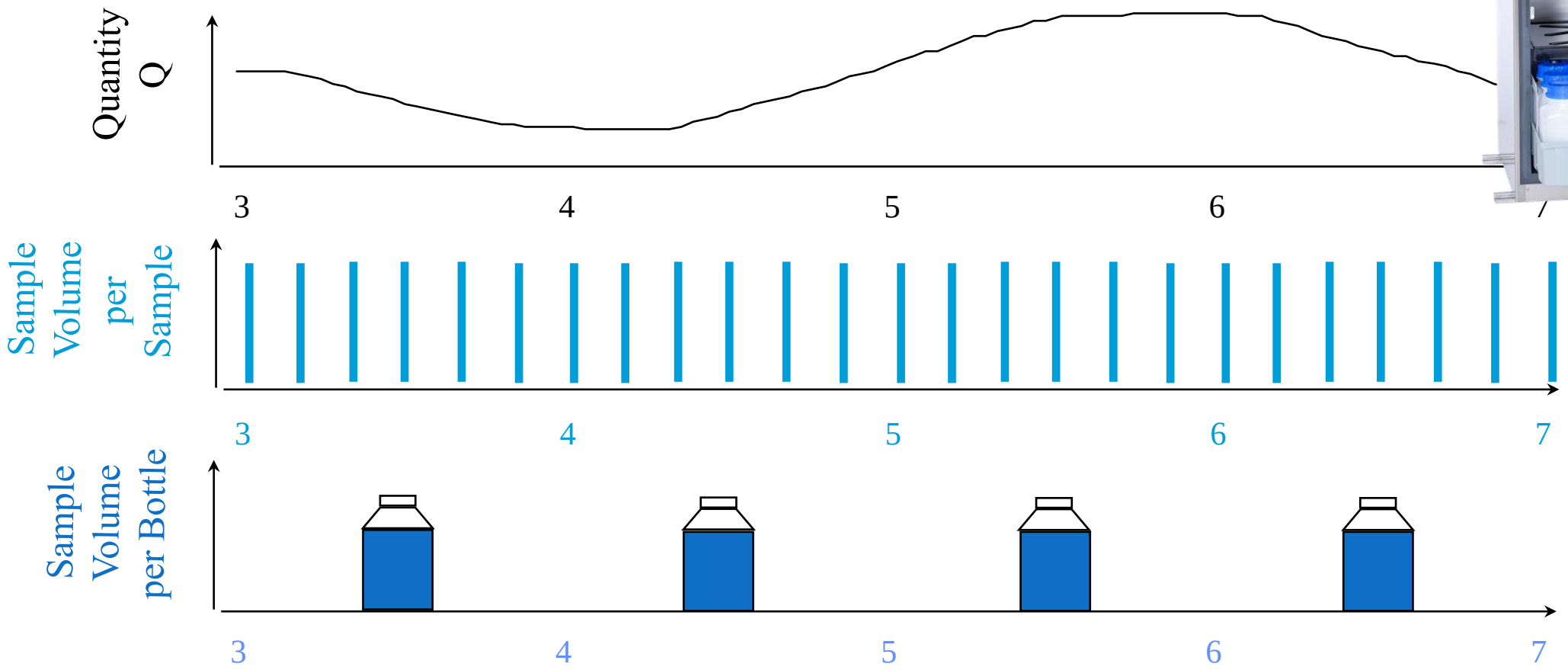
# AUTOMATIC WATER SAMPLING

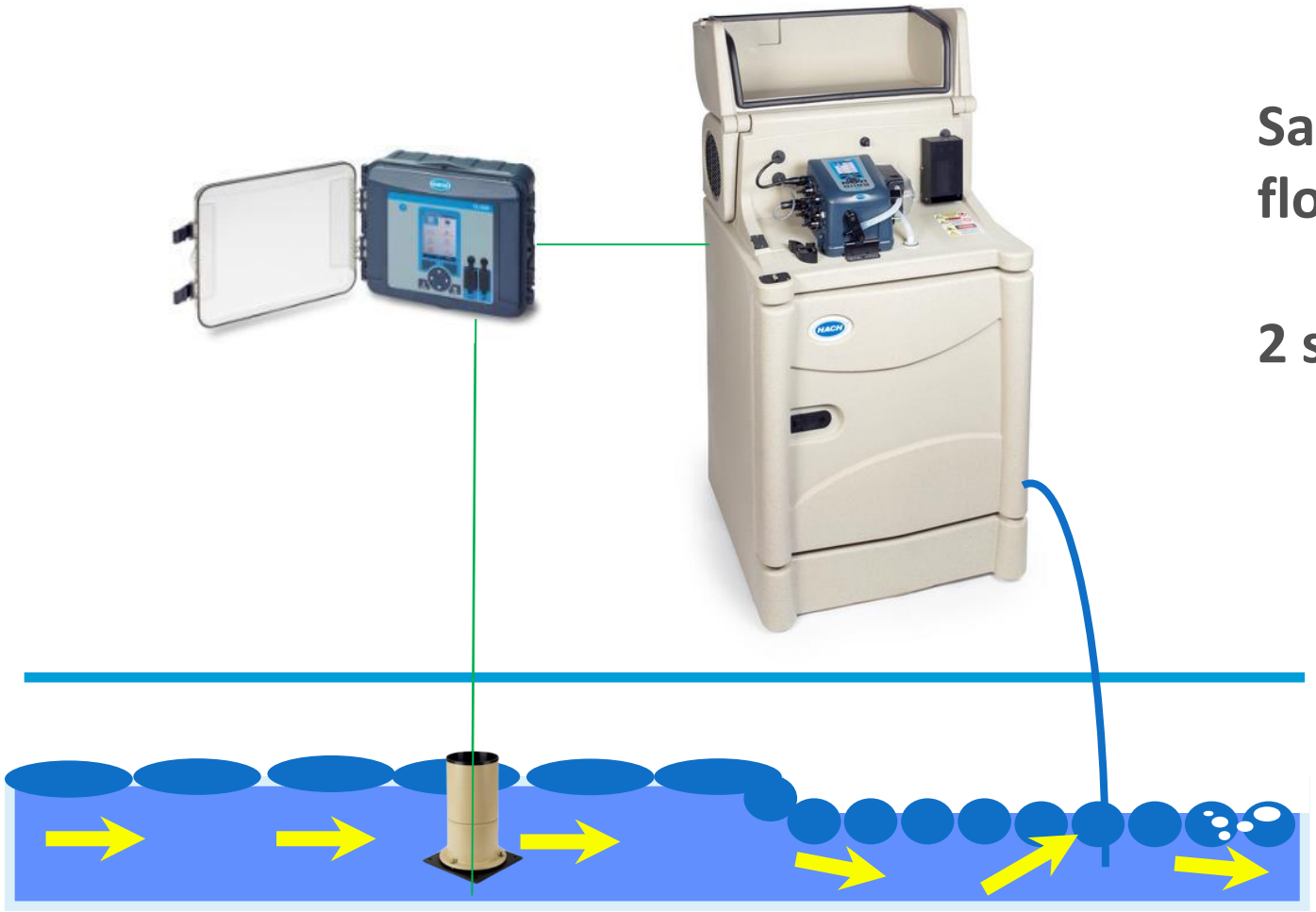
- **Sampling methods**
  - Time related
  - Connected to flow meter
    - Constant Volume/Variable Time (CV/VT)
    - Constant Time/Variable Volume(CT/VV)

- **2 sampling techniques**
  - Peristaltic pumps
  - Pressure vacuum

# TIME RELATED SAMPLE



# Automatic water sampler with connected flow meter

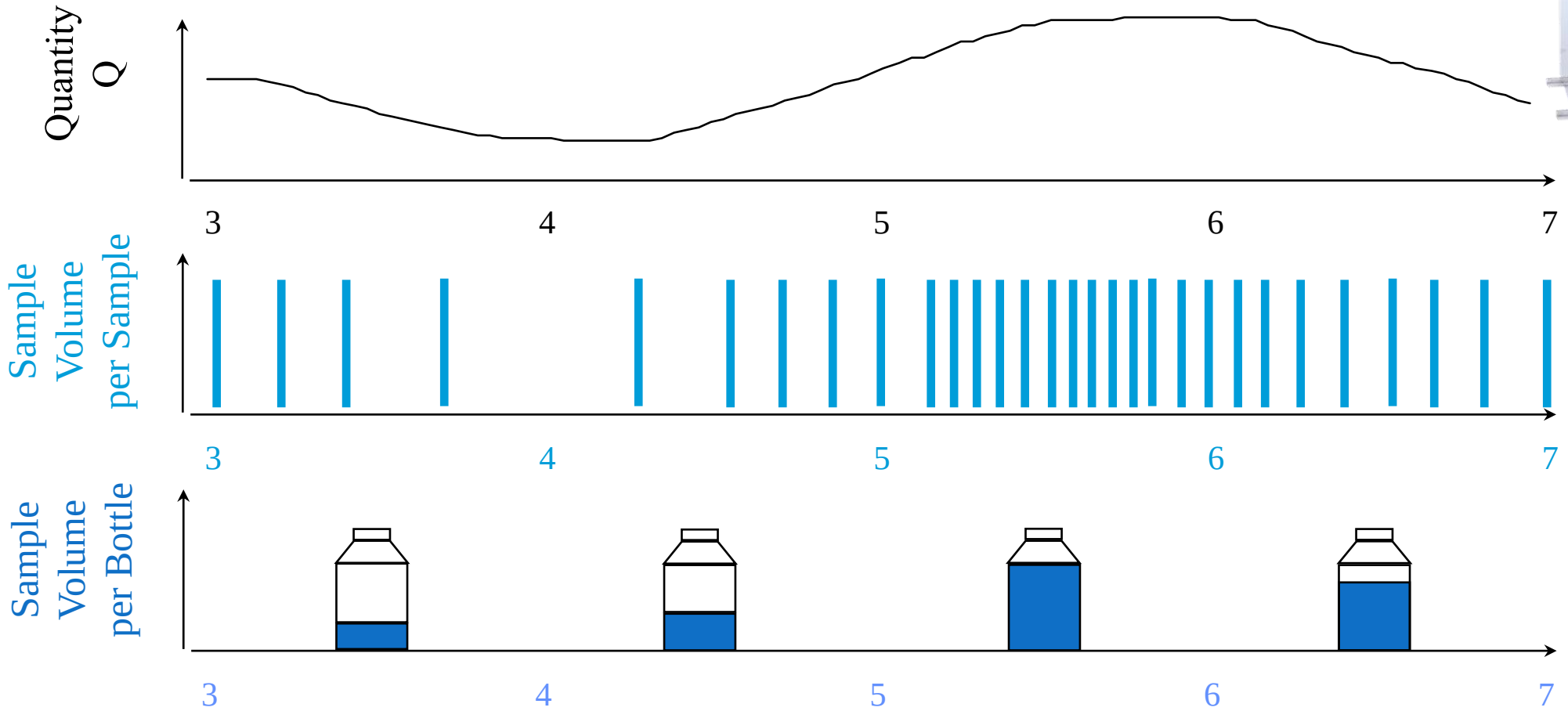


**Sampler takes in consideration the sample flow**

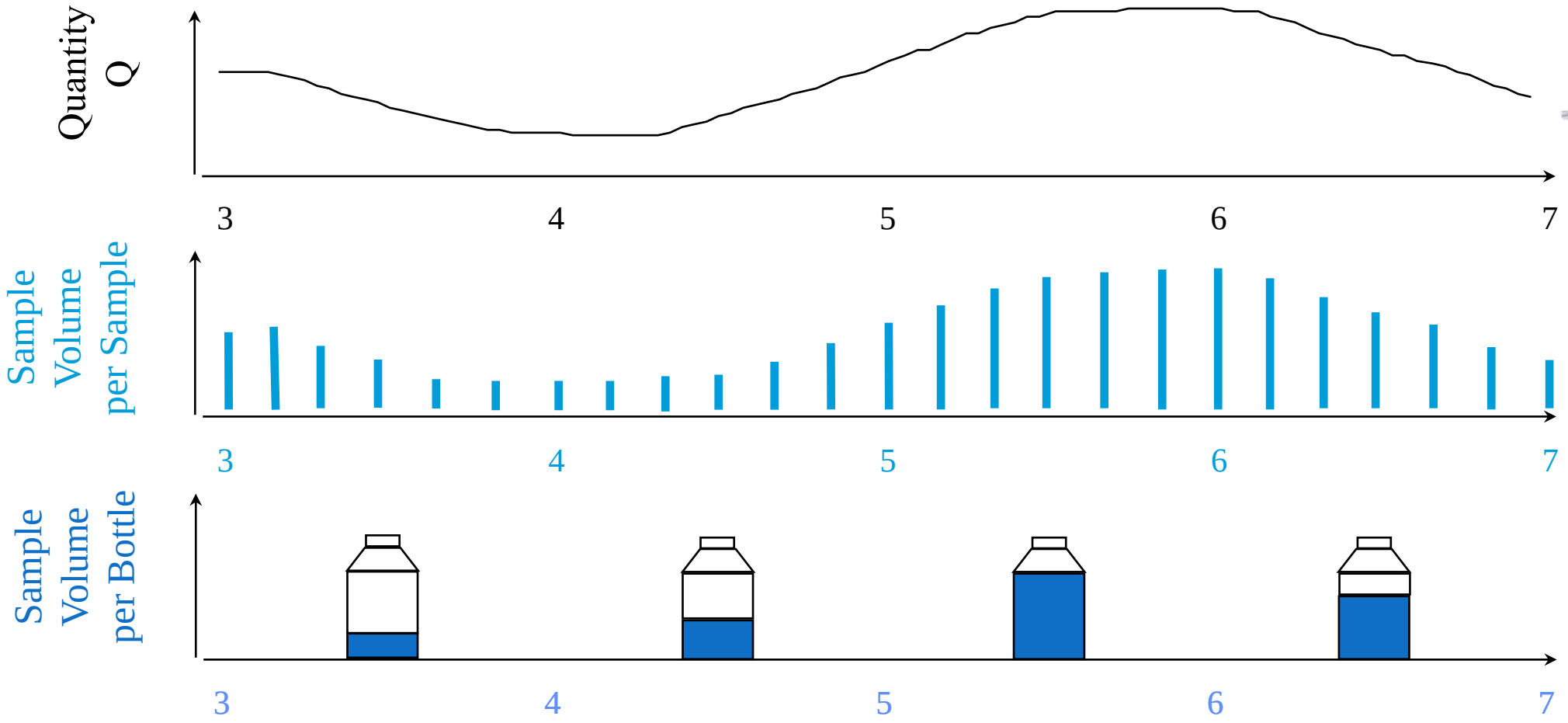
**2 sampling methods**

- Constant Volume/Variable Time (CV/VT)
- Constant Time/Variable Volume(CT/VV)

# FLOW PROPORTIONAL SAMPLE: Constant Volume/Variable Time (CV/VT)

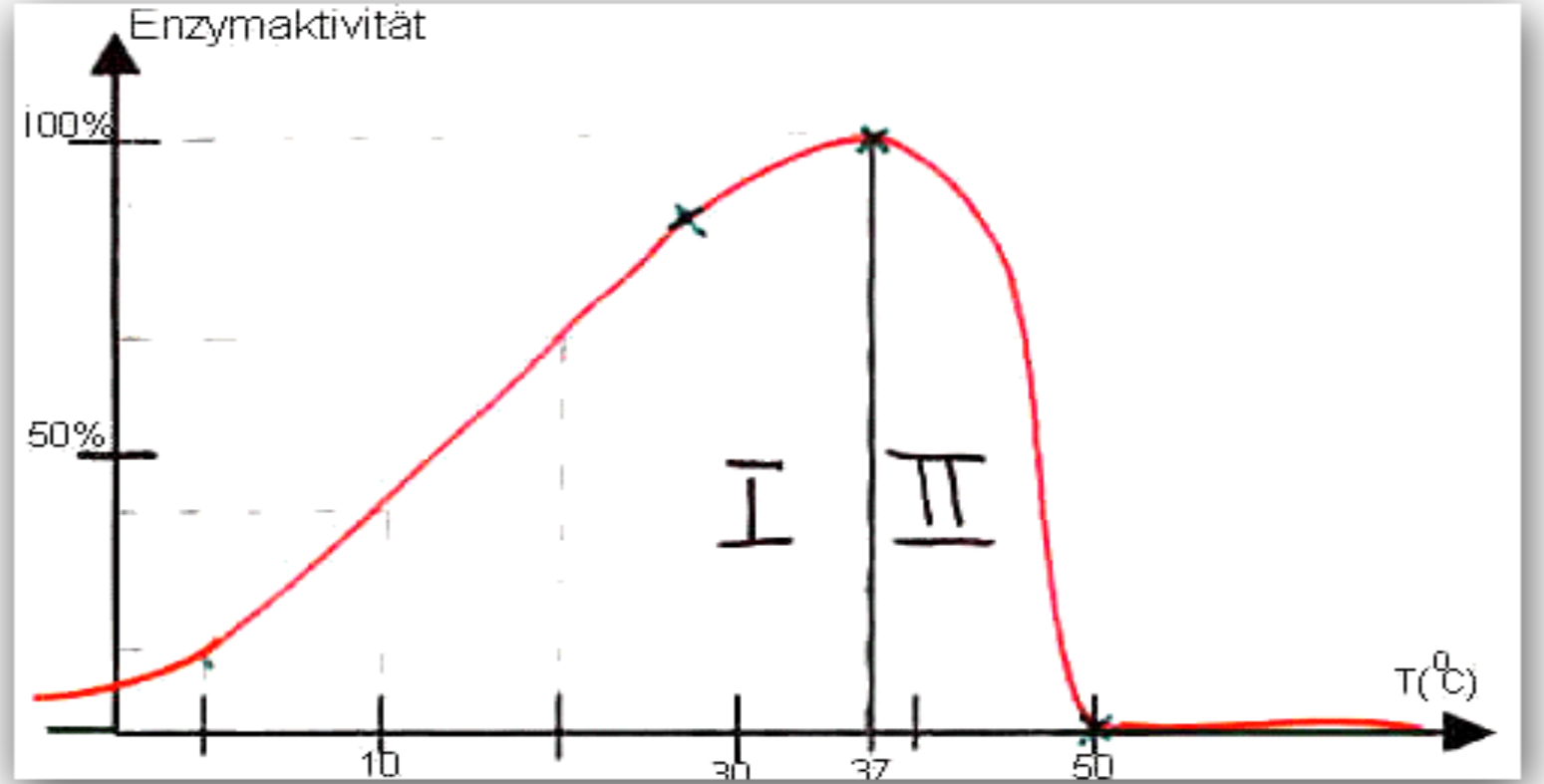


# FLOW PROPORTIONAL SAMPLE: Constant Time/Variable Volume(CT/VV)



# Why to cool samples?

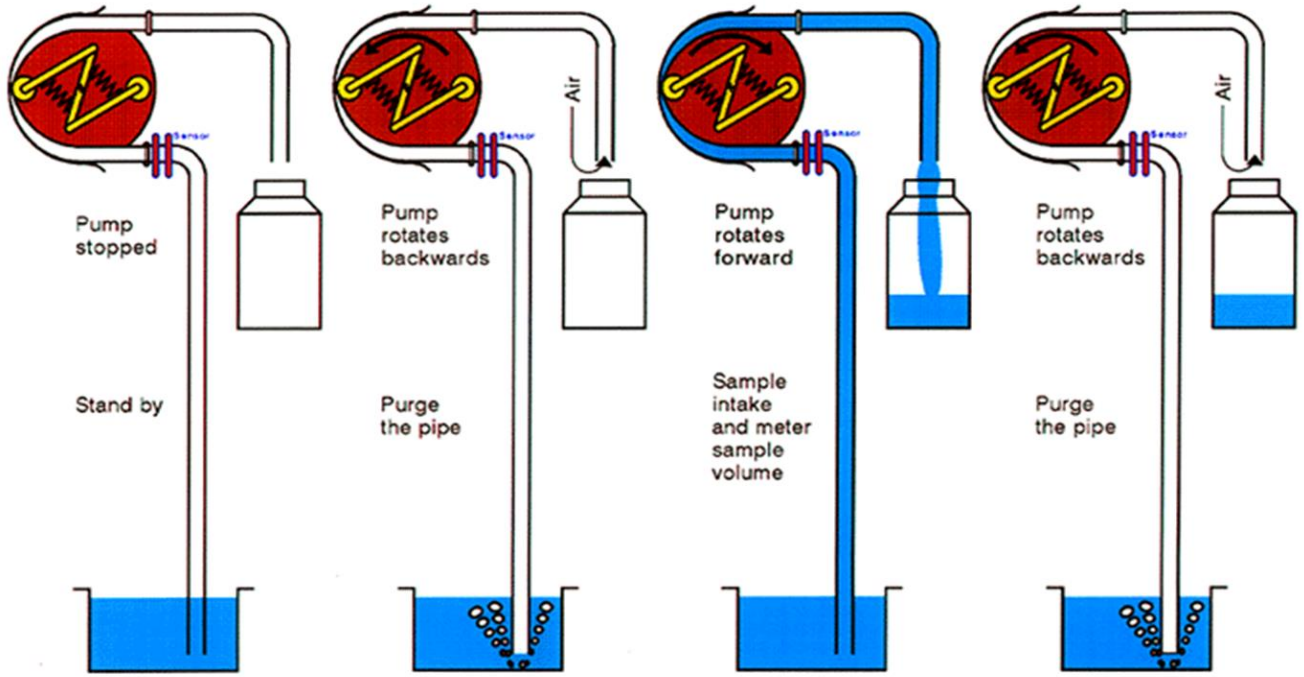
Cooling samples at 4°C inhibits bacteria activity → sample content won‘t be modified



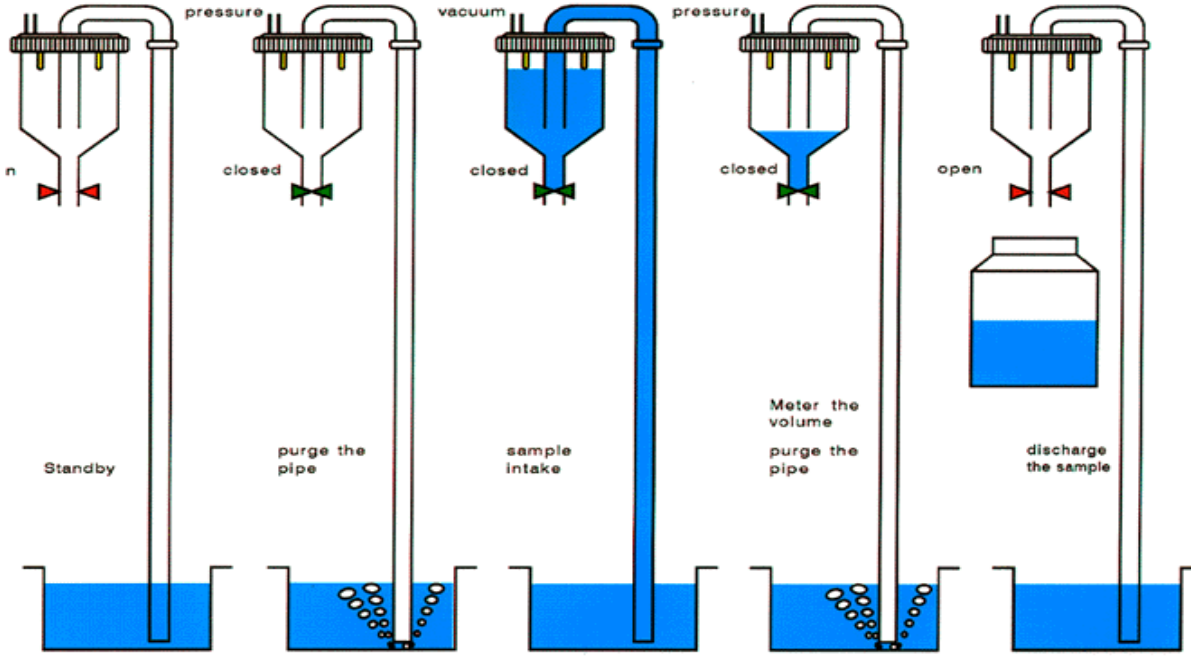

**Active or passive cooling available**

# Technologies, how to take samples automatically?

## Peristaltic technology (Sigma)




## Pressure vacuum (Buehler)




# What says the norm regarding Peristaltic pump?

**ISO 5667-10:2020**
**Annex F**

**Table F.1 — Advantages and disadvantages of two main types of pumping**

| Pumping type | Advantages | Disadvantages |
|---|---|---|
| Peristaltic pump (PP) | Only the desired volume of sample is pumped | Accuracy of unit volume: difficult to obtain especially for small volumes (<100 ml) |
| | Possible rinsing with sample to avoid cross contamination | Checking the unit volume required over time |
| | Sample contact only with the inside of the suction pipe and the liquid detector | Possibility of deposits in pipes which can lead to cross contamination |
| | No sedimentation of solids because sample is in permanent movement from the sampling point to the collecting flask | Unstained solid integrity due to pipe crushing (less representative sample for suspended solids, possible biological modification) |
| | Cleaning and preventive maintenance low, easy and less expensive | Internal diameter limited to 9,5 mm |
| | Crushing pipe and rollers are the only wear parts. Easy to change and low cost | Suction hard solids (sand) can damage the pump and result in high maintenance costs |
| | Better overall behaviour under particular sampling conditions (hot fluids, fouling, presence of suspended matter) | Frequent exchange of the crushing pipe. Risk of rupture if rarely replaced and / or in the presence of hard solids in the sample. |
| | Slower fouling of elements in contact with the fluid | |
| | High suction heights | |

# Peristaltic pump samplers = HACH SIGMA

All Weather
Refrigerated (AWR)

Refrigerated

Portable

# What says the norm regarding Vaccum pump

**ISO 5667-10:2020**
**Annex F**

Table F.1 *(continued)*

| Pumping type | Advantages | Disadvantages |
|---|---|---|
| Vacuum pump (VAP) | Repeatable and accurate sample volumes | Possible sedimentation and degassing in the bowl during adjustment to the requested volume |
| | Easy calibration of the unit volume | Risk of clogging the pressure sensor |
| | Reduced risk of cross-contamination by pre- and post-sampling purges | Mandatory detection of the arrival of the sample |
| | Solids integrity | Risk of permanent deposition in the bowl (e.g. grease) which can alter the volume and composition of the sample |
| | Pipe diameter may be greater than 9 mm | Various materials in contact with the sample |
| | Easy cleaning of the bowl (disassembly) | More complex system |
| | Less frequent change of wear parts (vacuum pump diaphragm, pinch valve pipe) | Cleaning or rinsing of pipes more difficult to carry out "in-line" without disassembly (problem of absence of conductivity when rinsing with ultra-pure water) |
| | Less Energy Consumption | |
| | Possible rinsing with sample to avoid cross contamination | Limited pumping height (7 m) |

# Pressure/Vacuum samplers = BÜHLER


# How to select the correct sampler?

## STATIONARY

✓ Conditions of sampling

*Is the sampling done on loaded pipe or at athmospheric pressure?*

✓ Numbers of bottles

*Which bottle do you need?*

✓ Bottle material

*Do you prefer plastic or glass bottles?*

✓ Refrigered model (portable)

*Do you need refrigerated model?*

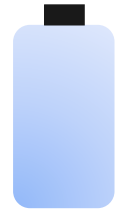
✓ STAINLESS STEEL ou PE

*What materials do you want to take it?*

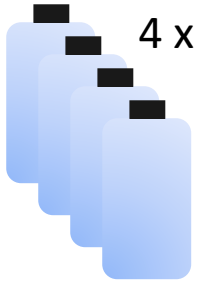
✓ Presence of H2S

*Is there H2S?*

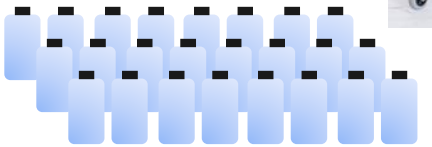
*If yes, choose reinforced stainless steel 316/GF*



1 x 25L



4 x 14L



24 x 1L

# How to select the correct sampler?

## PORTABLE

- ✓ Peristaltic pump or vacuum technique

*Is the sampling done on loaded pipe or at athmospheric pressure? At which height?*

- ✓ Numbers of bottles

*Which bottle do you need?*

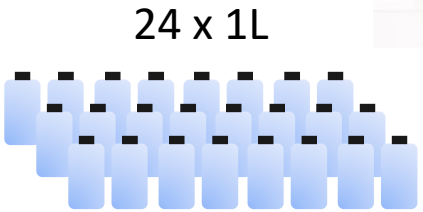
- ✓ Bottle material

*Do you want plastic or glass bottles?*

- ✓ Insulated or refrigered model

*Do you want an insulated or refrigerated model?*






# Laboratory
## Instruments and analytical technique

# Analytical Technologies

**Photometric** (Light)

- Visual
- **Spectrophotometry (Colorimetry)**
- Nephelometry (Turbidity)
- Luminescent (LDO)

**Electrochemical** (Probe)

- Potentiometric (pH, ISE…)
- Polarographic (DO)
- Conductometric
- ORP

**Titrametric**

- Drop Count
- Digital Titrator
- Traditional Buret
- Electrochemical titration (Probes)

**Microbiological**

- Qualitative
- Quantitative

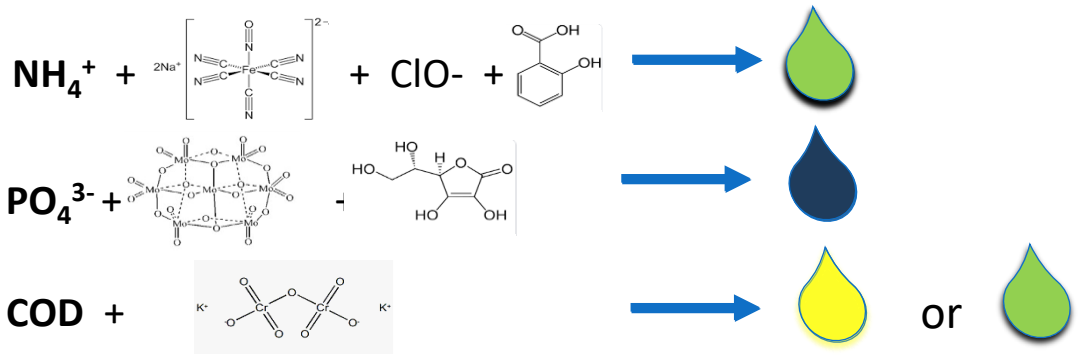
**Gravimetric**

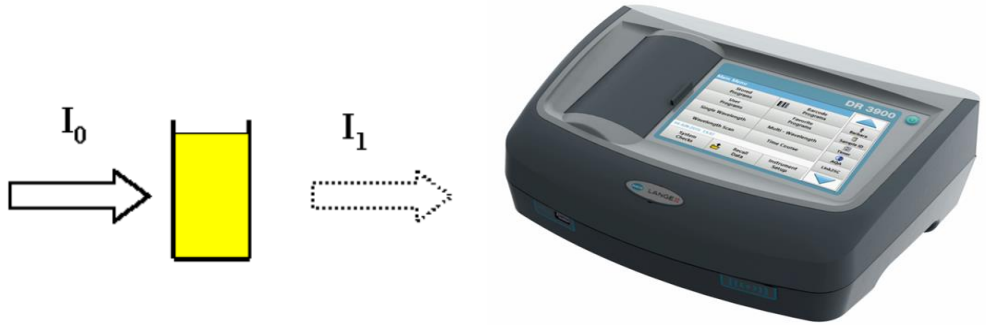
- Total Dissolved Solids
- Total Suspended Solids

# Spectrophotometry

# Principle of photometry


- Water parameters do not have an apparant color
- When adding specific reagents, specific colors develop




- The colored sample absorbs light
- The absorption of the light is proportional to the concentration of the parameter

# Photometric System

**Designed as a system**
Hach chemistries and instruments are designed to work as an integrated system, eliminating calibration and variability errors from the outset so you can be certain of your results.

**Reagent stability**
Formulations and packaging are designed to provide long product life to ensure accurate results after shipping and storage and reduce the effects of common sample interferences.

**Support**
We offer a dedicated support team who are trained to solve your technical problems, backed by decades of experience.




# Traditional Hach Tests

- Bulk liquids
- AccuVac Ampules
- Powder Pillows
- PermaChem powder reagents
- **LCK cuvette tests**
- Chemkey


# Why Perform Self Monitoring with Cuvette

# Benefits of cuvette tests

- Safety
  - No contact with chemistries
  - Less chemical reagent than other methods
- Easy to use & ideal for wastewater parameters
- Rapid and accurate results
- Easy updates
- Environmental protection (recycling)
- Standardized Methods

# Safety

**No contact with chemistries**


- Cap with reagent
  - DosiCap / DosiCap Zip for freeze-dried reagents
  - No powder or liquid reagent handling with several tests

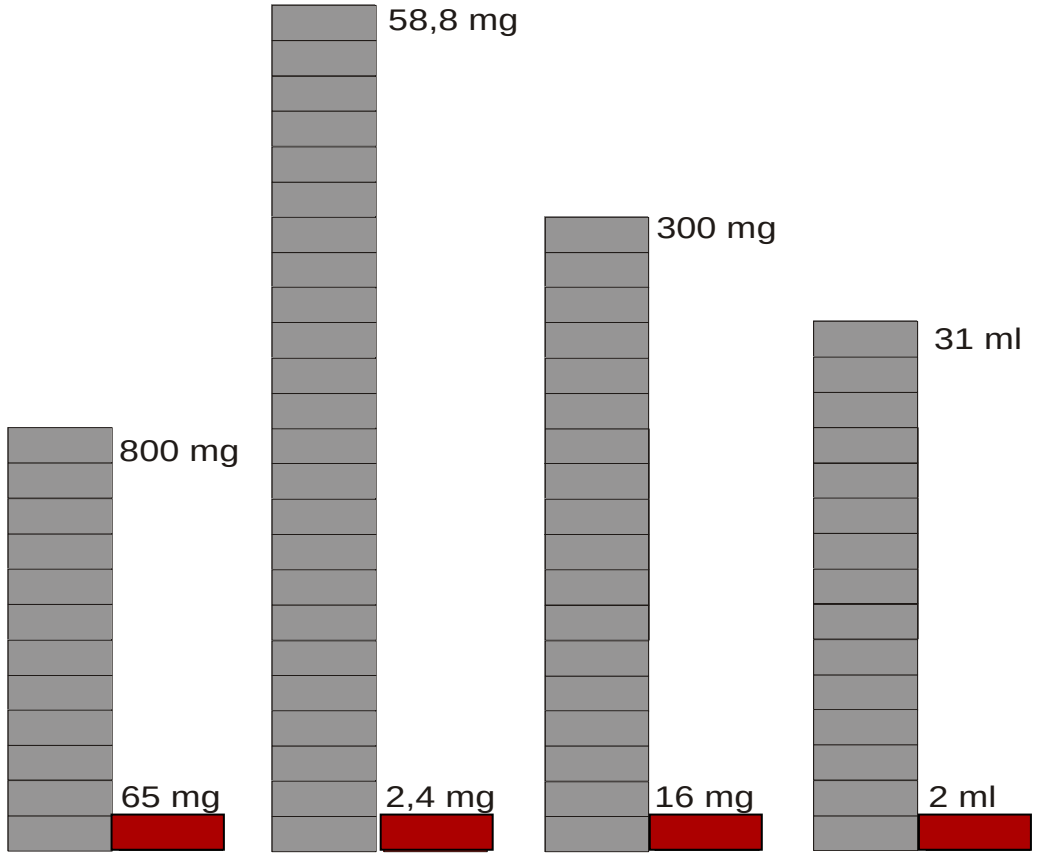
- Cuvette pre-filled reagent
- No waste handling
- No glassware cleaning

# Safety

**~95% fewer chemical reagents than traditional standard method**

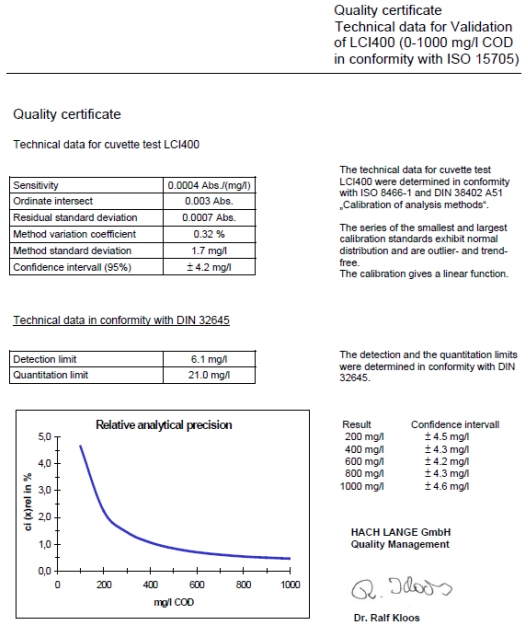
**COD with Standard Method**


**Hach COD Test**



# Easy to use

- Complete solution & ready to use
- All required reagents in one box
- Ideal for wastewater parameters (digestion)
- Easy-to understand  and structured working procedure
  - Pictograms inside box lid
  - Full procedure available by download
- Quality certificate by download



Quality certificate
Technical data for Validation of LCI400 (0-1000 mg/l COD in conformity with ISO 15705)

Quality certificate

Technical data for cuvette test LCI400

| | |
|---|---|
| Sensitivity | 0.0004 Abs./(mg/l) |
| Ordinate intersect | 0.003 Abs. |
| Residual standard deviation | 0.0007 Abs. |
| Method variation coefficient | 0.32 % |
| Method standard deviation | 1.7 mg/l |
| Confidence intervall (95%) | ± 4.2 mg/l |

The technical data for cuvette test LCI400 were determined in conformity with ISO 8466-1 and DIN 38402 A51 „Calibration of analysis methods".

The series of the smallest and largest calibration standards exhibit normal distribution and are outlier- and trend-free.
The calibration gives a linear function.

Technical data in conformity with DIN 32645

| | |
|---|---|
| Detection limit | 6.1 mg/l |
| Quantitation limit | 21.0 mg/l |

The detection and the quantitation limits were determined in conformity with DIN 32645.

Relative analytical precision

cl (x)rel in %

mg/l COD

| Result | Confidence intervall |
|---|---|
| 200 mg/l | ± 4.5 mg/l |
| 400 mg/l | ± 4.3 mg/l |
| 600 mg/l | ± 4.2 mg/l |
| 800 mg/l | ± 4.3 mg/l |
| 1000 mg/l | ± 4.6 mg/l |

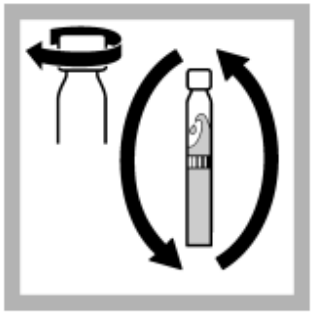
HACH LANGE GmbH
Quality Management

Dr. Ralf Kloos


## Procedure

**1.** Carefully pipet **1.0 mL** of **sample**.

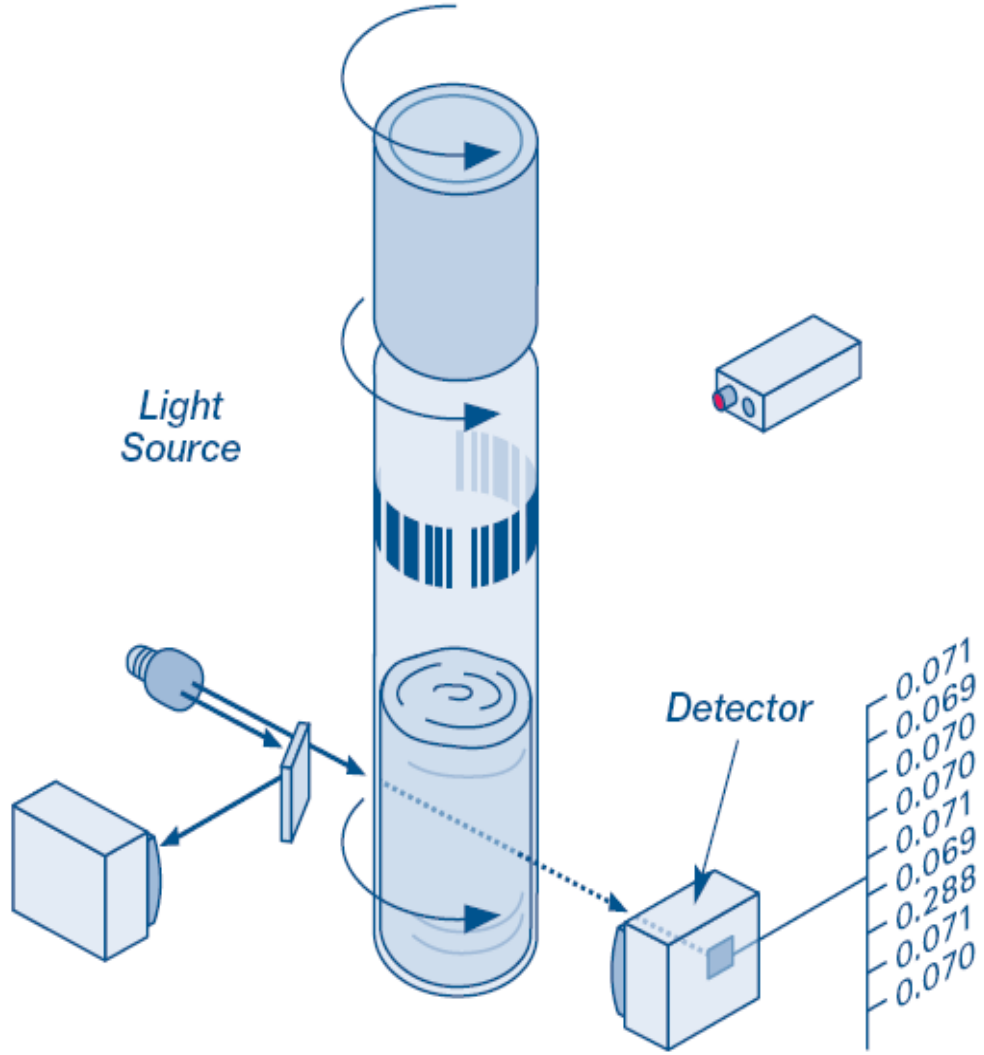
**2.** Carefully pipet **0.2 mL** of **solution A**.



**3.** Close the cuvette and invert a few times until **no more streaks** can be seen.

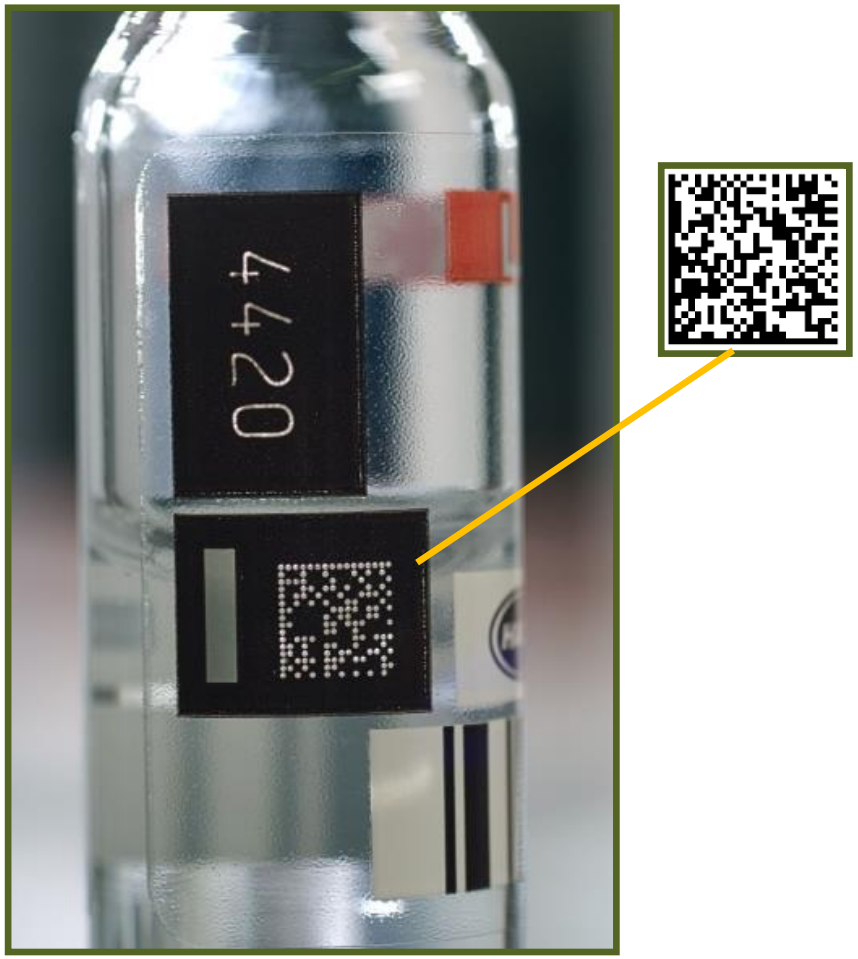
**4.** After **15 minutes**, thoroughly clean the outside of the cuvette and evaluate.

# Accurate Results – 10fold measurement



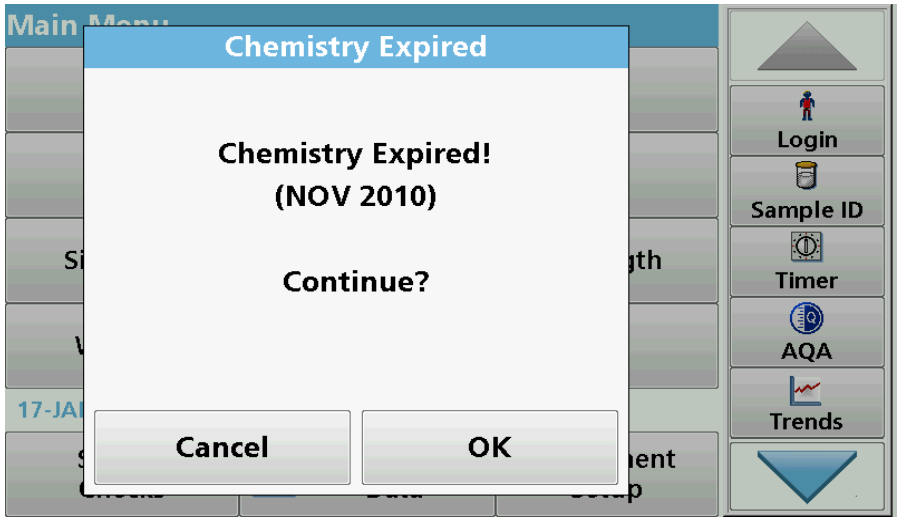

- **Reference beam** technology corrects net deviation or lamp aging effects
- **10-fold-measurement** (including averaging and outlier elimination ) to avoid wrong results from scratches, dirt and fingerprints
- **Warning** in clear text messages  when turbidity or dirty cuvettes in place

# Accurate Results – 2D code

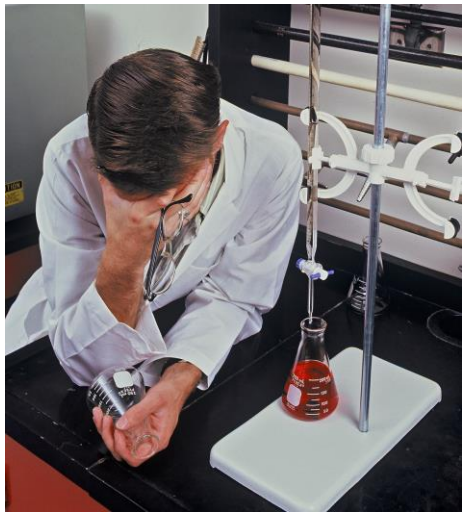



**What comes with the 2D-code:**

- **Test #** and automated check if right test data are available
- **Test Expiration date:** Message if teagents are expired
- **Lot number** (traceability)
- **Lot specific factor** (Truecal)



# Accurate Results – Truecal



**The problem:**
**Inaccurate & Unreliable Testing**

- 8-10% of labs in the EU fail proficiency testing on an annual basis
- Bad readings and potential limit violations are not identified
- Failing proficiency testing with potential loss of laboratory accreditation

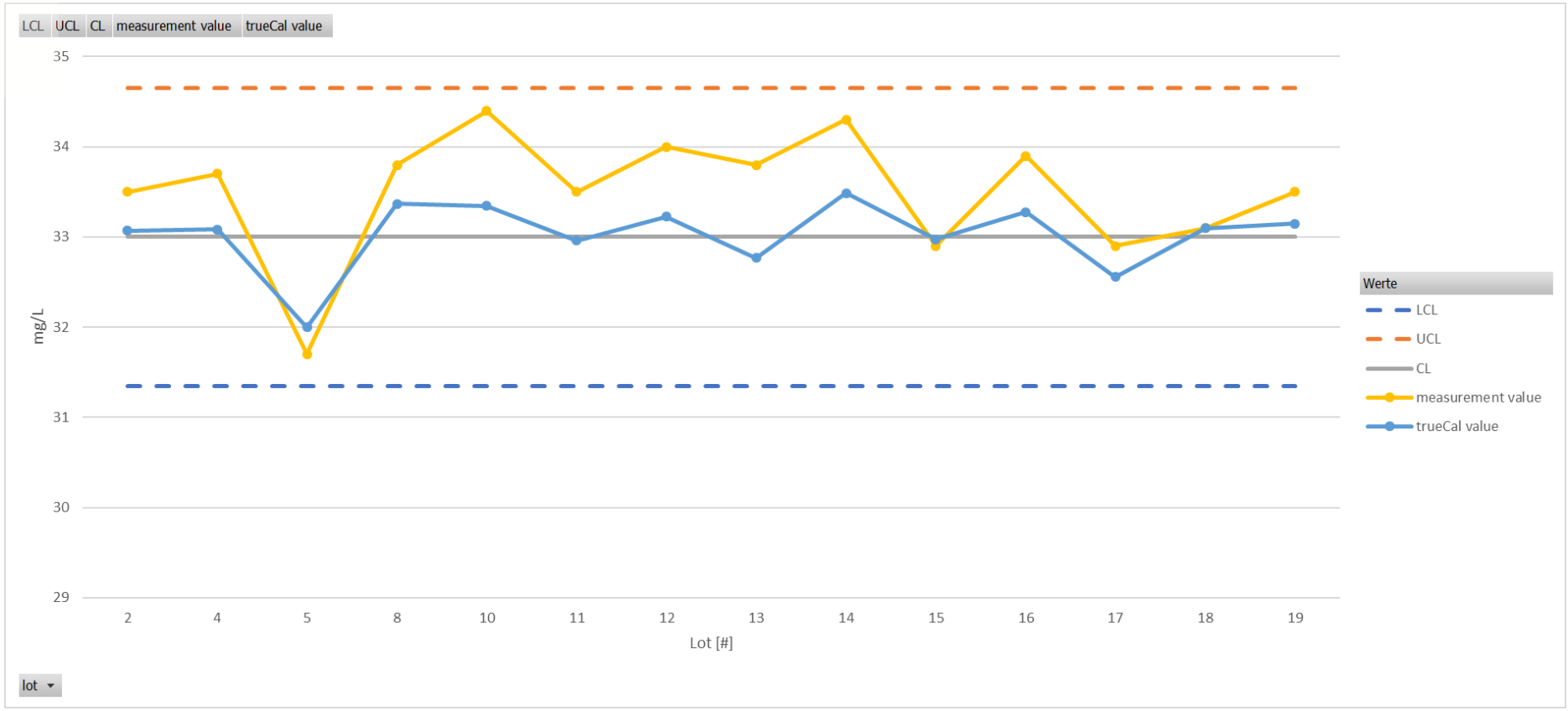
**The solution:**
**Truecal™**

- Lot after lot - Be Right
- Truecal with each vial includes the calibration data for each individual lot, reducing variation in results.
- This allows to meet reporting results and to perform proficiency testing with higher confidence.

- Test #
- Lot/Batch #
- Shelf-life Information
- **Truecal: Lot Specific Calibration**

# Accurate Results – Impact of Truecal

Example: LCK303 High Range Ammonium




- Reduces variation
- Increases accuracy of results
- Higher Confidence

**Compatible with DR3900 and DR6000**

**Focus on WW parameters**: COD (LCK014 / 1414 /114 / 314 / 514 / 614 / 714 / 914 / 1014) - Total N (LCK138 / 238 / 338 / 438) - Ammonium (LCK302 / 303 / 304 / 305 / 503 / 505) - Nitrate (LCK339 / 340 / 540) - Nitrite (LCK341 / 342) - Phosphate (LCK348 / 349 / 350)

# Accurate Results – Always up-to-date with RFID


## Reliable updates in a flash

**Step 1**

The DR 3900 reads the barcode on the cuvette and identifies that a data update is required for the test in question.

**Step 2**

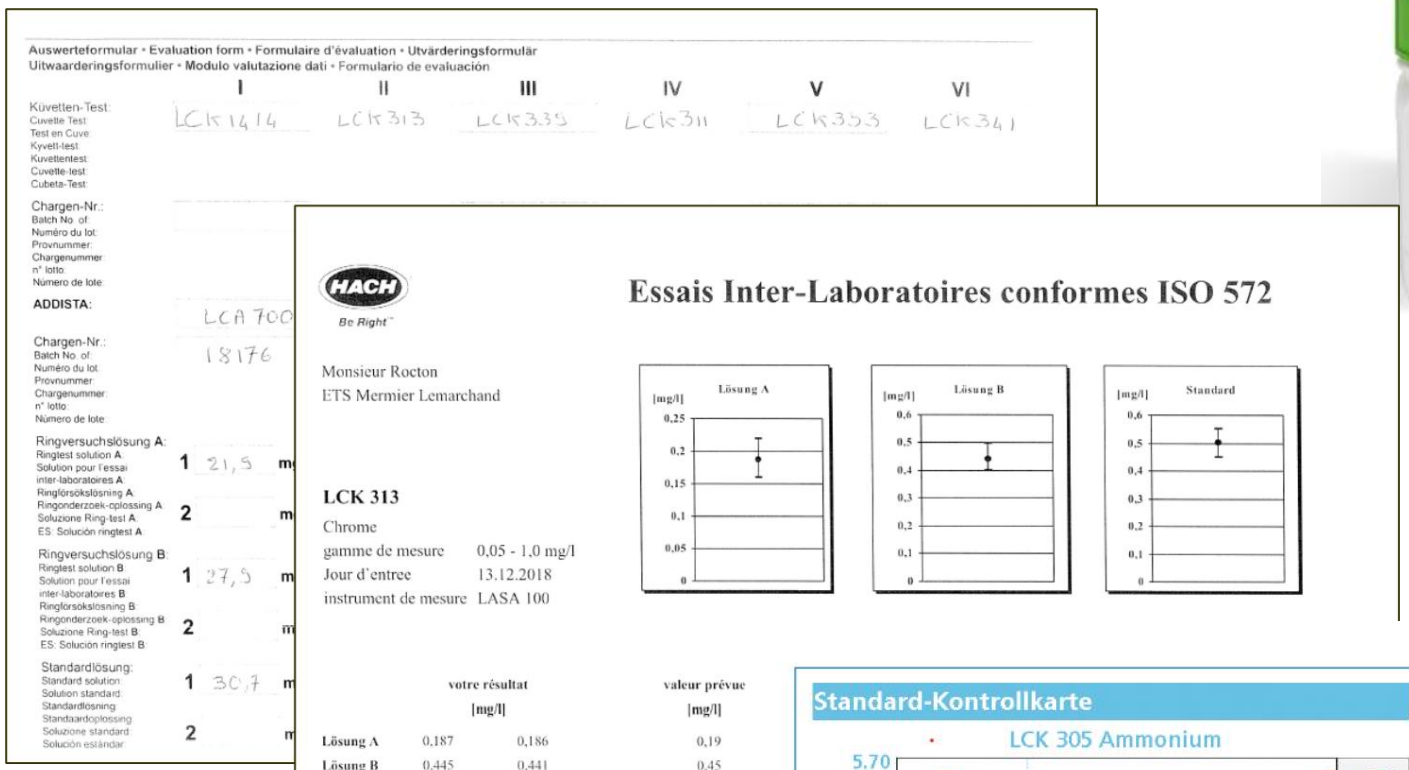
It then indicates that the cuvette packaging should be placed in front of the photometer. After two seconds, an audio signal confirms that the data has been updated.

**Step 3**

Measurement is initiated automatically once the update is complete — using the correct factors to make sure that the measurement result is also correct.

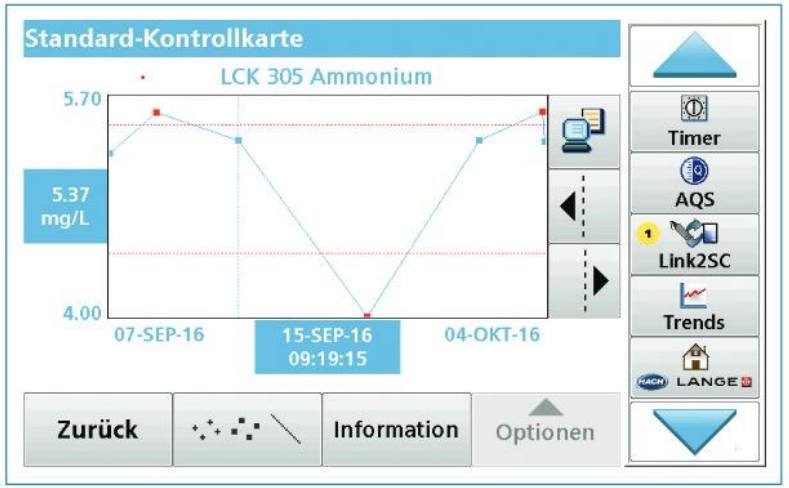
Without RFID sensor the method can be updated via file download from www.hach.com

# Accurate Results – Addista





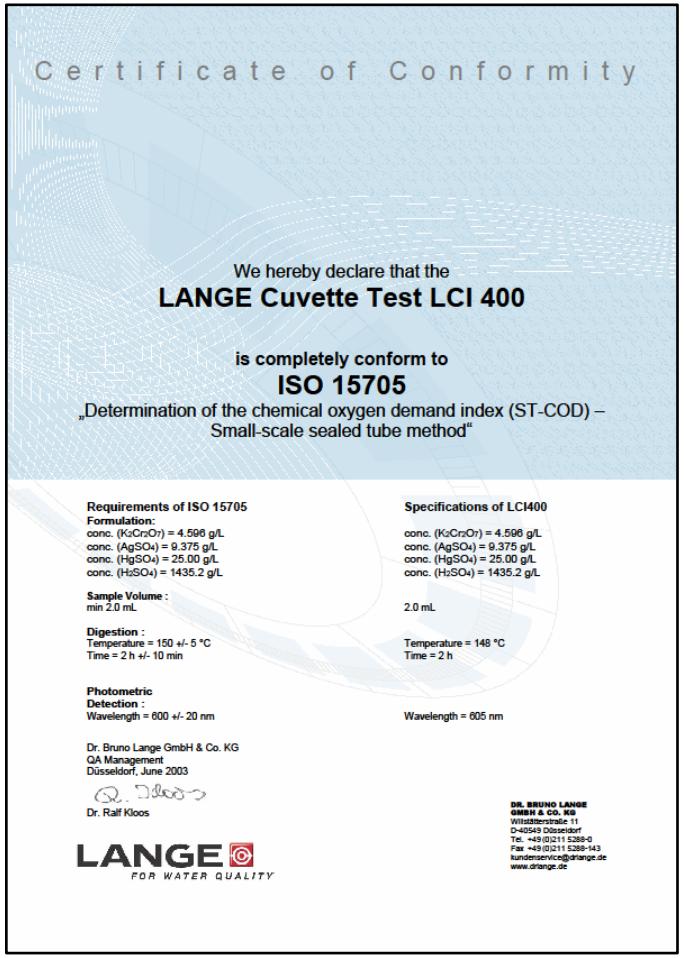
**Several parameters in the same standard solution**




Addista-Standards for system control and free participation in HACH round robin test

Traceable Multi-Standards for accreditated labs

# Accurate Results – ISO Standards



Certificate of Conformity

We hereby declare that the

**LANGE Cuvette Test LCI 400**

**is completely conform to**

**ISO 15705**

„Determination of the chemical oxygen demand index (ST-COD) – Small-scale sealed tube method“

| Requirements of ISO 15705 | Specifications of LCI400 |
|---|---|
| **Formulation:** | |
| conc. ($K_2Cr_2O_7$) = 4.596 g/L | conc. ($K_2Cr_2O_7$) = 4.596 g/L |
| conc. ($AgSO_4$) = 9.375 g/L | conc. ($AgSO_4$) = 9.375 g/L |
| conc. ($HgSO_4$) = 25.00 g/L | conc. ($HgSO_4$) = 25.00 g/L |
| conc. ($H_2SO_4$) = 1435.2 g/L | conc. ($H_2SO_4$) = 1435.2 g/L |
| **Sample Volume :** min 2.0 mL | 2.0 mL |
| **Digestion :** Temperature = 150 +/- 5 °C, Time = 2 h +/- 10 min | Temperature = 148 °C, Time = 2 h |
| **Photometric Detection :** Wavelength = 600 +/- 20 nm | Wavelength = 605 nm |

Dr. Bruno Lange GmbH & Co. KG
QA Management
Düsseldorf, June 2003

Dr. Ralf Kloos

LANGE FOR WATER QUALITY

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D-40549 Düsseldorf
Tel. +49 (0)211 5288-0
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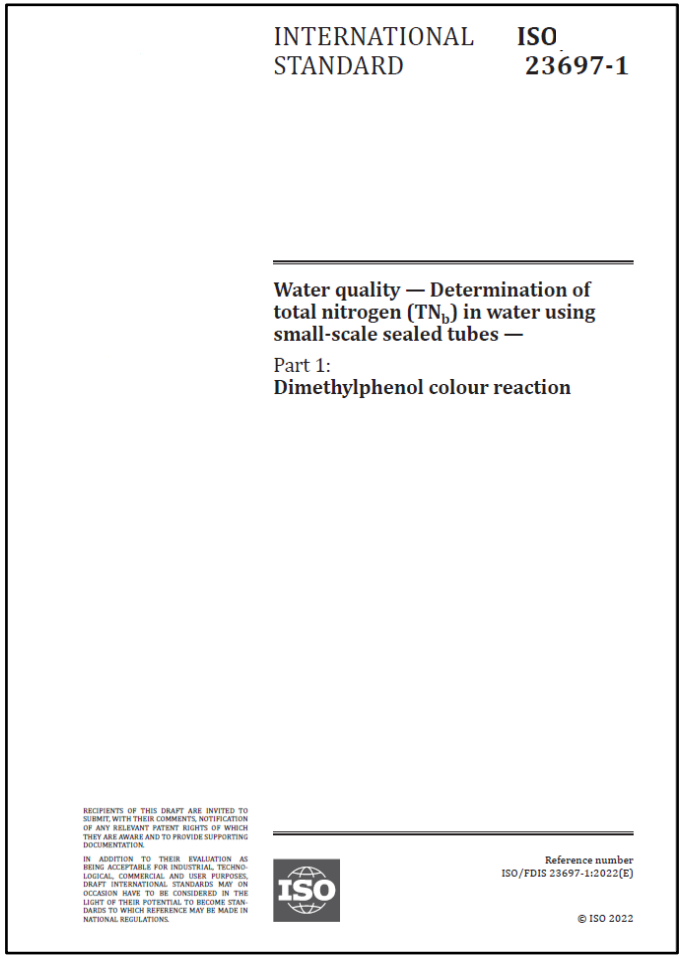
kundenservice@drlange.de
www.drlange.de

**COD ISO 15705:2002**



INTERNATIONAL STANDARD **ISO 23697-1**

**Water quality — Determination of total nitrogen ($TN_b$) in water using small-scale sealed tubes —**

Part 1:
**Dimethylphenol colour reaction**

RECIPIENTS OF THIS DRAFT ARE INVITED TO SUBMIT, WITH THEIR COMMENTS, NOTIFICATION OF ANY RELEVANT PATENT RIGHTS OF WHICH THEY ARE AWARE AND TO PROVIDE SUPPORTING DOCUMENTATION.

IN ADDITION TO THEIR EVALUATION AS BEING ACCEPTABLE FOR INDUSTRIAL, TECHNOLOGICAL, COMMERCIAL AND USER PURPOSES, DRAFT INTERNATIONAL STANDARDS MAY ON OCCASION HAVE TO BE CONSIDERED IN THE LIGHT OF THEIR POTENTIAL TO BECOME STANDARDS TO WHICH REFERENCE MAY BE MADE IN NATIONAL REGULATIONS.

ISO

Reference number
ISO/FDIS 23697-1:2022(E)

© ISO 2022

**Ammonium: ISO 23695**

**TN: ISO 23697-1**

**Nitrate: ISO 23696-1**

# Environmental Protection - Recycling

**Waste Handling in Düsseldorf**

- ~75% of test components returned from our customers to the environment center will be re-used or recycled.

- Certified disposal company & registered as an official recycling center

- Commitment to protect the environment (ISO14001 certified) and a safe working place (ISO45001 certified)

- New technologies which enhance the process are actively implemented if an environmental benefit is found.



GOLD 2022 ecovadis Sustainability Rating

Deutscher Nachhaltigkeitspreis

ENTSORGUNGSFACHBETRIEB bvse ENTSORGER-GEMEINSCHAFT e.V.

# COD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# COD - Chemical Oxygen Demand

**What is COD?**

- Chemical Oxygen Demand
- Sum parameter, determined from a homogenized sample
- Organic compounds are oxidized
- Method derived parameter: Defined conditions K2Cr2O7, 148 °C and 2 h digestion silver-catalysed in strong sulfuric acid)

- Determination by photometry (e.g. ISO 15705) or titration (e.g. ISO 6060) with (NH4)2Fe(SO4)2


ISO 6060 TOC (macro size, titration based)

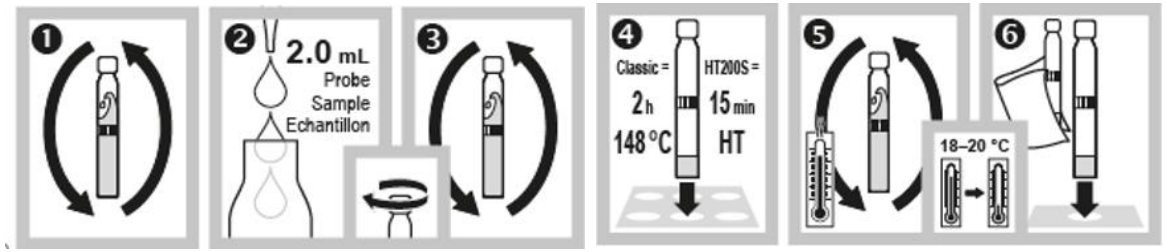

ISO 15705 ST COD with 95% less reagents (micro size, sealed tube COD, photometric based)

# COD – Sample Preparation

- **Homogenization** of sample **is mandatory,** according standards (e.g. DIN 38402-30)
- Particles, fibers or flakes (precipitation) are part **sum parameter**
- **Representative sample**
- **Dispersing tool** needed for homogenization
- Specification: **20,000 rpm for 60 sec.**
- Longer time frames **can influence** the sample
- Final **sample taking** for analysis purposes with **magnetic stirrer**

# COD – Procedure

**Precise COD measurement in six steps**




- Shake cuvette before adding sample
- Add sample into “cloud”
- Close cuvette, start digestion
- Shake warm cuvette again after digestion and cool down
- Make sure the precipitation has settled completely before reading and do not swirl cuvettes just before reading
- Start reading on photometer

**Note**

- The color is stable ($Cr^{3+}$) in the cuvette
- COD tests readings can be done next morning


# COD – Chloride Interference


- Chloride in **high concentrations** lead to false positive results, check **interference – table** in each test manual!
- **Check chloride** content in sample prior to COD analysis (e.g. LCK 311, Chloride test strips)
- If the **chloride** concentration **is above** the **interference limit** of e.g. **1500 mg/l**, sample must be diluted with **COD-free** water

**or better: apply COD tests** with **higher Chloride** tolerance:

- **LCK 1014 COD** (100-2000 mg/l), **$Cl^-$ Tolerance 4,000mg/l**
- **LCK1714 COD salt water** (70 – 250 mg/L), **$Cl^-$ Tolerance 20,000 mg/l**
- **LCK 1814 COD salt water** (7 - 70 mg/L), **$Cl^-$ Tolerance 20,000 mg/l**
- **LCK 1914 COD salt water** (250 - 1000 mg/L), **$Cl^-$ Tolerance 20,000 mg/l**

# COD – Choosing the correct range

- Samples with **COD** values higher than measuring range can be diluted, but usually **not preferred** for COD measurements
- **Different ratio** between dichromate and COD concentration in cuvette, different **oxidation performances**
- Highest accuracy and precision **in the middle of the range**
- **Different test ranges** available to avoid **inaccuracies**

5 – 60 mg/l

15 – 150 mg/l

50 – 300 mg/l

150 – 1000 mg/l

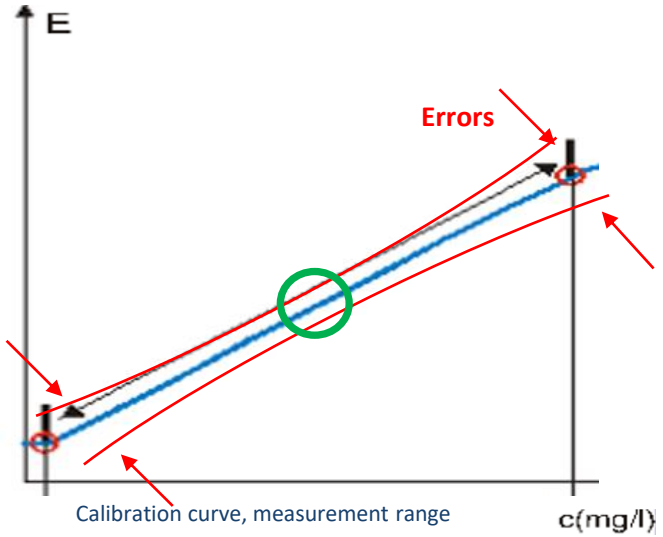
100 – 600 mg/l

100 – 2000 mg/l

1000 – 10000 mg/l

5000 – 60000 mg/l

- Example: COD is 145 mg/l (LCK 314: 15 – 150 mg/L)
- Better to choose LCK 614 (50 – 300 mg/l)



# COD – High Temperature Application

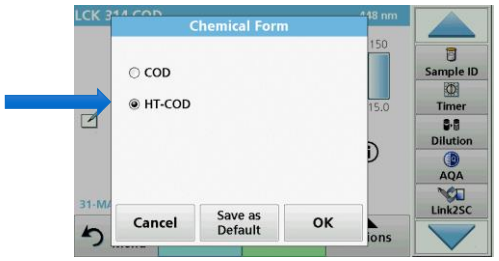
**HT COD application:**

- Companies that **need fast COD results** (examples):
  - unload waste truck
  - fast results for plant control
- HT 200S allows COD digestion **at 170°C in 15 minutes**

- **HT application**: If sample **is unknown** start first with **comparative trials** (HT

- **Municipal wastewater** shows in general **good matches** to standard (ISO 15705, 148°C, 2h)

- For correct documentation the results can be **marked** as **HT-COD**




# COD – Standard Methods









**COD Saltwater Application LCK1714, 1814 1914 – Flemish Standard WAC/III/D/020**

- New Flemish (Belgium) COD Standard: WAC/III/D/020 (1/2021) Vito (independent Flemish research organization)
- WAC/III/D/020 is mandatory to use for COD analytics in saltwater, launched Jan 2021
- Macro size reflux method (e.g. ISO 6060) not used for such samples any longer
- Only micro size Cuvette Tests
- Together with Vito, - Hach introduced a greener analysis method for measuring COD in wastewater (s. “Vision” newsletter, page 14-15):
- https://vito.be/sites/vito.be/files/newsletters/vito_vision_en_april20_lr.pdf

# COD – Regulatory Shift to TOC?

REACH

- **REACH directive:** 2012 **ECHA** (EU Commission) started activities to ban $Cr^{6+}$ , SVHCs ("Substance of very high concerns")
- **Conflict:** COD as **wastewater** parameter, COD **requested by UWWTD**
- **Authorization** needed to **keep working** with $Cr^{6+}$ and COD test **Sunset Date (09/2017)**
- ECHA **exempted** SVHC's ($Cr^{6+}$ ), if used for **scientific research & development** (monitoring of water) and in **amounts < 1t/a**

Current state:

- **~ 2016:** DG Environment (EU Commission) **seeking for alternatives** to COD (go green strategy)
- Several drafts to replace COD by TOC short term
- Plant **specific conversion factors** suggested, for each WWTP (Waste Water Treatment Plant)
- **General replacement not accepted**, but **total revision** of UWWTD started
- Some Member States,e.g. NL start investigations to **replace COD by TOC**

Future state:

Revised EU UWWT Directive October 2022

- TOC official monitoring parameter, member states can choose between TOC or COD
- Lower discharge limits for TN and TP
- Removal and Monitoring of Micropollutants (e.g. painkiller, antibiotics, anti-corrosion agents…)
- Wastewater surveillance for multiple viruses (incl SARS-CoV- II)
- **NL moves away from COD to TOC in 2025 for all sewage charge testing**

# TOC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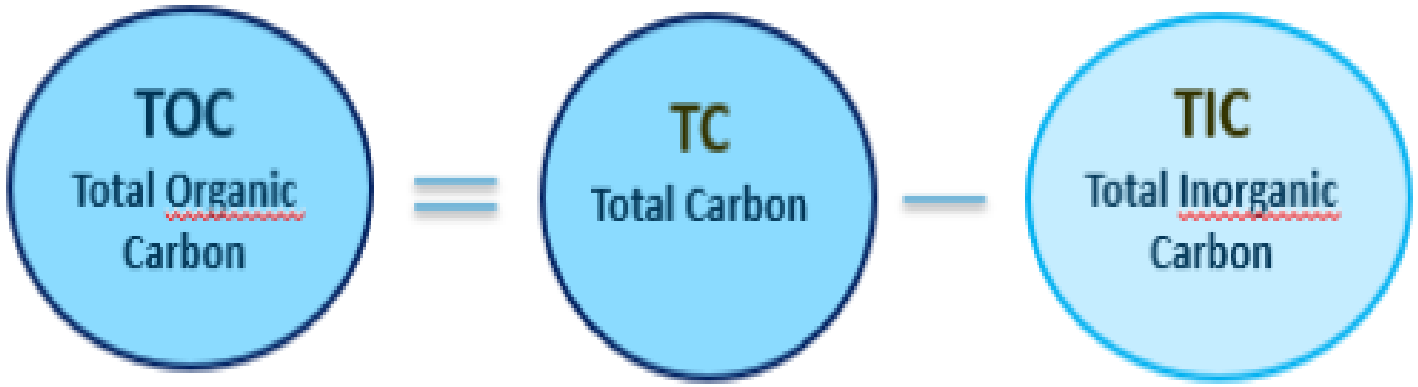
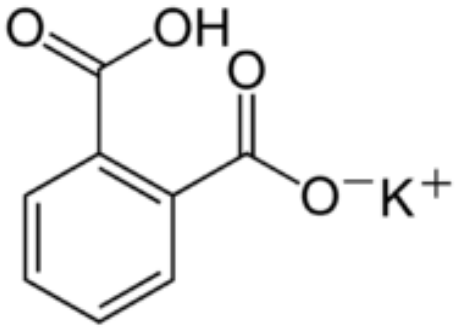
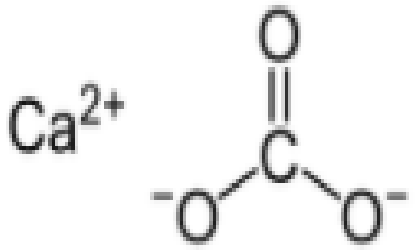
# What is TOC?




**KHP** Potassium hydrogen phthalate

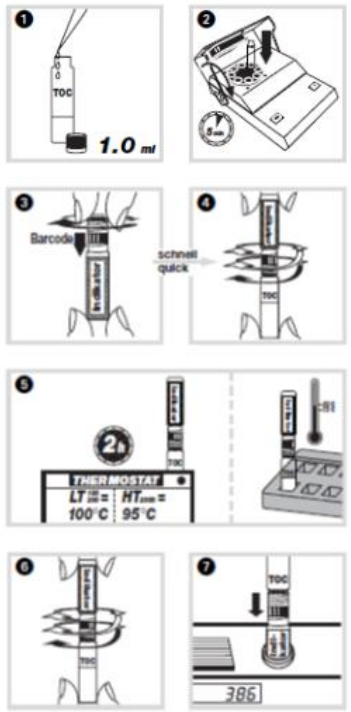



Calcium Carbonate

TOC Detection methods:
1) Direct Method
2) Difference Method

# TOC Direct Method

## LCK385 - LCK387: Persulfate Oxidation after IC removal



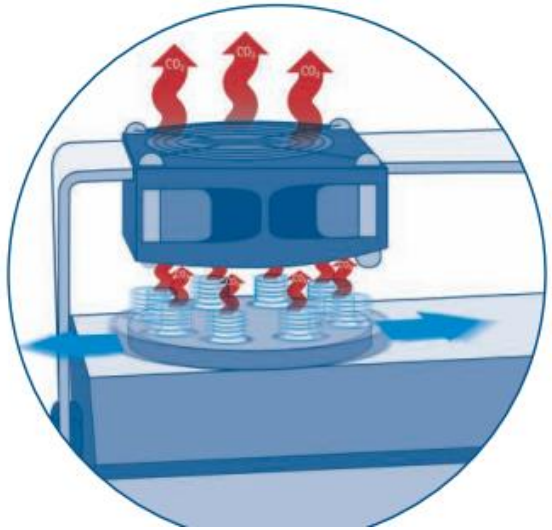


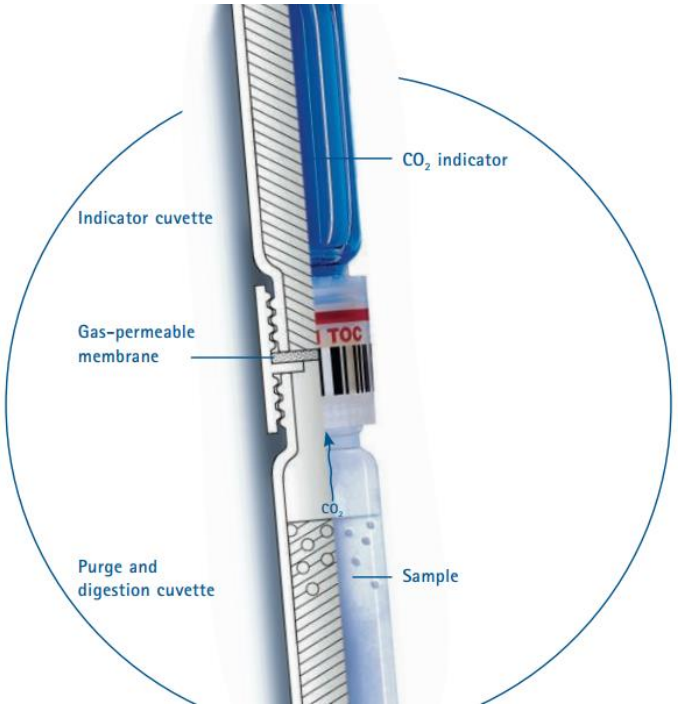
**IC removal**

- **Sample + diluted sulfuric acid -> vibration and fan in TOC-X5 shaker**
- **5 min vibration sufficient to remove 250mg/L TIC**

**Mechanism**

- **persulfate digestion 100° C / 120 min**
- **Oxidation of organic carbon**
- **$CO_2$ passes gas permeable membrane**
- **Color change of pH indicator**
- **Ranges: 3-30mg/L; 30-300mg/L;300-3000 mg/L**





# TOC Difference Method

## LCK380-LCK381: difference method

- **For samples containing VOC or low TIC**
- **2 cuvettes required: 1 for TC and 1 for TIC**
- **Photometer calculates**

  **TOC = TC-TIC**

# Phosphate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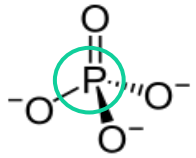
# Phosphate Overview

Sum parameter
$P_{total}$

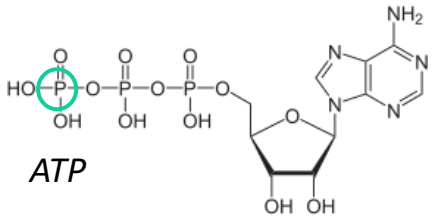
soluble

nonsoluble/bounded

**ortho-Phosphate:**

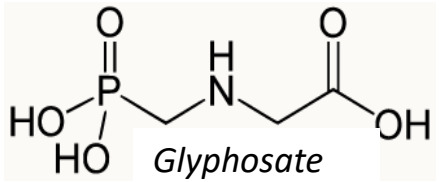


**Polyphosphate**



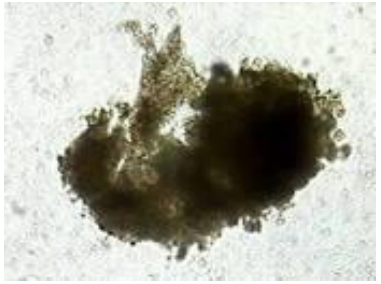
*ATP*

**Phosphonates** (C-bounded phosphorus compounds)



*Glyphosate*

**Specially bound Phosphate** (Organic and inorganic compounds)



*Mud flake*

# Phosphate – Regulatory Outlook

**Water Framework Directive (WFD)**

- WFD‘s goal is to **increase water quality** by 2027
- Achieving **“good status“** for rivers, lakes, coastal waters and groundwater.
- Wastewater Treatment Plants (WWTP‘s) **“point-sources“**

**Outlook:**

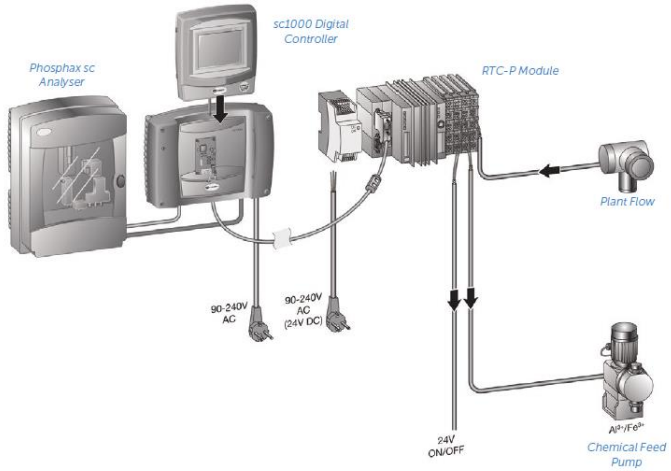
- Ongoing **lowering of Phosphorus concentrations** in surface waters **until 2027 to 0.05 mg/L P**
- **Challenging treatment** of existing WWTP‘s
- **Precipitation methods** of WWTP’s can reach their limits
- **New treatment** techniques & **new monitoring** systems to come

# Phosphate – Hach solutions adressing WFD goals

**Laboratory based measurement**
Ultra-low range Phosphate
Range: **0.01-0.5mg/l $PO_4$-P** (ortho)
50mm cuvette with Dosicap
DR3900/DR6000
Phosphor molybdenum blue-method
Method according ISO 6878-1-1986



**Continuously measurement solution**
Phosphax sc LR (Low Range)
Range: **0.015-2 mg/L $PO_4$-P** (ortho)
Yellow method
Aeration tank and WWTP effluent
Surface water monitoring





**Claros Process Management**
Claros RTC (Real Time Control)
RTC-P module for Phosphorous removal

# Phosphate – Different options

- Phosphate tests to measure different phosphate components
- Different sample **preparation** & **digestion** of sample
- Evaluation as **ortho $PO_4$ –P** or **TP** (total Phosphorous)
- Legal reporting: **WW** as **$PO_4$-P, DW** as **$PO_4$**


| Target | Sample | Oxidation | Digestion |
|---|---|---|---|
| **Total Phosphate** | Homogenization | Yes | Yes |
| **Ortho-Phosphate** | Filtration | No | No |
| **Polyphosphate** (Ortho-phosphate is co-determined) | Filtration | No | Yes |
| **Phosphonates** (O-Phosphate & Polyphosphates are co-determined) | Filtration | Yes | Yes |

# Phosphate – Procedure

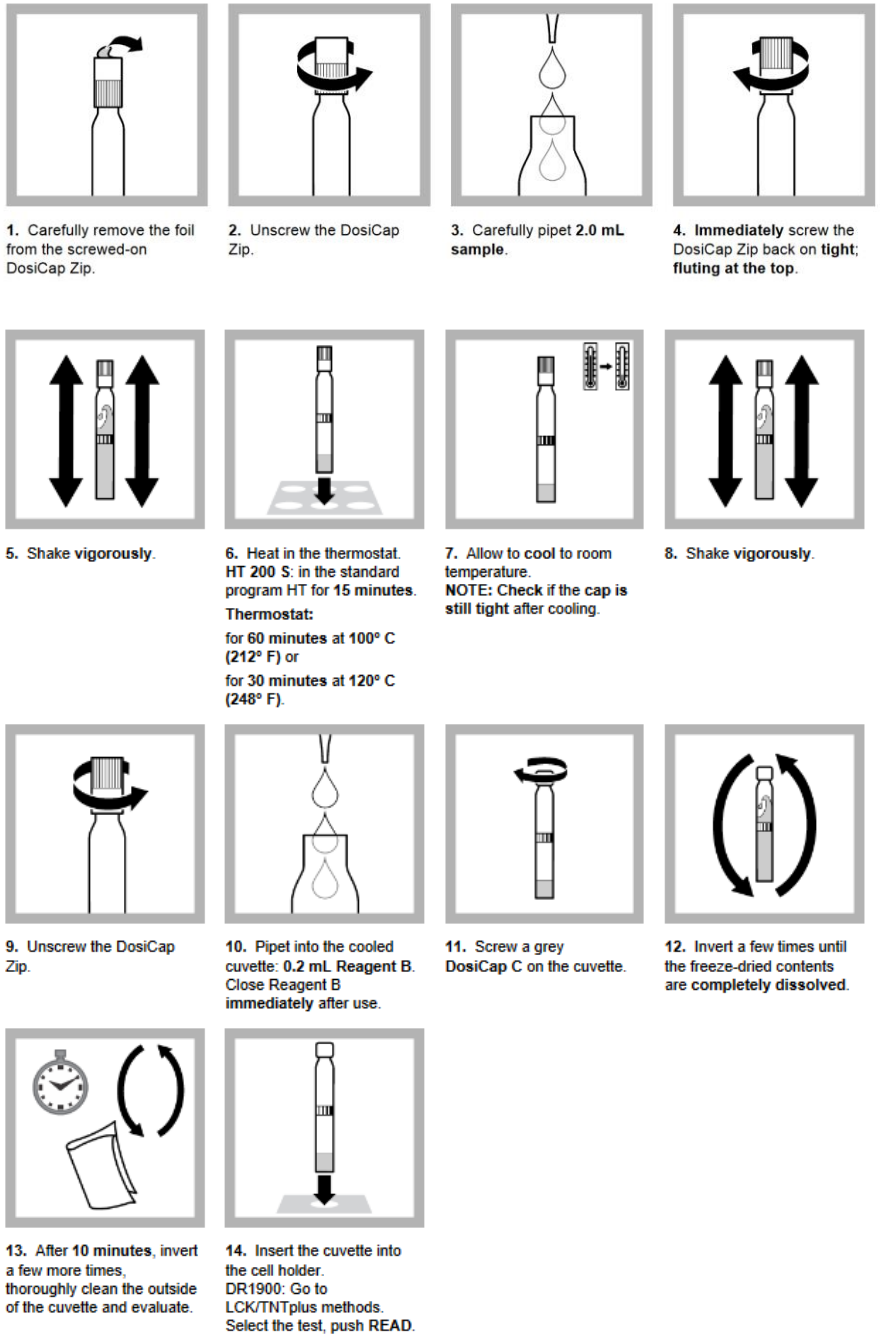
- Analysis done out of **homogenized** sample:
  - Shake (up to 5 l)
  - Magnetic stirrer
  - Disperser
  - Ultrasonic bath

- Choose correct **measuring range** of test
- Otherwise, dilute sample

- **Oxidation in Reactor:**
  - HT200S: 15 mins
  - LT200: 30 mins, 120°C
  - LT200: 60 minutes at 100° C

➔ Higher Temperature to speed up digestion time

**Procedure total phosphorus**



1. Carefully remove the foil from the screwed-on DosiCap Zip.
2. Unscrew the DosiCap Zip.
3. Carefully pipet **2.0 mL sample**.
4. **Immediately** screw the DosiCap Zip back on **tight**; **fluting at the top**.
5. Shake **vigorously**.
6. Heat in the thermostat. **HT 200 S**: in the standard program HT for **15 minutes**. **Thermostat:** for **60 minutes** at **100° C (212° F)** or for **30 minutes** at **120° C (248° F)**.
7. Allow to **cool** to room temperature. **NOTE: Check** if the **cap is still tight** after cooling.
8. Shake **vigorously**.
9. Unscrew the DosiCap Zip.
10. Pipet into the cooled cuvette: **0.2 mL Reagent B**. Close Reagent B **immediately** after use.
11. Screw a grey **DosiCap C** on the cuvette.
12. Invert a few times until the freeze-dried contents are **completely dissolved**.
13. After **10 minutes**, invert a few more times, thoroughly clean the outside of the cuvette and evaluate.
14. Insert the cuvette into the cell holder. DR1900: Go to LCK/TNTplus methods. Select the test, push **READ**.

# Nitrogen Parameters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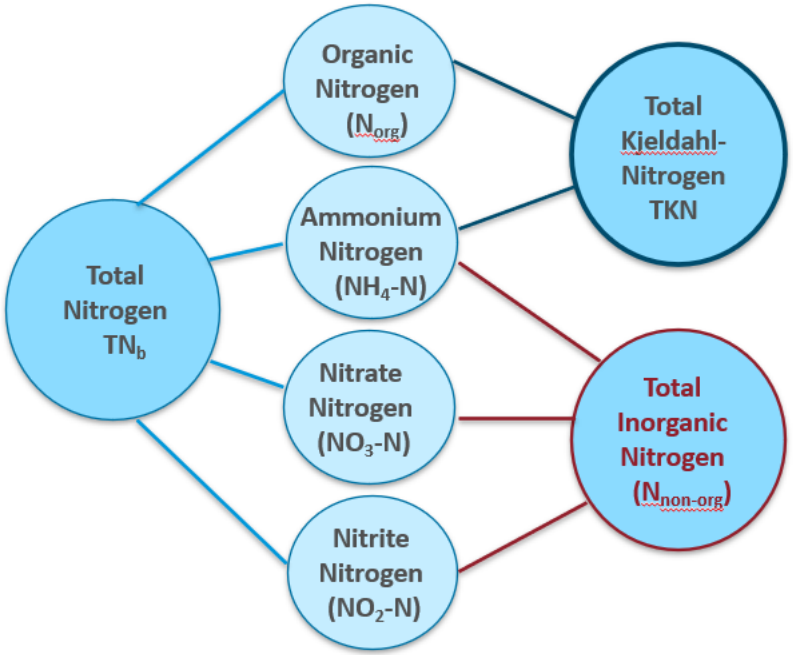
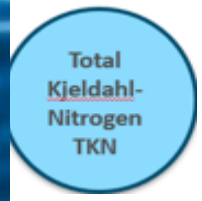
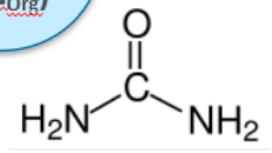
# Nitrogen – Definition Nitrogen Parameters



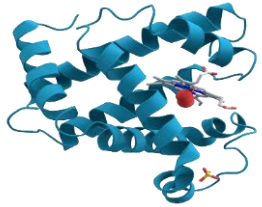




**Total Kjeldahl-Nitrogen:**

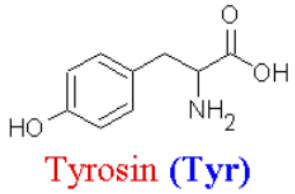
- Sum of Ammonium + Organic Nitrogen
- Analyzed by "Kjeldahl-Method"


**Urea:**
Important role in biological processes, e.g. metabolism of proteins



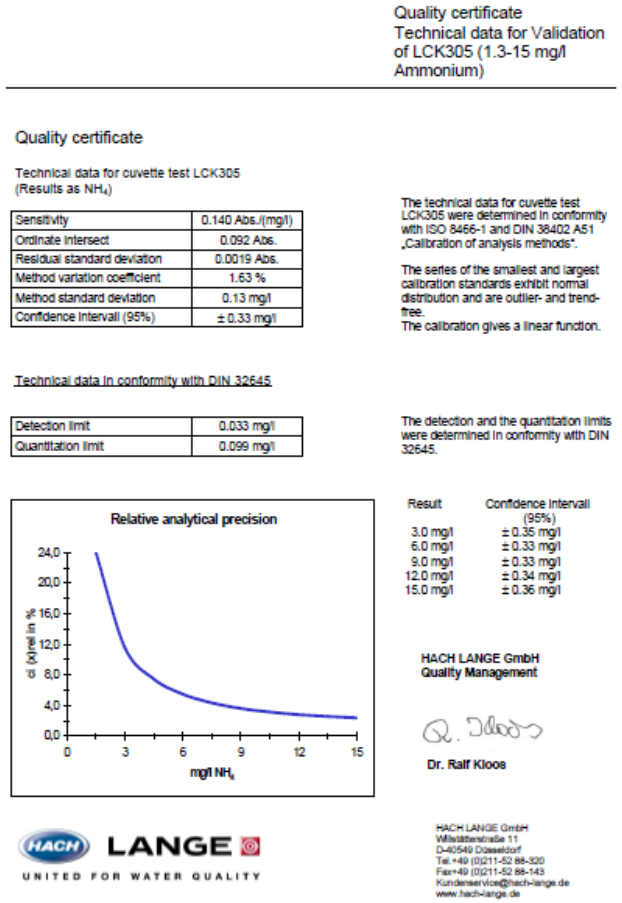
**Protein** (protein):
Biological macromolecule, formed from amino acids by peptide bonds




**Organic acids** (amino acids):
e.g. Tyrosine, non-essential proteinogenic α-Amino acid, casein (cheese)

# Ammonium

- ISO standard **(ISO 23695)**
- Ammonium ions are not bounded/soluble, direct readings
- Filtering if turbidity is present
- 
- Highest precision/accuracy in the middle of MR
- Multiple ranges enable most accurate testing without diluting, e.g. Ammonium



Quality certificate
Technical data for Validation of LCK305 (1.3-15 mg/l Ammonium)

Quality certificate

Technical data for cuvette test LCK305
(Results as $NH_4$)

| | |
|---|---|
| Sensitivity | 0.140 Abs./(mg/l) |
| Ordinate intersect | 0.092 Abs. |
| Residual standard deviation | 0.0019 Abs. |
| Method variation coefficient | 1.63 % |
| Method standard deviation | 0.13 mg/l |
| Confidence intervall (95%) | ± 0.33 mg/l |

The technical data for cuvette test LCK305 were determined in conformity with ISO 8466-1 and DIN 38402 A51 „Calibration of analysis methods".

The series of the smallest and largest calibration standards exhibit normal distribution and are outlier- and trend-free.
The calibration gives a linear function.

Technical data in conformity with DIN 32645

| | |
|---|---|
| Detection limit | 0.033 mg/l |
| Quantitation limit | 0.099 mg/l |

The detection and the quantitation limits were determined in conformity with DIN 32645.

Relative analytical precision

σ (rel) in %

mg/l $NH_4$

| Result | Confidence intervall (95%) |
|---|---|
| 3.0 mg/l | ± 0.35 mg/l |
| 6.0 mg/l | ± 0.33 mg/l |
| 9.0 mg/l | ± 0.33 mg/l |
| 12.0 mg/l | ± 0.34 mg/l |
| 15.0 mg/l | ± 0.36 mg/l |

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Quality Management

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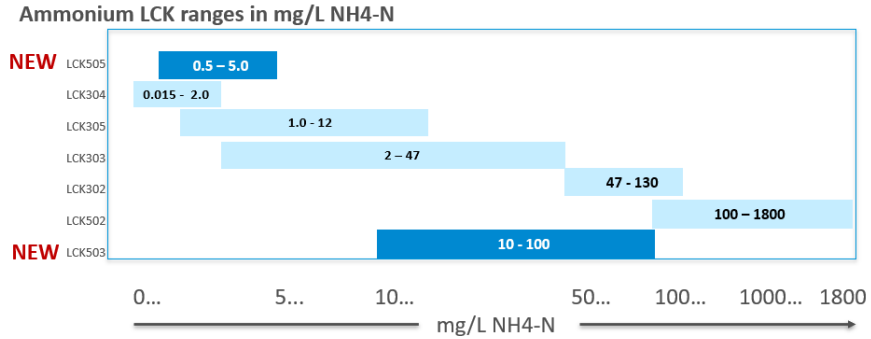
UNITED FOR WATER QUALITY

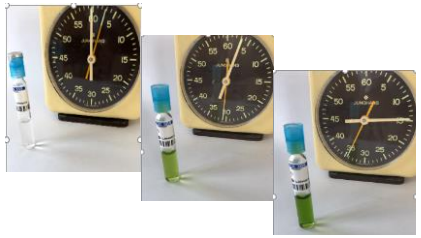


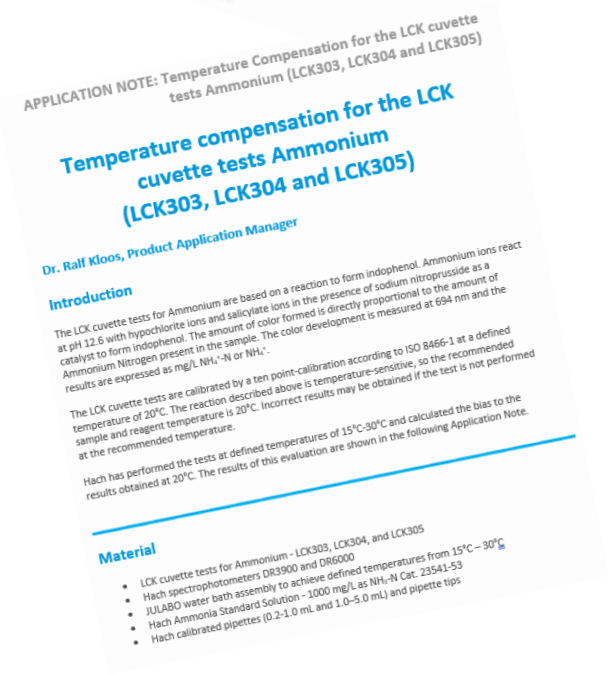

# Ammonium – Tipps & Tricks

- Interferences from water sample are stated in each working manual
- If colored sample or turbidity is present, a separate determination of a **sample-specific-blank** according **Hach's Application A 130 might be required**

| Test | Cuvette | Sample | Dist. water | Cap | Reagent A | Reagent B |
|---|---|---|---|---|---|---|
| LCK 302 Ammonium | Analysis cuvette | 0.2 mL | — | Original cap | — | — |
| LCK 303 Ammonium | Analysis cuvette | 0.2 mL | — | Original cap | — | — |
| LCK 304 Ammonium | Analysis cuvette | 5.0 mL | — | Original cap | — | — |
| LCK 305 Ammonium | Analysis cuvette | 0.5 mL | — | Original cap | — | — |
| LCK 307 Boron | Empty cuvette* | 2.5 mL | — | Red plug | 1.0 mL | — |
| LCK 310 Chlorine | Empty cuvette* | 2.0 mL | — | Red plug | — | — |


- The chemical reaction is temperature-dependent (room temperature)
- If temperature is too warm (e.g. non-air conditioned laboratory in mid-summer): **Application „Temperature Compensation"** is recommended (only DR3900/6000)
- The chemical reaction is very time-dependent (15 min) and must be strictly observed

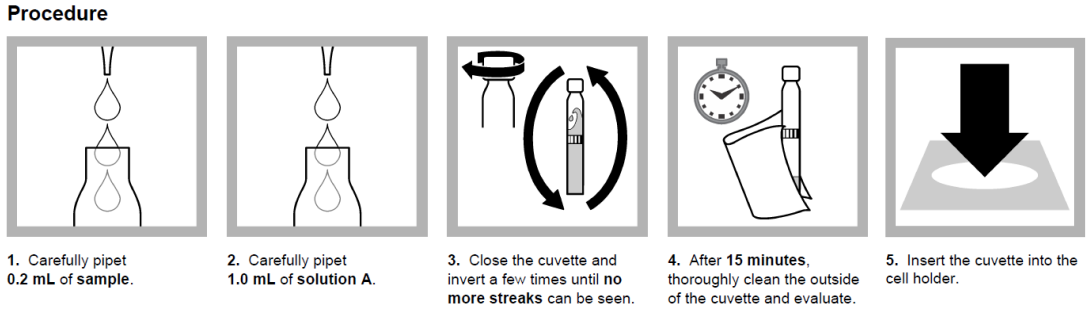




# Nitrate – Tipps & Tricks

- ISO standard **(ISO 23696)**

- Reliable results in 5 steps (example LCK340):





- Perform analysis in a timely manner after sampling or preserve the sample
- Not more than 3 hours should elapse between sampling and analysis.
- High loads with **oxidizable organic substances (COD > 200 mg/l)** lead to **additional coloration** of the reagent (false positive results)
- Chloride concentrations > 500 mg/L in a samples interfere (false negative results)
- If dilution is no option due to too low NO3 concentration, Chloride removal using Silver Oxide (LCW 925, up to 20 g/l $Cl^-$ ) is recommended

# Total N – Tipps & Tricks


1-16 mg/L TNb


5-40 mg/L TNb


20-100 mg/L TNb

**Principle:**

- ISO standard (**ISO 23697**)
- **Inorganic and organically** bound **Nitrogen** is oxidized to Nitrate
- Thermal digestion in **reaction tubes** with Peroxydisulfate
  - 30 minutes at 120 °C (LT200)
  - 15 minutes with HT200s
- **Photometric determination** and calculation to TNb

**Interferences:**

- **Sample homogenization** is mandatory
- Dependent on TN range, specific concentrations of chloride or high COD may interfere with the digestion and result in low findings (see test procedures!)
- Reaction tubes (20 mm) recommended to use **max 7 times** (carry over effects, **Nitrogen-free** water needed)
- Slight **turbidities present** do not interfere
- During the reaction, a slight pink coloration may form. The coloration does not affect the evaluation.

**New range available! LCK438 100-250 mg/L TNb**

# Thank you!