

Validation of COD method (MDP) – Experience report



Changing the paradigm of water pollution monitoring

Dr. Christian Prokisch, 03.08.2018

Agenda



Company



MN Water Analysis



ATP Protocol



ATP for *NANOCOLOR® COD*



Summary



Company

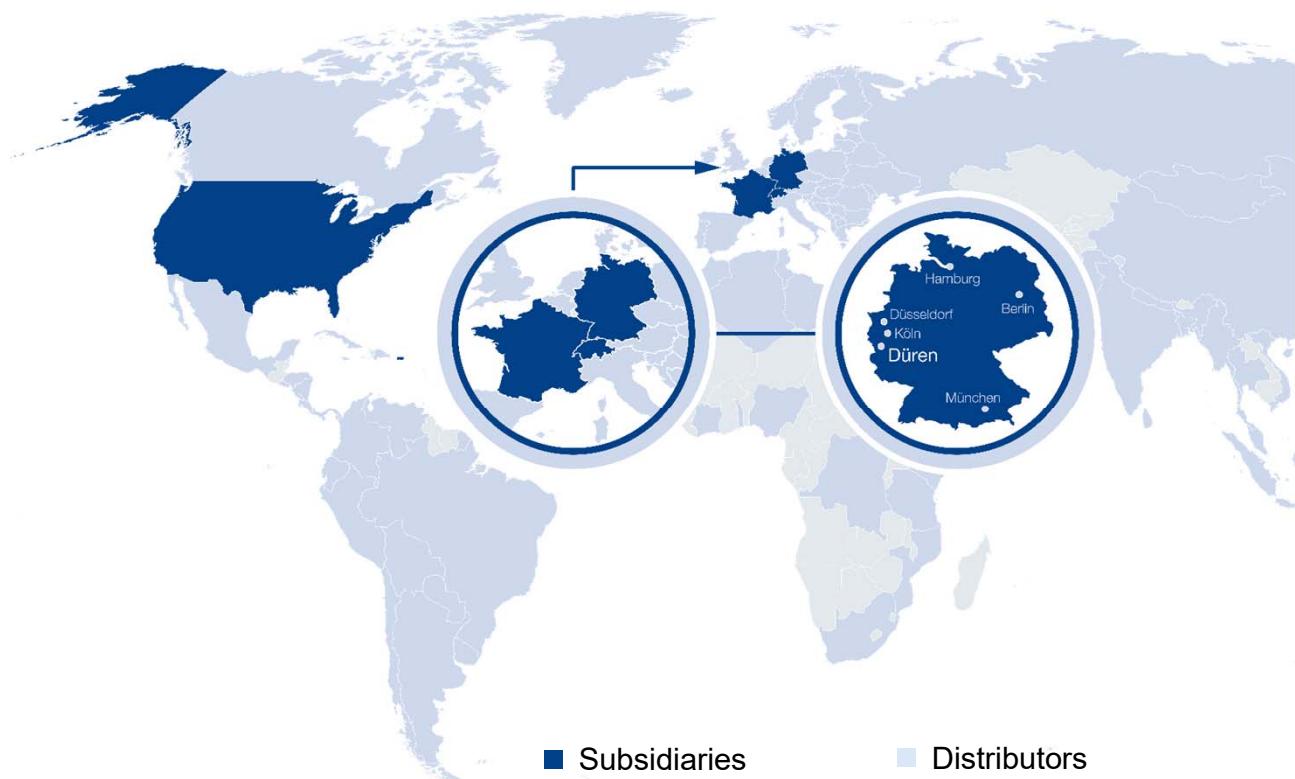




Company

MN today

- 4th Generation family owned
- More than 650 employees
- More than 25.000 products
- Turnover 115 Mio. €



Company



Business units

1911



Filtration

1959



Rapid Tests

1961



Chromatography

1970



Water Analysis

1989



Bioanalysis



MN Water Analysis





MN Water Analysis

Why are we here?

- Market share NANOCOLOR®
 - Germany: ca. 40%
 - US: 0%
- Get experience with US regulations



Get acceptance for COD tube tests



MN Water Analysis

Outstanding photometers

- NANOCOLOR® VIS II
 - Revolutionary user experience with 10 inch HD touch screen display
 - Intuitive, icon-based menu guidance
 - Integrated turbidity control





MN Water Analysis

Competitive heating blocks

- NANOCOLOR® VARIO 4
 - Touch screen with intuitive menu navigation
 - Lockable protective lids and safety covers
 - Calibrated sensors to control digestion temperature optional

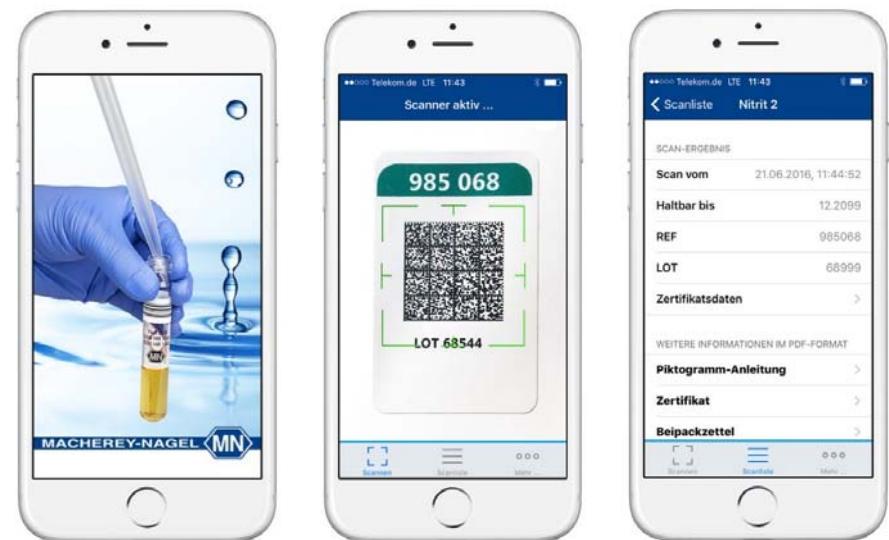




MN Water Analysis

Innovative access to test data

- NANOCOLOR® App
 - LOT specific data
 - Instructions for use
 - Safety information



Small things make a difference



ATP protocol appendix H





ATP protocol appendix H

Method defined parameter (MDP)

- “[...] defined solely by the method used to determine the analyte [...]”
- Examples:
 - BOD
 - Color
 - COD
- “[...] any modifications [...] requires EPA review [...]”





ATP protocol appendix H

What the EPA writes on MDP...

- “An ATP that achieves **better** results is not an appropriate goal”
- “common statistical tests are not useful [...] for MDPs”
- “EPA would not [...] approve any applications [...] that failed [...] side-by-side comparison studies”





ATP protocol appendix H

New: Phase 1

- 1 laboratory
- 9 matrices
- Side-by-side analysis
- “*EPA employs the Root Means Square Deviation (RMSD) ” ...*



Goal: no statistical difference



ATP protocol appendix H

Statistic for Phase 1

- For the case of 3 replicates

$$\bullet RMSD = \sqrt{\frac{\sum_{j=1}^J (\bar{x}_{RMj} - \bar{x}_{ATPj})^2}{J}}$$

$$\bullet RMSD_{max} = \sqrt{\frac{2MSE}{n}} F(0.95; J; 2J(n - 1))$$

$$\bullet MSE = \frac{1}{2J} \sum_{j=1}^J \sum_{k=1}^2 s_{jk}^2$$

$\bar{x}_{RMj}; \bar{x}_{ATPj}$ = j^{th} sample mean
for reference method and ATP

J = total number of samples

s_{jk} = standard deviation for sample
 j and method k



Correlate difference of means to standard deviation



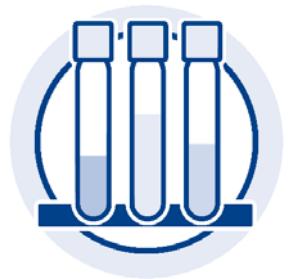
ATP protocol appendix H

Phase 2

- 9 laboratories
- 9 matrices
- QC testing
- Use statistical methods from “New Methods” protocol



Goal: obtain QC acceptance criteria



ATP for NANOCOLOR® COD





ATP for NANOCOLOR® COD

Methods to detect oxygen demand

- BOD₅ – established in US
 - „the original“
 - Takes 5 days
- TOC – not yet widely established
- COD – established in Europe
 - Uses poisonous and carcinogenic chemistry
 - Quick and reliable results

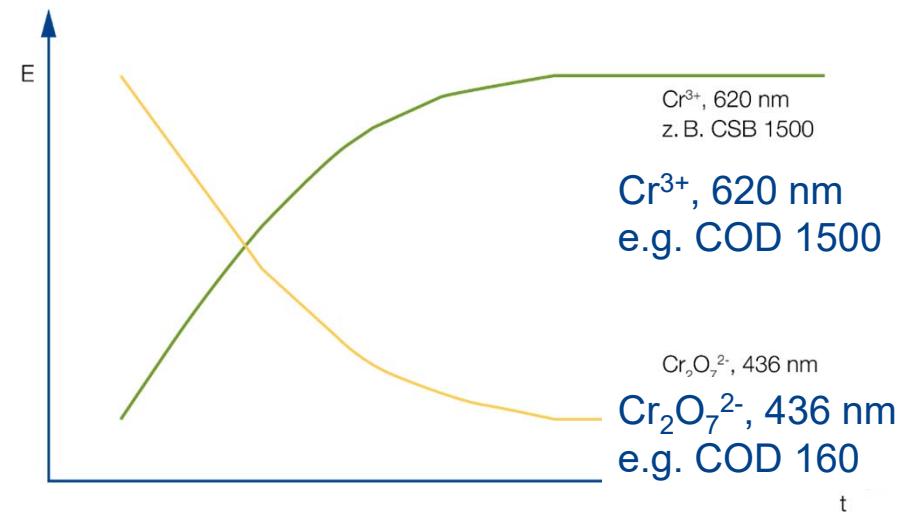




ATP for NANOCOLOR® COD

Method summary

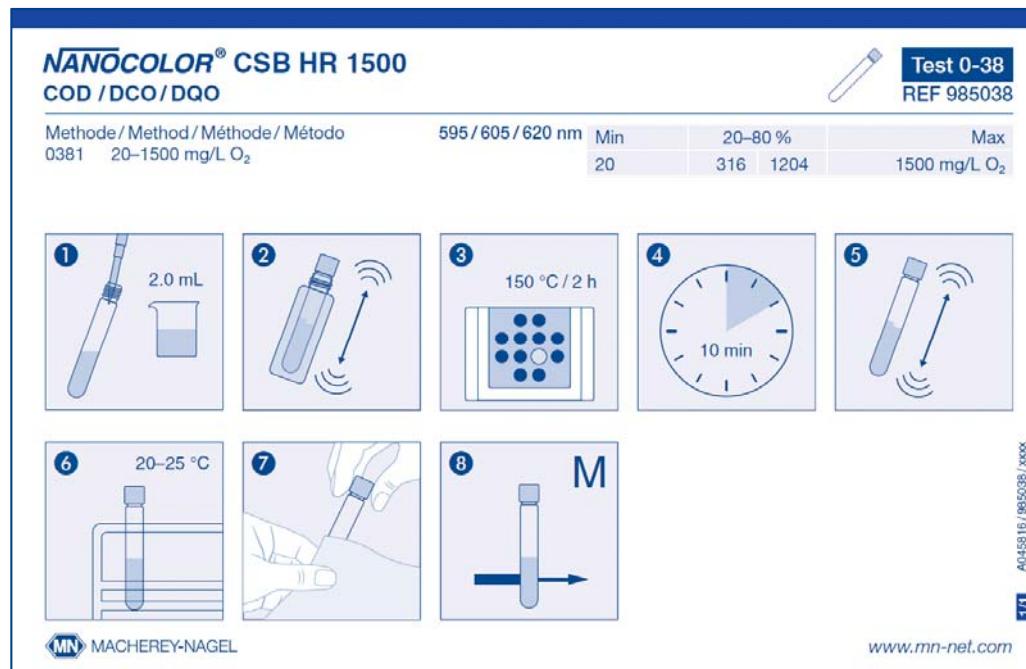
- Tube tests for chemical oxygen demand
- Principle
 - $\text{Cr}_2\text{O}_7^{2-}$ + "Dirt" → 2 Cr^{3+}
- NANOCOLOR® COD HR 1500
- NANOCOLOR® COD LR 150





ATP for NANOCOLOR® COD

Procedure



ATP for NANOCOLOR® COD



Study Design

- Phase 1
 - Flowers Chemical Laboratories
 - 9 different matrices
 - Compared to HACH 8000
- Phase 2
 - Study Management by Flowers Chemical Laboratories
 - A total of nine different labs
 - 9 matrices, 1 per lab
 - QC data





ATP for NANOCOLOR® COD

Matrix Samples

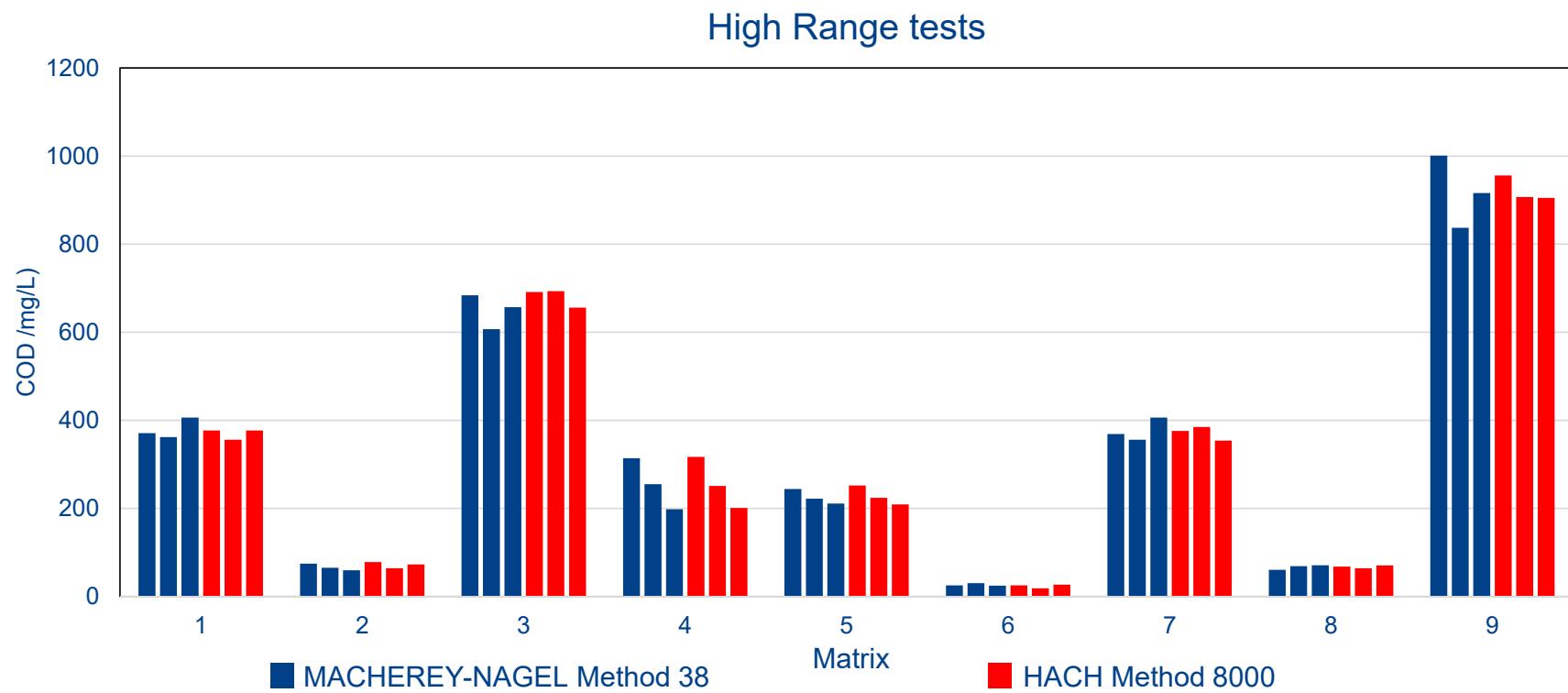
- ATP requirement: real life samples
- COD Low Range
 - POTW effluents
- COD High Range
 - Industrial user influents
 - POTW influents
 - Primary Clarifier effluent



ATP for NANOCOLOR® COD



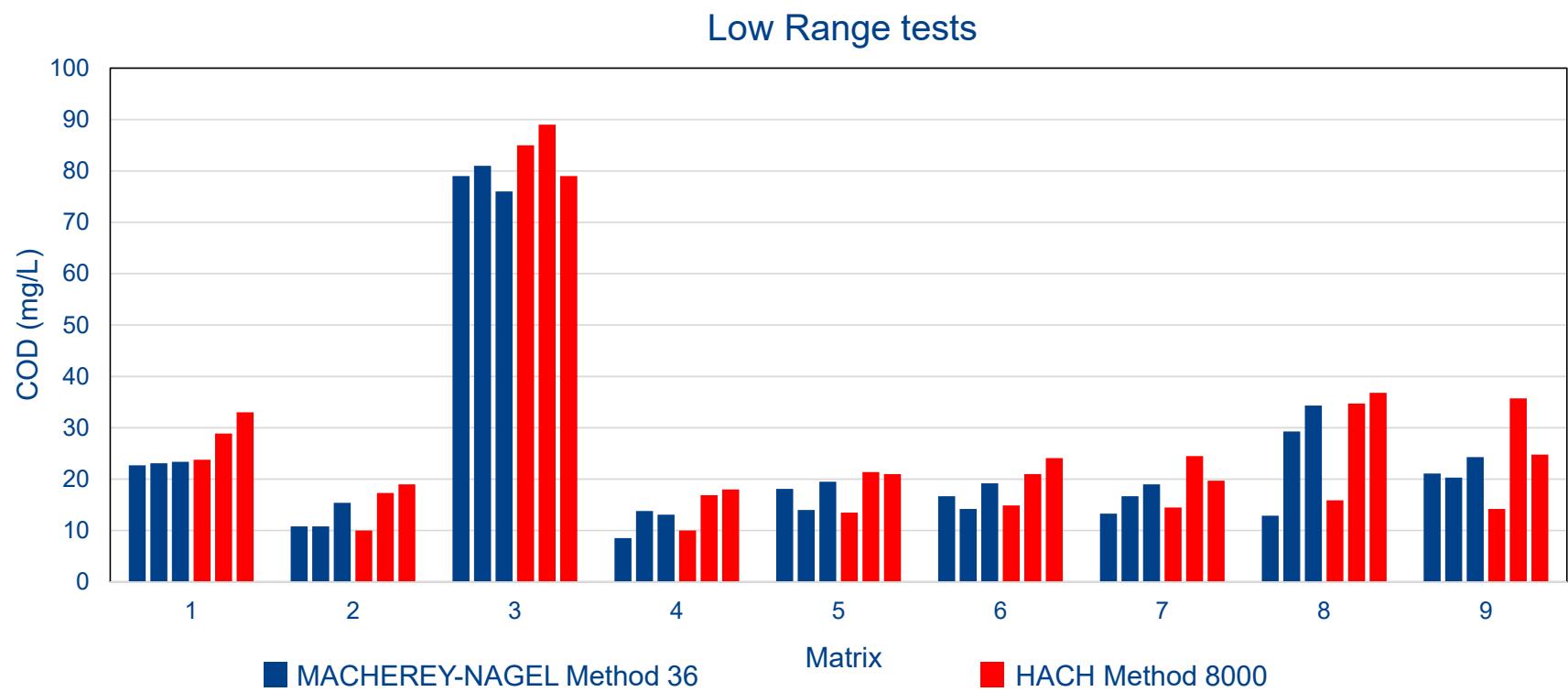
Phase 1: Side-by-side results High Range





ATP for NANOCOLOR® COD

Phase 1: Side-by-side results Low Range





ATP for NANOCOLOR® COD

Results for Phase 1

- COD High Range
 - RMSD (11.2) < RMSD max (38.7)
 - No statistical difference
- COD Low Range
 - RMSD (3.76) < RMSD max (6.78)
 - No statistical difference

$$\begin{aligned} \bullet \quad RMSD &= \sqrt{\frac{\sum_1^j (\bar{x}_{RMj} - \bar{x}_{ATPj})^2}{J}} \\ \bullet \quad RMSD_{max} &= \sqrt{\frac{2MSE}{n} F(0.95; J; 2J(n - 1))} \\ \bullet \quad MSE &= \frac{1}{2J} \sum_{j=1}^J \sum_{k=1}^2 s_{jk}^2 \end{aligned}$$



No significant difference between COD methods from MN and HACH



ATP for NANOCOLOR® COD

Results of phase 2

	COD LR (3 – 150 mg/L)	COD HR (20 – 1500 mg/L)
IPR mean percent recovery	90% – 110%	90% – 110%
IPR maximum RSD	10%	10%
MS/MSD recovery	78% – 110%	80% – 110%
MS/MSD maximum relative percent difference (RPD)	20%	15%
CCV or LFB recovery	90% – 110%	90% – 110%
ICV	± 10%	± 10%
LRB	≤ 50% of the MRL	≤ 50% of the MRL



Summary





Summary

- ATP Protocol for method defined parameters
 - Requires effort
 - Is feasible
 - Provides good information
 - RMSD-statistic seems to be useful
- NANOCOLOR® COD tests from MN
 - No significant difference to HACH Method 8000
 - Easy to use
 - Outstanding photometers



MACHEREY-NAGEL COD tests are comparable to HACH's



Summary

Thanks to (in order of appearance)

- Antoinette Ruschmann (Cardinal Laboratories)
- Andy Eaton, Nilda Cox, Shu Liu ... (Eurofins Eaton Analytics)
- Lem Walker & colleagues (US EPA)
- Jeff Flowers, Travis Wright ... (Flowers Labs)

Thank you for your attention!

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