

COD method (MDP) – processed through USEPA CWA program



Collaborative efforts to improve environmental monitoring

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Agenda



Company



MN Water Analysis



ATP Protocol



ATP for *NANOCOLOR*® COD



Summary



Company

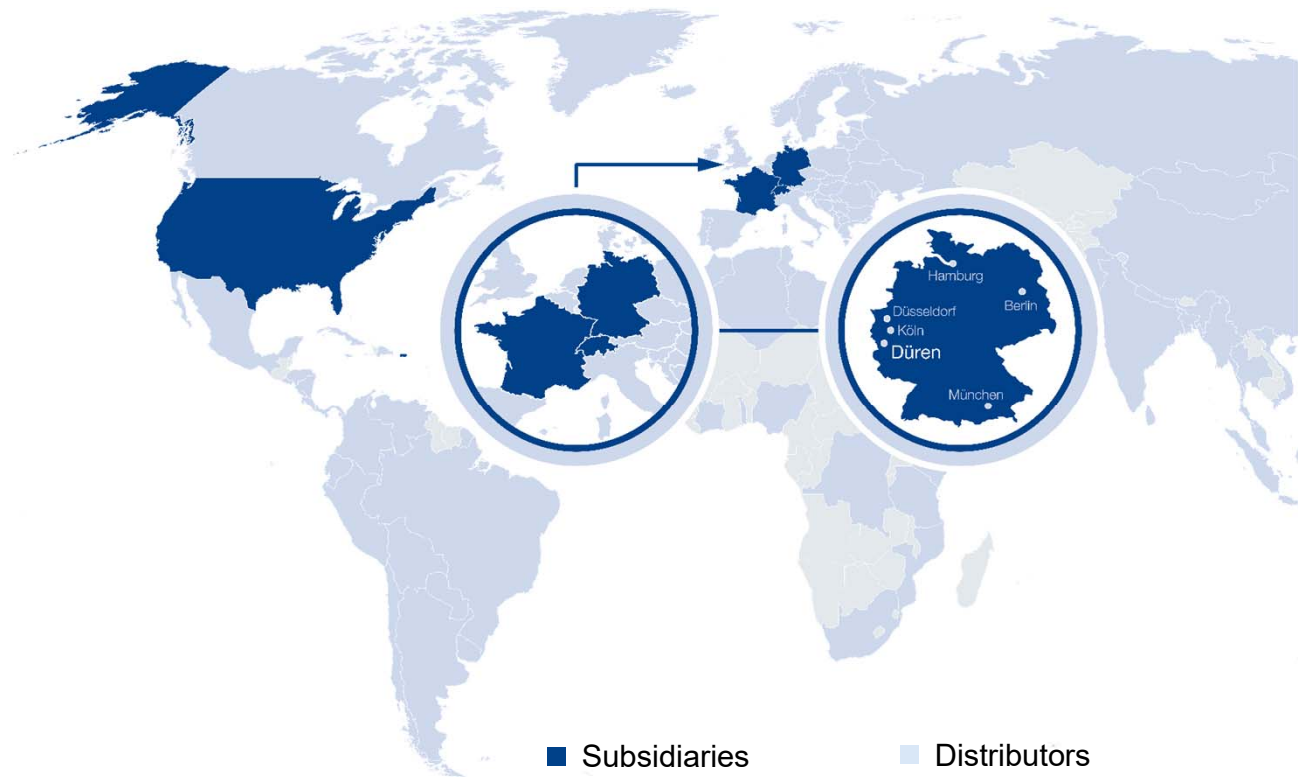




Company

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

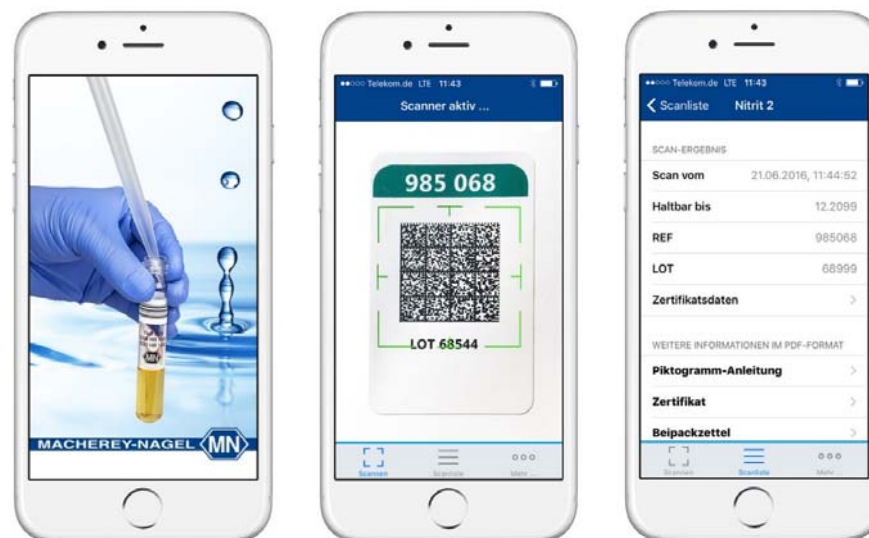




MN Water Analysis

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

$$• \text{RMSE} = \sqrt{\frac{\sum_1^j (\bar{x}_{RMj} - \bar{x}_{ATPj})^2}{J}}$$

$$• \text{RMSE}_{max} = \sqrt{\frac{2\text{MSE}}{n} F(0.95; J; 2J(n - 1))}$$

$$• \text{MSE} = \frac{1}{2J} \sum_{j=1}^j \sum_{k=1}^2 S_{jk}^2$$

$\bar{x}_{RMj}; \bar{x}_{ATPj} = j^{\text{th}}$ 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

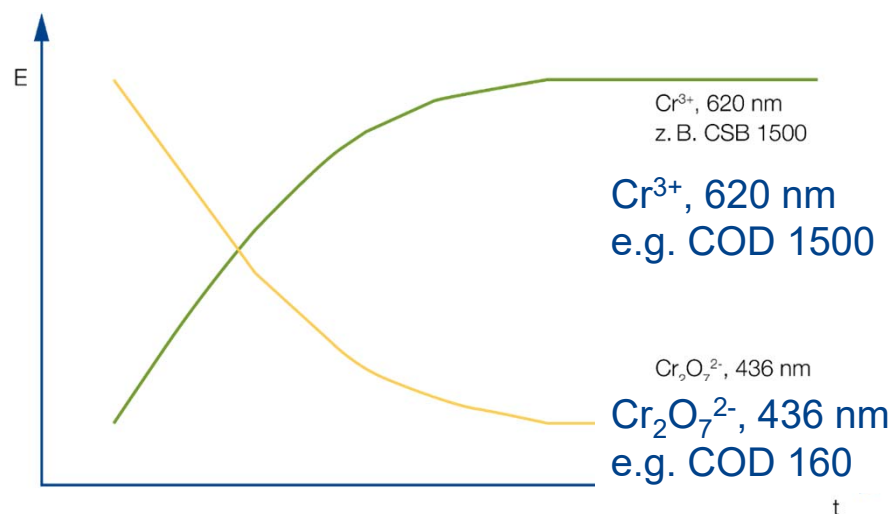




ATP for NANOCOLOR® COD

Method summary

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





ATP for NANOCOLOR® COD

Procedure

NANOCOLOR® CSB HR 1500
COD / DCO / DQO

Test 0-38
REF 985038

Methode / Method / Méthode / Método 595 / 605 / 620 nm Min 20–80 % Max
0381 20–1500 mg/L O₂ 20 316 1204 1500 mg/L O₂

1. Add 2.0 mL of sample to the test tube.
2. Mix the contents of the test tube.
3. Incubate at 150 °C for 2 hours.
4. Wait 10 minutes.
5. Mix the contents of the test tube.
6. Incubate at 20–25 °C.
7. Add the reagent to the test tube.
8. Read the result (M).

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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

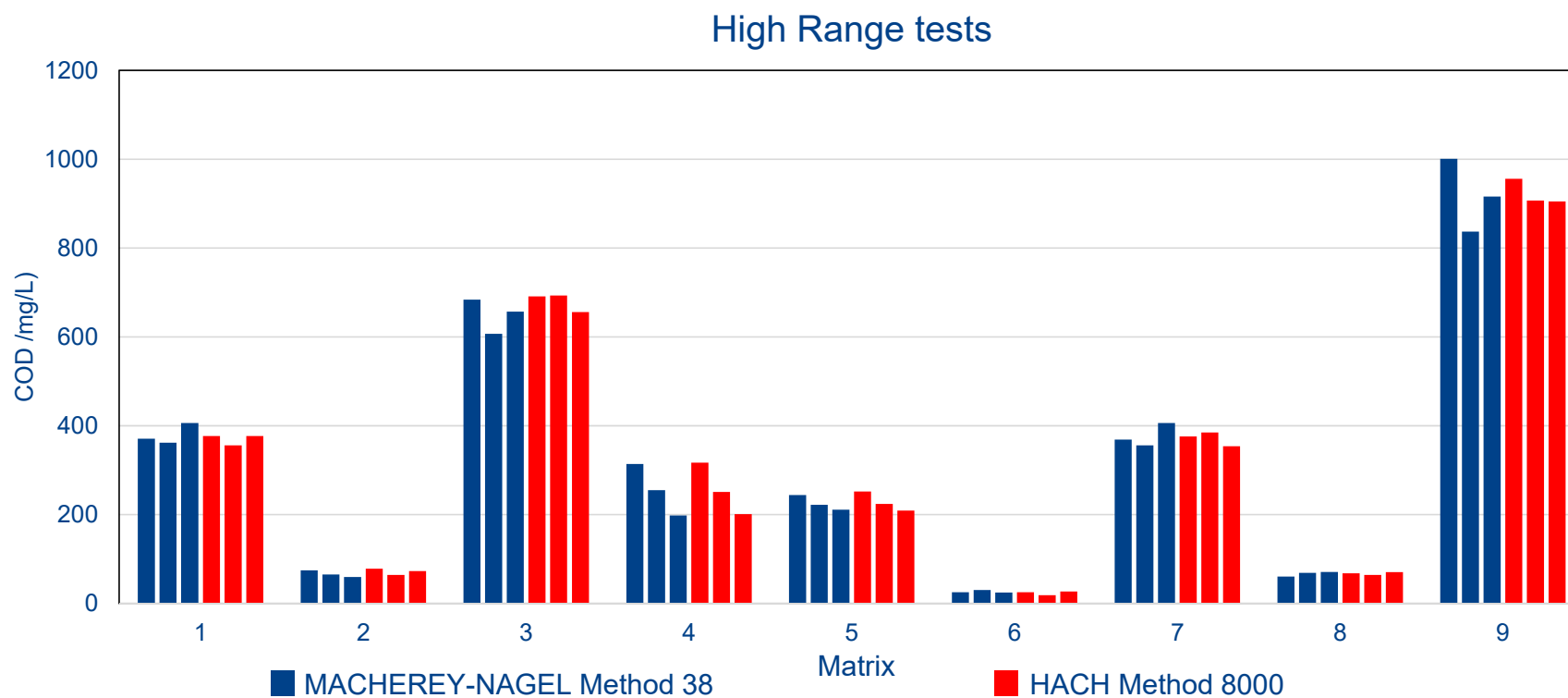
- ATP requirement: real life samples
- COD Low Range
 - POTW effluents
- COD High Range
 - Industrial user influents
 - POTW influents
 - Primary Clarifier effluent





ATP for NANOCOLOR[®] COD

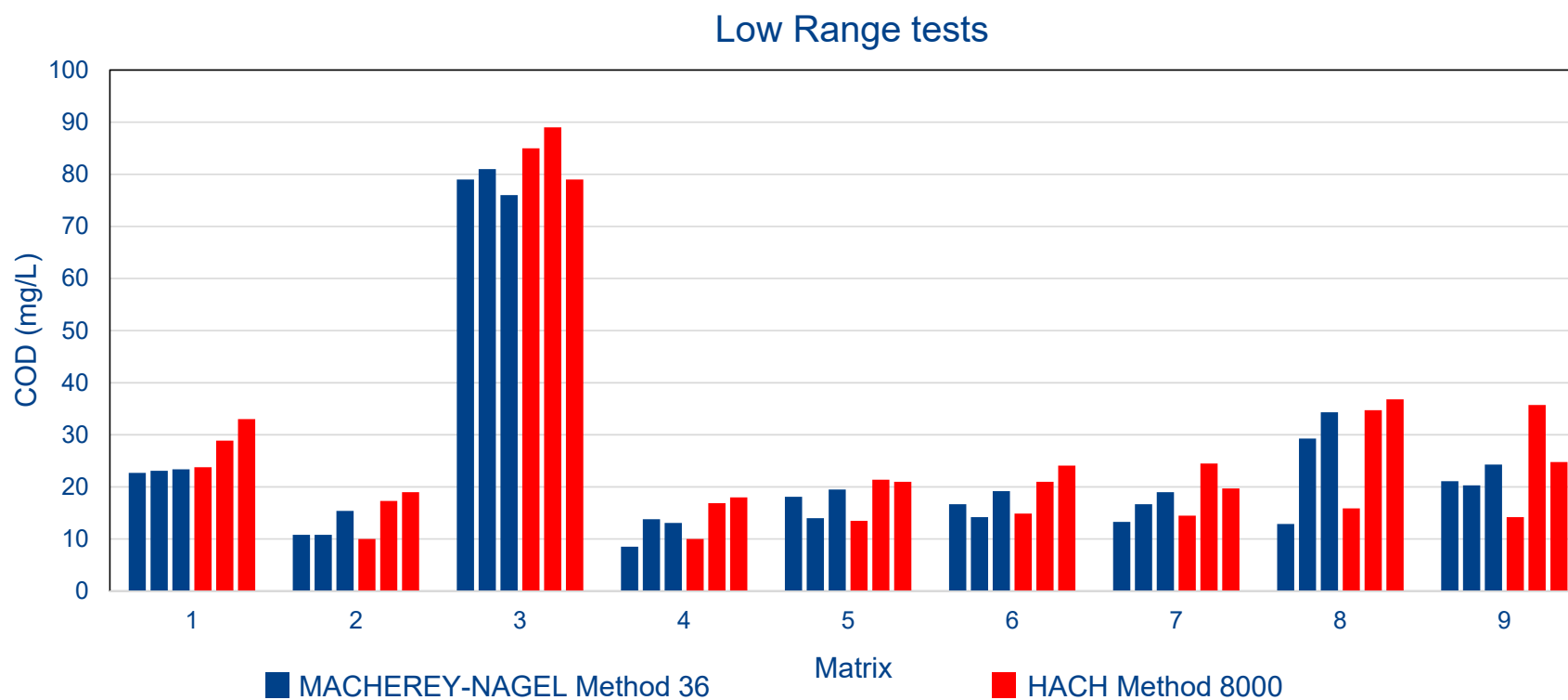
Phase 1: Side-by-side results High Range





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

$$• RMSD = \sqrt{\frac{\sum_1^j (\bar{x}_{RMj} - \bar{x}_{ATPj})^2}{J}}$$

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

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



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



MACHERY-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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