Skalar

Analyses of inorganic parameters by Flow Analyses

Water Workshop
University of Novi Sad
1 – 5 September 2008
Program

- Introduction of Skalar Analytical
- Skalar Continuous Flow Analyses
- Practical applications on CFA
  - Nutrients
  - Cyanide
  - Phenol
  - Total Nitrogen
  - Total Phosphate
  - Dissolved Organic Carbon
Skalar Worldwide

Germany
Belgium
United Kingdom
India
The Netherlands
Serbia
France
Austria
United States
Czech Republic

Represented in more than 60 countries
Thousands of Skalar Analyzers operational worldwide

- Commercial laboratories
- Industrial laboratories
- Universities and Research laboratories
- Process control

Applications:
- Water
- Soil, Plant & Fertilizer
- Beer & Malt
- Food & Beverage
- Wine
- Tobacco
- Pharmaceutical
- Detergents
- Mining & Metallurgical
- Petrochemical
According International standards

Skalar applications are according to international directives such as

- ISO
- EPA
- ASTM
- CEN
- AFNOR
- AOAC
- DIN
- NEN
- ASBC
- EBC
- Mebak
- User’s methods
Skalar Product Lines

- SAN++ Analyzer
- Wet Chemistry automation
- FormacsSERIES and PrimacsSERIES
- TOC & TN Analyzers
- Robotic Analyzers
- BOD, COD, Titations, ISE etc
- Fluo Imager
- Oil in water, Chlorofyll
- Toxtracer
- Bio-assay for Toxicity
Program

- Introduction of Skalar Analytical
- Skalar Continuous Flow Analyses
- Practical applications on CFA
  - Nutrients
  - Cyanide
  - Phenol
  - Total Nitrogen
  - Total Phosphate
  - Dissolved Organic Carbon
Skalar Products
Continuous Flow Analyzer

San++
Continuous Flow Analyzer
Advantages

• Fast, accurate, reliable and reproducible results
  (standardization of methods and operation conditions)

• High capacity and sample throughput
  (up to several hundreds per day)

• Less chance on human errors
  (No transcription or operator errors)

• money-saving
  (saving on reagents and time)

• Automated Data-acquisition and data-management

• Avoiding this in your laboratory
Continuous Flow Analyzer

Typical Automated Environmental Applications

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Analyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>Methyleneg Blue Active Substances (MBAS)</td>
</tr>
<tr>
<td>Aluminum</td>
<td>Molybdenum</td>
</tr>
<tr>
<td>Boron</td>
<td>Nitrate + Nitrite</td>
</tr>
<tr>
<td>Bromide</td>
<td>Permanganate value (COD)</td>
</tr>
<tr>
<td>Calcium</td>
<td>Potassium</td>
</tr>
<tr>
<td>Chloride</td>
<td>Total Amino Acids</td>
</tr>
<tr>
<td>Chemical Oxygen Demand</td>
<td>Total Alkalinity</td>
</tr>
<tr>
<td>Chlorine</td>
<td>Total Carbonates</td>
</tr>
<tr>
<td>Cholinesterase Inhibition</td>
<td>Total Hardness</td>
</tr>
<tr>
<td>Chromium VI</td>
<td>Total Nitrogen (UV and TKN)</td>
</tr>
<tr>
<td>Color</td>
<td>Total Phosphate (UV)</td>
</tr>
<tr>
<td>Conductivity</td>
<td>Total Phenols</td>
</tr>
<tr>
<td>Cyanide (Total - Free - WAD) Dissolved</td>
<td>Silicate</td>
</tr>
<tr>
<td>Organic Carbon</td>
<td>Sodium</td>
</tr>
<tr>
<td>Fluoride</td>
<td>Sulfate</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>Sulfur Dioxide</td>
</tr>
<tr>
<td>Iron (Total - Free - Hydrolysable)</td>
<td>Urea</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Volatile Acids</td>
</tr>
<tr>
<td>Manganese</td>
<td>Zinc</td>
</tr>
</tbody>
</table>
Continuous Flow Analyzer

Principle of the San⁺⁺

Full Instrument Control

Auto Sampler → Chemistry Section → Detection → Computer

From 1 to 16 channels simultaneously

Data Handling and Report Generation
Continuous Flow Analyzer

Modular Design

Auto Sampler → Chemistry Section and Detection → Data Acquisition
Data Reporting and Full Instrument Control

Full Instrument control
Continuous Flow Analyzer

Typical Advantages CFA compared to other techniques

- Implementation of complex analysis techniques like:
  - inline distillation, digestion, extraction, dialysis
- No blocking by dirty samples as of mini-bore coils
- Sub ppb level sensitivity (and expended range in ppm level)
- Full end point color development (optimal chemistry)
- No synchronization required to analyze data
- No degassing of reagents

( CFA = Continuous Flow Analysis )
Program

- Introduction of Skalar Analytical
- Skalar Continuous Flow Analyses
- Practical applications on CFA
  - Nutrients
  - Cyanide
  - Phenol
  - Total Nitrogen
  - Total Phosphate
  - Dissolved Organic Carbon
Practical Applications on CFA

Method Descriptions: Hardcopy and Digital

- **Preparation:** Dissolve the 4-aminoantipyrine in 20 ml distilled water. Fill up to 100 ml with distilled water, add the lig 35 and mix. Store this solution for at least two weeks.

- **Preparation:** Dissolve the potassium ferricyanide, the boric acid and the potassium chloride in 20 ml distilled water. Adjust the pH to 10.3 with potassium hydroxide solution (M). Fill up to 100 ml with distilled water.

- **Preparation:** Dissolve the phenol in 100 ml distilled water. Fill up to 1 litre with distilled water and mix.

**LABORATORY FACILITIES**
- 1. Maximum power consumption depending on the analyser configuration, 2000 VA. Check voltage at the back of the instrument before installation.

**PROCEDURE**
- **SAMPLE PREPARATION**
  - Glass or polytetrafluoroethylene (PTFE) containers are suitable for sampling. Prior to use, all containers and devices the sample may come into contact with, shall be rinsed with sulfuric acid of approximately pH 2.
  - Analyse the samples immediately after their collection. Alternatively, adjust a pH of approximately 2 with sulfuric acid (H2SO4 97% or diluted solution) or hydrochloric acid (HCl w/w 50% or diluted solution), store in the dark at a temperature of 2 to 5°C, and analyse within 24 hours.

- In exceptional cases, after acidification and membrane (pressure) filtration of the sample, a storage of up to two weeks is possible. The applicability of this preservation method shall be checked for the individual case of examination.

- Filtration of the sample prior to measurement is necessary, if there is a risk of clogging the transport tubes.

- **REAGENTS**
  - **A. Distillation reagent**
    - Required chemicals: Phosphoric acid (H3PO4)(85%) and water.
    - Preparation: Distill the phosphoric acid in 70 ml distilled water, while cooling. Fill up to 100 ml with distilled water and mix. Store the stock solution at 4°C. Solution is stable for 1 week. Note: Prepare fresh solution every day.

- **Preparation:** Dissolve the phenol in 100 ml distilled water. Fill up to 1 litre with distilled water and mix.

- **Preparation:** Dissolve the 4-aminoantipyrine in 80 ml distilled water. Fill up to 100 ml with distilled water, add the lig 35 and mix. Store this solution for at least two weeks.

- **Preparation:** Dissolve the potassium ferricyanide, the boric acid and the potassium chloride in 80 ml distilled water. Adjust the pH to 10.3 with potassium hydroxide solution (M). Fill up to 100 ml with distilled water.

- **Note:** Prepare a fresh solution every day.

- **Note:** Prepare a fresh solution every day.

- **Note:** Store the stock solution at 4°C. Solution is stable for 1 week.

**REFERENCE**
- Water Quality - Determination of the Phenol Index by Flow Analysis, ISO 14402.

**STANDARDS**
- **A. Distillation reagent**
  - Maximum power consumption depending on the analyser configuration, 2000 VA. Check voltage at the back of the instrument before installation.
  - Facilities for chemical wastes. Check environmental regulations for proper disposal of waste.

- **PROCEDURE**
  - **SAMPLE PREPARATION**
    - Glass or polytetrafluoroethylene (PTFE) containers are suitable for sampling. Prior to use, all containers and devices the sample may come into contact with, shall be rinsed with sulfuric acid of approximately pH 2.
    - Analyse the samples immediately after their collection. Alternatively, adjust a pH of approximately 2 with sulfuric acid (H2SO4 97% or diluted solution) or hydrochloric acid (HCl w/w 50% or diluted solution), store in the dark at a temperature of 2 to 5°C, and analyse within 24 hours.

- In exceptional cases, after acidification and membrane (pressure) filtration of the sample, a storage of up to two weeks is possible. The applicability of this preservation method shall be checked for the individual case of examination.

- Filtration of the sample prior to measurement is necessary, if there is a risk of clogging the transport tubes.

- **REAGENTS**
  - **A. Distillation reagent**
    - Required chemicals: Phosphoric acid (H3PO4)(85%) and water.
    - Preparation: Distill the phosphoric acid in 70 ml distilled water, while cooling. Fill up to 100 ml with distilled water and mix. Store the stock solution at 4°C. Solution is stable for 1 week. Note: Prepare fresh solution every day.

- **Preparation:** Dissolve the phenol in 100 ml distilled water. Fill up to 1 litre with distilled water and mix.

- **Preparation:** Dissolve the 4-aminoantipyrine in 80 ml distilled water. Fill up to 100 ml with distilled water, add the lig 35 and mix. Store this solution for at least two weeks.

<table>
<thead>
<tr>
<th>Method Description</th>
<th>Supplier and catalog number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled water</td>
<td>Merck 100317 corrosive</td>
</tr>
<tr>
<td>Boric acid</td>
<td>Merck 10317 corrosive</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>Merck 100573 corrosive</td>
</tr>
<tr>
<td>Potassium ferricyanide</td>
<td>Merck 107255 harmful</td>
</tr>
<tr>
<td>Baking soda</td>
<td>Merck 105017 corrosive</td>
</tr>
<tr>
<td>Distillation unit</td>
<td>Merck 107255 harmful</td>
</tr>
<tr>
<td>Sample pump tube</td>
<td>Merck 105021 corrosive</td>
</tr>
</tbody>
</table>

**CATALOGUE NUMBERS**
- Required chemicals: Distilled water, Boric acid, Hydrochloric acid.
- Distilled water *.......................
- Boric acid ............................
- Hydrochloric acid (32%) Merck 100317 corrosive
- 4-Aminoantipyrine Merck 107293 harmful

**ANALYSIS:** PHENOL INDEX
- **RANGE:** 2 - 100 ppb C6H5OH

**SAMPLE:** WASTE WATER

**INTERFERENCES**
- Interferences caused by clogging of the distillation capillary may occur when the salt content of the sample exceeds 10 gr/litre. In these cases, dilute the sample with water.

- The interlaboratory trial has shown that detergents in waste water can strongly influence the determination, because the foam produced in the flow system can disturb both the steam distillation of volatile phenolic compounds, is the mixed with continuously flowing solutions of 4-aminoantipyrine and potassium hexacyanoferrate(III). Phenolic compounds in the distillate are oxidised by hexacyanoferrate(III), and the resulting quinones react with 4-aminoantipyrine forming yellow condensation products, which are measured spectrometrically at 505 nm. (Method according to ISO/DIS 14402)

**CHARTS**
- Benzene hydroxide solution
- Aminoantipyrine solution
- Distillation reagent
- Flow cell 5B in white waste

**FILTERS**
- Merck 100017 corrosive
- Merck 100117 corrosive
- Merck 100573 corrosive
- Merck 107255 harmful
- Merck 109873 corrosive
- Merck 10986 corrosive
- Merck 109021 corrosive
- Merck 109206 toxic

**RESOURCES REQUIRED CHEMICALS**
- **Supplier and catalog number**
- **Deposit classification**

- **A. Distillation reagent**
  - Required chemicals: Phosphoric acid (H3PO4)(85%) and water.
  - Preparation: Distill the phosphoric acid in 70 ml distilled water, while cooling. Fill up to 100 ml with distilled water and mix. Store the stock solution at 4°C. Solution is stable for 1 week. Note: Prepare fresh solution every day.

- **Preparation:** Dissolve the phenol in 100 ml distilled water. Fill up to 1 litre with distilled water and mix.

- **Preparation:** Dissolve the 4-aminoantipyrine in 80 ml distilled water. Fill up to 100 ml with distilled water, add the lig 35 and mix. Store this solution for at least two weeks.

- **Preparation:** Dissolve the potassium ferricyanide, the boric acid and the potassium chloride in 80 ml distilled water. Adjust the pH to 10.3 with potassium hydroxide solution (M). Fill up to 100 ml with distilled water.

- **Note:** Prepare a fresh solution every day.

- **Note:** Prepare a fresh solution every day.

- **Note:** Store the stock solution at 4°C. Solution is stable for 1 week.

**REFERENCES**
- Water Quality - Determination of the Phenol Index by Flow Analysis, ISO 14402.

**STANDARDS**
- **A. Distillation reagent**
  - Maximum power consumption depending on the analyser configuration, 2000 VA. Check voltage at the back of the instrument before installation.
  - Facilities for chemical wastes. Check environmental regulations for proper disposal of waste.

- **PROCEDURE**
  - **SAMPLE PREPARATION**
    - Glass or polytetrafluoroethylene (PTFE) containers are suitable for sampling. Prior to use, all containers and devices the sample may come into contact with, shall be rinsed with sulfuric acid of approximately pH 2.
    - Analyse the samples immediately after their collection. Alternatively, adjust a pH of approximately 2 with sulfuric acid (H2SO4 97% or diluted solution) or hydrochloric acid (HCl w/w 50% or diluted solution), store in the dark at a temperature of 2 to 5°C, and analyse within 24 hours.

- In exceptional cases, after acidification and membrane (pressure) filtration of the sample, a storage of up to two weeks is possible. The applicability of this preservation method shall be checked for the individual case of examination.

- Filtration of the sample prior to measurement is necessary, if there is a risk of clogging the transport tubes.

- **REAGENTS**
  - **A. Distillation reagent**
    - Required chemicals: Phosphoric acid (H3PO4)(85%) and water.
    - Preparation: Distill the phosphoric acid in 70 ml distilled water, while cooling. Fill up to 100 ml with distilled water and mix. Store the stock solution at 4°C. Solution is stable for 1 week. Note: Prepare fresh solution every day.

- **Preparation:** Dissolve the phenol in 100 ml distilled water. Fill up to 1 litre with distilled water and mix.

- **Preparation:** Dissolve the 4-aminoantipyrine in 80 ml distilled water. Fill up to 100 ml with distilled water, add the lig 35 and mix. Store this solution for at least two weeks.

- **Preparation:** Dissolve the potassium ferricyanide, the boric acid and the potassium chloride in 80 ml distilled water. Adjust the pH to 10.3 with potassium hydroxide solution (M). Fill up to 100 ml with distilled water.

- **Note:** Prepare a fresh solution every day.
Practical Applications on CFA
Skalar SAN++ Example Configuration

SYSTEM 1, CONFIGURATION FOR THE SKALAR AUTOMATIC ANALYSER FOR THE ANALYSIS OF AMMONIA, SILICATE, ORTHO PHOSPHATE, NITRATE-NITRITE AND NITRITE IN WATER/SEAWATER SAMPLES
Practical Applications on CFA

Nitrite: Colorization method

According ISO 13395

Sulfanylamide

\[ \Downarrow + \text{NO}_2 + H^+ \]

Diazonium compound

\[ \Downarrow \alpha\text{-naphtylethylenediamine dihydrochloride} \]

Red-purple color measured at 540 nm

Identical to the manual method
Practical Applications on CFA

Nitrite: Colorization method

Flow Diagram

Photometric detection

Color Reaction

Reagent addition

Sampling
Practical Applications on CFA

Nitrate: Colorization method (NO₂ + NO₃)

According ISO 13395

\[ \text{NO}_3 \rightarrow \text{NO}_2 \text{ by reduction} \]

**Reduction methods:**
- Cd-reduction
- Reduction with hydraziniumsulfate
- Enzymatic reduction

Sulfanylamide

\[ \downarrow + \text{NO}_2 + \text{H}^+ \]

Ziazonium compound

\[ \downarrow \alpha\text{-naphtylethylenediamine dihydrochloride} \]

Red-purplue color measured at 540 nm
Practical Applications on CFA

Nitrate: Colorization method (NO$_2$ + NO$_3$)

FLOW DIAGRAM

Color Reaction

- Colour reagent
- Air
- Buffer solution
- Air
- Buffer solution + EDTA
- Sample
- Sampler

Photometric detection

- Cd-reduction column
- Dialyses

* standard membrane catnr. SA 5282
Practical Applications on CFA
Total Cyanide, a complete Analysis Process

Different methods:

1. **Photometric detection with UV-A destruction**
   Total determination of CN, including thiocyanates
   According ISO 14403

2. **Photometric detection with UV-B destruction**
   Total determination of CN, excluding thiocyanates
   According ISO 14403

3. **Amperometric detection**
   with a silver working electrode and silver/silver chloride reference electrode
   According ISO 14403

4. **Photometric detection of WAD (Weak and Dissociable cyanides)**
   According ISO 14403
Practical Applications on CFA

Total Cyanide: Photometric detection with UV-B destruction
Total determination of CN, excluding thiocyanates, according ISO 14403

CN-complex

\[ + \text{UV-light} ( + \text{pH 3.8} \]

HCN

\[ \downarrow \text{Separation by distillation at 125°C under vacuum} \]

\[ \downarrow \text{Chloramine-T,} \]

Cyanogene chloride

\[ \downarrow \text{Colorisation with 4-pyridine carboxylic acid} \]

\[ \downarrow \text{and 1,3-dimethylbarbituric acid} \]

Red colour, measured at 600 nm
Practical Applications on CFA

Total Cyanide: Photometric detection with UV-B destruction

FLOW DIAGRAM

Color Reaction

- Colour reagent
- Chloramine-T solution
- Air
- Buffer solution
- (Re)sample

Photometric detection

- Flow cell 10
- Filter 600 nm
- Cor. filter 650 nm

In-line distillation

- In-line UV digestion
- vacuum pump 9031
- condenser 5371
- built up in glass sleeved with acidflex

In-line UV digestion

- Sodium hydroxide solution (0.1M)
- Distillation reagent
- Distilled water
- Sodium hydroxide solution (1M)

Sampling

- Sampler
- In-line distillation unit is situated at the back panel of the module support holder
- Glass tubing SA 5359 (2.0mm I.D., 4.0mm O.D.)
- Air linlet via 50 cm 5133 tube with restrictor (3 cm 5142 tube)
- Air restrictor (2CA14031)
Cyanide, Total & Free: Method Amperometric

**PRINCIPLE (total cyanide)**
The automated procedure for the determination of Total Cyanide is based on the following reaction: Complex bound cyanide is decomposed by the radiation of UV light, in a continuously flowing stream at pH 3.8. A UV-B lamp (± 312 nm) and a coil of borosilicate glass is used to avoid UV light, with a wavelength of less than 290 nm, and thus preventing the conversion of thiocyanate into cyanide. The Cyanide, decomposed at pH 3.8, is kept in solution by addition of a liquid to increase the pH to > 10 and then pumped to the dialyser where the sample is acidified to form hydrogen cyanide gas.

The hydrogen cyanide gas diffuses through the hydrophobic Teflon membrane into the alkaline receptor stream. The cyanide is measured amperometrically with a silver working electrode and silver/silver chloride reference electrode. (the method is according ISO 14403)
Practical Applications on CFA

Phenol Index: a complete Analysis Process
Total determination of phenols, according ISO 14402

- phenol-complex
  - distillation at pH 1.4
- volatile phenolic compounds
  - potassium hexacyanoferrate(III)
- Quinones
  - 4-aminoantipyrine
- yellow condensation products, measured at 505 nm
Practical Applications on CFA

Phenol Index: a complete Analysis Process

Photometric detection

FLOW DIAGRAM

Color Reaction

Distilled water

Potassium ferricyanide solution

Air

Resample

4-Aminoantipyrine solution

Nitrogen gas 70 - 80 units

Air

Sample

Distillation reagent

Sampling

Distillation unit is situated beside the module support holder

**always close the clamp after

In-line distillation

Flow cell 50 mm

Filter 505 nm

Cor. filter 720 nm

ml/min

Potassium ferricyanide solution

Air

Resample

4-Aminoantipyrine solution

Distilled water

Nitrogen gas 70 - 80 units

Air

Sample

Distillation reagent

Sampling

Distillation unit is situated beside the module support holder

**always close the clamp after

In-line distillation

Flow cell 50 mm

Filter 505 nm

Cor. filter 720 nm

ml/min

Potassium ferricyanide solution

Air

Resample

4-Aminoantipyrine solution

Distilled water

Nitrogen gas 70 - 80 units

Air

Sample

Distillation reagent

Sampling

Distillation unit is situated beside the module support holder

**always close the clamp after
### Practical Applications on CFA

#### Total Nitrogen

**Different methods:**

<table>
<thead>
<tr>
<th>Element</th>
<th>Legislation</th>
<th>Description</th>
<th>Skalar system</th>
<th>Skalar Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Nitrogen</td>
<td>ISO/CD 29441</td>
<td>Online measurement after UV-destruction</td>
<td>San++ with online UV-destruction</td>
<td>M475-424</td>
</tr>
<tr>
<td>Kjeldahl-N total phosphate</td>
<td>Offline destruction, followed by colorimetric detection of ammonium and phosphate on CFA</td>
<td>San++ with prior destruction on SA5640</td>
<td>M155-056, M503-004</td>
<td></td>
</tr>
<tr>
<td>Kjeldahl-N</td>
<td>Offline destruction, followed by colorimetric detection of ammonium on CFA</td>
<td>San++ with prior destruction on SA5640</td>
<td>M155-056</td>
<td></td>
</tr>
<tr>
<td>Total Nitrogen</td>
<td>EN 12260:2003 or EN-ISO 11905-2:1997</td>
<td>High Temperature combustion</td>
<td>Formacs™N</td>
<td></td>
</tr>
<tr>
<td>Totaal Nitrogen</td>
<td>EN-ISO 11905-1:1998</td>
<td>Offline destruction, followed by colorimetric detection of nitrate on CFA</td>
<td>San++ with prior destruction on SA5640</td>
<td>M461-032</td>
</tr>
</tbody>
</table>
Practical Applications on CFA
Total Nitrogen by in-line UV-destruction

According ISO/CD 29441

N-compounds

\[ \downarrow \text{Oxidation reagent} + \text{UV-destruction} \]

Organic carbon to Nitrate

\[ \downarrow +T\ (C) \]

Ammonium to nitrate

\[ \downarrow +\text{Cd-reduction} \]

Nitrate to nitrite

\[ \downarrow +\text{sulfanilamide} , \]
\[ \text{N-1-naftyl-ethyleen-diamine-dihydrochloride} \]

Red colored complex, measured at 540 nm

Identical to nitrate measurement
Practical Applications on CFA

Total Nitrogen by in-line UV-destruction

- Color reaction
- In-line dialysis
- In-line UV digestion
- Sampling
- Photometric detection
- Back pressure Regulation

FLOW DIAGRAM

H2O + Brj 38
Air
Sample
Oxidizing reagent
Borsic buffer solution

Distilled water
Air
Distilled water

Predilution built up in glass

6307 + 5112 Godemis column

Sampling

Backpressure unit
Practical Applications on CFA
Total Nitrogen by in-line UV-destruction

Calibration curve TN (UV) on Skalar CFA (method 475-427)
Conc: 0 – 20 mg N/l

\[ a = -3844.20063 \quad b/(\text{Slope}) = 35268.8038 \quad RSD = 4780 \cdot 0.25 \quad r = 0.9976 \]
Practical Applications on CFA

Total Nitrogen: Result comparison versus manual method

<table>
<thead>
<tr>
<th>Sample Identity</th>
<th>Result Skalar (TN)</th>
<th>Result ref (TN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10443292</td>
<td>7.5</td>
<td>7.5</td>
</tr>
<tr>
<td>22034434</td>
<td>32.9</td>
<td>33.7</td>
</tr>
<tr>
<td>10441790</td>
<td>292.2</td>
<td>294.0</td>
</tr>
<tr>
<td>22036038</td>
<td>59.8</td>
<td>60.6</td>
</tr>
<tr>
<td>22036040</td>
<td>78.8</td>
<td>79.3</td>
</tr>
<tr>
<td>22036043</td>
<td>53.2</td>
<td>53.1</td>
</tr>
<tr>
<td>22036149</td>
<td>50.5</td>
<td>51.8</td>
</tr>
<tr>
<td>88050901</td>
<td>20.9</td>
<td>20.6</td>
</tr>
<tr>
<td>88051101</td>
<td>33.0</td>
<td>33.4</td>
</tr>
<tr>
<td>88053301</td>
<td>28.9</td>
<td>30.3</td>
</tr>
<tr>
<td>88053501</td>
<td>61.1</td>
<td>61.9</td>
</tr>
<tr>
<td>88053601</td>
<td>49.3</td>
<td>50.6</td>
</tr>
<tr>
<td>88053602</td>
<td>3.8</td>
<td>3.7</td>
</tr>
<tr>
<td>88053701</td>
<td>56.8</td>
<td>58.0</td>
</tr>
<tr>
<td>88053801</td>
<td>113.4</td>
<td>111.0</td>
</tr>
</tbody>
</table>
## Practical Applications on CFA

### Total Phosphate by in-line UV-destruction

<table>
<thead>
<tr>
<th>Element</th>
<th>Norm</th>
<th>Omschrijving</th>
<th>Skalar Systeem</th>
<th>Skalar Methode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphate ortho &amp; total</td>
<td>EN-ISO 15681-2:2003</td>
<td>Off-line destruction or in-line destruction</td>
<td>San** with in-line UV-destruction or off-line destruction</td>
<td>M503-004</td>
</tr>
<tr>
<td>Kjeldahl-N total phosphate</td>
<td></td>
<td>Offline destruction, followed by colorimetric detection of ammonium and phosphate on CFA</td>
<td>San** with prior destruction on SA5640</td>
<td>M155-056, M503-004</td>
</tr>
</tbody>
</table>
Practical Applications on CFA

Total Phosphate by in-line UV-destruction

According ISO 15681-2

P-compounds

\[ \downarrow \text{Oxidation reagent + UV-destruction} \]

Organic phosphate to ortho-phosphate

\[ \downarrow +T \, (^{\circ}C) \]

Inorganic phosphate to ortho-phosphate

\[ \downarrow +\text{katalyst} \]

ammonium haptamolybdate

phospho-molybdic acid complex, measured at 540 nm

Identical to o-phosphate measurement
Practical Applications on CFA

Total Phosphate by in-line UV-destruction

FLOW DIAGRAM

Photometric detection

Color reaction

UV + 107°C Digestion

Back pressure Regulation
Practical Applications on CFA
Total Phosphate by in-line UV-destruction

Calibration curve TP (UV) on Skalar CFA
Conc: 0 – 1 mg P/l
Practical Applications on CFA
Total Phosphate / Total Nitrogen

Graph Results (UV-Digestion vv Manual)

Total Phosphate UV-P:
Range: 1 - 500 μg P/l.

Total Nitrogen UV-N:
Range: 20 - 5000 μg N/l.

According to international standard regulations (ISO, DIN, etc.) accredited!
Practical Applications on CFA
Total Organic Carbon

How to measure TOC?

- **UV-promoted persulfate oxidation (TOC)**
  - On CFA using a TOC module, followed by IR-detection

- **High temperature catalytic combustion (TOC & TN)**
  - On Formacs SERIES TOC Analyzer
Practical Applications on CFA

What is Total Organic Carbon?

- TC: Total Carbon
  - TIC: Total Inorganic Carbon
    - Particulate (Carbonates)
      - Dissolved (CO₂, HCO⁻³, CO₃²⁻)
    - Dissolved (CO₂, HCO⁻³, CO₃²⁻)
  - TOC: Total Organic Carbon
    - Particulate (Carbonates)
    - Dissolved (CO₂, HCO⁻³, CO₃²⁻)
    - POC: Purgable Organic Carbon
    - NPOC: Non Purgable Organic Carbon
Practical Applications on CFA
Total Organic Carbon – UV promoted on CFA

Sample

เราจะใช้กรดเพื่อเตรียมตัวให้แก่สารประกอบไอCAPEU และสเปรจ์ (N2)

liberates and disperses any inorganic or volatile organic carbon

Organic carbon rests in sample

¶ persulfate / tetra borate reagent
+ UV digestion coil

All organic carbon oxidised to CO₂

¶ acidification and sparging

to release CO₂ from solution

IR-measurement of CO₂
Practical Applications on CFA

Total Organic Carbon – UV promoted on CFA
TOC / TN Analyses

Formacs\textsuperscript{HT} TOC Analyzer

New model High Temperature Combustion Analyzer

Optional Sampler  TOC Analyzer  Data acquisition & instrument control
TOC / TN Analyses

Formacs\textsuperscript{HT}: Schematics of TOC Analyzer

New model High Temperature Combustion Analyzer
TOC / TN Analyses

Formacs \textsuperscript{TN}: Schematics of ND20 TN Detector

\[
\text{Combusted sample gas} \rightarrow \text{Air/Oxygen in} \rightarrow \text{Ozonator} \rightarrow \text{Detector (PMT)} \rightarrow \text{Scrubber}
\]

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2^* + \text{O}_2 \rightarrow \text{NO}_2 + \text{O}_2 + h_v
\]
TOC / TN Analyses

Formacs $^{TN}$: With TKN reactor

Skalar offers a true Kjeldahl Alternative

$$TKN = TN - NN$$

- NN application offers fast and economical alternative for classical Total Kjeldahl Nitrogen analysis
- NN Reactor can also be used for IC analysis
- Low maintenance
TOC / TN Analyses

Formacs TN: With TKN reactor

Case Study
Italian National Research Council

Section of Hydrobiology and Ecology of Inland Waters, Verbania - Italy

For many years the water quality of the Italian lakes has been monitored on nutrients to obtain long-term trends for evaluation.

Nitrogen concentrations is an important parameter for the ecosystem functioning and needs to be monitored accurately.

Typical specifications
Range : 0.05 – 5.00 mg/l N
CV : < 1 % F.S.
MDL : 10 µg/l N

<table>
<thead>
<tr>
<th></th>
<th>Range (mg/l N)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaNO3 Std 2.00</td>
<td>TN 2.00</td>
<td>102</td>
</tr>
<tr>
<td>NaNO3 Std 4.00</td>
<td>TN 4.00</td>
<td></td>
</tr>
<tr>
<td>KNO3 2 mg/l</td>
<td>TN 2.04</td>
<td>102</td>
</tr>
<tr>
<td>NaNO2 2 mg/l</td>
<td>TN 2.08</td>
<td>104</td>
</tr>
<tr>
<td>NH4Cl 2 mg/l</td>
<td>TN 2.02</td>
<td>101</td>
</tr>
<tr>
<td>NH4Cl 4 mg/l</td>
<td>TN 4.2</td>
<td>105</td>
</tr>
<tr>
<td>NH4Acetate 2 mg/l</td>
<td>TN 2.1</td>
<td>105</td>
</tr>
<tr>
<td>Glycine 2 mg/l</td>
<td>TN 2.07</td>
<td>104</td>
</tr>
<tr>
<td>Creatinine 2 mg/l</td>
<td>TN 2.11</td>
<td>106</td>
</tr>
<tr>
<td>Creatinine 4 mg/l</td>
<td>TN 4.27</td>
<td>107</td>
</tr>
</tbody>
</table>
TOC / TN Analyses

Formacs™ TN Vs Traditional TKN

- Much faster than the Kjeldahl method; 3 minutes per measurement to 1-2 hours for TKN
- Combustion technique handles more difficult matrices (Particulate & Brines)
- No toxic chemicals.
- Many samples are measured automatically
- Better precision
- Wide dynamic range
- Elimination of operator error

Conclusion: Cost reduction for working hours, chemical waste disposal and laboratory space.
Thank you for your attention.
We hope to see you at the Hands-on demonstration.

SKALAR,
Your Partner in Chemistry Automation