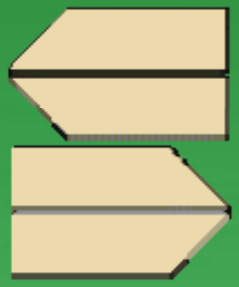
Skalar



Analyses of inorganic parameters by Flow Analyses

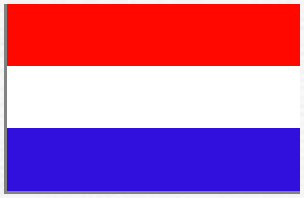
Water Workshop
University of Novi Sad
1 – 5 september 2008

Program

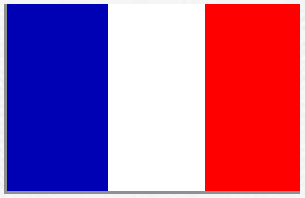
- Introduction of Skalar Analytical
- Skalar Continuous Flow Analyses
- Practical applications on CFA
  - Nutrients
  - Cyanide
  - Phenol
  - Total Nitrogen
  - Total Phosphate
  - Dissolved Organic Carbon

Skalar Worldwide

Germany



The Netherlands

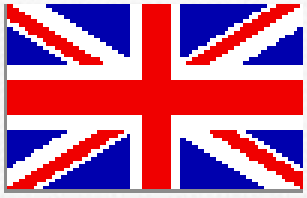


France

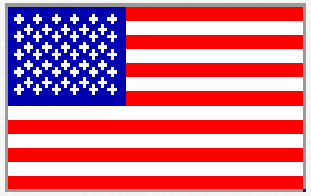
Belgium

Represented in more than 60 countries

Austria



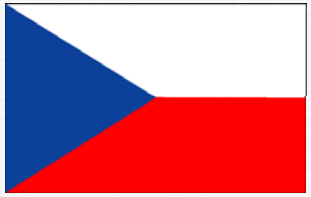
United Kingdom



United States

India

Serbia



Czech Republic

Thousands of Skalar Analyzers operational worldwide

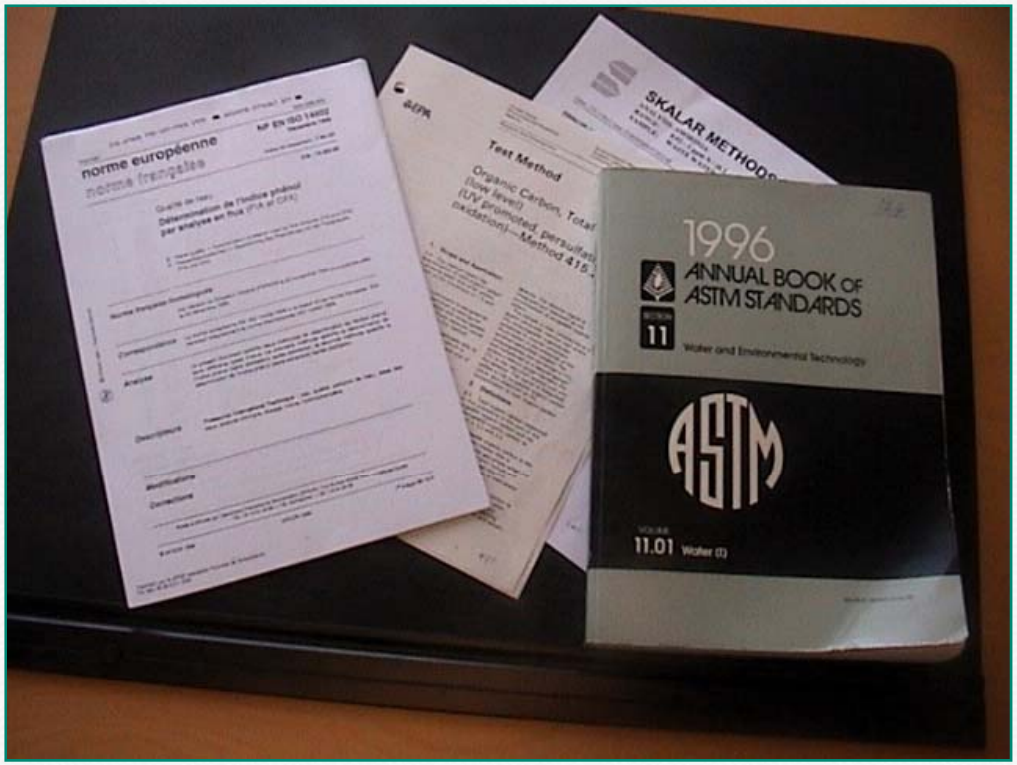
- ✓Commercial laboratories
- ✓Industrial laboratories
- ✓Universities and Research laboratories
- ✓Process control

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

Formacs^{SERIES} and Primacs^{SERIES}

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
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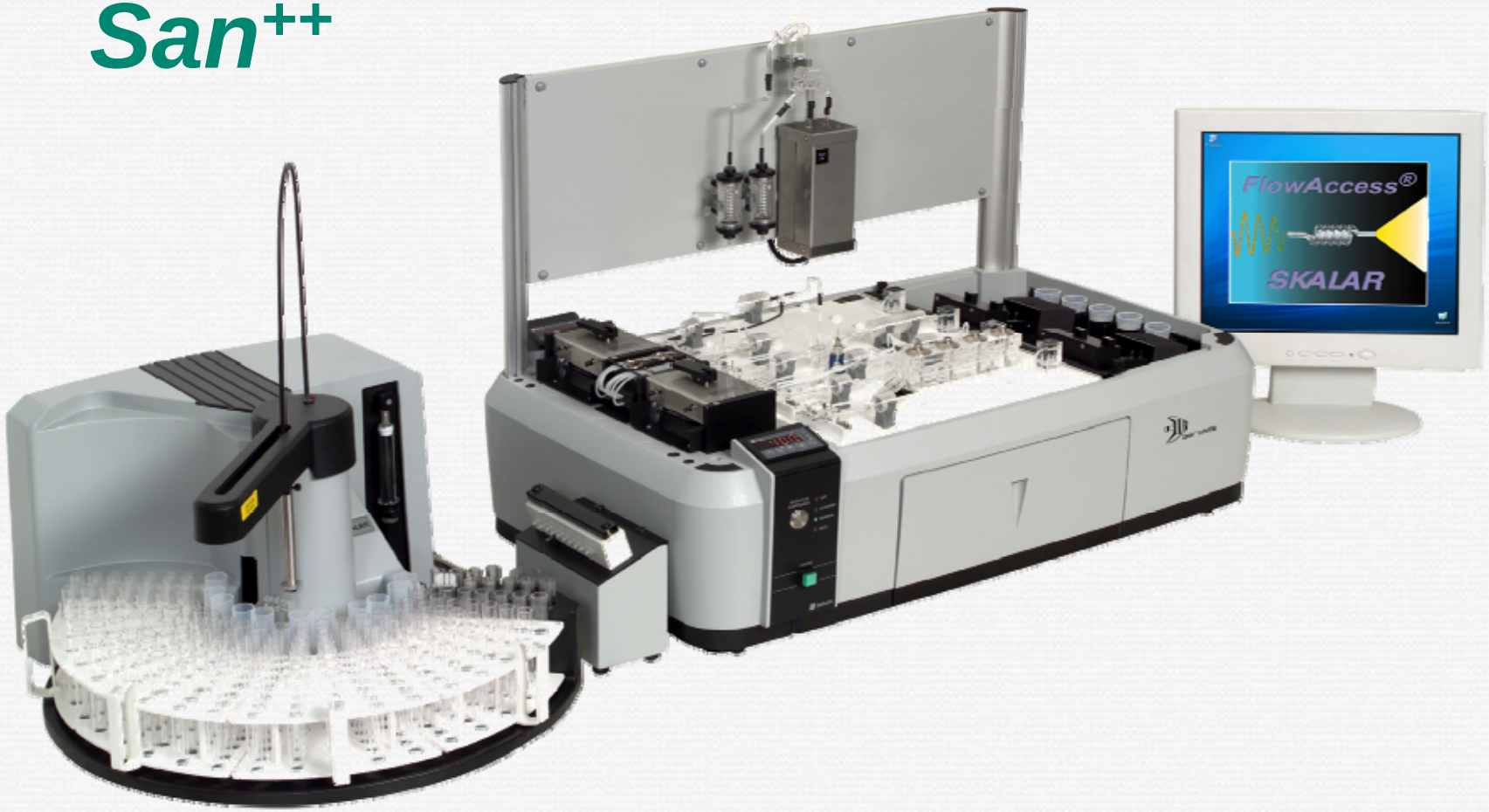
  - Nutrients
  - Cyanide
  - Phenol
  - Total Nitrogen
  - Total Phosphate
  - Dissolved Organic Carbon

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**

SKALAR

Continuous Flow Analyzer

Typical Automated Environmental Applications

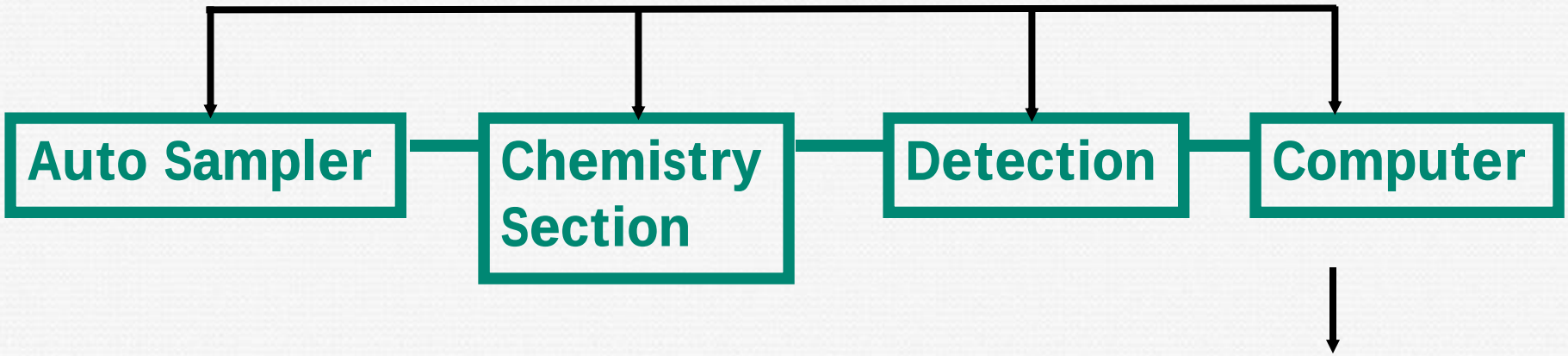
Ammonia
Aluminum
Boron
Bromide
Calcium
Chloride
Chemical Oxygen Demand
Chlorine
Cholinesterase Inhibition
Chromium VI
Color
Conductivity
Cyanide (Total – Free – WAD) Dissolved
Organic Carbon
Fluoride
Formaldehyde
Iron (Total – Free – Hydrolysable)
Magnesium
Manganese
Methylene Blue Active Substances (MBAS)
Molybdenum
Nitrate + Nitrite
Permanganate value (COD) Potassium
Total Amino Acids
Total Alkalinity
Total Carbonates
Total Hardness
Total Nitrogen (UV and TKN)
Total Phosphate (UV)
Total Phenols
Silicate
Sodium
Sulfate
Sulfur Dioxide
Urea
Volatile Acids
Zinc

SKALAR

Continuous Flow Analyzer

Principle of the San^{++}

Full Instrument Control

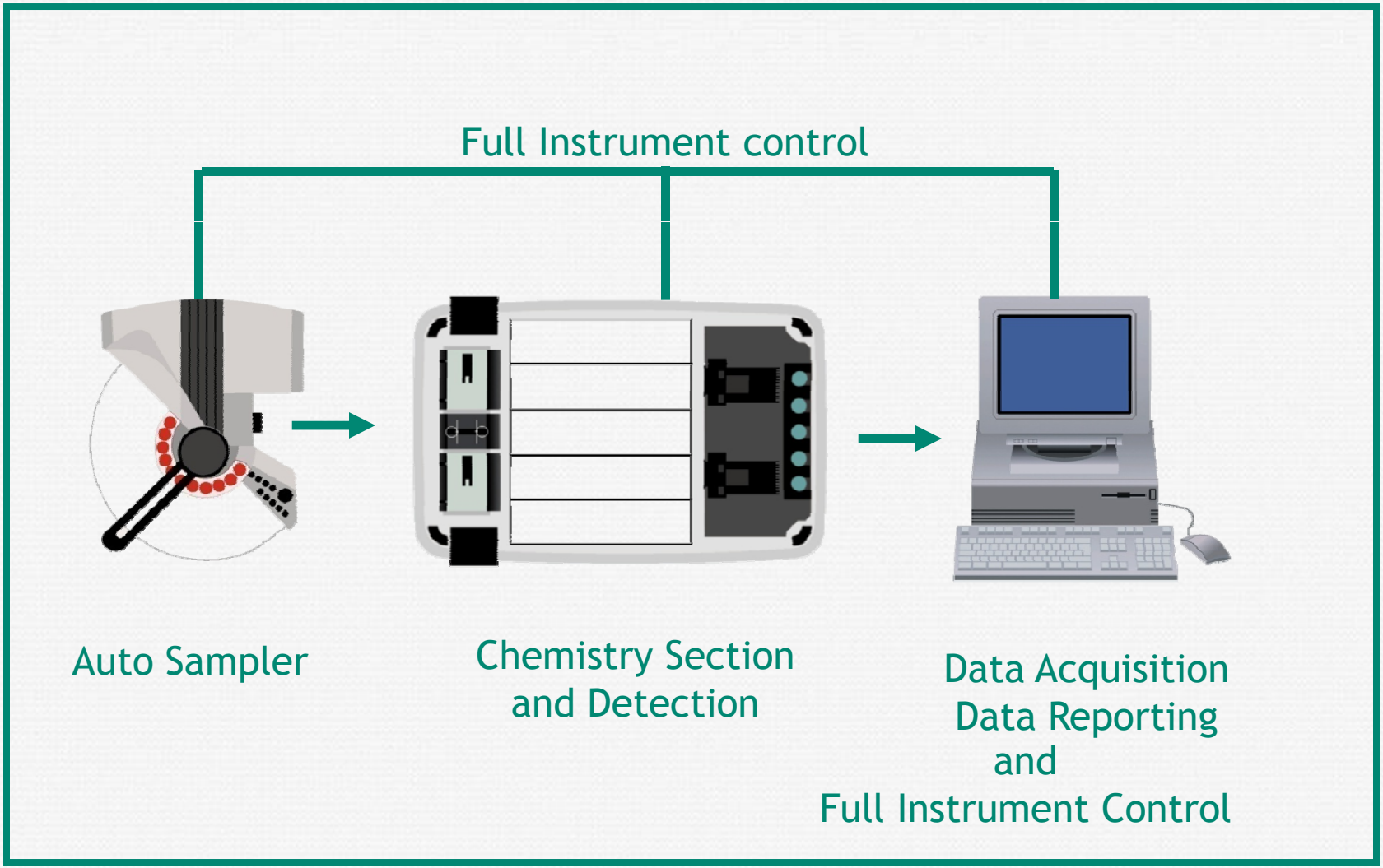


From 1 to 16 channels simultaneously

Data Handling and Report Generation

Continuous Flow Analyzer

Modular Design



SKALAR

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

SKALAR METHODS

ANALYSIS: PHENOL INDEX
RANGE: 2 - 100 ppb C_6H_5OH
SAMPLE: WASTE WATER

Catnr. I497-001 issue 112399/MH/99208370

PRINCIPLE

The automated procedure for the determination of the Phenol Index is based on the following: the sample is fed into a stream, mixed with phosphoric acid, and inline distilled at pH 1.4. The distillate, containing steam 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)

LABORATORY FACILITIES

1. Maximum power consumption depending on the analyser configuration, 2000 VA. Check voltage at the back of the instrument before installation.
2. 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 (H_2SO_4 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: o-Phosphoric acid ..... Preparation: Dilute the phosphoric acid in ± 70 ml
H_3PO_4 (85%) distilled water while cooling. Fill up to
Distilled water *..... 100 ml with distilled water and mix.
H_2O

Note: Prepare a fresh solution every day.

. Preparation: Dissolve the 4-amino antipyrine in ± 80 ml distilled water. Fill up to 100 ml with distilled water, add the Brij 35 and mix.

. Note: Prepare a fresh solution every day.

Preparation: Dissolve the potassium ferricyanide, the boric acid and the potassium chloride ± 80 ml distilled water. Adjust the pH to 10.3 with potassium hydroxide solution (1M). Fill up to 100 ml with distilled water.

Note: Prepare a fresh solution every day.

. Preparation: Dissolve the phenol in ± 800 ml distilled water. Fill up to 1 litre with distilled water and mix.

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

Stock solution 10 ppm C_6H_5OH

Dilute 1 ml stock solution 1000 ppm C_6H_5OH to 100 ml with distilled water.*

Note: Prepare the stock solution 10 ppm C_6H_5OH fresh weekly.

g of the distillation capillary may occur when the salt
0 gr/litre. In these cases, dilute the sample with water.
late matter. Turbid or coloured samples and samples
ot interfere with the determination.
wn that detergents in waste water can strongly influence
oam produced in the flow system can disturb both the
nols and phase segmentation and phase separation
rferences can easily be discovered in flow systems.
nt content, this international standard is only applicable
bove 0.1 mg/litre.

ndard 100 ppb C_6H_5OH is ± 96 A.U.
80 sec, air: 1 sec.
pler and the sample pump tube is made of 5141 tube.
em is approximately 45 minutes.

? or 2005 is in use, the pump tubes with catnr. SA 3020 up

catnr. SA 5020 up to 5039.

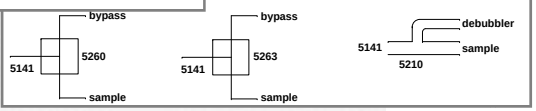
e sample matrix after sample pretreatment.

S

w cell catnr. SA 6425 and filters catnr. SA 6534 and SA
added to the module:

components

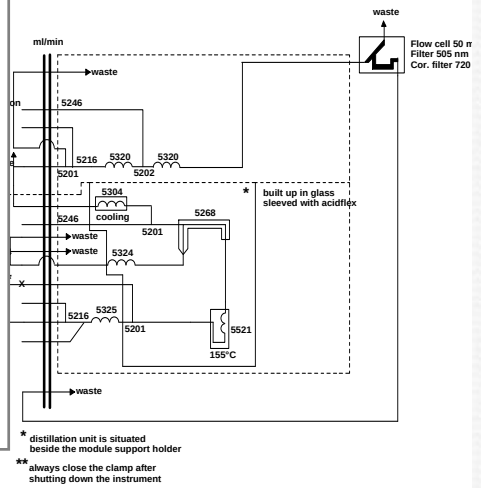
module, the following items are added to the cartridge
0 (standard), 5263 (for digest and acid) and debubbler



BERS REQUIRED CHEMICALS

oduct	Supplier and catnr.	Danger classification
	Merck 100100731	corrosive
	Merck 100317	corrosive
	Merck 100573	corrosive
	Merck 107293	harmful
	Skalar SC13900	
	Merck 104973	
	Merck 100165	
	Merck 104936	
	Merck 105021	corrosive
	Merck 100206	toxic

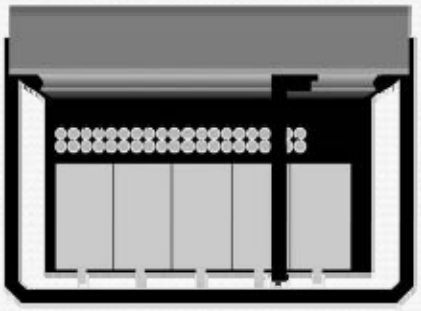
rmination of the Phenol Index by Flow Analysis, ISO 14402.

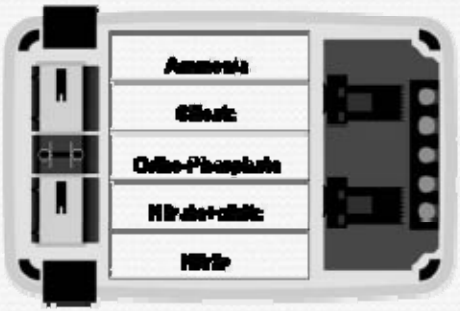


Practical Applications on CFA

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

⇩ + NO_2 + H^+

Diazonium compound

⇩ α-naphtylethylenediamine dihydrochloride

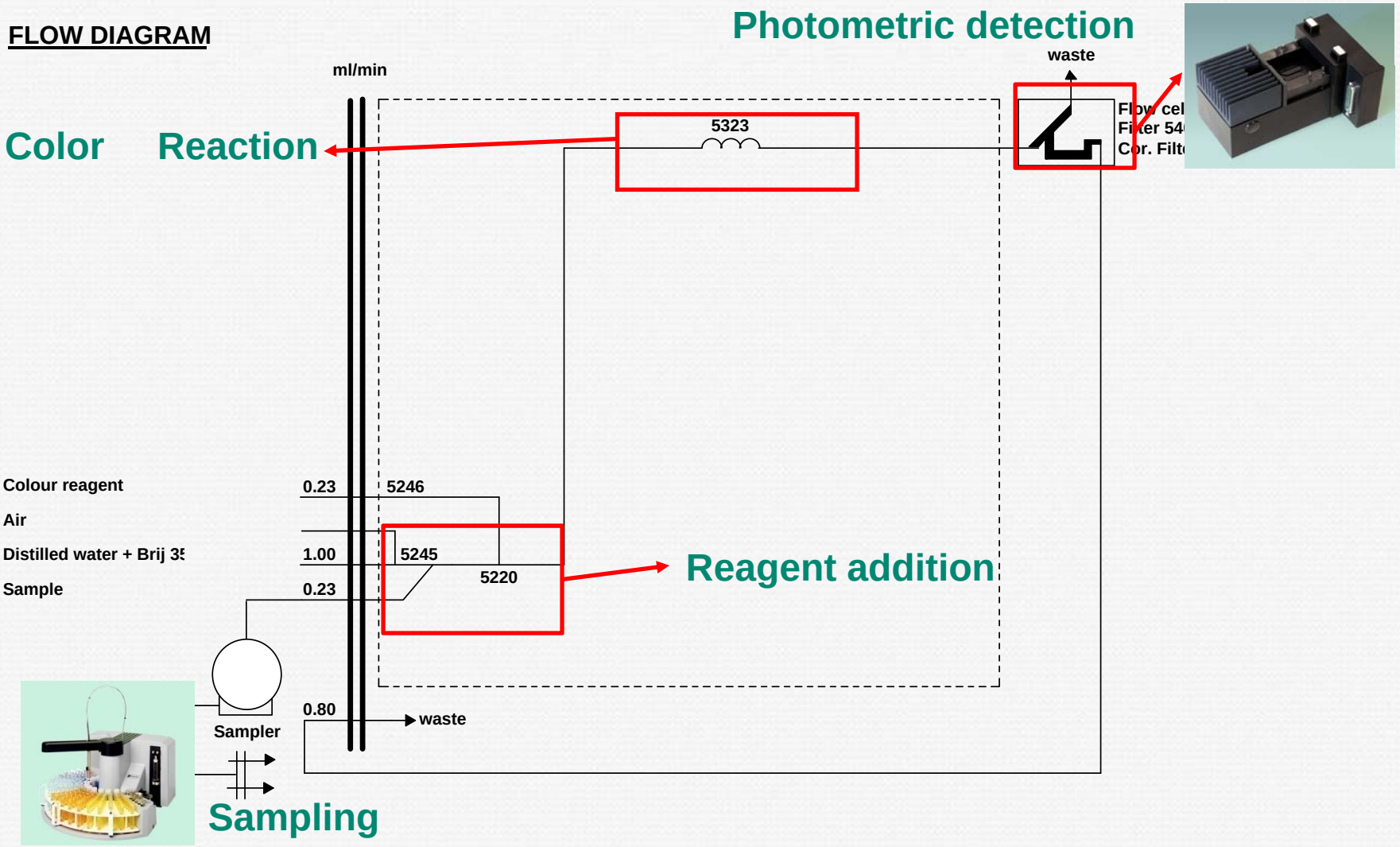
Red-purple color measured at 540 nm

Identical to the manual method

Practical Applications on CFA

Nitrite: Colorization method

FLOW DIAGRAM



Practical Applications on CFA

Nitrate: Colorization method (NO_2 + NO_3)

According ISO 13395

NO_3 ⇨ NO_2 by reduction

Reductionmethods:
- ✓Cd-reduction
- ✓ reduction with hydraziniumsulfate
- ✓enzymatic reduction

After reduction of NO_3 to NO_2: Identical measurement as NO_2-application

Sulfanylamide

⇩+ NO_2 + H^+

Ziazonium compound

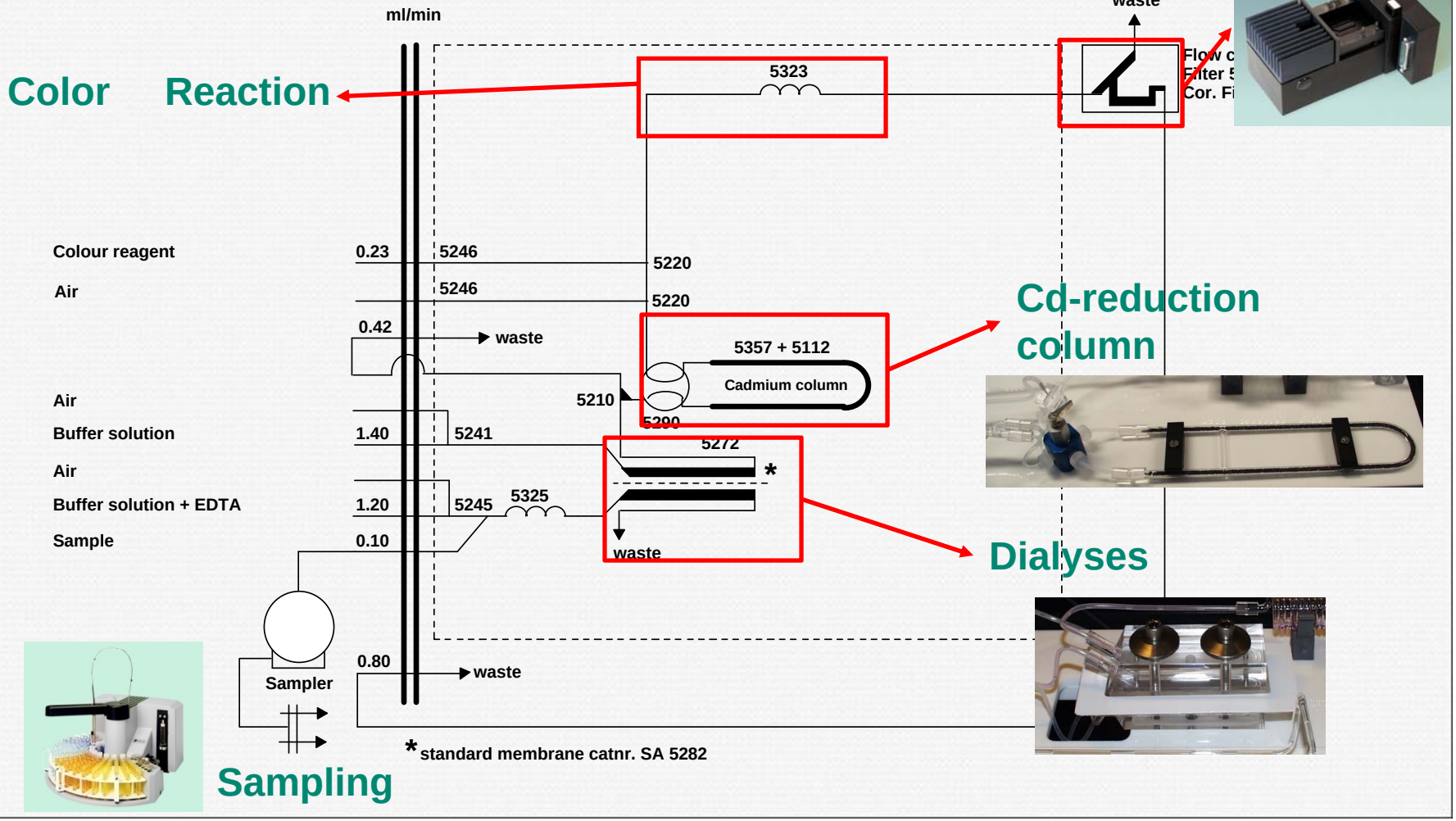
⇩α-naphtylethylenediamine dihydrochloride

Red- purple color measured at 540 nm

Practical Applications on CFA

Nitrate: Colorization method (NO_2 + NO_3)

FLOW DIAGRAM



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

⇩ + UV-light (+ pH 3.8

HCN

⇩ Separation by distillation at 125°C under vacuum

⇩ Chloramine-T,

Cyanogene chloride

⇩ Colorisation with 4-pyridine carboxylic acid

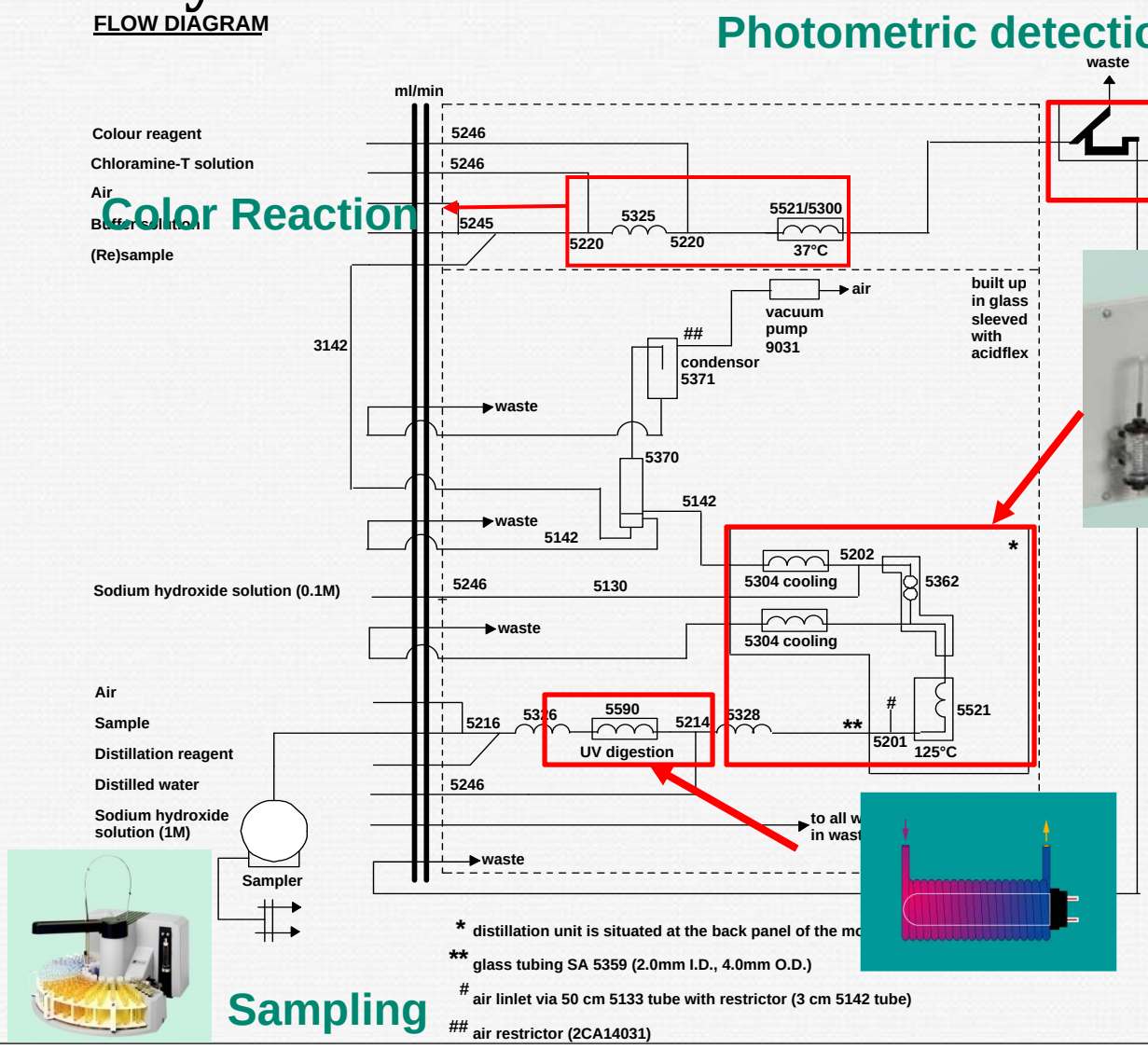
⇩ and 1,3-dimethylbarbituric acid

Red colour, measured at 600 nm

Practical Applications on CFA

Total Cyanide: Photometric detection with UV-B destruction

FLOW DIAGRAM



Photometric detection

Color Reaction

In-line distillation

In-line UV digestion

Sampling

* distillation unit is situated at the back panel of the mo

** 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)

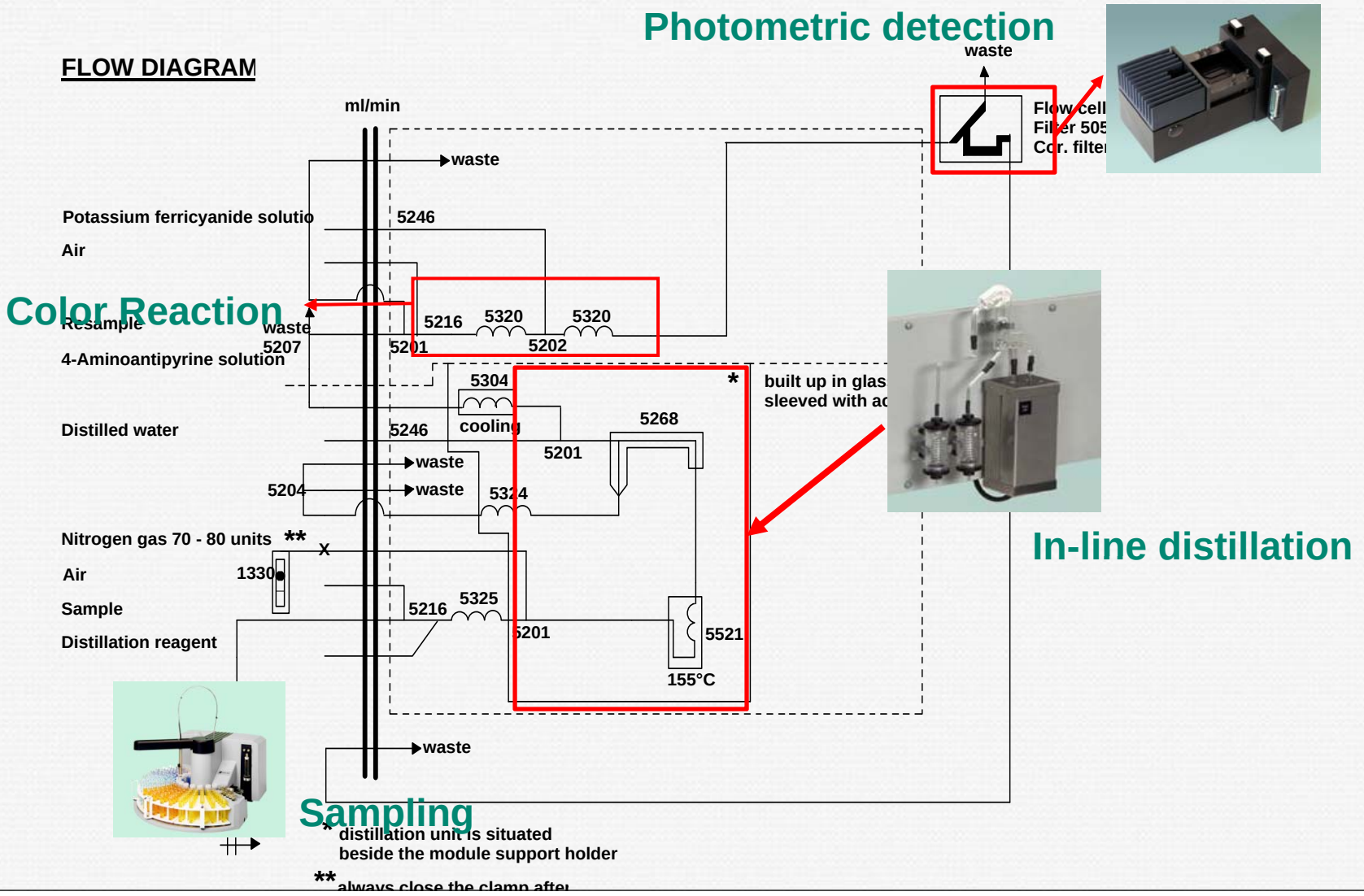
Quinones

⇩ 4-aminoantipyrine

yellow condensation products, measured at 505 nm

Practical Applications on CFA

Phenol Index: a complete Analysis Process



Practical Applications on CFA

Total Nitrogen

Different methods:

Element	Legislation	Description	Skalar system	Skalar Method
Total Nitrogen	ISO/CD 29441	Online measurement after UV-destruction	San^{++} with online UV-destruction	M475-424
Kjeldahl-N total phosphate		Offline destruction, followed by colorimetric detection of ammonium and phosphate on CFA	San^{++} with prior destruction on SA5640	M155-056 M503-004
Kjeldahl-N		Offline destruction, followed by colorimetric detection of ammonium on CFA	San^{++} with prior destruction on SA5640	M155-056
Total Nitrogen	EN 12260:2003 or EN-ISO 11905-2:1997	High Temperature combustion	Formacs^{TN}	
Totaal Nitrogen	EN-ISO 11905-1:1998	Offline destruction, followed by colorimetric detection of nitrate on CFA	San^{++} with prior destruction on SA5640	M461-032

Practical Applications on CFA

Total Nitrogen by in-line UV-destruction

According ISO/CD 29441

N-compounds

⇩ Oxidation reagent + UV-destruction

Organic carbon to Nitrate

⇩ +T (C)

Ammonium to nitrate

⇩ +Cd-reduction

Identical to nitrate measurement

Nitrate to nitrite

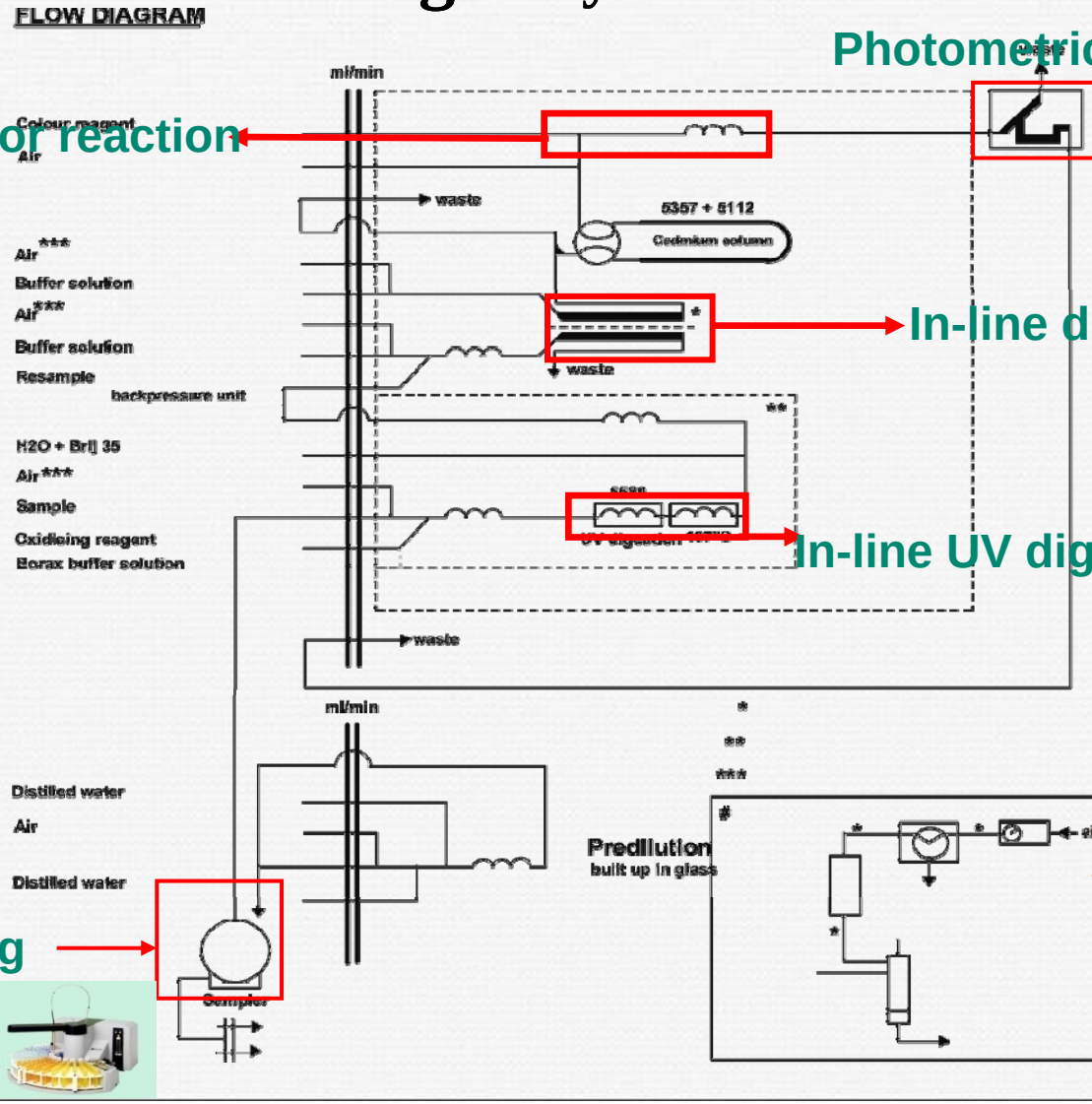
⇩ +sulfanilamide ,
N-1-nafthyl-ethyleen-diamine-dihydrochloride

Red colored complex, measured at 540 nm

Alternative for Kjeldahl

Practical Applications on CFA

Total Nitrogen by in-line UV-destruction

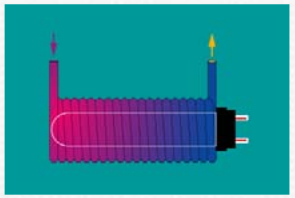


Color reaction

Photometric detection

In-line dialysis

In-line UV digestion

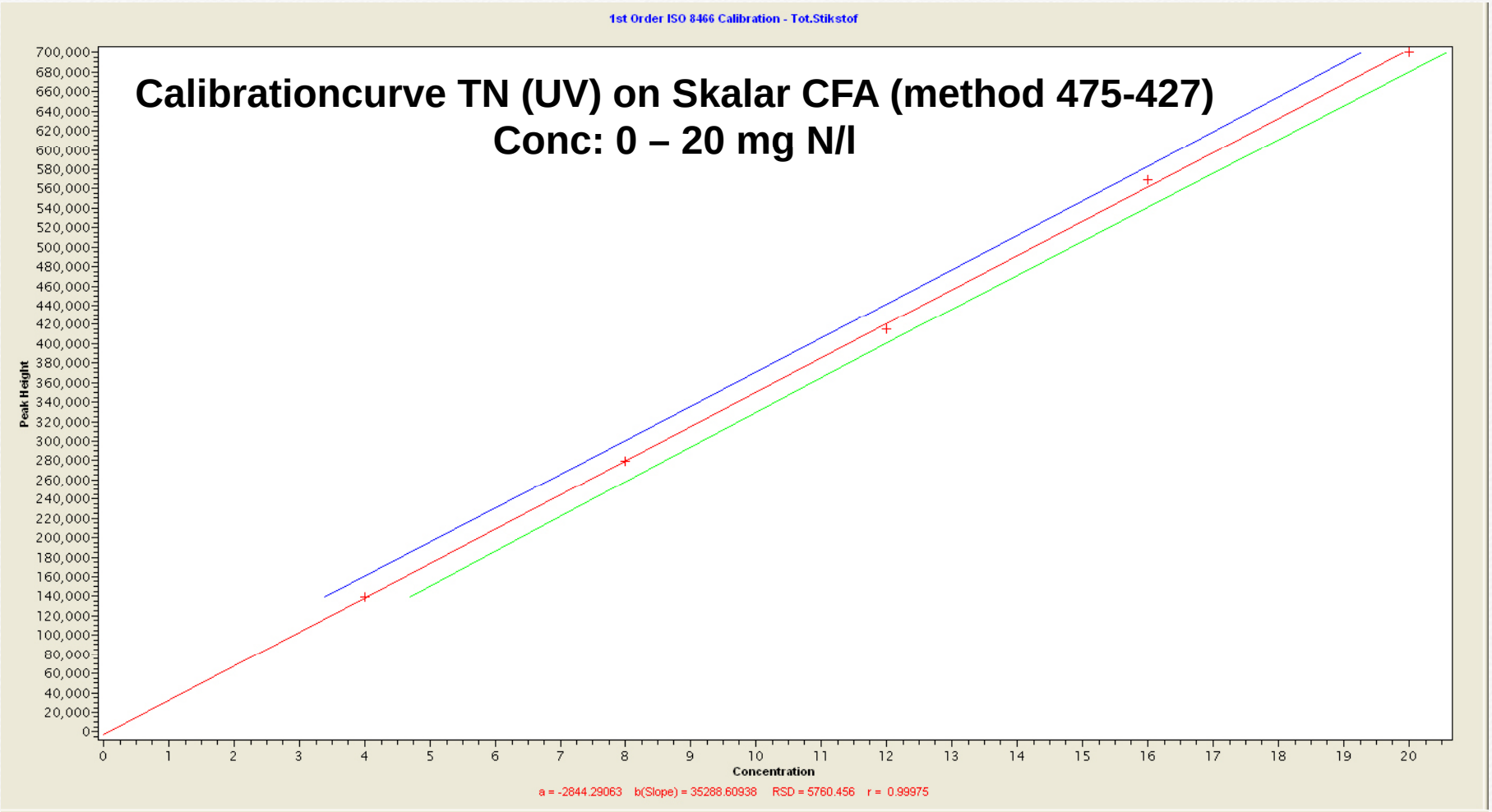


Sampling

Back pressure Regulation

Practical Applications on CFA

Total Nitrogen by in-line UV-destruction



Practical Applications on CFA

Total Nitrogen: Result comparison versus manual method

Sample Identity	Result Skalar (TN)	Result ref (TN)
10443292	7.5	7.5
22034434	32.9	33.7
10441790	292.2	294.0
22036038	59.8	60.6
22036040	78.8	79.3
22036043	53.2	53.1
22036149	50.5	51.8
88050901	20.9	20.6
88051101	33.0	33.4
88053301	28.9	30.3
88053501	61.1	61.9
88053601	49.3	50.6
88053602	3.8	3.7
88053701	56.8	58.0
88053801	113.4	111.0

Practical Applications on CFA

Total Phosphate by in-line UV-destruction

Element	Norm	Omschrijving	Skalar Systeem	Skalar Methode
Phosphate ortho & total	EN-ISO 15681-2:2003	Off-line destruction or in-line destruction	San^{++} with in-line UV-destruction or off-line destruction	M503-004
Kjeldahl-N total phosphate		Offline destruction, followed by colorimetric detection of ammonium and phosphate on CFA	San^{++} with prior destruction on SA5640	M155-056 M503-004

Practical Applications on CFA

Total Phosphate by in-line UV-destruction

According ISO 15681-2

P-compounds

⇩ Oxidation reagent + UV-destruction

Organic phosphate to ortho-phosphate

⇩ +T (°C)

Inorganic phosphate to ortho-phosphate

⇩ +katalyst
ammonium haptamolybdate

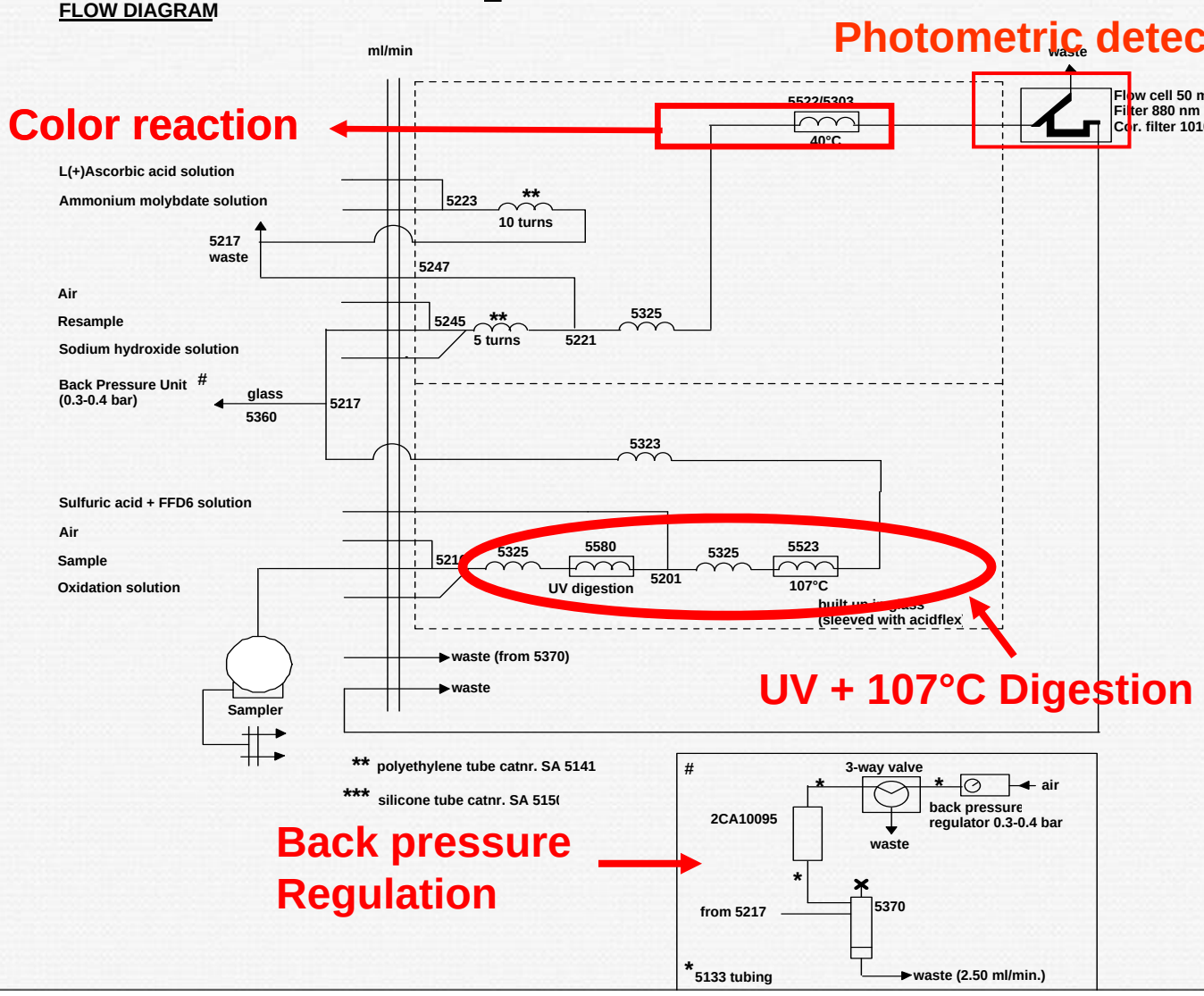
Identical to o-phosphate measurement

phospho-molybdic acid complex, measured at 540 nm

Practical Applications on CFA

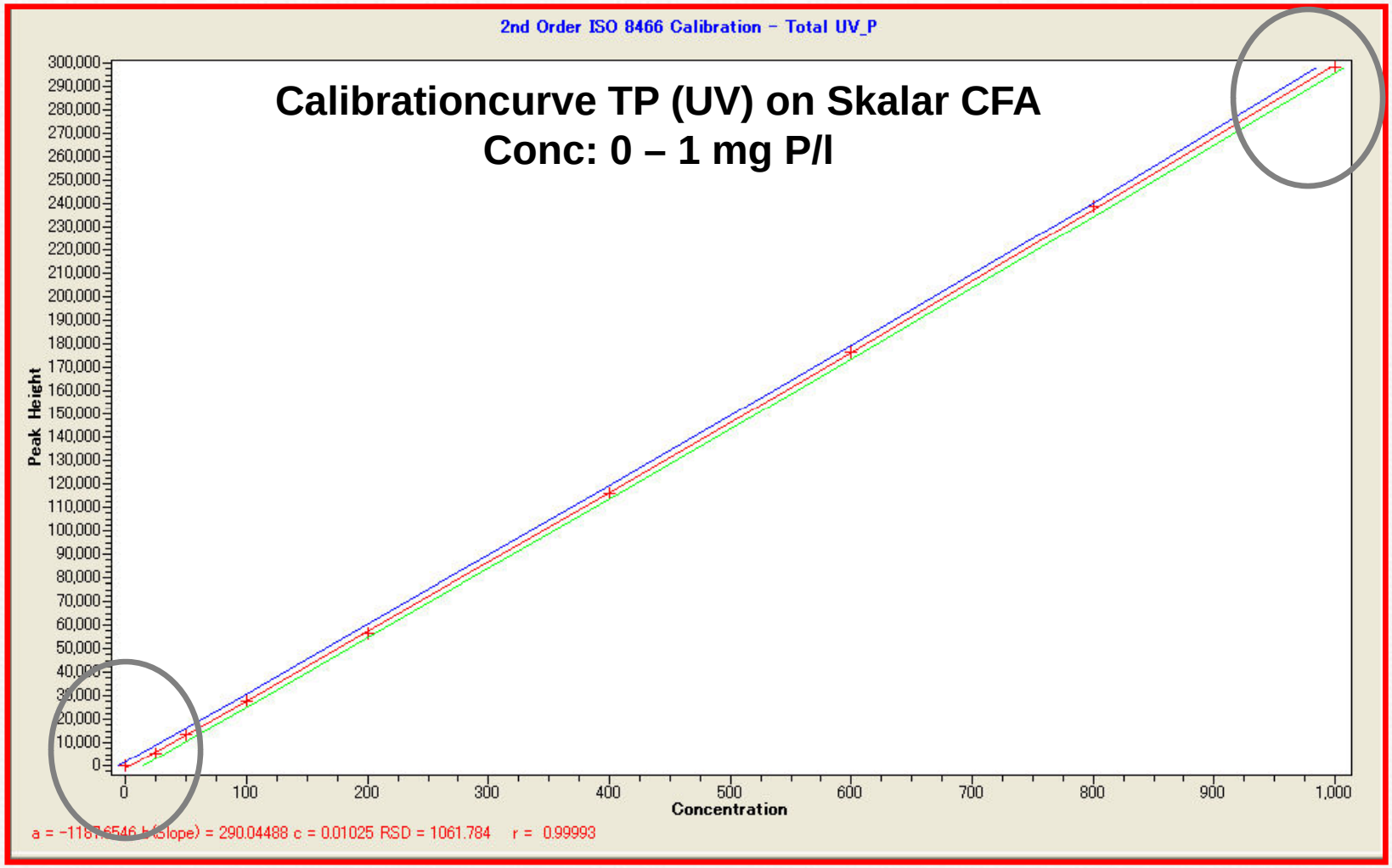
Total Phosphate by in-line UV-destruction

FLOW DIAGRAM



Practical Applications on CFA

Total Phosphate by in-line UV-destruction

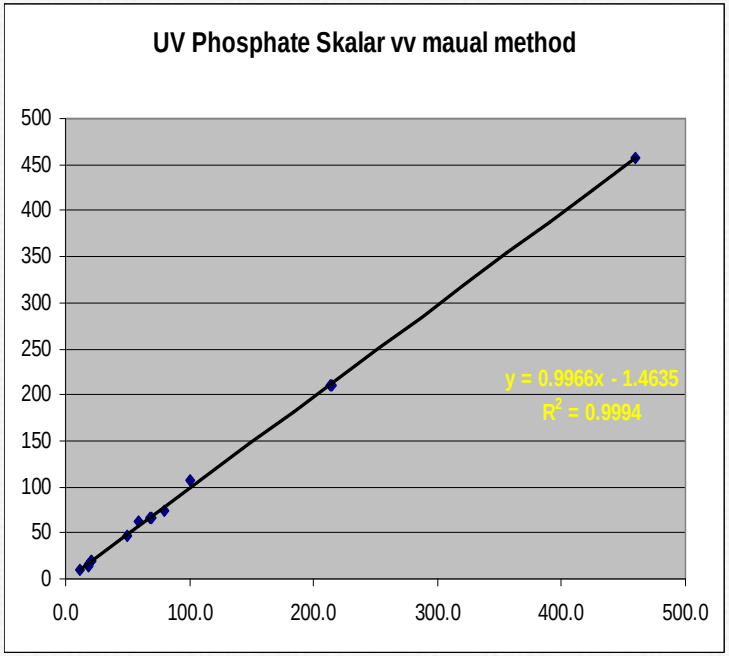


Practical Applications on CFA

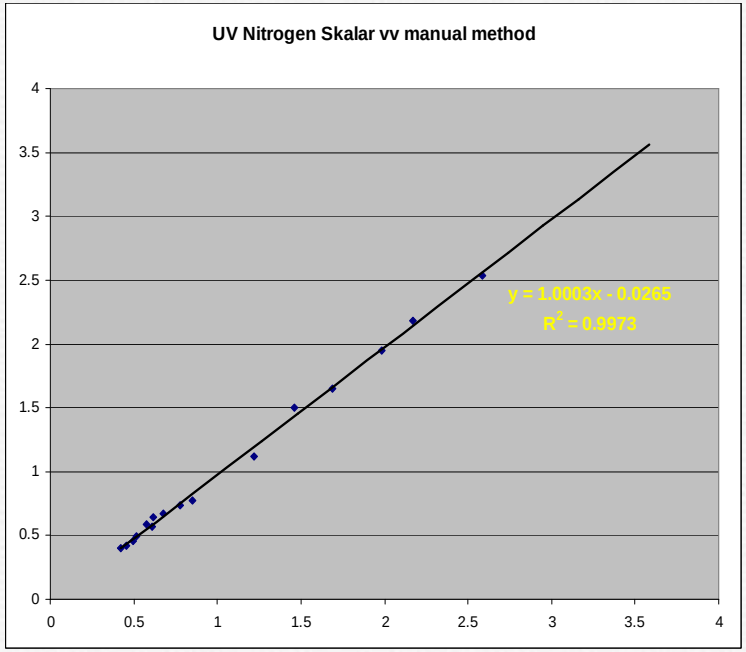
Total Phosphate / Total Nitrogen

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.



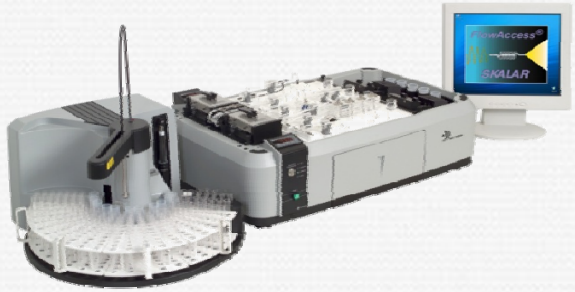
According to international standard regulations (ISO, DIN, etc.) accredited!

Practical Applications on CFA

Total Organic Carbon

How to measure TOC?

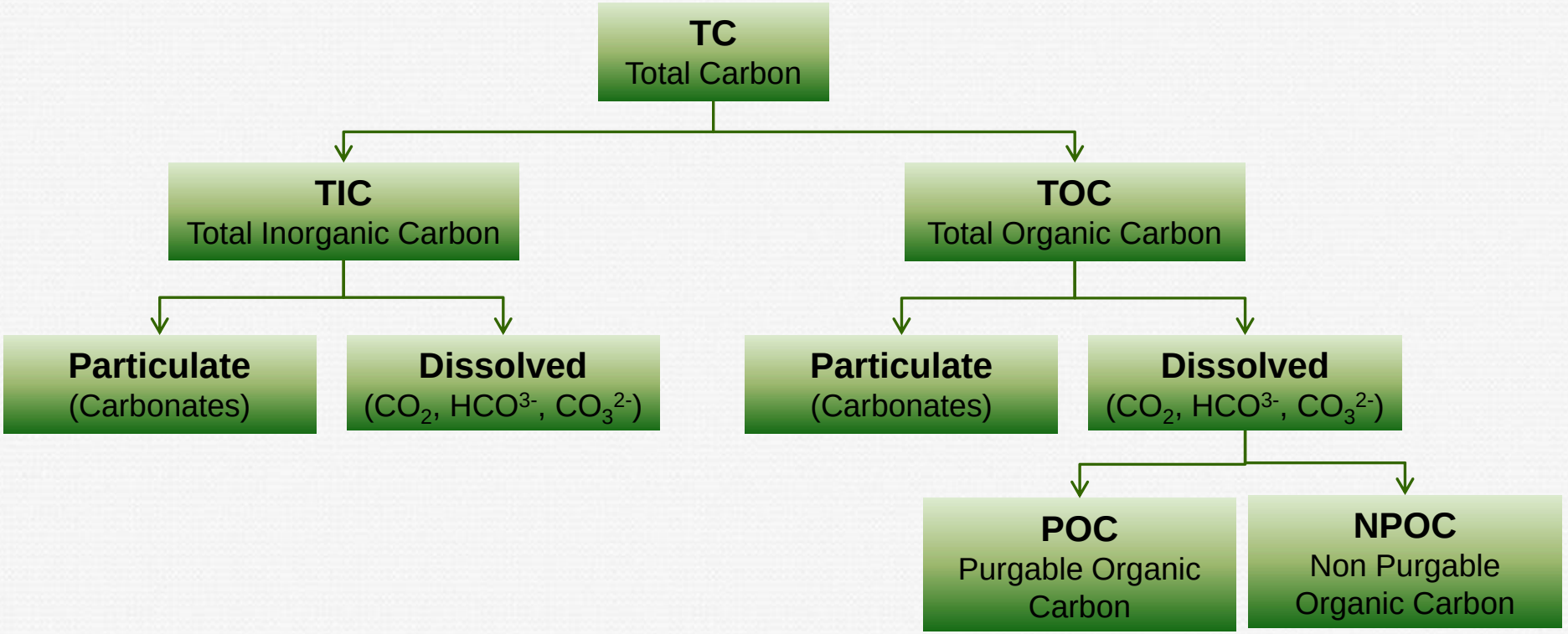
- UV-promoted persulfate oxidation (TOC)
  - ↳ On CFA using A TOC module, followed by IR-detection



- High temperature catalytic combustion (TOC & TN)
  - ↳ On Formacs^{SERIES} TOC Analyzer

Practical Applications on CFA

What is Total Organic Carbon?



Practical Applications on CFA

Total Organic Carbon – UV promoted on CFA

Sample

⇩acidified + sparged (N_2)

liberates and disperses any inorganic or volatile organic carbon
Organic carbon rests in sample

⇩ persulfate / tetra borate reagent
+ UV digestion coil

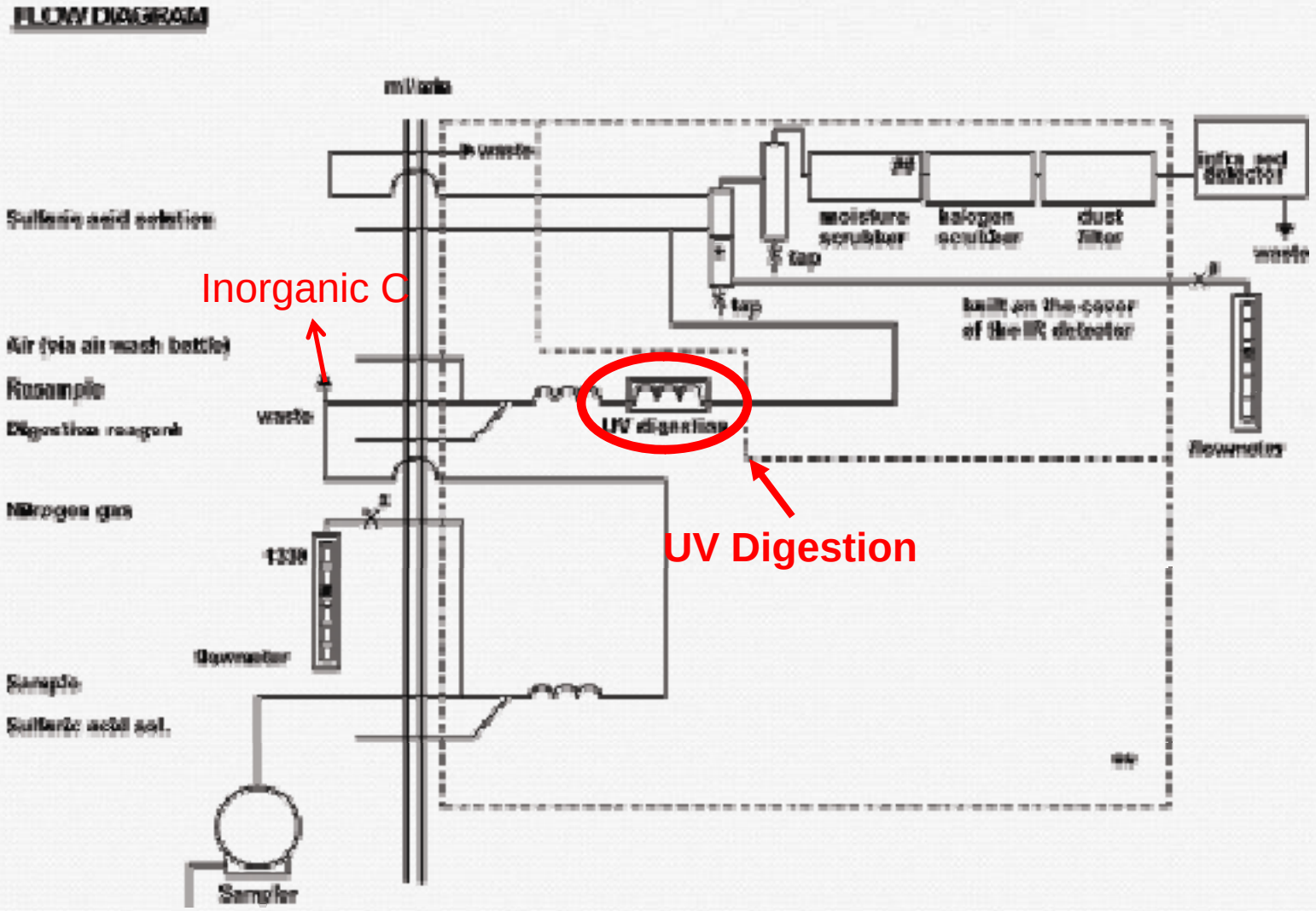
All organic carbon oxidised to CO_2

⇩ acidification and sparging
to release CO_2 from solution

IR-measurement of CO_2

Practical Applications on CFA

Total Organic Carbon – UV promoted on CFA



TOC / TN Analyses

Formacs^{HT} TOC Analyzer

New model High Temperature Combustion Analyzer

Optional Sampler

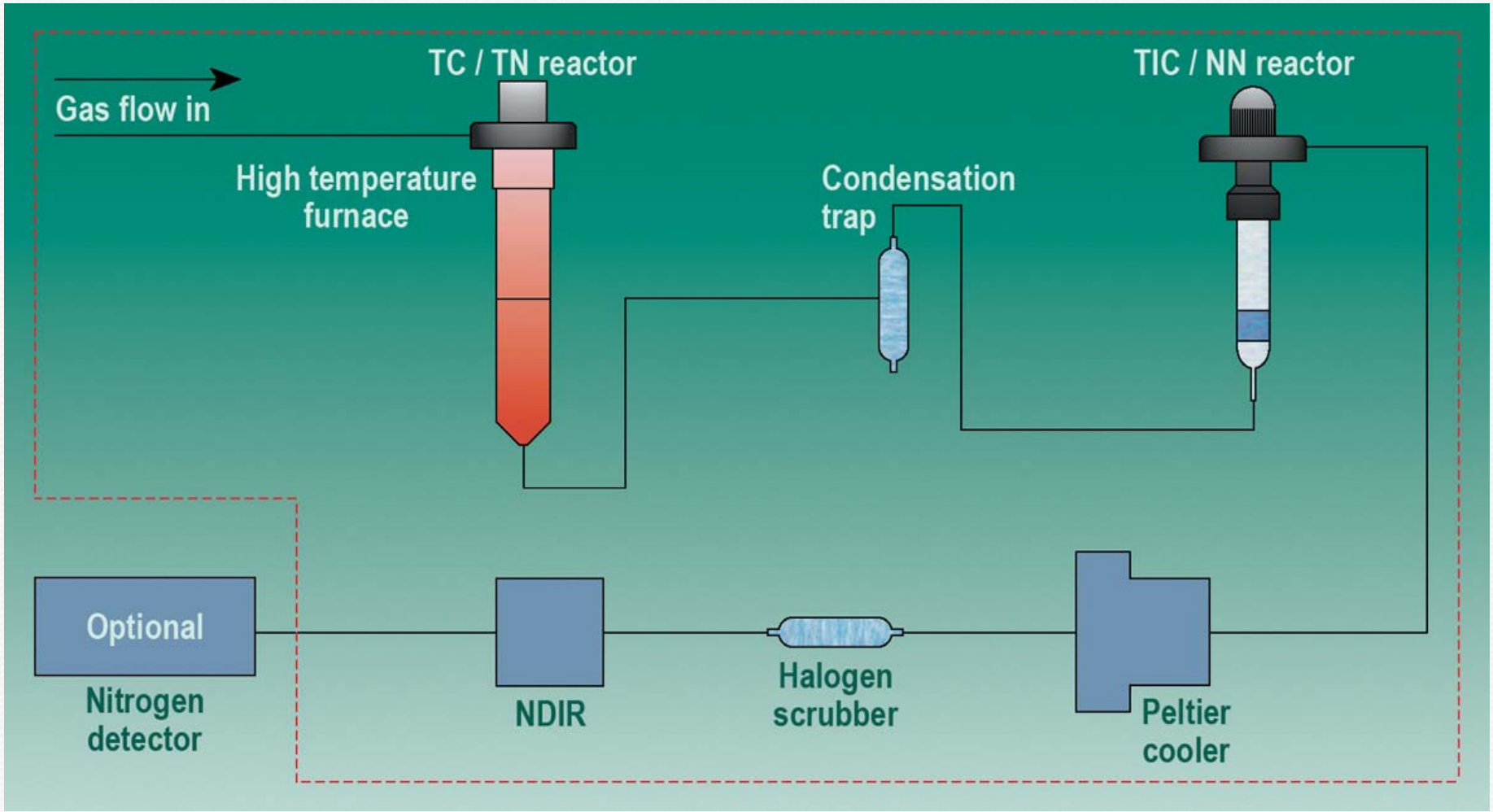
TOC Analyzer

Data aquisition & instrument cotrol

TOC / TN Analyses

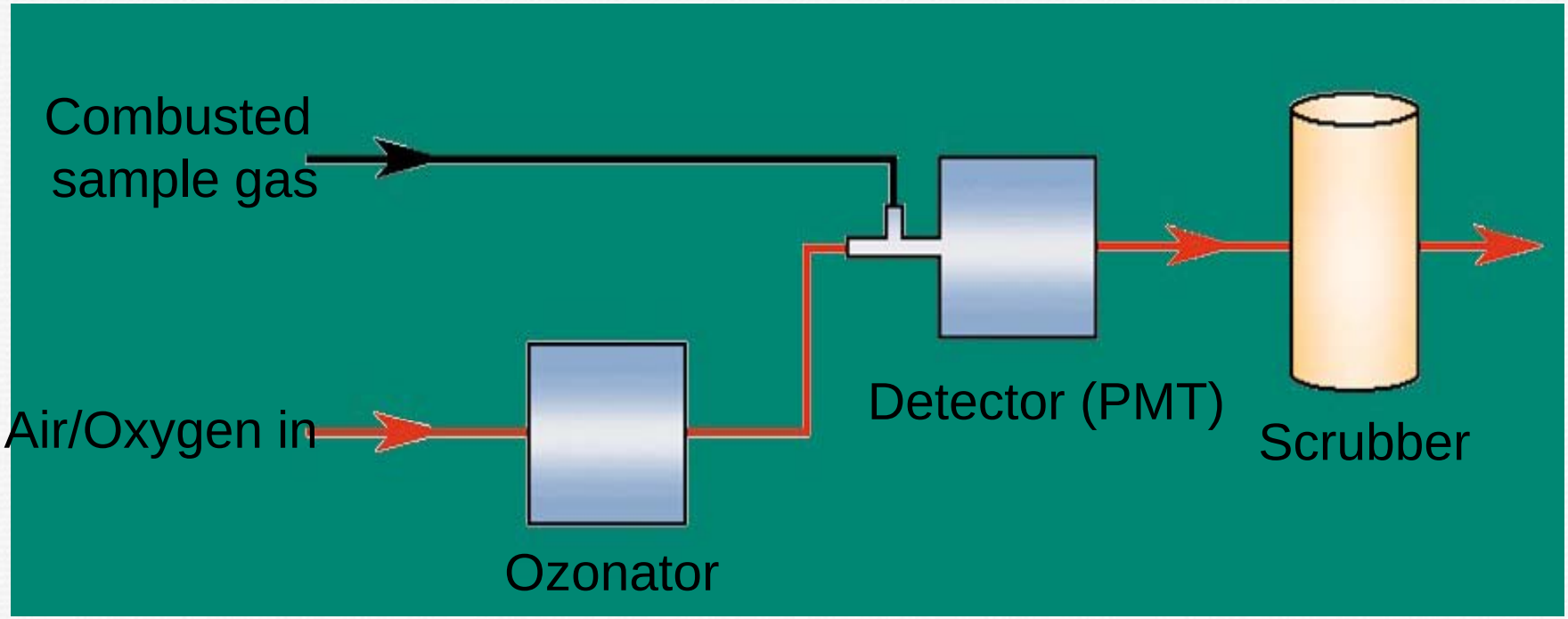
Formacs^{HT}: Schematics of TOC Analyzer

New model High Temperature Combustion Analyzer



TOC / TN Analyses

Formacs ^{TN}: Schematics of ND20 TN Detector



$$NO + O_3 \rightarrow NO_2^* + O_2 \rightarrow NO_2 + O_2 + h_v$$

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

		Results	
NaNO3 Std 2.00 mg/l	TN	2.00	Recovery
NaNO3 Std 4.00 mg/l	TN	4.00	%
KNO3 2 mg/l N	TN	2.04	102
NaNO2 2mg/l N	TN	2.08	104
NH4Cl 2 mg/l N	TN	2.02	101
NH4Cl 4 mg/l N	TN	4.2	105
NH4Acetate 2mg/l N	TN	2.1	105
Glycine 2 mg/l N	TN	2.07	104
Creatinine 2 mg/l N	TN	2.11	106
Creatinine 4 mg/l N	TN	4.27	107

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