Advanced technics in the determination of sum parameters (TIC/TOC/TNb)

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What is a „sum parameter“?

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Definition: sum parameter

A composite parameter achieved by the determination of a general characteristic (x) of various chemical compounds (x_i) as sum without specification of a single compound.

$$\sum_{i=1}^{i} x_i = x_1 + x_2 + \ldots\ldots\ldots + x_i$$

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sum parameters

...are commonly used in water and waste water analyses for the determination of its contamination with organic compounds.

Typical sum parameters are:

BOD_x	-	biological oxygen demand
COD	-	chemical oxygen demand
TOC	-	total organic carbon

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sum parameters

BOD_x and **CSB** are indirect methods to determine the amount of organic carbon by the determination of the biological and chemical oxygen demand during the decomposition of its compounds.

Disadvantage:

- slow
- insufficient or wrong oxidation
- depending from biological activity
- heavy metal containing reagents
- no automation

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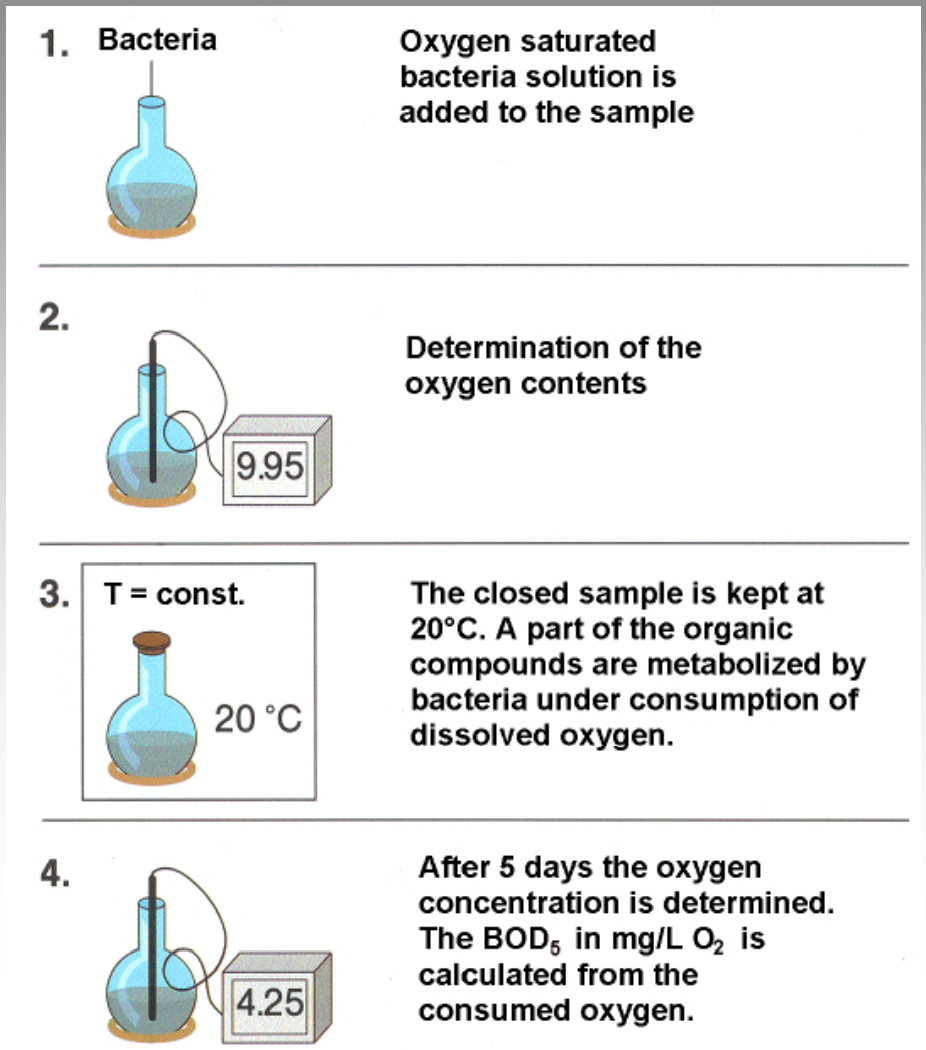
sum parameters



BOD_5 - biological oxygen demand after 5 days

DIN 38 409 H51
DIN 38 409 H52

Disadvantage:
particulates are not sufficiently oxidized

Reference: Fonds der chemischen Industrie - Umweltbereich Wasser

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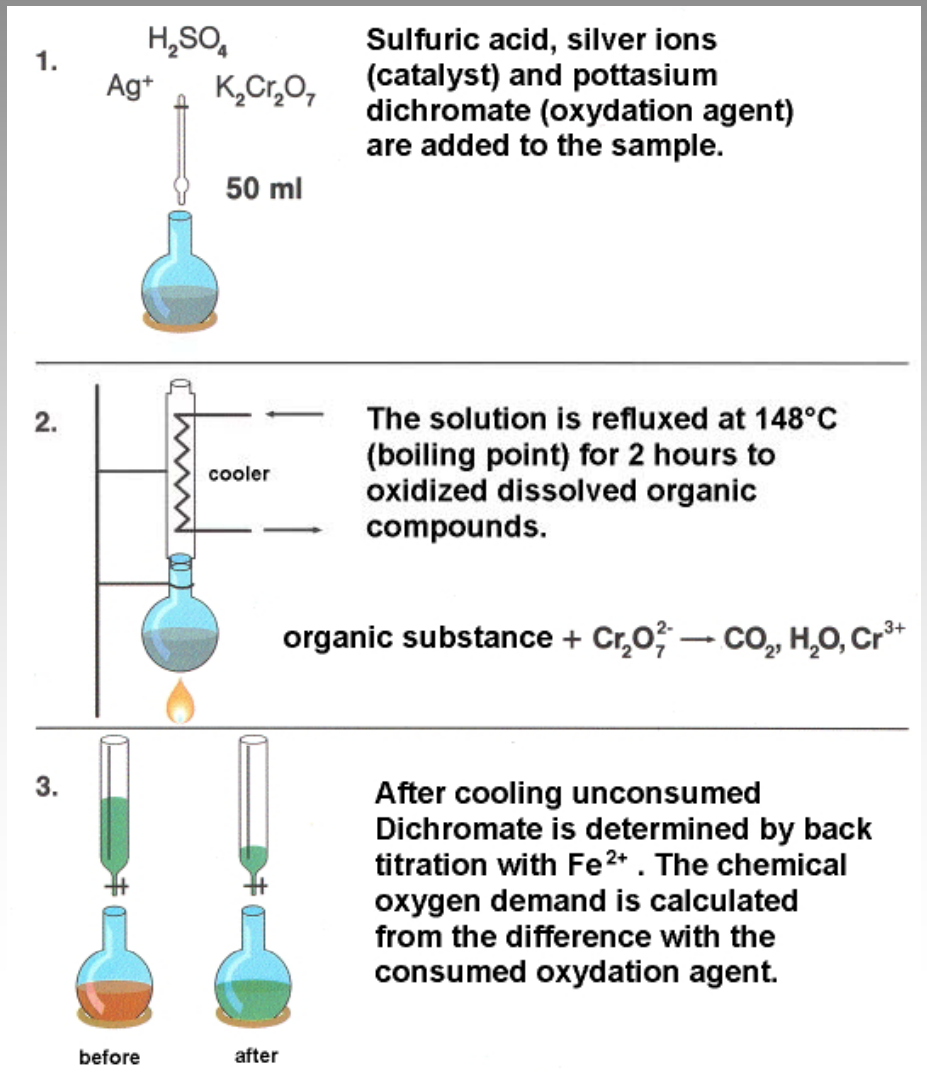
sum parameters



COD - chemical oxygen demand

DIN 38 409 H41

Disadvantage: higher or fluctuating results, if dichromate is consumed due to the oxidation of sulfur containing compounds

Reference: Fonds der chemischen Industrie - Umweltbereich Wasser

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sum parameters

EN 1484 - European Standard

Water analysis -
Guidlines for the determination of the total organic carbon (TOC) and dissolved organic carbon (DOC)

The EN 1484 approves the determination of TOC and DOC as appropriate method to determine the contamination of water with organic compounds.

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sum parameters

EN 1484 - European Standard

Determination of TOC and DOC by:

- **Wet chemical - UV-persulfat method**
- **Combustion method**

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Determination of TOC and DOC

Wet chemical - UV-persulfat method

Advantage:

- large sample volume (up to 20mL)
- high sensitivity

Disadvantage:

- insufficient oxidation of particulates
- not applicable for electrolytes
- not for highly contaminated samples
- not for solid samples

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Determination of TOC and DOC

Combustion method

Advantage:

- quantitative oxidation of all carbon containing compounds
- low matrix influence
- applicable for waste water and solids

Disadvantage:

- lower injection volume (up to 3mL)
- problematically with salts
- lower sensitivity

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Conclusion

The combustion method has the largest potential to be state of the art, when the disadvantages can be minimized.

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EN 1484 - European Standard

TC - total carbon

TIC - total inorganic carbon („H_2CO_3“)

TOC - total organic carbon (+ CN^-, OCN^-, SCN^-)

TIC + TOC = TC (additive determination)

TOC = TC - TIC (difference method)

Direct method:

TOC = (TC - TIC) after external acidification

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EN 1484 - European Standard

TOC - total organic carbon
NPOC - non-purgable organic carbon
POC (VOC) - purgable organic carbon

TOC = POC + NPOC

$\Rightarrow$ **TIC + POC + NPOC = TC**

or $\Rightarrow$ **NPOC = TC - TIC - POC**

POC = 0 $\Rightarrow$ **NPOC = TOC**

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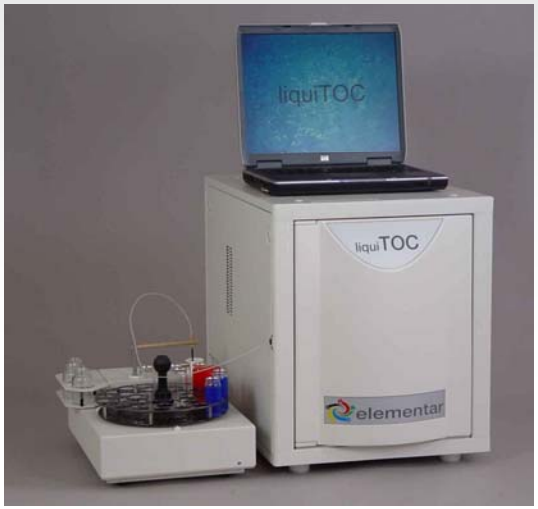
Additive determination

TIC + TOC = TC

or

TIC + POC + NPOC = TC



liqui TOC II
liqui TOC trace

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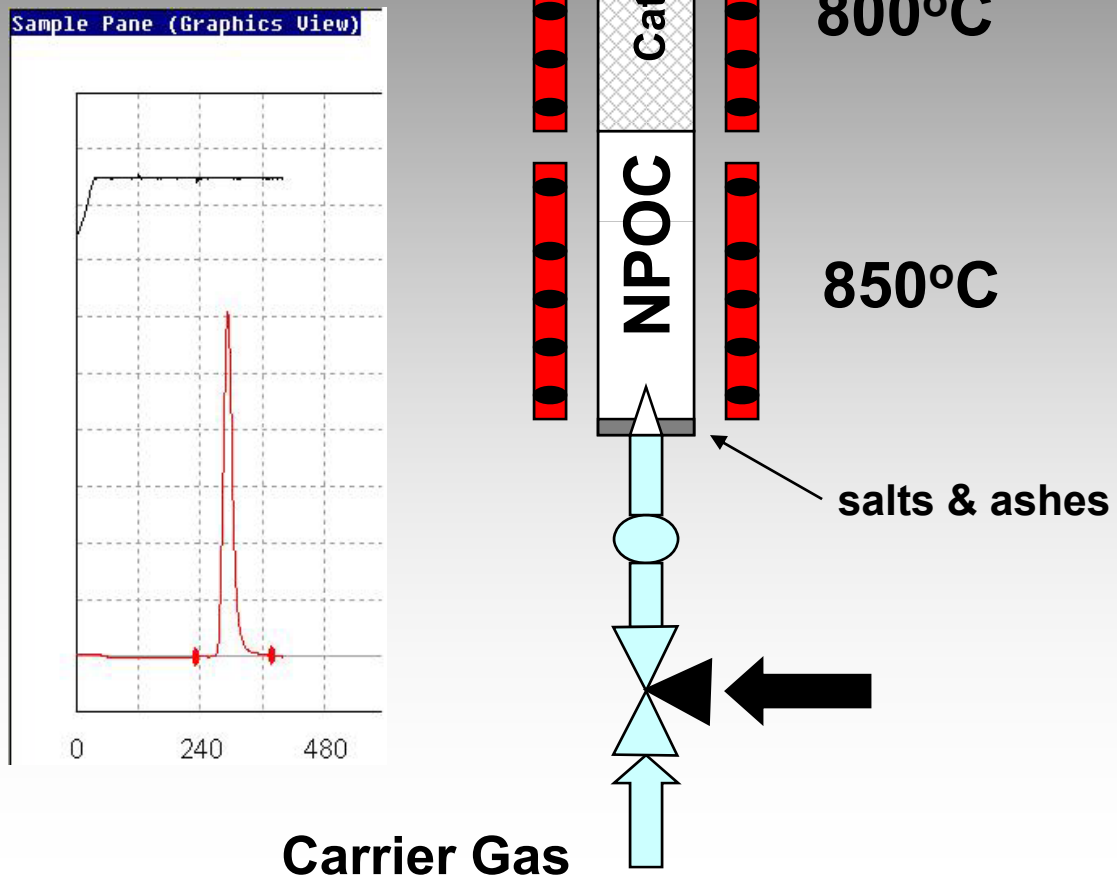
NPOC direct (after external acidification)



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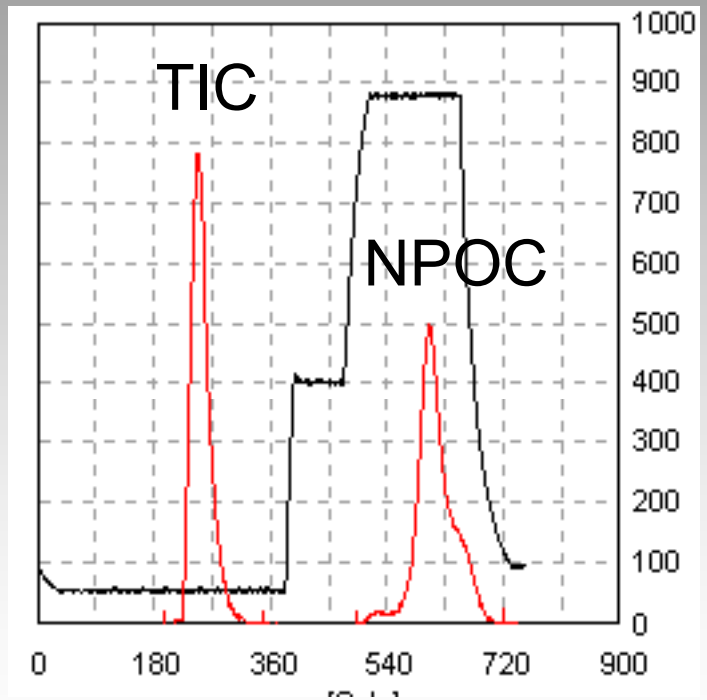
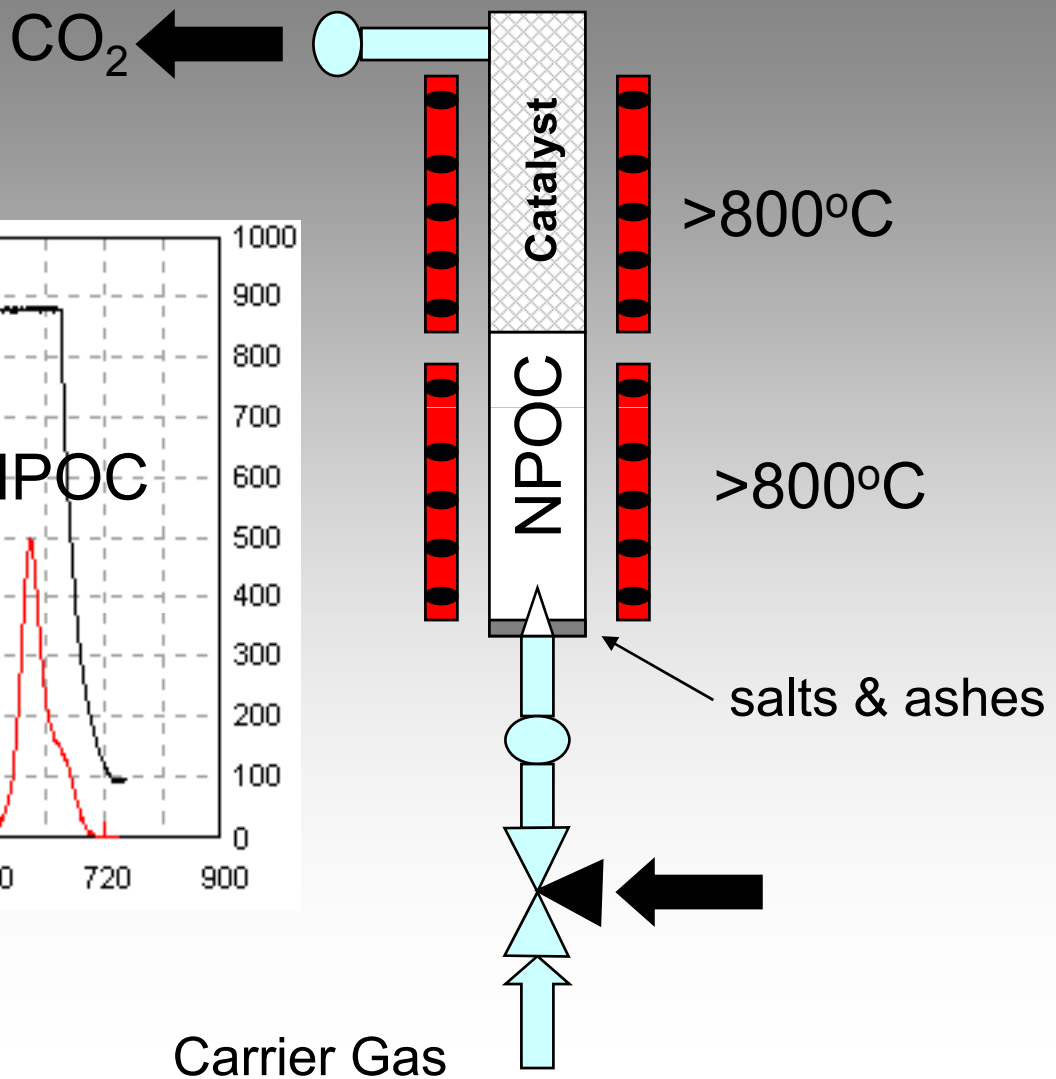
TIC/NPOC - determination





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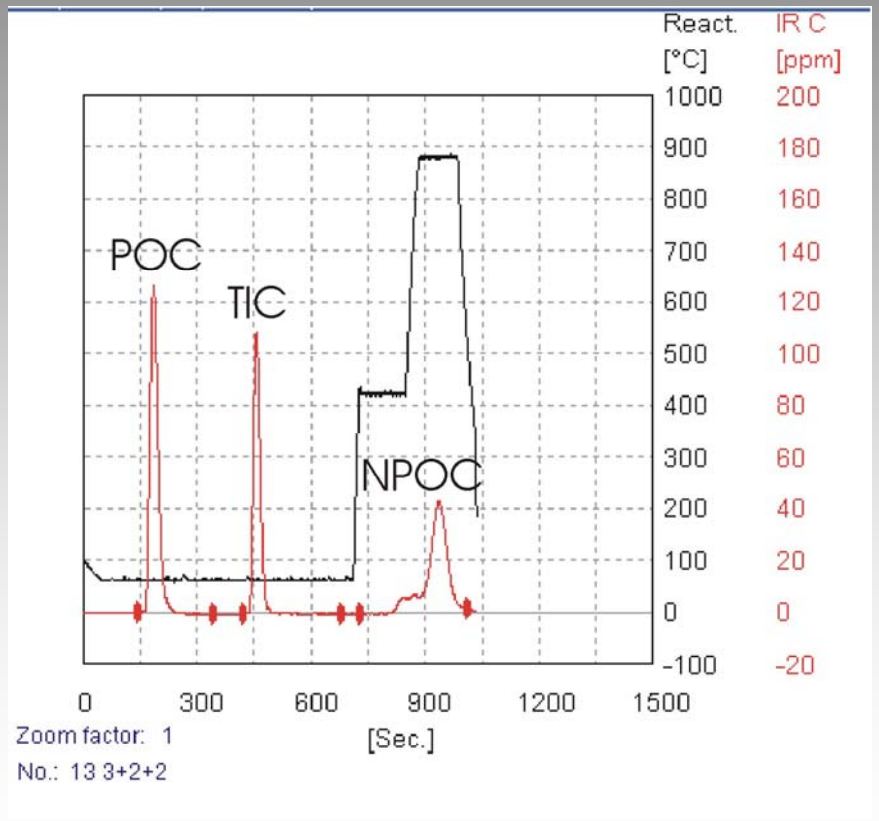
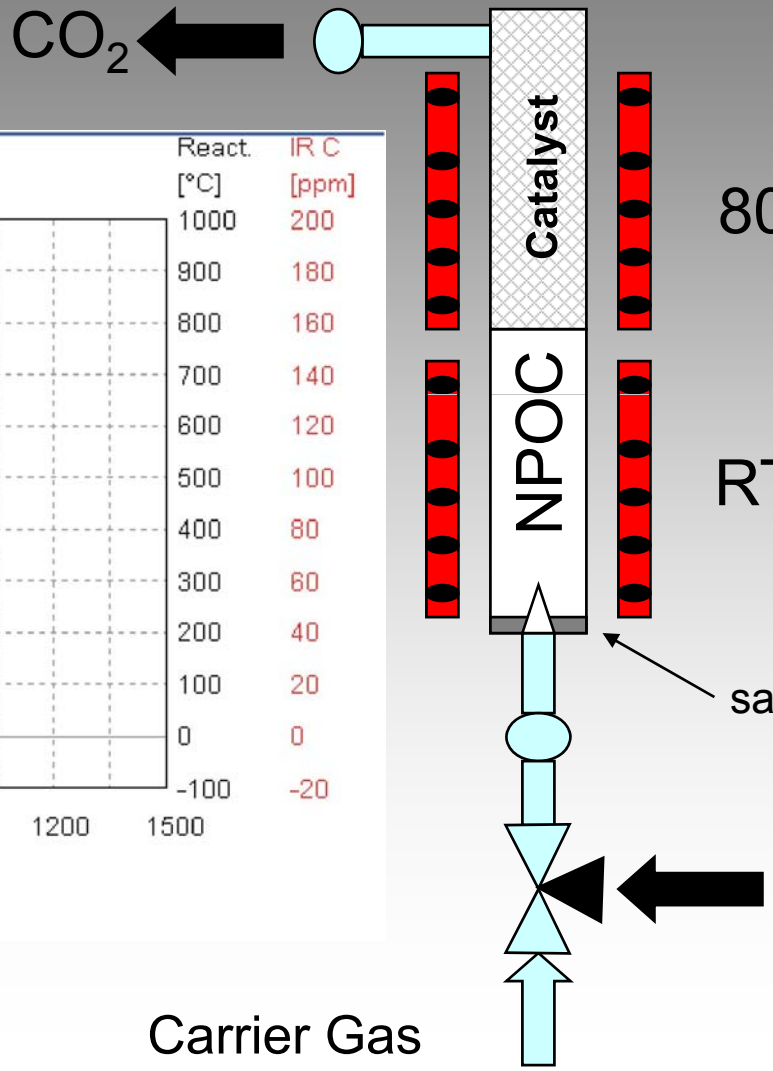
TIC/POC/ NPOC - determination





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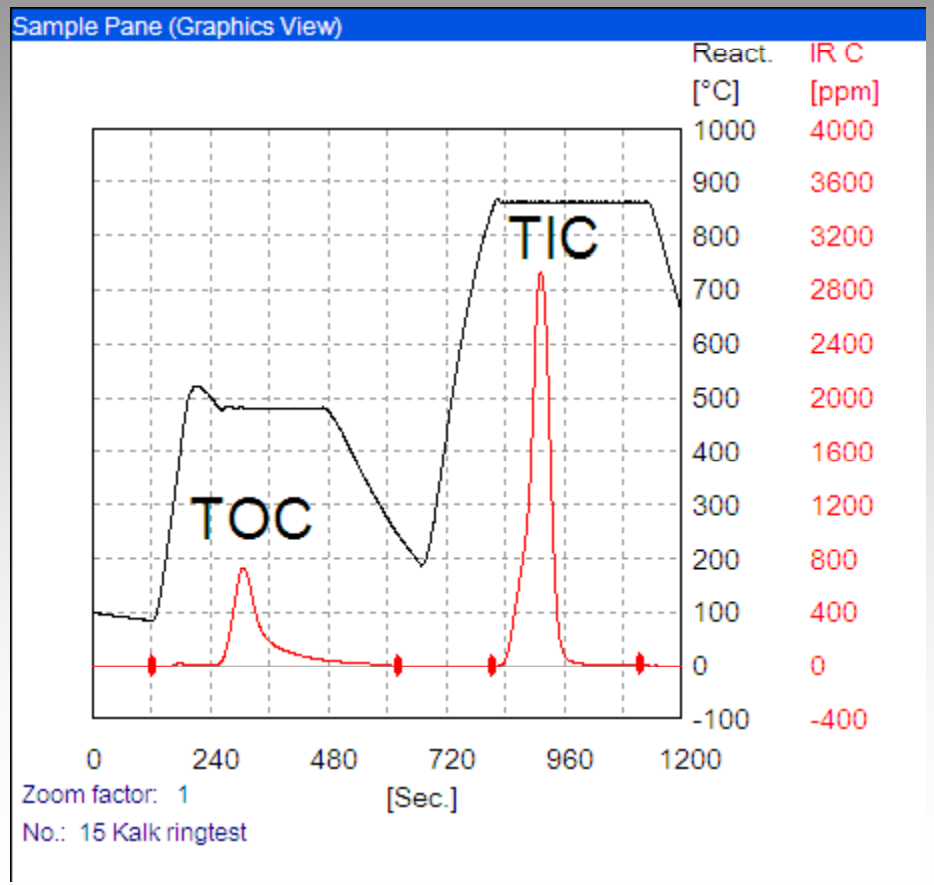
Dynamic 2-zone-furnace



Determination of TIC and TOC in solids without acidification by the temperature ramp method.

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Difference method

TOC = TC - TIC

or

NPOC = TC - TIC - POC

vario TOC cube

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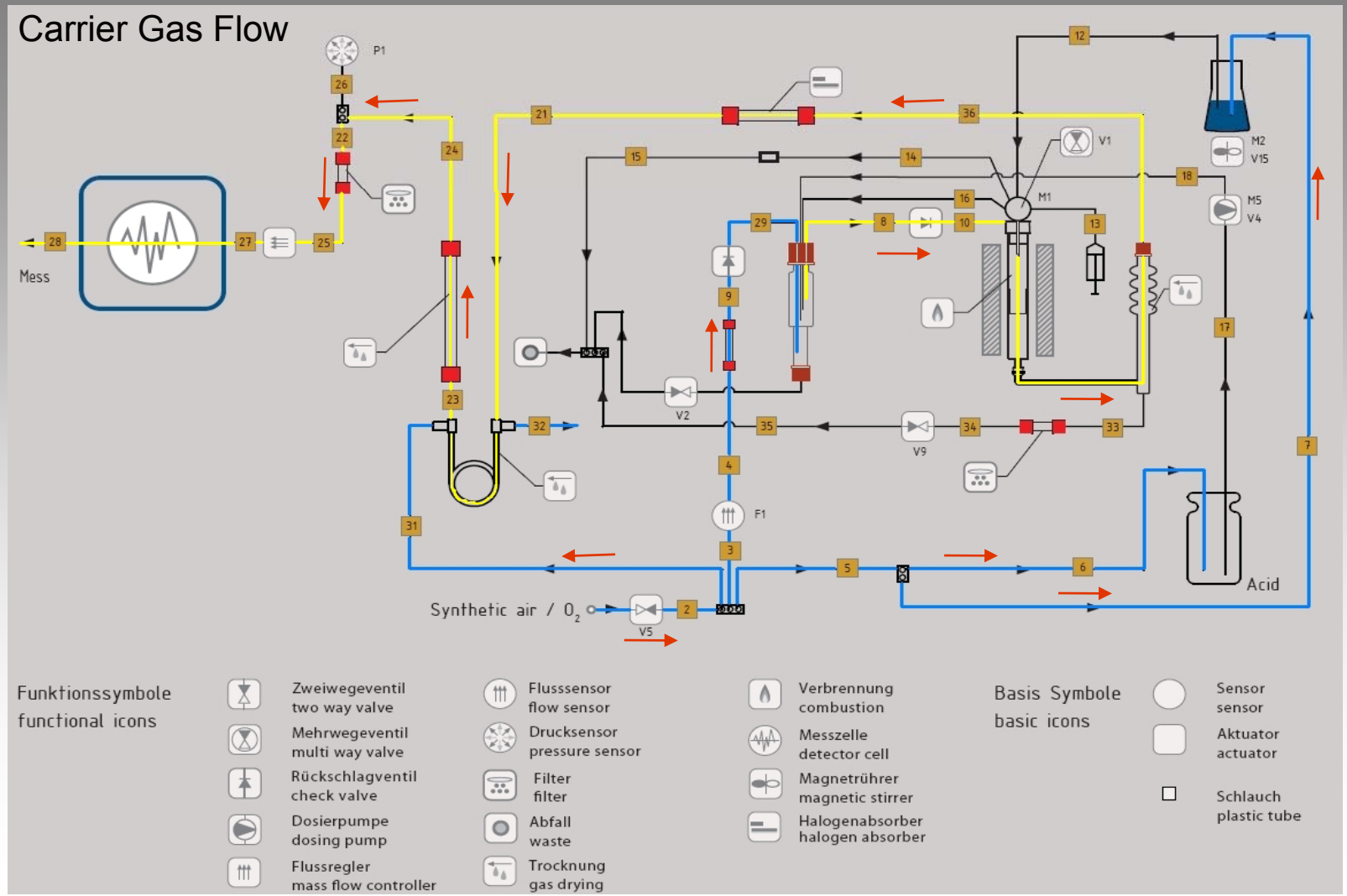

TIC/TC analysis

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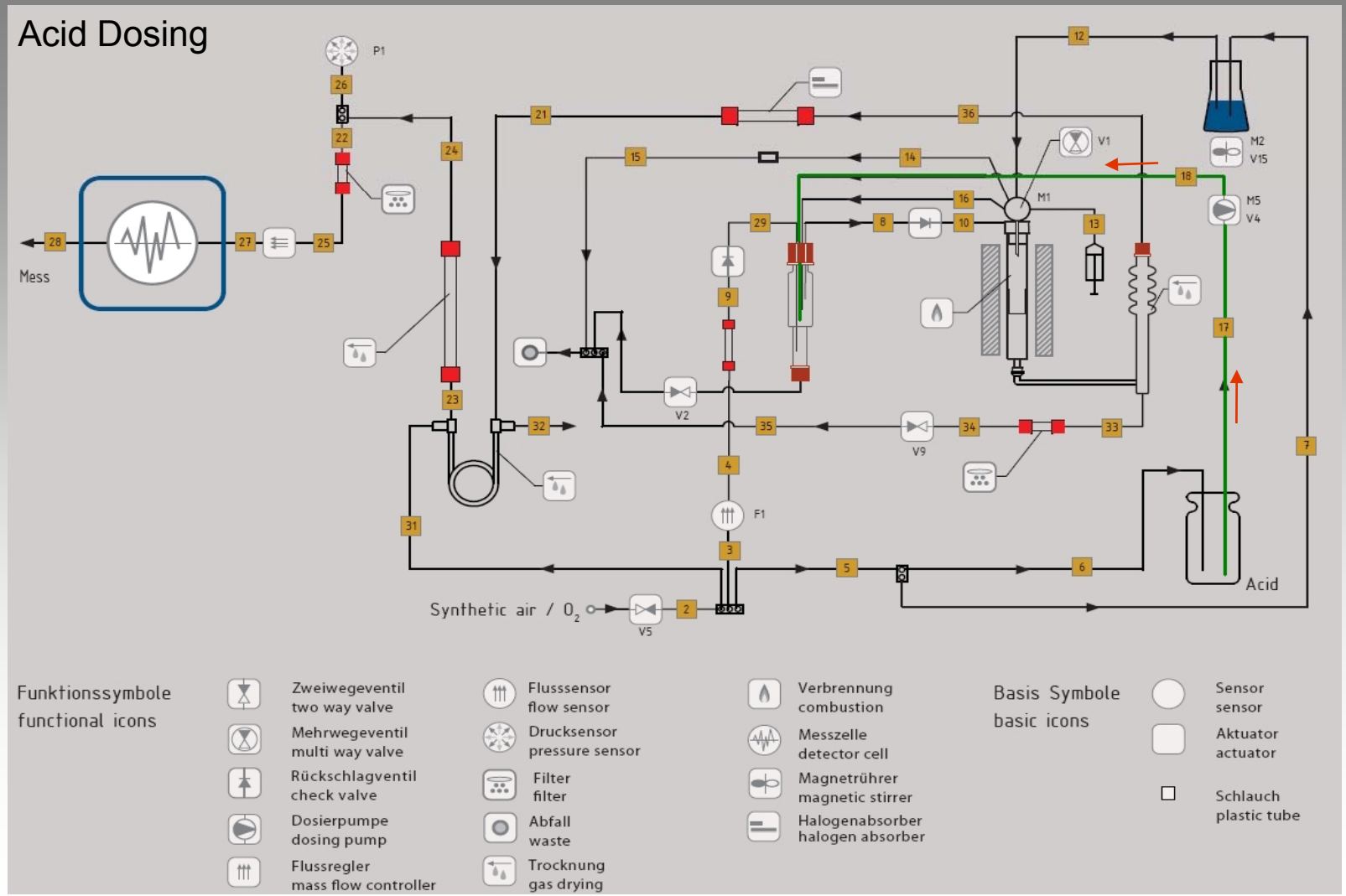

TIC/TC analysis

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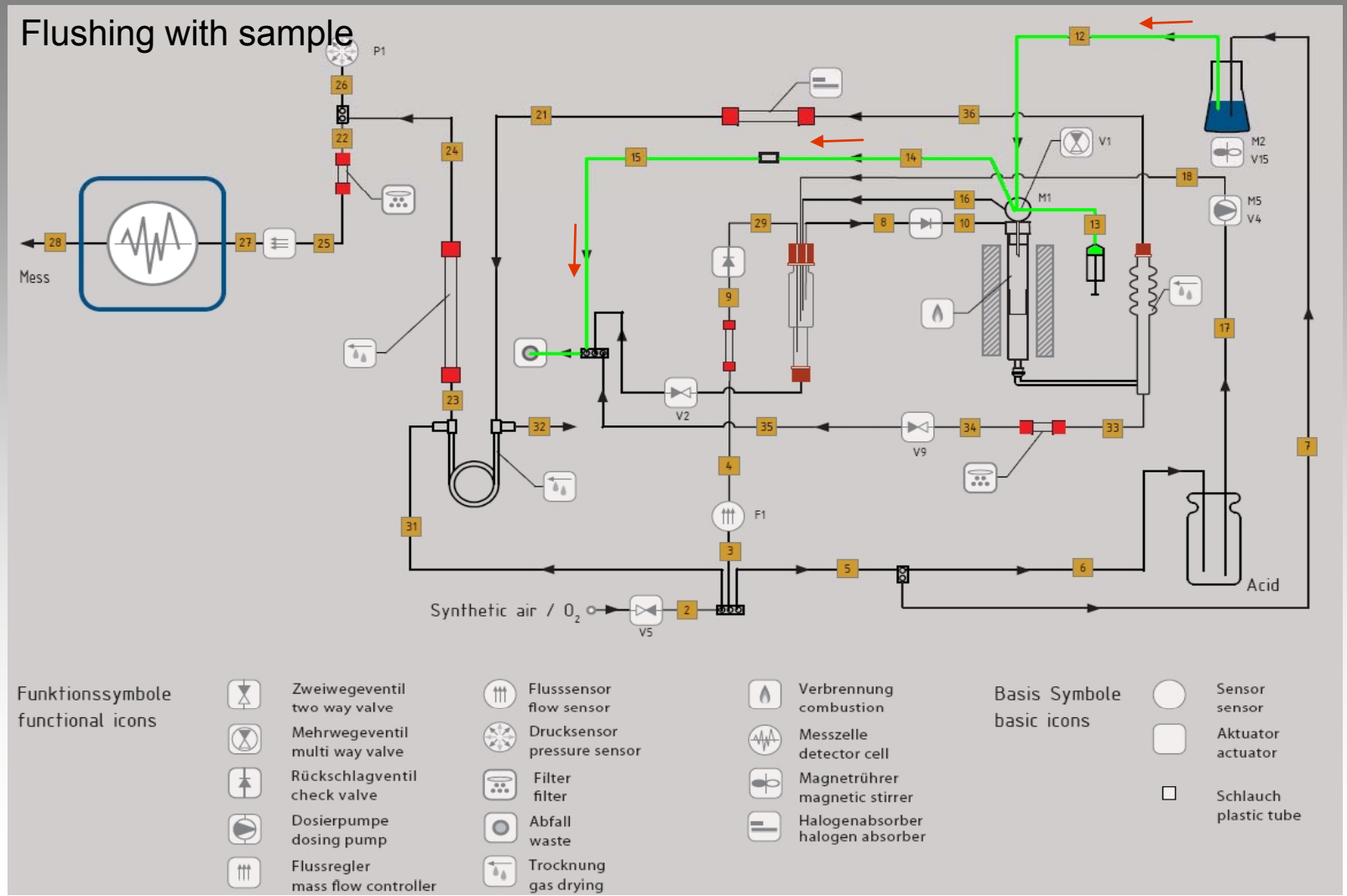

TIC/TC analysis

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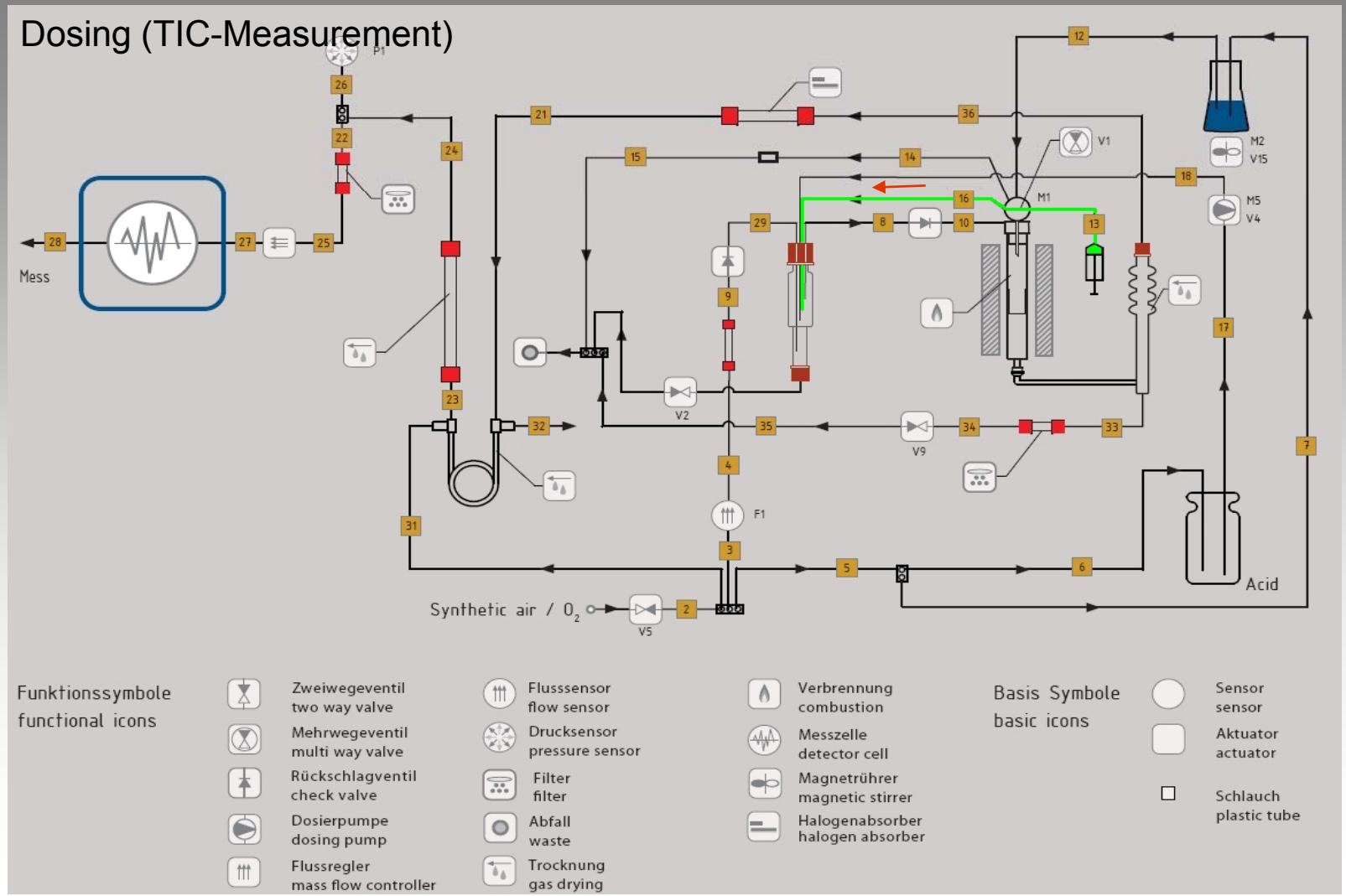

TIC/TC analysis

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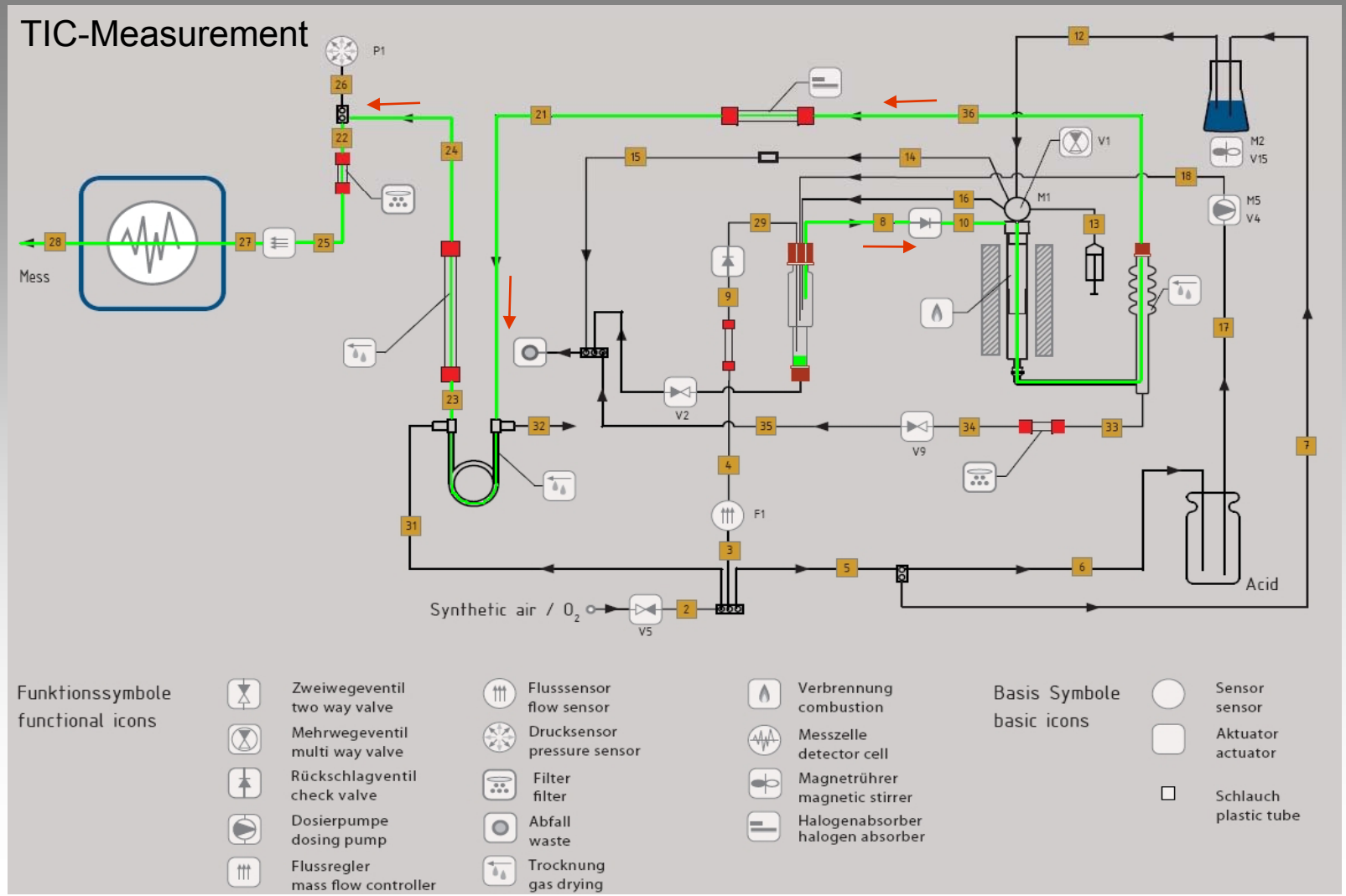

TIC/TC analysis

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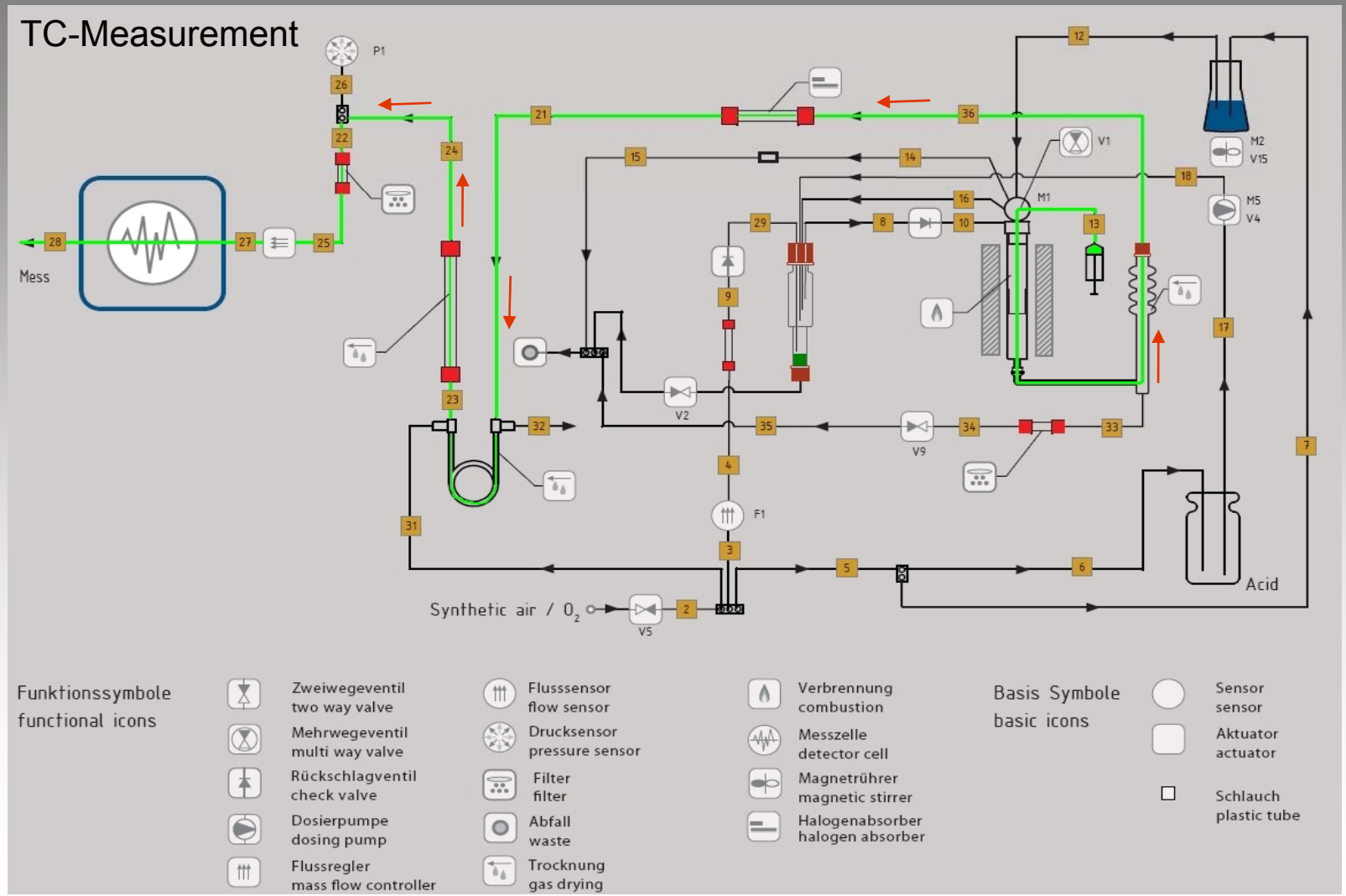

TIC/TC analysis

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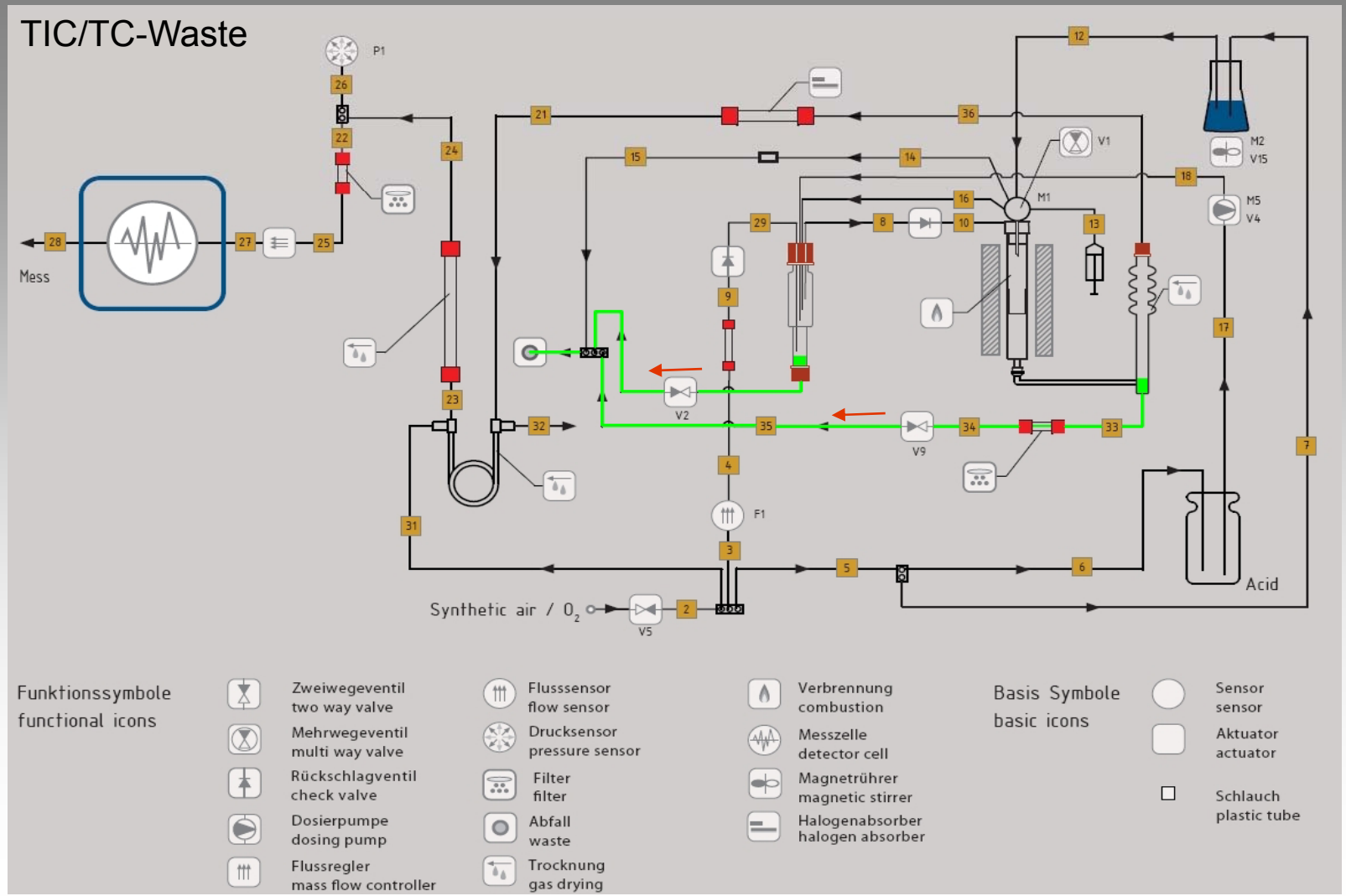

TIC/TC analysis

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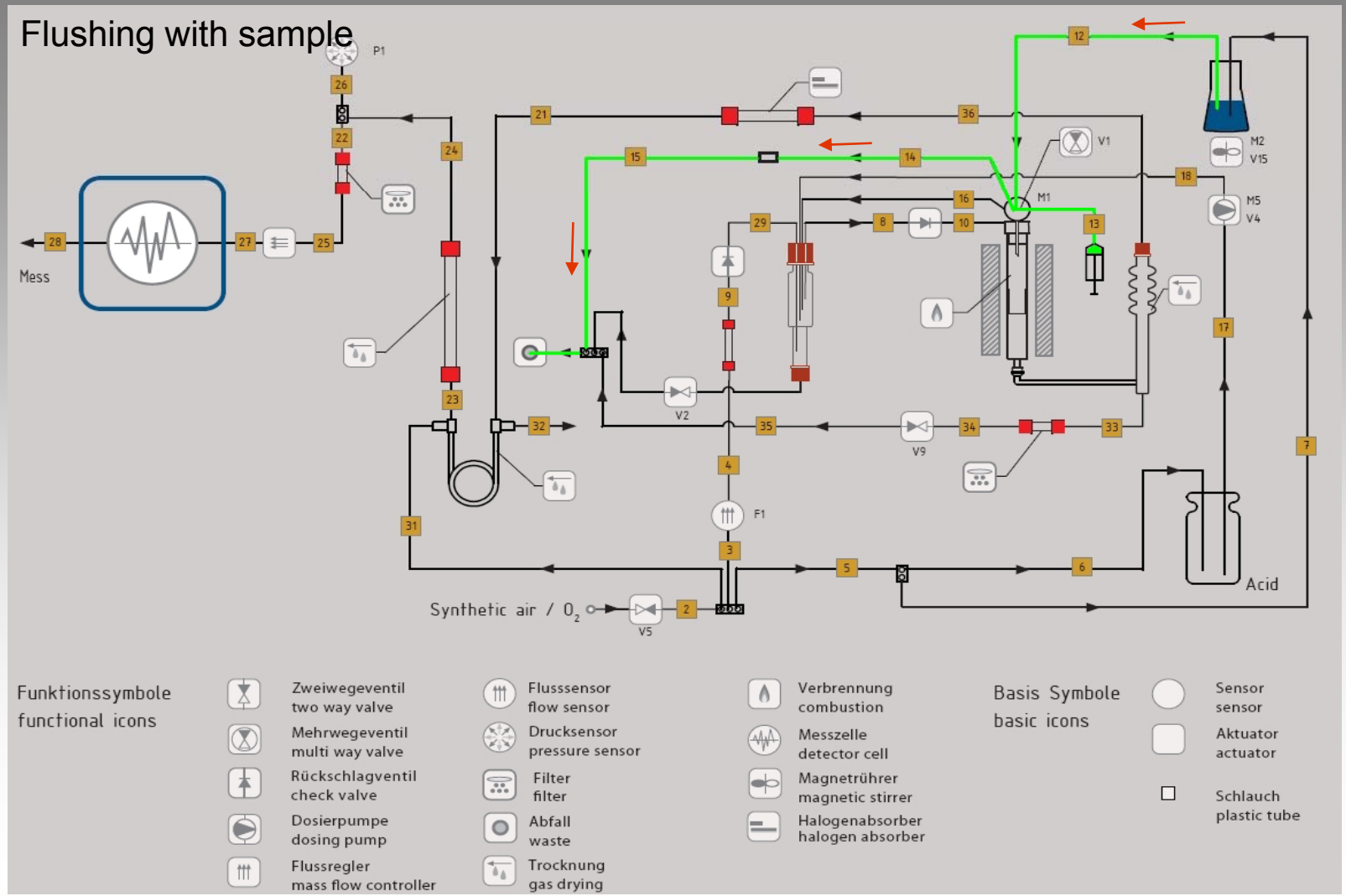

NPOC analysis

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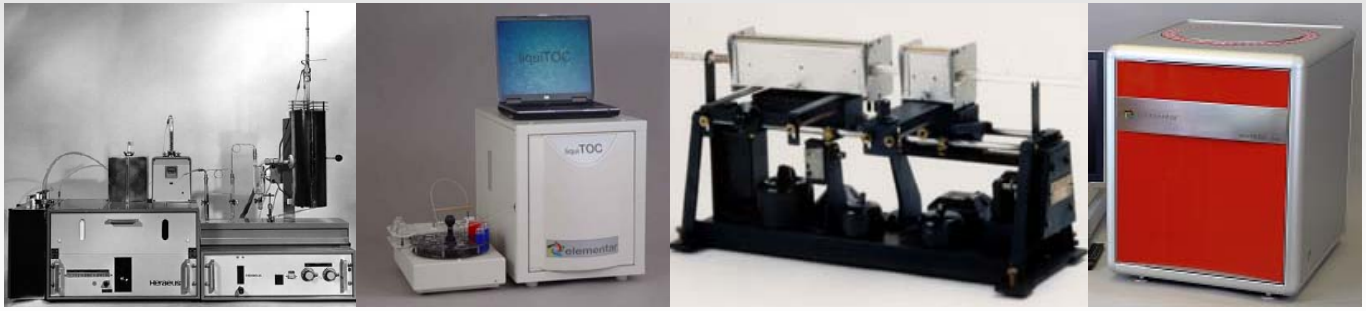
combines for the very first time

110 years of experience in elemental analysis

and more than

30 years of experience in TOC analysis



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THE POWER OF EXPERIENCE

Sets new standards in TOC analysis

measuring range for TOC from
2 ppb to 60.000 ppm

optional up to 50mg $C_{abs.}$ in solids

Makes „auto-dilution“ unnessesary.

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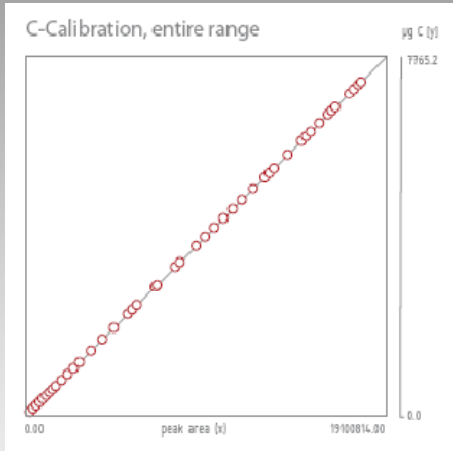

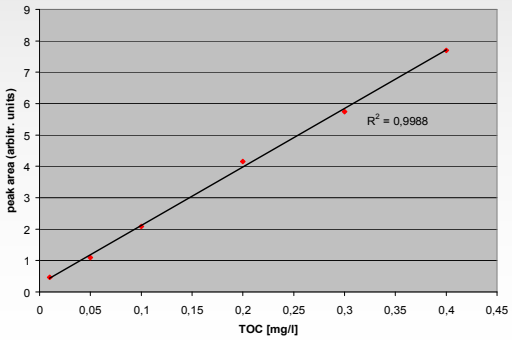

Sets new standards in TOC analysis

with new detectors – free of spectral interferences, e.g. of SO_2 and with extraordinary linearity over the entire detection range.

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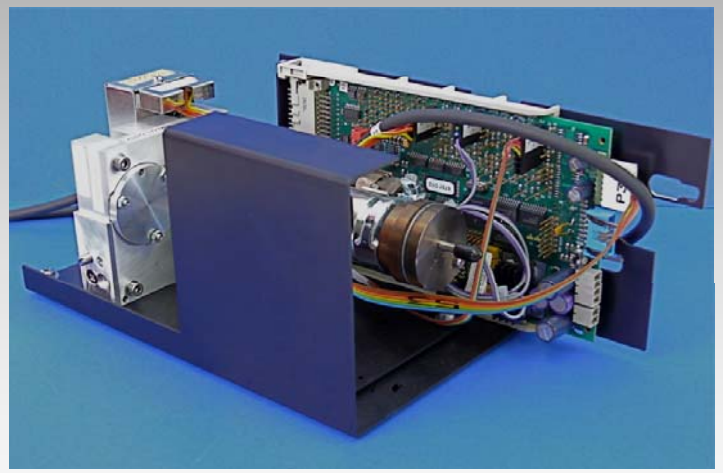

Also available for TN_b determination:

CLD 0.2ppm – 200ppm
ECD 0.2ppm – 500ppm

Sets new standards in TOC analysis

New NDIR detectors with outstanding performance in TN_b – determination.

Working range:
0.05ppm – 50,000ppm

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Sets new standards in TOC analysis

with its integrated automatic sample feeder for liquids

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available with

- 120 positions for up to 300 mg
- 80 positions for up to 1 g
- also applicable for liquids and suspensions by capsule sealing technique

Sets new standards in TOC analysis

with its revolutionary automated analysis of solids

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Sets new standards in TOC analysis

with its unique reusable ash/salt crucible for complete matrix separation, e.g. no restrictions on salt content in liquids and solids

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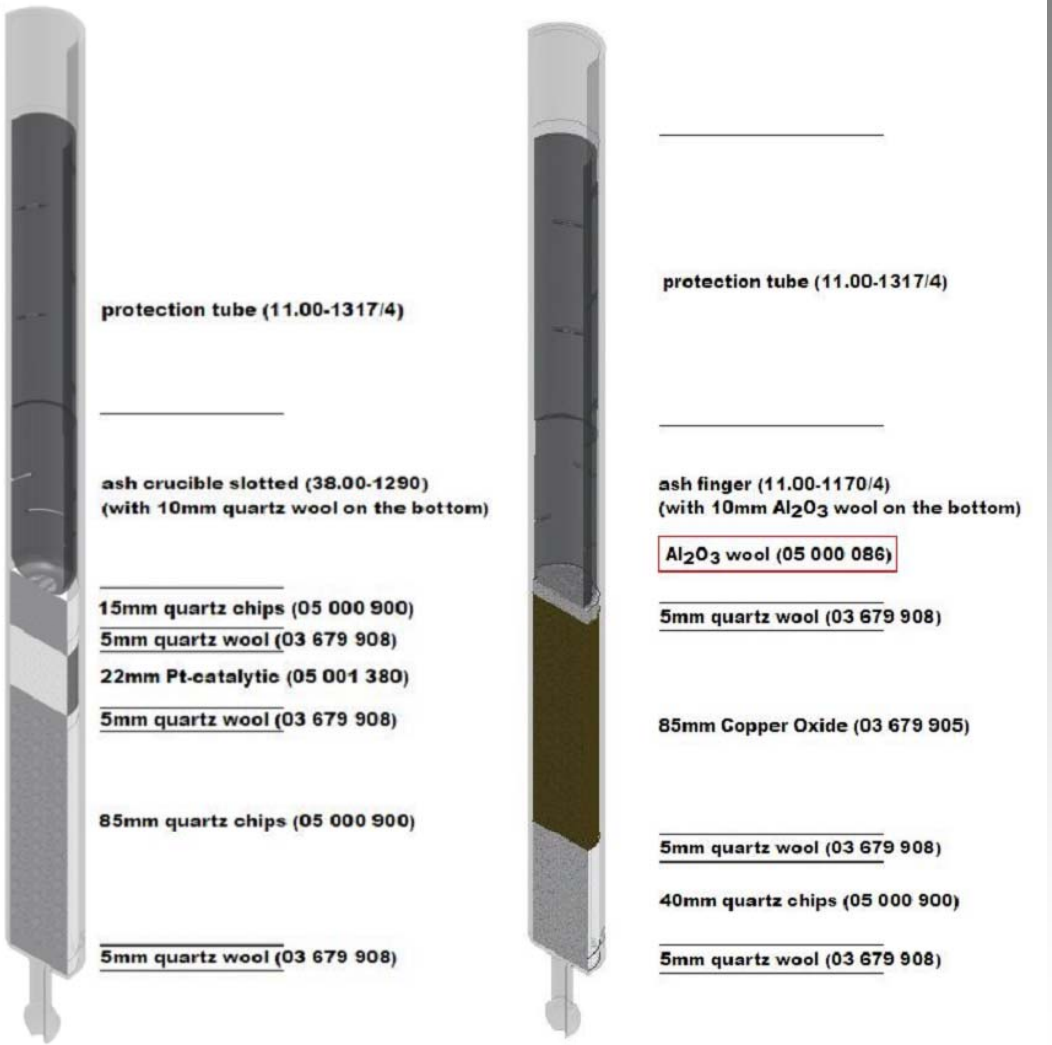
liquid samples



solid samples

Combustion tubes

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Combustion tube for solids

Combustion tube for liquids

Combustion tubes

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Sets new standards in TOC analysis

with no restrictions on the particle size in liquids

No need any more for inaccurate suspension method

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Applications from liquids to...

- reagent water
- drinking water
- waste water
- ...

- sea water
- saline solutions
- electrolytes
- ...

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... to solids

- particles
- suspensions
- slurries ...

- soils
- residues
- solids ...

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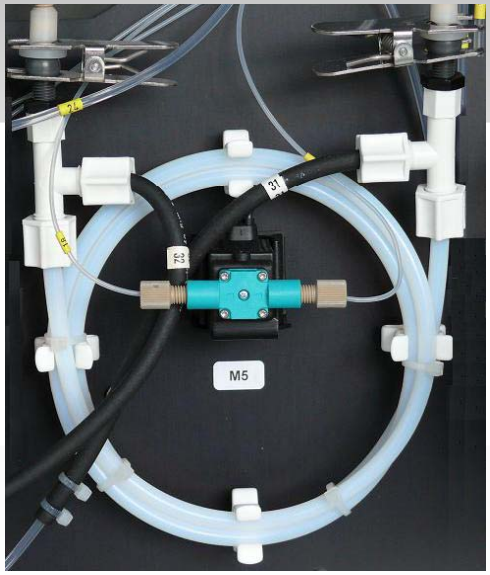
Approved methods, once again improved with IDS-3*

condensation

counter gas membrane drying



chemical drying

* 3-step intensive drying system

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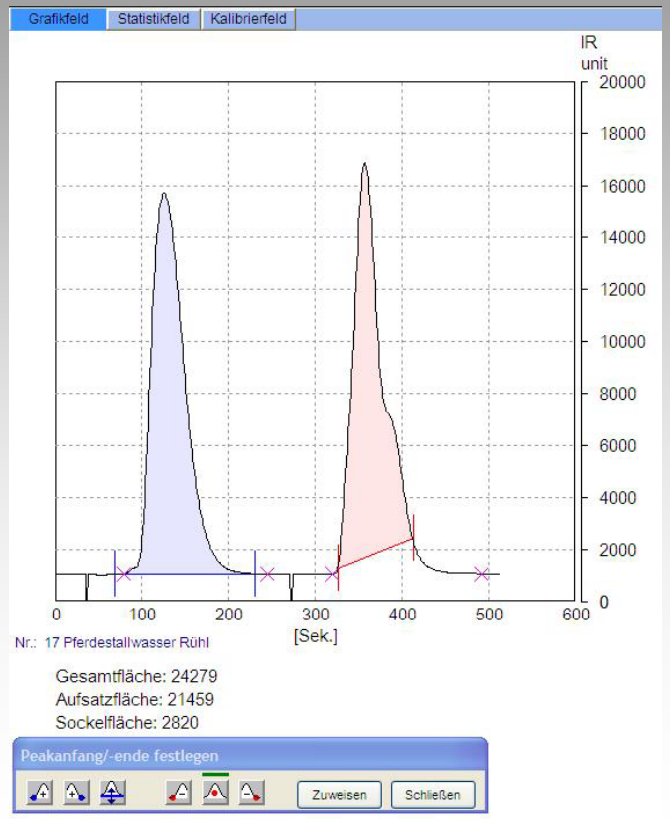

Comprehensive math data processing

- **Statistics**
- **Manual and automatic peak integration**
- **Base line correction**
- **Peak substraction**

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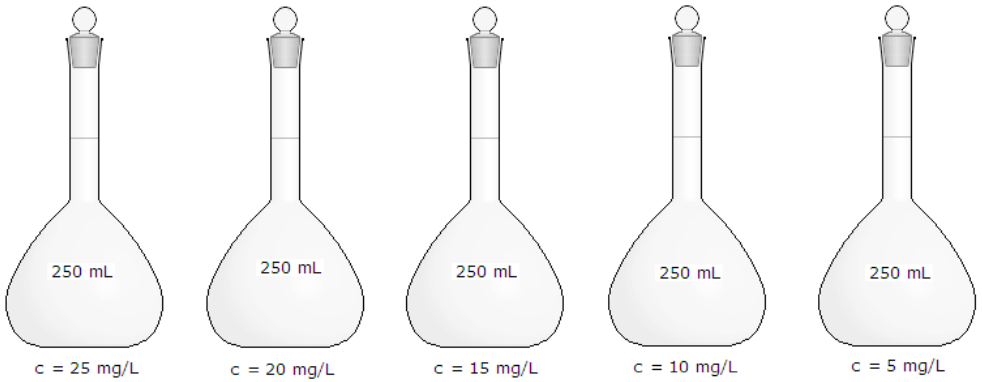


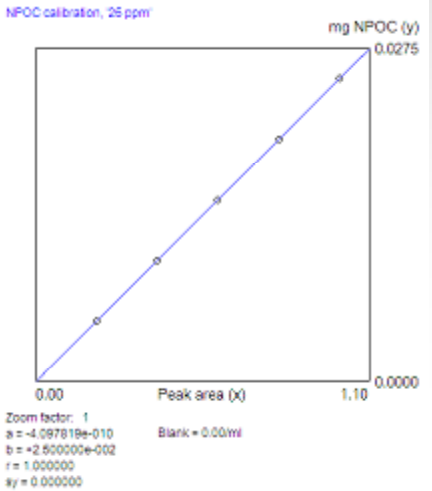
Automatic Calibration

by fixed volume
and different conc.

Dilution series

Sample Pane (Text View)

No.	Hole Pos.	Name	TIC Area	TIC [mg/L]	NPOC Area	Dil. Factor	NPOC [mg/L]
1	1	♦Std {1mL}	0.00	0.00	0.20	1.00	5.00
2	2	♦Std {1mL}	0.00	0.00	0.40	1.00	10.00
3	3	♦Std {1mL}	0.00	0.00	0.60	1.00	15.00
4	4	♦Std {1mL}	0.00	0.00	0.80	1.00	20.00
5	5	♦Std {1mL}	0.00	0.00	1.00	1.00	25.00



Automatic outlier elimination

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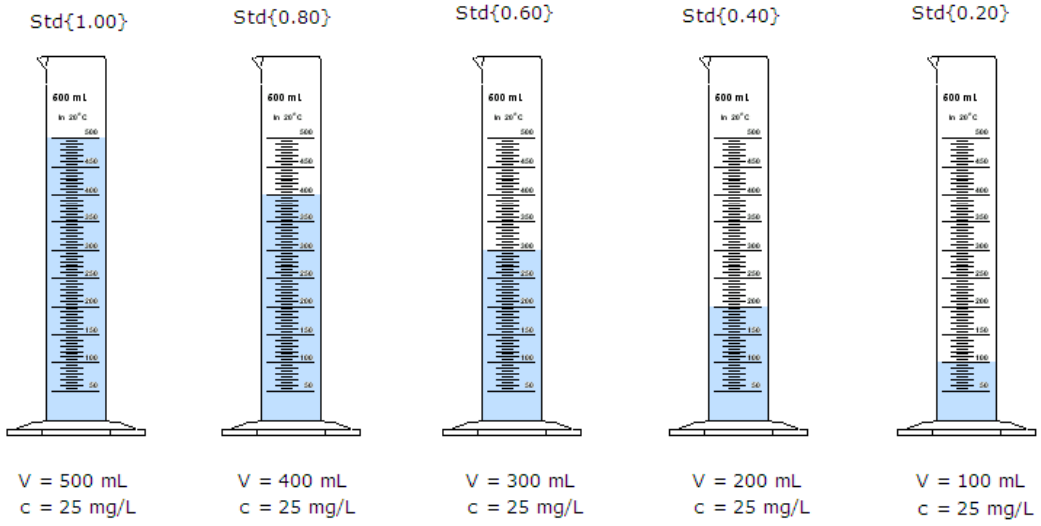
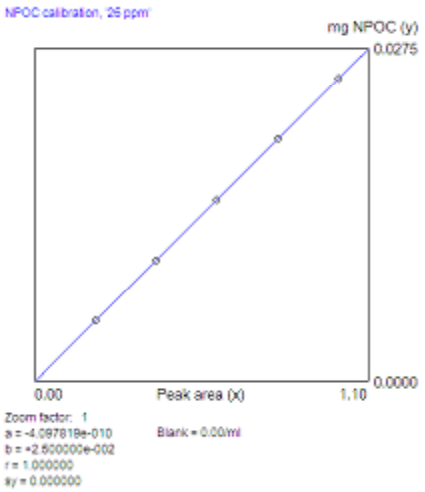


Sample Pane (Text View)

No.	Hole Pos.	Name	TIC Area	TIC [mg/L]	NPOC Area	Dil. Factor
1	1	Std{0.20}	0.00	0.00	0.20	1.00
2	1	Std{0.40}	0.00	0.00	0.40	1.00
3	1	Std{0.60}	0.00	0.00	0.60	1.00
4	2	Std{0.80}	0.00	0.00	0.80	1.00
5	2	Std{1.00}	0.00	0.00	1.00	1.00



Multi-point-calibration from a single standard solution

Automatic Calibration

by fixed concentration and different volumes

auto-dilution-effect without dilution errors

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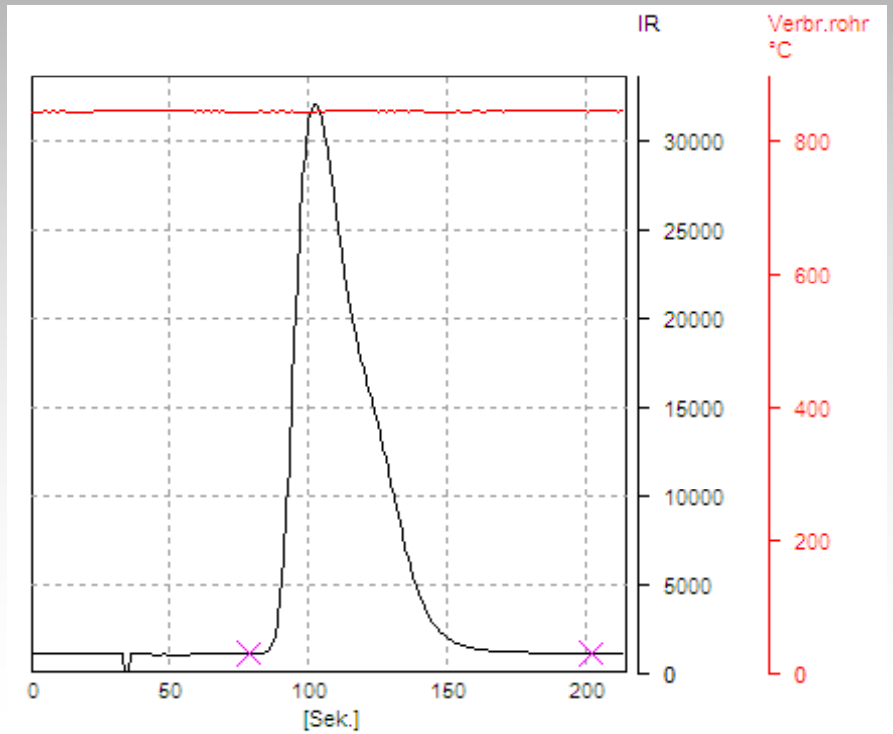
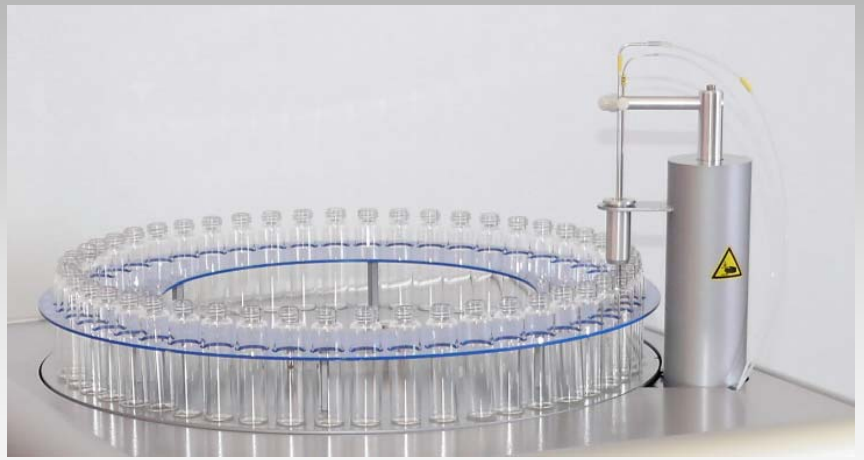
Analysis of well water for animals
(liquid samples, particles)





Method	Sample	TC [mg/L]
mean [%]	well water	76,520
RSD (absolute)		0,271
RSD (relative) %		0,354

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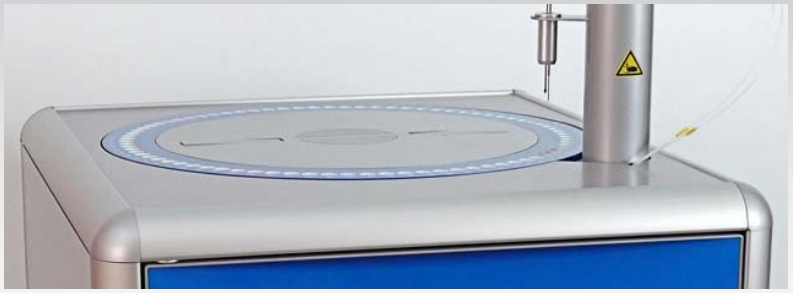
Analysis of hard digestible silicon carbid compounds (SiBCN)



Method	Sample	TOC [mg/L]
mean [%]	SiBCN	30,82
RSD (absolute)		0,0683
RSD (relative) %		0,0261

vario TOC cube shows excellent oxidation behaviour even in case of hard digestable compounds like SiBCN ceramics with decomposition temperatures of approx. 2000°C.

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Analysis of sea water (liquid samples, salt)

Method	Sample	TC [mg/L]
TC measurement of n = 50 sea water samples		
mean [%]	North Sea	24,282
RSD (absolute)		0,160

Method	Sample	TOC [mg/L]
TOC measurement of n = 50 sea water samples. External sample acidification was performed under stirring in the vials of the automatic sample feeder, followed by automatic stripping of CO_2 with synthetic air.		
mean [%]	North Sea	12,209
RSD (absolute)		0,074

Excellent for the analysis of brine solutions

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Analysis of river sediments (solid sample)

Method		
Analysis of 25 dried river sediments (Elbe/Germany) measured in solid mode		
	n	TC [%]
mean [%]	25	5,396
RSD (absolute)		0,088
Reference value (varioMAX)		5,35 %

Method		
Analysis of 25 dried river sediments (Hunte/Germany) measured in solid mode		
	n	TC [%]
mean [%]	25	4,202
RSD (absolute)		0,070
Reference value (varioMAX)		4,22 %

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THE FACTS I

Analytical method: Catalytic high temperature digestion

Standards: ISO 8245, EPA 415.1, European standard acc. to EN 1484, ENV 12260, European Pharmacopoeia 6.0, vol.1 (20244) 2008, U.S.Pharmacopoeia-NF, USP 30 ⟨643⟩ 2007; DIN 38409

Measured parameters: TC; TOC, TIC/NPOC; DOC; POC optional TN_b

Digestion temperature: free selectable up to 1200 °C, standard operating temperature in dependency on the chosen catalyst between 800 – 950 °C

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THE FACTS II

Measuring range (ppm):	C: 0 – 60,000 ppm (cube)
alternatively high%C	C: 0 – 100 % (up to 50mg $C_{abs.}$)
	C: 0 – 25,000 ppm (trace)
	N: 0 – 200 ppm(CLD); 500 ppm(EC)
	N: 0 – 50,000 ppm (NDIR)
Detection limit:	C: ± 6 µg/L SD (cube)
	C: ± 3 µg/L SD (trace)
	N: ± 0.02 mg/L SD (NDIR)
Precision:	< 1 % at > 5 mg/L C

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THE FACTS III

Injection volume (liquid-mode): 0.05 – 2 mL (cube)

0.2 – 4 mL (trace)

Sample weight (solid-mode):

organic substance 0.02 – 10 mg or up to 1 g soil

(depends on the sample matrix)

Particel size: **liquid mode:** inner tube diameter 0.8 mm

solid mode: free selectable in dependency on the chosen capsule size

Duration of analysis: 2 - 3 min. for TC (solids)

3 - 4 min. per parameter (liquids)

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THE FACTS IV

Gas:	synthetic air (hydrocarbon ≤ 0.1 $mg \cdot L^{-1}$ and CO_2 ≤ 1 $mg \cdot L^{-1}$) or oxygen (grade ≥ 4.5)
Gas flow:	200 $mL \cdot min^{-1}$ at 1 bar pre-pressure
Dimensions:	55 x 42 x 55 cm (L x W x H) – basic unit 55 x 42 x 72 cm (L x W x H) – basic unit with autosampler for liquids
Weight:	approx. 60 kg
Power supply:	100/110/200/230 V, 50/60 Hz, 1.6 kW

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Instrument control and data processing

Operation and control under Windows® XP or Windows® Vista. All instrument functions are digitally controllable, the comprehensive operation software includes e.g. automatic leak test, extensive fault diagnostics, monitoring of maintenance cycles, sleep- / awake function, statistical evaluation and almost unlimited memory capacity for storage of analytical data and graphics. Integration to data network and LIMS.

The possibility of remote control and diagnosis via the internet.

In full compliance with 21 CFR Part 11 (option).

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Thank you for your attention.

ХВАЛА!

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