

3. Chemical industry





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The most commonly used compound in the chemical industry is water – not only as a solvent in processing, but also as an energy carrier in the cooling or heating cycle. As vast amounts of water are needed, chemical industries are often located close to large bodies of flowing water. Water used as processing water or as cooling water is cleaned and subsequently led back to the river or stream. For environmental protection, these waters are subject to specific control and monitoring measures. As the TOC non-specifically detects all organic compounds, this parameter has also proven to be invaluable here.

Large chemical industrial parks have their own wastewater treatment plants for cleaning wastewaters emanating from the various chemical plants. In order to evenly distribute the wastewater charges over the participating companies, the TOC load of the individual wastewaters is often used as a basis for calculation. Companies delivering higher TOC loads are required to pay higher charges.

Incoming goods control is important in the chemical industry. Impurities present in reagents often also constitute the impurities in products. In addition to the targeted analysis of known compounds, sum parameters can help to assess the raw chemicals in terms of their impurities. The TOC plays an important role here: this parameter describes the contamination through organic compounds and specifies the total amount of organic carbon. TOC can, therefore, also be used for the assessment of inorganic chemicals.

The great challenge for TOC measurements in chemical products is to develop protective mechanisms to help protect instruments and their components, as well as to prevent damage by, for instance, acid fumes or high salt loads. For this purpose, Shimadzu's TOC-L series offers several gas washers and options to ensure safe and problem-free analyses.

A further challenge is to attain a stable and reproducible oxidation to ensure that no fluctuating or strongly tailing peaks are recorded. In addition, the measuring values should remain stable over a longer measuring interval.

In order to cover this wide range of analytical tasks in the chemical industry, flexible systems are needed that are easily adapted to the task in question via various options, kits and modules. Shimadzu offers TOC systems that are highly suitable for such analytical problems. Because of their modular design, the instruments in the TOC-L series can be equipped for any possible measurement task.

The individual application notes (for instance 'TOC determination in hydrochloric acid, brines or sodium hydroxide') contain further information. In addition to applications in the chemical industry, application notes are also available on 'Pharmaceutical industry', 'Environmental analysis', 'TOC special applications', 'TOC in daily practice' and 'TOC process analysis.'

Application News

Sum parameter – Total Organic Carbon

TOC – Determination in hydrochloric acid

No. SCA-130-301

Acids, in particular concentrated hydrochloric acid, represent a large group of inorganic chemicals frequently used in the chemical industry. TOC determination in concentrated hydrochloric acid poses an enormous challenge to the analyzers that are used for this purpose.



TOC-L CPH with OCT-L

■ Acid challenge

The great challenge is to develop protective mechanisms to help protect instruments and their components, as well as to prevent damage by acidic fumes. For this purpose, the TOC-L series offers several gas washers that bind and eliminate the chlorine gas formed in the flow line of the system in various ways.

Another challenge is to attain a stable and reproducible oxidation process to ensure that no fluctuating or tailing peaks are being recorded. In addition, the measuring values should remain stable over a longer measuring interval.

In general, it is possible to greatly dilute the substance to be analyzed in order to eliminate matrix interferences. But sometimes it is necessary to achieve very low limits of detection (with reference to 37% hydrochloric acid) of 1 mg/L.

■ TOC Measuring Method

The 37% hydrochloric acid solution was manually diluted to a ratio of 1:2 with water in order to obtain an 18.5% hydrochloric acid solution.

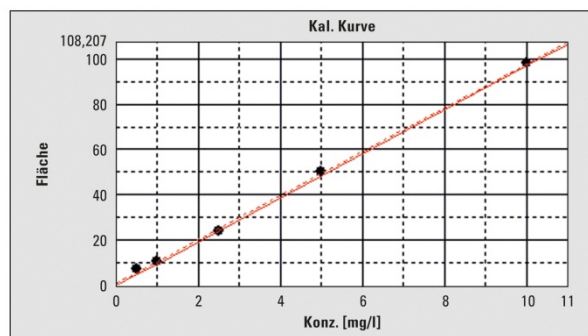


Abb.2 Mehrpunktkalibration mit
Verdünnungsfunktion

Calibration was carried out in the range of 0.5 to 10 ppm. The automatic dilution function of the analyzer automatically executes this calibration from a single stock solution. The injection volume was 150 μ L. In case the TOC contamination of the hydrochloric acid exceeds the measuring range of the calibration, the automatic dilution function of the analyzer will readjust the hydrochloric acid solution to fit the measuring range.

■ Verification the measuring method

After calibration, the TOC content of the concentrated hydrochloric acid solution was determined.

To investigate matrix influences, a potassium hydrogen phthalate solution was subsequently added to the 18.5% hydrochloric acid solution to increase the TOC by 5 ppm (Figure 3 and Table 1).

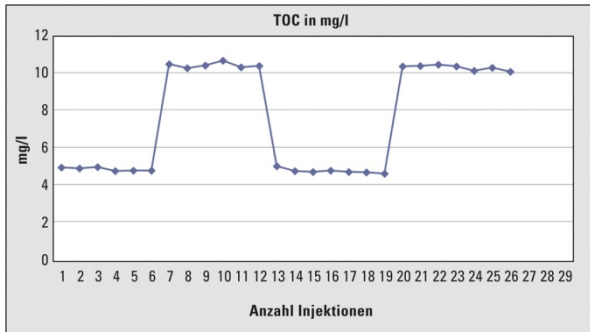


Fig.3: Results of original and spiked hydrochloric solution

Figure 3 and Table 1 show the results of the individual measurements of the hydrochloric acid as well as the measurements of the spiked hydrochloric acid.

TOC result of 18,5% hydrochloric acid in mg/l		
Injection	Original	Spiked with 5ppm TOC
1	4,901	10,46
2	4,858	10,24
3	4,91	10,39
4	4,716	10,64
5	4,728	10,28
6	4,739	10,35
7	4,966	10,34
8	4,71	10,36
9	4,662	10,42
10	4,733	10,33
11	4,659	10,11
12	4,625	10,27
13	4,552	10,06
Mean value	4,75	10,33
SD	0,12	0,15
RSD in %	2,6	1,4

Tab. 1: Values of each injection

■ Long-term stability

To investigate the long-term stability of the method, the 37% hydrochloric acid solution was again diluted to a ratio of 1:2 with water and injected 76 times (150 µL).

The relative standard deviation over all measurements was 3.4%. The following graph shows the progression of the TOC values of the hydrochloric acid injections.

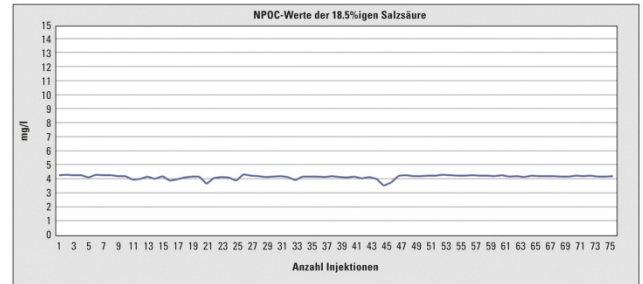


Fig.4: Result of longterm stability

Blank values and standards (10 ppm) were alternately measured between the individual measurements.

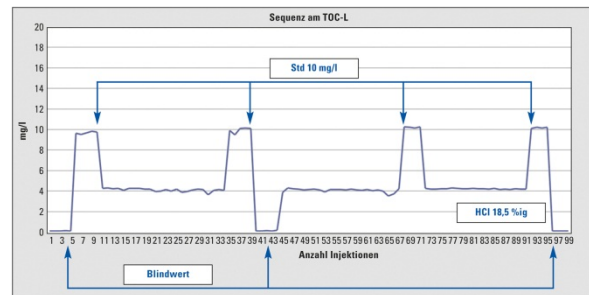


Fig. 5: Sequence of hydrochloric acid, blank (pure water) and Standards (10 mg/l)

■ Recommended analyzer / configuration

- TOC-L_{CPH} with a normal sensitive catalyst (without glass wool at the bottom of the catalyst tube)
- B-Type scrubber with SnCl₂ solution
- Copper bead scrubber with pH paper
- Bypassing the blank check vessel
- Substituting water for phosphoric acid (IC vessel)
- OCT-L 8-port sampler

Application News

Sum parameter – Total Organic Carbon

TOC – Determination in nitric acid

No. SCA-130-302

Organic contaminants present in basic chemicals may constitute the impurities in products. This is why quality control of the reactants is indispensable.



The determination of organic contaminations in concentrated nitric acid (69%) becomes a challenge when the required detection limit does not allow large dilution steps.

An example is the TOC determination in a 69% HNO₃ solution with a detection limit of < 10 mg/L.

■ Sample preparation

For sample preparation, the 69% HNO₃ solution was diluted to a ratio of 1:10 with ultrapure water.

Compound (concentration)	Dilution	Konz. [%]
Nitric Acid (69%)	1 : 10 diluted with water (5ml / 50ml)	Ca. 7%

Calibration of the TOC-L system was carried out using the automatic dilution function in the range of 0.5 mg/L to 10 mg/L.

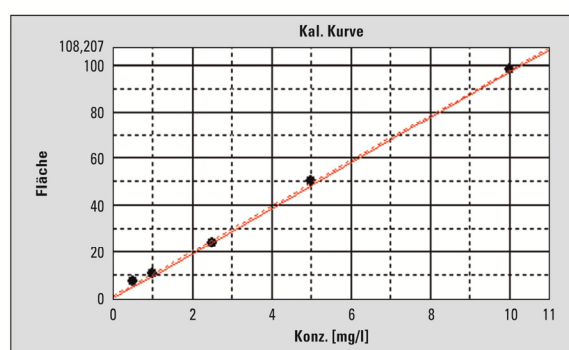


Fig. Multi-point calibration with dilution function

To protect the NDIR detector, the B-type scrubber was used together with the halogen scrubber.

■ Matrix interferences

In addition to CO₂, various nitrogen oxides are formed from the organic components during the combustion of nitric acid. Excessively high levels of NO₃ can lead to significant amounts of N₂O (nitrous oxide). Nitrous oxide exhibits absorption bands in the same IR detection range as CO₂ and can, therefore, be misinterpreted for CO₂. In addition, nitrous oxide can cause tailing and can affect the peak symmetry.

Due to the high solubility of N₂O in water, the gas is dissolved in the B-type scrubber and will not reach the detector.

■ **Result**

The duplicate NPOC determination of a nitric acid produced the following results:

Sample	NPOC [mg/l]	RSD [%]
Nitric Acid (69%)	36,9	1,4
Nitric Acid (69%)	33,4	3,0

To investigate this matrix influence, an additional dilution (1:10) of a 69% nitric acid solution was carried out and a potassium hydrogen phthalate stock solution was subsequently added to increase the NPOC content by 5 ppm. (Note: This corresponds to an increase to 50 ppm for the 1:10 dilution).

Sample	NPOC [mg/l]	RSD [%]
Nitric Acid (69%)	25,1	1,3
Nitric Acid (69%) Spiked with 50 ppm KHP	76,2	1,8

The use of suitable gas washers (scrubbers) enables reproducible TOC measurements in concentrated nitric acid.



■ **Recommended Analyzer / Configuration**

TOC-L_{CPH} with normal sensitive Catalyst

B-Type-Scrubber

OCT-L (8-port Sampler)

Application News

Sum parameter – Total Organic Carbon

TOC – Determination in sulfuric acid

No. SCA-130-303

Acids are a group of frequently used inorganic chemicals used in the chemical industry. In particular, sulfuric acid is used in a wide range of applications.



Sulfuric acid in a concentration range to 1% can be directly measured using a TOC-L analyzer. Higher sulfuric acid concentrations can lead to tailing and, consequently to increased measurement values because high sulfate concentrations (> 5000 mg/L) can lead to the formation of large amounts of SO₂ vapors. SO₂ exhibits absorption bands in the same IR detection range as CO₂ and can, therefore, be misinterpreted for CO₂.

To determine organic contaminations in highly concentrated sulfuric acid, additional SO₂ scrubbers are used.

The following SO₂ scrubbers are available:

- Sulfix (WAKO Chemicals, Fuggerstr. 12, 41468 Neuss, Germany). The Sulfix scrubber is installed underneath the normal sensitive catalyst and enables selective filtration of the formed SO₂.
- Mist scrubber (cartridge)
Just like the halogen scrubber, the 'Mist scrubber' is used in the flow line for SO₂ absorption.

In the experiment described below, the NPOC content of a 98% sulfuric acid solution is determined.

The required purity criterion and the required limit of detection was < 10 mg/L.

■ Sample preparation

The concentrated sulfuric acid was diluted with ultrapure water to a ratio of 1:10 to decrease the concentration as well as the viscosity of the sulfuric acid.

Compound (Concentration)	Dilution	Conc.
Sulfuric acid (98%)	1 : 10 diluted with water (5m/50ml)	Ca. 10%

The dilution has to be carried out with the utmost care and caution, as the sulfuric acid reacts violently upon the addition of water (heat generation).

The system is calibrated using the automatic dilution function in the range of 0.5 mg/L to 10 mg/L.

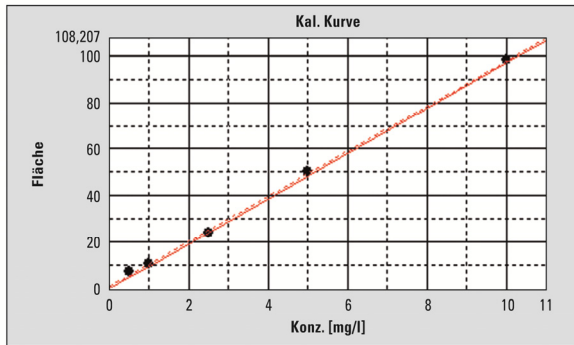


Fig. Multi-point calibration with dilution function

■ Kit for high-salt samples

For the determination, a TOC-L_{CPH} equipped with a kit for high salt loads was used. The kit consists of a special catalyst tube, a special mixture of various catalyst beads and a ceramics grid, which replaces the platinum net.

Sample acidification when using the high-salt kit, is carried out with sulfuric acid. Sulfuric acid is used to modify the sample matrix. While NaCl has a melting point of 801 °C, the melting point of NaSO₄ is higher (881 °C). This has a positive effect on the lifetime of the combustion tube.

For this reason, sulfuric acid is measured directly using the high-salt kit.

■ Result

The duplicate determination of sulfuric acid yielded the following results:

Sample	NPOC [mg/l]	RSD [%]
Sulfuric acid (98%)	<10 (4,6)	-
Sulfuric acid (98%)	<10 (5,4)	-

The sulfuric acid fulfilled the required purity criteria of TOC < 10 mg/L.

The use of suitable gas washers (scrubbers) enables reproducible TOC measurements in concentrated sulfuric acid.



■ Recommended analyzer / Configuration

- TOC-L_{CPH}
- OCT-L
- High-Salt-Kit
- B-Type-Scrubber with diluted hydrochloric acid with wire net.
- Mist-Scrubber

Application News

Sum parameter – Total Organic Carbon

TOC – Determination in brines

No. SCA-130-304

The determination in difficult matrices, such as brines or heavily contaminated wastewaters, presents a special challenge for TOC analyzers. In the chemical industry, brines with a salt load (NaCl) of up to 28% are used for chlor-alkali electrolysis. For this process it is important to know the TOC content.

The unique feature of this application does not inherently lie in the conversion of the carbon components to carbon dioxide, but in the salt load associated with the matrix. This leads to higher maintenance needs, as the salt can crystallize in the combustion system.

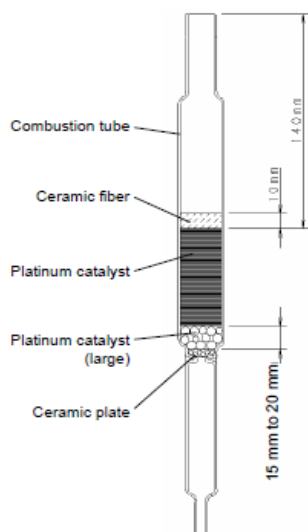
■ Kit or high-salt samples

The TOC-L series features a kit for high-salt samples, which significantly increases the instrument's availability. The kit consists of a combustion tube of a special geometry and a unique catalyst mixture.

In this application, sample acidification is carried out with sulfuric acid. Sulfuric acid modifies the sample matrix. Whereas the melting point of NaCl is 801 °C, NaSO₄ has a higher melting point is (888 °C). The potassium salts of sulfuric acid also have a significantly higher melting point than those of hydrochloric acid. This extends the lifetime of the combustion tube.

Compound	Melting point
NaCl	801°C
KCl	773°C
Na ₂ SO ₄	888°C
MgCl ₂	708°C
CaCl ₂	782°C
K ₂ SO ₄	1.069°C

Tab. Melting point of different salts



■ Sample preparation

The determination of organic contaminations in a pure brine (30% sodium chloride solution) is described below. For such highly concentrated salt solutions, the principle of diluting the sample as much as possible applies. As the required detection limit was at < 1 mg/L, the samples were diluted with ultrapure water to a ratio of 1:1. Dilution was carried out manually in a 50 mL volumetric flask under the addition of several drops of concentrated sulfuric acid (25%).

Compound (Concentration)	Dilution	Conc.
Brine solution (30%)	1 : 2 diluted with water (25ml/50ml) add. 1-2 drops Sulfuric acid until pH<7	ca. 15%ig

For the analysis a TOC-L_{CPH} equipped with a kit for high salt loads was used. The system is calibrated using the automated dilution function in the range of 0.5 mg/L to 10 mg/L.

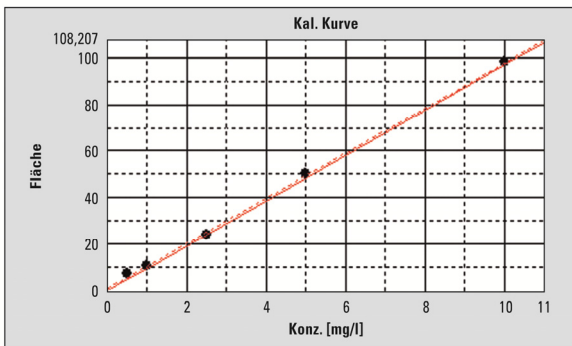


Fig. Multi-point calibration with dilution function

Result

The duplicate determination of the TOC analysis yielded the following results:

Sample	NPOC [mg/l]	RSD [%]
Brine solution (30%)	3,6	1,8
Brine solution (30%)	3,6	1,8

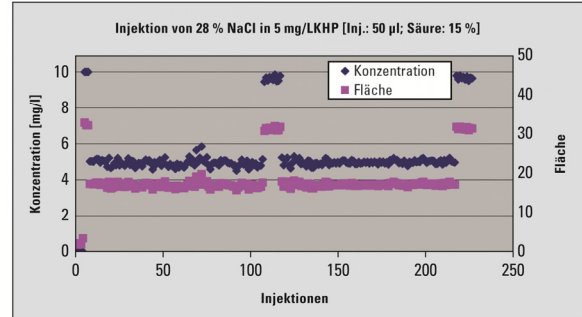
Stability test

In this test, the long-term stability of the combustion system was tested. The system was calibrated to 10 mg/L with an injection volume of 50 µL.

A 28% NaCl solution was prepared and spiked with a KHP solution to obtain a 5 mg/L TOC solution and a 15% sulfuric acid solution was added.

Initially, a blank value and a control standard (10 mg/L) were measured, and the NaCl solution was subsequently injected.

The control standards were tested after 110 and 220 injections of the brine solution, respectively.



Maintenance of the combustion tube and the catalyst was not necessary after the measurements were completed. Only the TC-slider needed to be cleaned. The figure above shows the excellent reproducibility's and the stability of the measurement.



Recommended Analyzer / Configuration

TOC-L_{CPH}
High-Salt-Kit
B-Type-Scrubber

Application News

Sum parameter – Total Organic Carbon

TOC – Determination in sodium hydroxide solution

No. SCA-130-305

Organic contaminants in basic chemicals may lead to impurities in the products. Therefore, quality control of the reactants is necessary.



The TOC determination in sodium hydroxide can lead to various problems. The catalyst and the combustion tube wear out very rapidly. This, in turn, will lower the sensitivity at an equally fast rate and leads to very poor reproducibilities.

NaOH can also absorb CO₂ from the environment. As air contains approximately 400 ppm CO₂, direct TC determination in sodium hydroxide can lead to much higher values. The NPOC method is, therefore, recommended for the determination of organic contaminations in sodium hydroxide. The sample should also be diluted as much as possible.

In the present case, a 50% sodium hydroxide solution was analyzed. The purity criterion and the required limit of detection was < 10 mg/L.

■ Sample Preparation

The sample was first manually diluted to a ratio of 1:10 with ultrapure water and a suitable amount of acid.

Several mL of ultrapure water were placed in a 50 mL volumetric flask. Subsequently, 5 mL of the concentrated sodium hydroxide was pipetted into the flask. Finally, concentrated sulfuric acid was added until the solution has reached a pH < 2. The flask was then filled with ultrapure water up to the mark. The addition of sodium hydroxide, as well as the addition of sulfuric acid to the water must be done with the utmost care and caution, as a violent chemical reaction occurs.

Compound (Concentration)	Dilution	Conz. [%]
Sodium hydroxide solution (50%)	1 : 10 diluted (5 ml / 50 ml) add. 1-2 drops Sulfuric acid until pH<7 (Note: generation of heat)	approx. 5% + Sulfuric acid

Calibration of the TOC-L system was carried out using the automatic dilution function within the range of 0.5 mg/L to 10 mg/L.

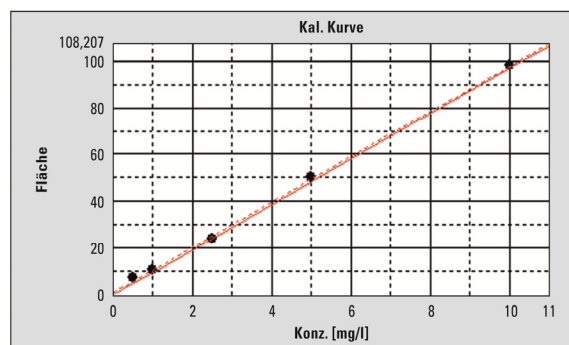
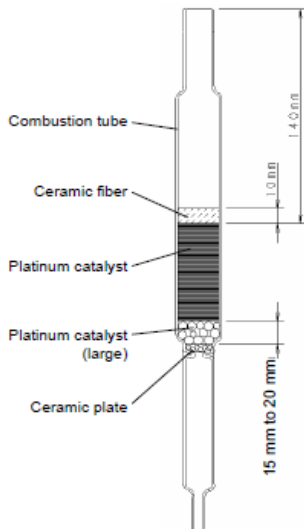


Fig. Multi-point calibration with dilution function

■ **Kit for high salt samples**

For the determination, a TOC-L_{CPH} was equipped with a kit for high salt loads. The kit consists of a special catalyst tube, a special mixture of various catalyst beads and a ceramics grid, which replaces the platinum net.



When using the high-salt kit, sample acidification is carried out with sulfuric acid, which is used here to modify the sample matrix. Compared to NaCl with a melting point of 801 °C, the melting point of NaSO₄ is higher (881 °C) which extends the lifetime of the combustion tube.

■ **Results**

The 5% sodium hydroxide can now be measured using the NPOC method. The duplicate determination of the sodium hydroxide yielded the following results.

Sample	NPOC [mg/l]	RSD [%]
Sodium hydroxide (50%)	<10 (8,2)	-
Sodium hydroxide (50%)	<10 (8,3)	-

The sodium hydroxide met the required purity criteria of < 10 mg/L TOC.

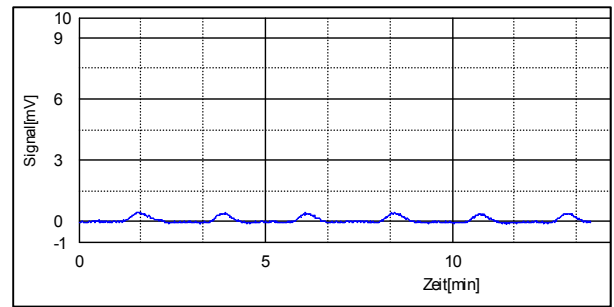


Fig. Example peaks of 50% sodium hydroxide solution



■ **Recommended Analyzer / Configuration**

- TOC-L_{CPH}
- OCT-L (8-port samples)
- High-Salt-Kit
- B-Type-Scrubber

Application News

Sum parameter – Total Organic Carbon

TOC – Determination in soda solution

No. SCA-130-306

Impurities in products can be caused by organic contaminants present in basic chemicals to. That is a reason why quality control of the reactants is indispensable.



In the determination of organic contaminations in concentrated soda solutions, various issues must be considered. In comparison to organic carbon, the soda solution to be investigated has a very high inorganic carbon content in the form of carbonates. In addition, the solution has a high pH value and tends to absorb carbon dioxide from the air.

A soda solution must, therefore, be analyzed using the NPOC method.

In the case described here, a 50% soda solution was investigated. The required detection limit was 10 mg/L.

■ Sample preparation

The sample was first manually diluted to a ratio of 1:10 with ultrapure water and a corresponding amount of acid. Several mL of ultrapure water were placed in a 50 mL volumetric flask. Subsequently, 5 mL of the concentrated soda solution was pipetted into the flask. Finally, concentrated sulfuric acid was added until the solution has reached a pH < 2.

The flask was then filled with ultrapure water up to the mark.

Compound (Concentration)	Dilution	Conc.
Soda hydroxide solution (50%)	1 : 10 diluted with water (5ml/50ml) add. 1-2 drops Sulfuric acid until pH<7	Approx. 5%

Caution: During the addition of the sulfuric acid, the carbonates decompose under a violent reaction (heat dissipation / gas formation).

Calibration of the TOC-L system was carried out using the automatic dilution function in the range of 0.5 mg/L to 10 mg/L.

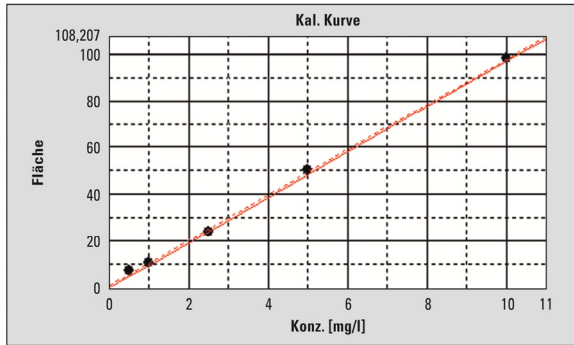
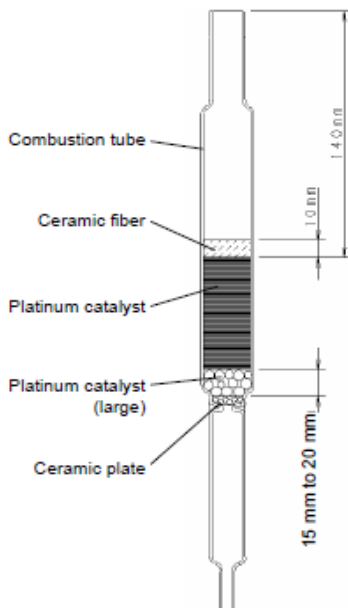


Fig. Multi-point calibration with dilution function

For the determination, a TOC-L_{CPH} was equipped with a kit for high salt loads. A special catalyst tube, a special mixture of various catalyst beads and a ceramics grid, which replaces the platinum net are part of the kit.



Sample acidification when using the high-salt kit, is carried out with sulfuric acid in order to modify the sample matrix.

The higher melting point point of NaSO₄ (881 °C) compared to NaCl (801 °C) has a positive influence on the lifetime of the combustion tube.

■ Results

The duplicate determination of the soda solution yielded the following results:

Sample	NPOC [mg/l]	RSD [%]
Soda solution (50%)	56,4	7,1
Soda solution (50%)	54,8	4,9

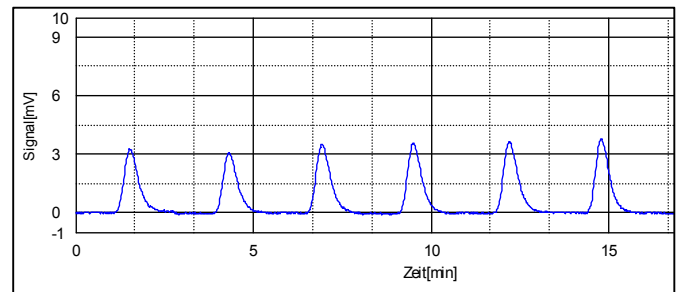


Fig. Peak graphs of a diluted soda solution (ca.5%)



■ Recommended Analyzer / Configuration

- TOC-L_{CPH}
- ASI-L
- High-Salt-Kit
- B-Type- Scrubber

Application News

Sum parameter – Total Organic Carbon

TOC – Determination in ammonia or ammonium salt solutions

No. SCA-130-307

Basic chemicals may contain organic contaminants polluting end products. This is why quality control of the reactants is a must.

In the TOC determination of ammonia water or concentrated ammonium salt solutions, various issues must be considered. Ammonia and some ammonium salts are alkaline. The catalyst and combustion tube are sensitive to alkaline media and are subjected to increased wear.



The solutions should, therefore, be acidified and possibly be diluted.

The decomposition during oxidation of the ammonium or ammonia proceeds to completion without the formation of residues on the catalyst. Therefore, it is not necessary to use a high-salt kit.

In the case described below, the NPOC content of a 40% ammonium nitrate solution was determined. The required detection limit was < 10 mg/L.

■ Sample preparation

The ammonium nitrate solution was diluted with ultrapure water to a ratio of 1:10. Dilution was carried out manually in a 50 mL volumetric flask under addition of several drops of concentrated sulfuric acid (25%).

Compound (Concentration)	Dilution	Conc.
Ammonium nitrate solution (40%)	1 : 10 diluted (5 ml / 50 ml) add. 1-2 drops Sulfuric acid until pH<7 (Note: generation of heat)	Approx. 4%

Calibration of the TOC-L system was executed using the automatic dilution function in the range of 0.5 mg/L to 10 mg/L.

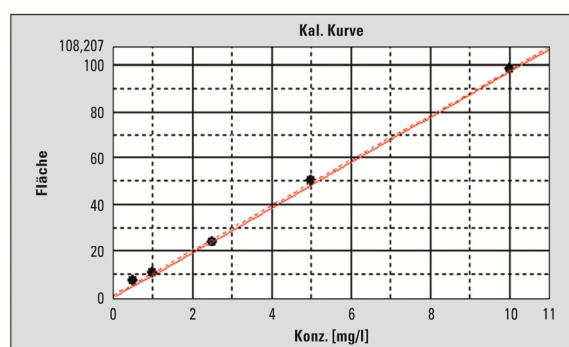


Fig. Multi-point calibration with dilution function

■ Interferences

In addition to CO₂ formed from the organic components, various nitrogen oxides are formed during the combustion of ammonium salts or ammonia water. Excessively high nitrogen levels can lead to the formation of significant amounts of N₂O (nitrous oxide). Nitrous oxide exhibits absorption bands in the same IR detection range as CO₂ and can, therefore, be misinterpreted for CO₂. In addition, nitrous oxide can cause tailing and can affect the peak symmetry.

A B-type scrubber is used to eliminate possible interference by nitrous oxide. Due to the high solubility of N₂O in water, the gas is dissolved in the B-type scrubber and will not reach the detector.

■ Results

The duplicate determination of the ammonium nitrate solution yielded the following results:

Probe	NPOC [mg/l]	RSD [%]
Ammonium nitrate solution (40%)	56,5	0,8
Ammonium nitrate solution (40%)	56,7	1,2

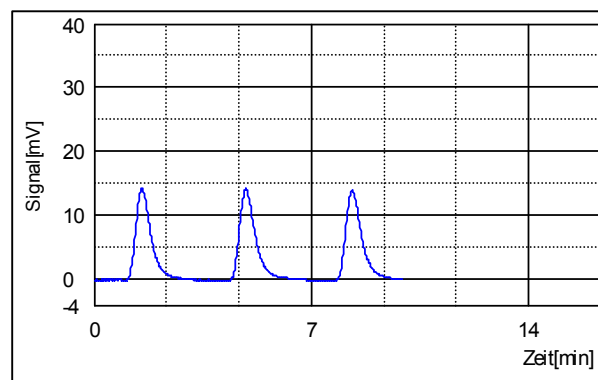


Fig. Example peaks of 40% ammonium nitrate solution



■ Recommended analyzer / Configuration

TOC-L CPH

OCT-L (8-port sampler)

B-Type- Scrubber

Application News

No. SCA-130-308

Sum parameter – Total Organic Carbon

TOC – Determination in sodium nitrate and sodium nitrite

Basic chemicals may contain organic contaminants influencing the quality of products. Quality control procedures of the reactants are, therefore, necessary in order to detect impurities.

For the determination of organic contaminations in salts, solutions of these salts can be prepared and subsequently measured using a TOC-L analyzer.



High salt concentrations generally present a problem for TOC analysis. These salts can crystallize in the combustion system and lead to higher maintenance needs.

In the case described below, the NPOC content of two salts was determined. The difficulty was the required detection limit of 10 mg/kg.

■ Sample preparation

For sample preparation, 5 g of both salts (sodium nitrite and sodium nitrate) were weighed into a 50 mL volumetric flask and diluted with ultrapure water. During dilution, the solutions were acidified with concentrated sulfuric acid (25%).

Compound (Concentration)	Dilution	Conz.
Sodium nitrate (>99,9%)	Weighted Sample 5 g / 50 ml add. 1-2 drops Sulfuric acid until pH<7	approx. 10%
Sodium nitrite (>99,9%)	Weighted Sample 5 g / 50 ml add. 1-2 drops Sulfuric acid until pH<7 Caution: Nitrogen oxide gas is released	approx. 10%

Caution: Nitrite salts react to form of toxic nitrous gases. Sample preparation should, therefore, always be carried out under a hood. The samples should only be removed from the hood, when no more nitrous gases escape.

Calibration of the TOC-L system was done applying the automatic dilution function in the range of 0.5 mg/L to 10 mg/L.

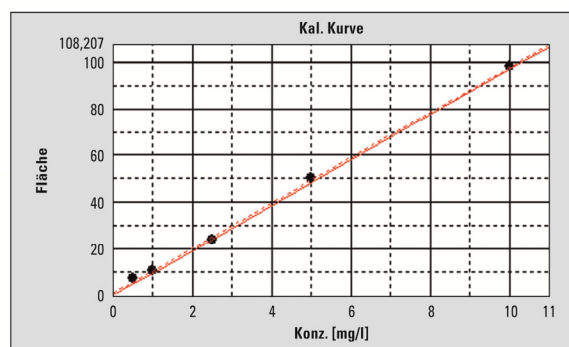
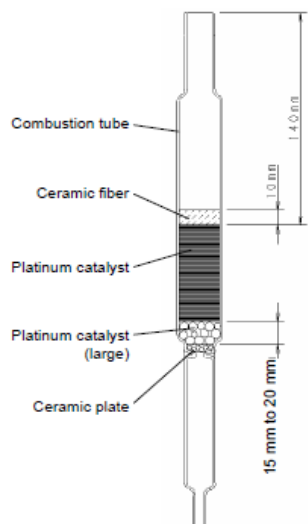


Fig. Multi-point calibration with dilution function

■ Kit for high-salt samples

The TOC-L series features a kit for high-salt samples, which significantly increases the instrument's availability. The kit consists of a combustion tube of a special geometry and a unique catalyst mixture.



In this application, sample acidification is carried out with sulfuric acid which is used to modify the sample matrix. Due to the higher melting point of NaSO_4 (888 °C) compared to 801 °C of NaCl the lifetime of the combustion tube is longer.

■ Interferences

The combustion of nitrogen compounds can lead to the formation of nitrous oxide gas. Nitrous oxide exhibits absorption bands in the same IR detection range as CO_2 and can, therefore, be misinterpreted for CO_2 . In addition, nitrous oxide can cause tailing and can affect the peak symmetry.

A B-type scrubber is used to eliminate possible interference by nitrous oxide. Due to the high solubility of N_2O in water, the gas is dissolved in the B-type scrubber and will not reach the detector.

■ Results

The duplicate determination of the salt solutions yielded the following results:

Sample	NPOC [mg/kg]	RSD [%]
Sodium nitrate (>99,9%)	22,8	4,7
Sodium nitrate (>99,9%)	24,0	6,8
Sodium nitrate (>99,9%)	<10 (9,0)	-
Sodium nitrate (>99,9%)	10,2	5,4

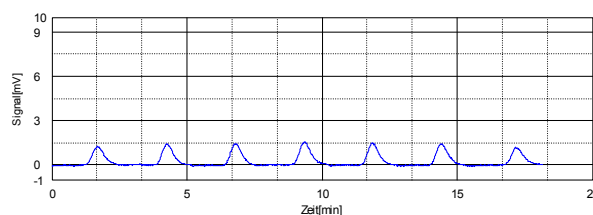


Fig. Example peaks: Sodium nitrate



■ Recommended Analyzer / Configuration

TOC-L_{CPH}
ASI-L
High-Salt-Kit
B-Type-Scrubber

Application News

No. SCA-130-309

Sum parameter – Total Organic Carbon

TOC determination in phosphoric acid

Phosphoric acid is one of the most frequently used inorganic acids in industrial applications. It is applied as starting material for the manufacture of phosphate-containing fertilizers as well as for the production of water-softening agents such as detergent additives.

Phosphoric acid is also used in the food industry – as acidification agent and preservative in beverages or as antioxidant in meats and meat products.



Particularly for these types of applications, it is important to apply acids that are pure and free from foreign substances. Manufacturers and processors of phosphoric acids are increasingly using the TOC (Total Organic Carbon) sum parameter for quality control. This parameter is a measure of the contamination of phosphoric acids by organic components.

The TOC method by using the catalytic combustion is not suitable for the determination of phosphoric acid,

because the phosphoric acid damages the combustion tube and the catalyst.

Due to this, the wet chemical TOC method is used to measure TOC in phosphoric acid.

■ Wet-chemical UV oxidation at 80 °C

The determination of the TOC content in phosphoric acid is carried out via wet-chemical UV oxidation using Shimadzu's TOC-V_{WP}.



Its core technology is the powerful oxidation applying a combination of sodium persulfate and UV oxidation at 80 °C. This ensures that all dissolved carbon compounds are converted to CO₂.

In the presence of persulfate ions and UV illumination, OH-radicals are formed which have a strong oxidative effect and convert organic compounds to carbon dioxide. A carrier gas transports the carbon dioxide formed to the NDIR detector where they are detected.

Automated reagent preparation eliminates any contamination of the reagent solutions and minimizes the blank value of the instrument.

■ TOC determination

Due to lower TOC concentration, the instrument is calibrated in a range of 0,1 – 1 mg/L.

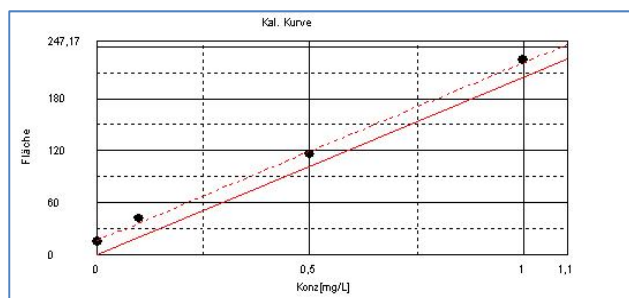


Figure: Calibration of NPOC between 0,1 – 1 mg/l.

Concentration of the phosphoric acid does not play a significant role in the determination; it is only necessary to ensure that the acid is not too viscous. The 85% phosphoric acid solution was therefore diluted 1:5 with water.

The resulting 17% acid solution was transferred into the instrument using an OCT-1 autosampler.



The autosampler OCT-1 has a big advantage for the measurement of aggressive matrices, because its parts are done of Teflon.

■ Method of phosphoric acid measurement

The concentrated phosphoric acid (85%) is diluted by 1:5.

TOC determination in phosphoric acid was carried out using the NPOC (Non-Purgeable Organic Carbon) method. Prior to TOC determination, neutral or alkaline samples are acidified in order to decompose all inorganic carbonates and bicarbonates. This step could be omitted for phosphoric acid.

Acidification: 0%
Spurge-time: 2 minutes
Injection volume: 3000µl

■ Results

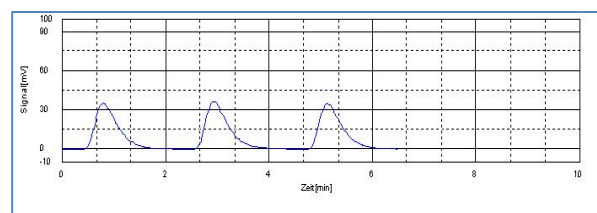


Abb.: Peak graph of diluted phosphoric acid(17%)

The 17% phosphoric acid solution measured in this way resulted in a TOC concentration of 0.61 mg/L. The relative standard deviation over three injections was 1.8%.

■ Recommended Analyser / Configuration

- TOC-V_{WP/WS}
- OCT-1

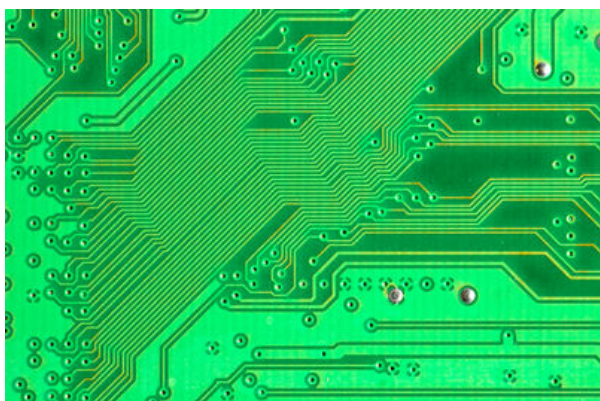
Application News

No. SCA-130-310

Sum parameter – Total Organic Carbon

TOC – Determination in diluted hydrofluoric acid

Hydrofluoric acid is the only acid that attacks glass (glass etching). Because of this chemical property, it plays a distinct role in several industrial processes, for instance in the manufacturing of solar cells and wafers as well as in microchip production. Hydrofluoric acid is the most widely used etching agent in the semiconductor industry.



When carrying out etching processes, it is important to ensure that the etching agent used will etch the respective layers and not leave any contaminants.

This raises questions on the impurities of etching agents, where both the purity of the starting acid and that of the etching solutions after the etching process are of interest.

To determine the degree of contamination, the TOC parameter is particularly suitable, as it is a sum parameter that detects all organic carbon compounds.

■ TOC determination

In the following measurement, a 4% hydrofluoric acid was manually diluted to 1:10 with water and measured using the TOC-L_{CPH}. Given the acidity of the hydrofluoric acid, the IC content can be neglected. With regard to the dilution, the solution was slightly acidified and sparged for 3 minutes. The NPOC was subsequently determined by means of combustion oxidation.

An aliquot of the sample is injected onto a hot (680 °C) platinum catalyst. The organic substances are converted to CO₂ and detected via an NDIR detector.

■ Calibration

Due to mostly working in a small measuring range, calibration was carried out in a range of 0.25 mg/L – 5.0 mg/L. For dilutions, the automatic dilution function of the TOC-L system was applied. The injection volume was 150 µL respectively.

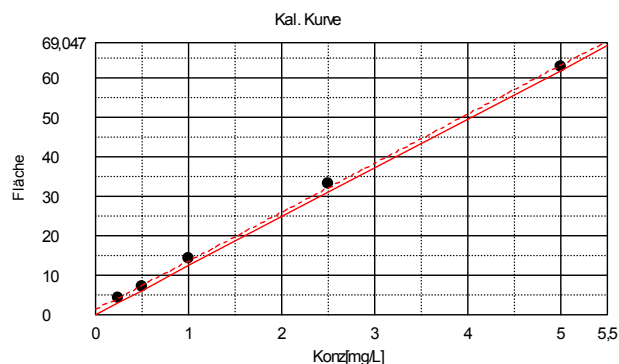


Figure: Calibration curve, TC 5 mg/L.

■ Measurement example

A total of 3 different hydrofluoric acids (0,4%) were measured:

- Hydrofluoric acid prior to etching (**HF1**)
- Hydrofluoric acid after etching (a seemingly clean wafer (**HF2**))
- Hydrofluoric acid after etching (a seemingly dirty wafer (**HF3**))



■ NPOC method

Acidification: 1.5%
Purging time: 3 minutes
Injection volume: 150 µL
Number of injections: 3

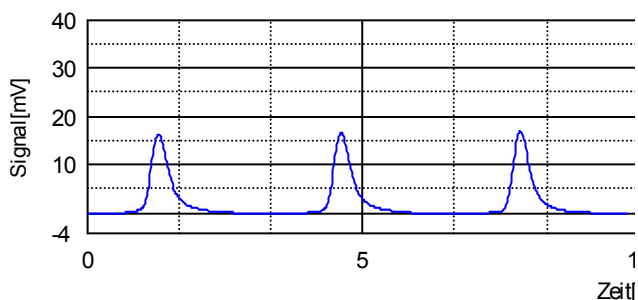


Figure: Peaks of the diluted HF solution.

The measurements were already stable after two or three injections. It is advantageous to carry out several HF injections prior to the actual sample measurement.

■ Results

Sample	NPOC [mg/L]	RSD [%]
HF 1	2.42	4.8
HF 2	3.09	3.2
HF 3	4.38	2.1

■ Protection and safety

For such measurements, comprehensive protective measures for dealing with hydrofluoric acid must be urgently observed. This also includes wearing protective clothing, gloves and safety goggles.

After measurement, the instrument must be rinsed several times with water. In addition, 20 injections with ultrapure water must be carried out.

Nevertheless the lifetime of syringe, combustion tube and catalyst will be shortening, due to HF solution.

■ Recommended instrument/ equipment

TOC-L_{CPH} / CPN
OCT-L

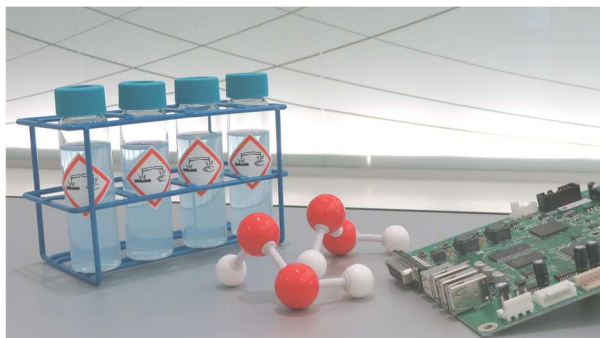
Application News

No. SCA-130-311

Sum parameters – Total Organic Carbon

Combined TOC and TN_b determination in hydrogen peroxide solution (H₂O₂)

Hydrogen peroxide (H₂O₂) is a mostly odorless, colorless liquid which could be described simply as water with an additional oxygen atom attached. This additional oxygen atom is keeping the molecule barely together in the so-called peroxide bond, but defines its large variety of uses in chemistry as a potent oxidizing agent. As the only byproducts of its reactions are water and oxygen, it can be considered environmentally friendly when used properly.



■ Economic importance of H₂O₂

Hydrogen peroxide is frequently used as a bleaching agent of pulp, natural fiber and chemical fibers in both industrial and household applications. In water treatment, in so called UVOX-processes (UV and Oxidation), UV radiation causes the formation of hydroxyl radicals that are used to decompose organic impurities in drinking water. Additionally, it is used in the synthesis of chemical materials, pharmaceuticals, as rocket propellant, disinfectant, in metal surface treatment and many more.

Hydrogen peroxide tends to decompose into water and oxygen with increasing pH value, but especially when coming into contact with metal surfaces, causing a catalytic reaction. That is why stabilizers (organophosphorus compounds and others) are being added to

commercially available H₂O₂ solutions, creating a wide range of available purity levels for various applications.

The level of purity required in the various industrial fields is becoming increasingly higher, a strong example being the semiconductor industry. To determine the purity of hydrogen peroxide solutions, combined TOC and TN_b measurement is an effective tool, as meaningful results can be obtained within minutes.

■ TOC / TN_b determination

In the following measurements, a 30% hydrogen peroxide solution was measured using a Shimadzu TOC-L CPH with TNM-L module. Calibration of the system was carried out using the automatic dilution function within a range of 10 – 50 mg/L TOC and 1 – 10mg/L TN_b.

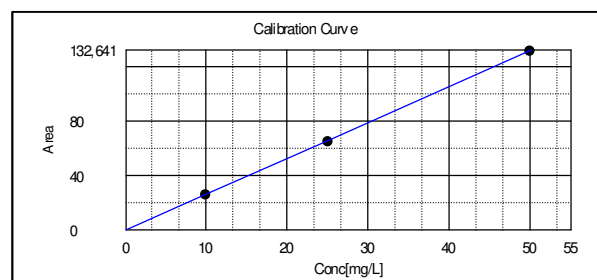


Fig. 1: TOC Multi-point calibration with dilution function

The undiluted hydrogen peroxide solution is placed in the autosampler in septum-sealed 40mL vials. The sample is then acidified and sparged out to remove inorganic carbon and CO₂ using the external sparge kit (NPOC determination). An undiluted aliquot of the sample is injected onto a hot (720°C) platinum catalyst. Organic substances are converted to CO₂ and detected using a NDIR detector. At the same time, nitrogen compounds are converted to NO and detected by a chemiluminescence detector.

■ Measurement method and results

Measurement type: NPOC
Addition of acid: 1.5%
Spurge time: 5 minutes
Injection volume.: 50 µL

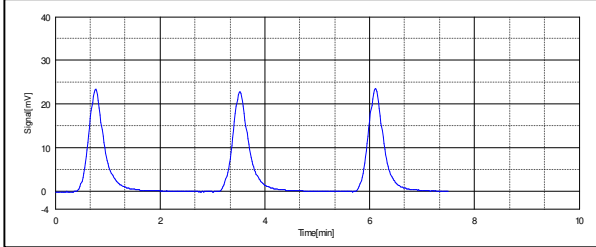


Fig.2: 3 NPOC Injections of 30% H₂O₂.

Multiple injections of the untreated 30% hydrogen peroxide solution were conducted successfully and with good reproducibility.

To investigate matrix influences, a potassium hydrogen phthalate solution was subsequently added to increase the TOC content by 10 and 20mg/L respectively. Concurrently, a mixed Potassium nitrate and Ammonium sulfate solution was added to increase the TN_b by 1 and 2mg/L (Figure 3).

Sample	NPOC [mg/l]	TN _b [mg/l]	RSD [%]
H ₂ O ₂ (30%)	19,4	2,76	1,0
H ₂ O ₂ (30%) (spiked with 10mgC/l and 1mgN/l)	29,0	3,71	1,5
H ₂ O ₂ (30%) (spiked with 20mgC/l and 2mgN/l)	38,9	4,71	0,5

Fig.3: Results of original and spiked H₂O₂

The NPOC and TN_b contents were found precisely according to the added amounts. The validity and efficiency of the measurement method was thereby considered verified.

■ Further considerations

The oxidation products of H₂O₂ pose no harm to the liquid handling system, catalyst and detectors of the TOC-L. The samples themselves however should be placed in septum-sealed vials in the autosampler, to exclude accidental spilling of the aggressive substance. The injection volume for both TOC and TN_b determination can be increased further to be able to measure in lower ranges.

Higher concentrated solutions (e.g. 55%) can be measured as well. Unstabilized solutions might tend to create foam when applying the NPOC method. In such cases it is advised to use the difference method (TOC=TC-IC) to prevent bad reproducibility.



■ Recommended analyzer / configuration

TOC-L_{CXH}
TNM-L for TN_b determination
ASI-L with external spurge kit