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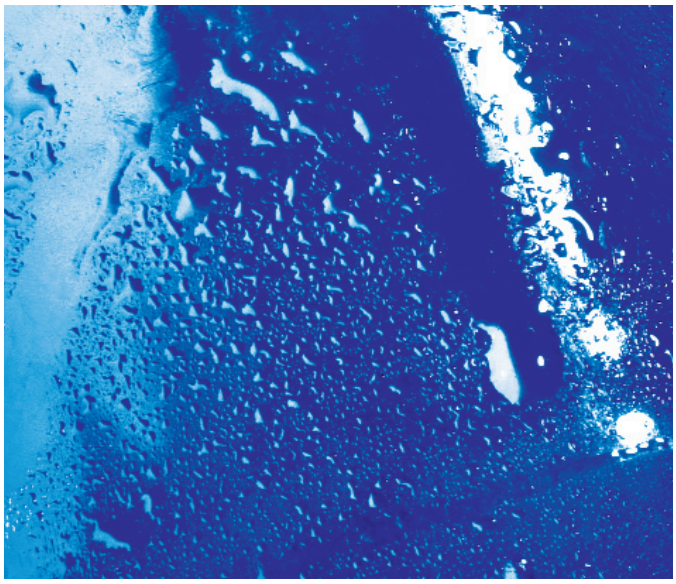
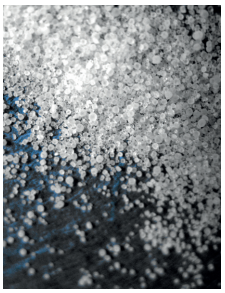
TOC Measurement in the Chemical Industry





Chemical Industry

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.'

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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.

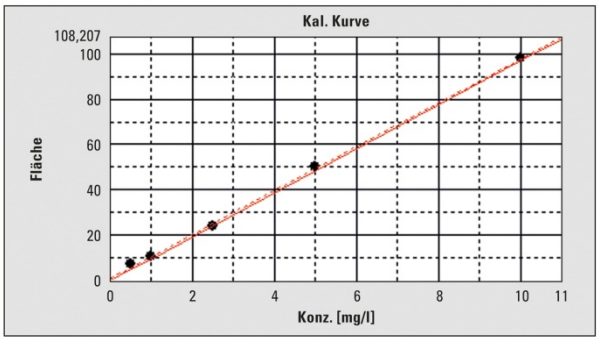

Abb.2 Mehrpunktkalibration mit Verdünnungsfunktion

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 µL. 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).

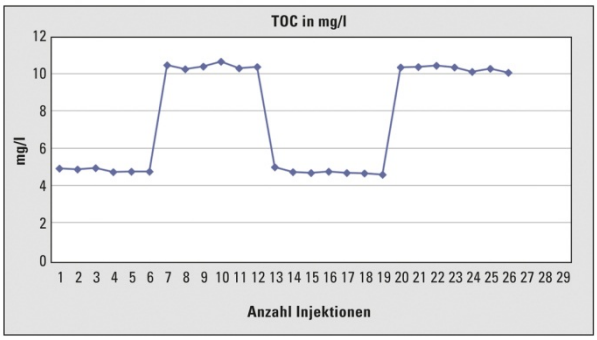

Fig.3: Results of original and spiked hydrochloric solution

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.

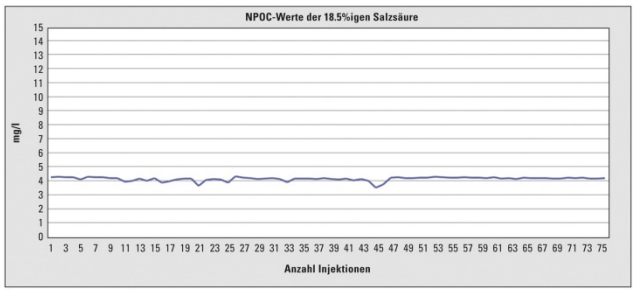

Fig.4: Result of longterm stability

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

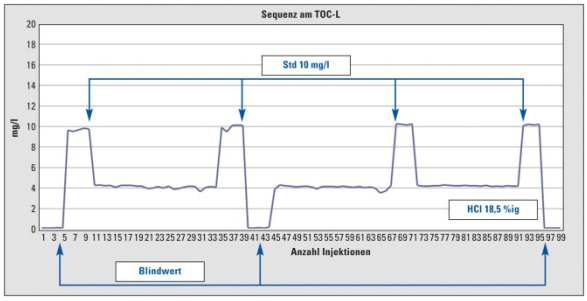

Fig. 5: Sequence of hydrochloric acid, blank (pure water) and Standards (10 mg/l)

■ 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 $SnCl_2$ solution
- Copper bead scrubber with pH paper
- Bypassing the blank check vessel
- Substituting water for phosphoric acid (IC vessel)
- OCT-L 8-port sampler

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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% HNO_3 solution with a detection limit of < 10 mg/L.

■ Sample preparation

For sample preparation, the 69% HNO_3 solution was diluted to a ratio of 1:10 with ultrapure water.

Compound (concen-tration)	Dilution	Conz. [%]
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.

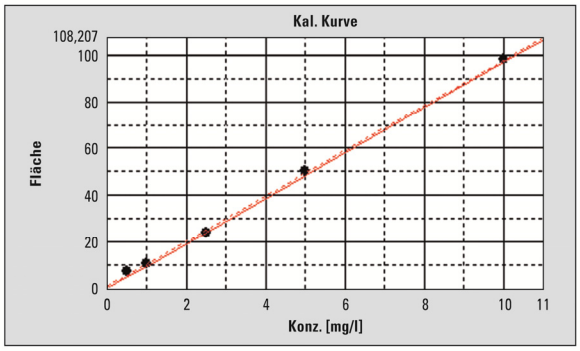

Fig. Multi-point calibration with dilution function

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

■ Matrix interferences

In addition to CO_2, various nitrogen oxides are formed from the organic components during the combustion of nitric acid. Excessively high levels of NO_3 can lead to significant amounts of N_2O (nitrous oxide). 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.

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.

■ 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)

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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 SO_2 vapors. SO_2 exhibits absorption bands in the same IR detection range as CO_2 and can, therefore, be misinterpreted for CO_2.

To determine organic contaminations in highly concentrated sulfuric acid, additional SO_2 scrubbers are used.

The following SO_2 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 SO_2.
- Mist scrubber (cartridge)
  Just like the halogen scrubber, the 'Mist scrubber' is used in the flow line for SO_2 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 (Concen-tration)	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.

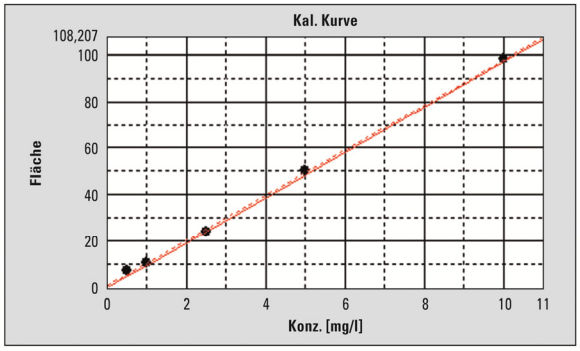

Fig. Multi-point calibration with dilution function

■ 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 $NaSO_4$ 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

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Application News

Sum parameter – Total Organic Carbon

TOC – Determination in brines

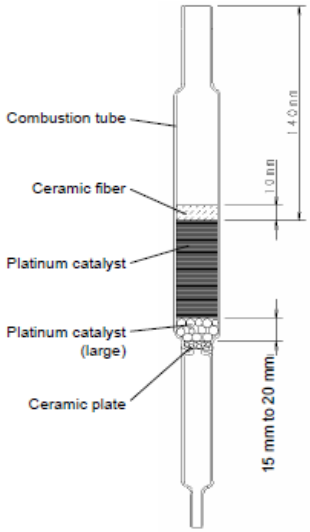
No. SCA-130-304

The determination in difficult matrices, such as brines or heavily contaminated waste-waters, 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 ia 801 °C, $NaSO_4$ 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_2SO_4	888°C
$MgCl_2$	708°C
$CaCl_2$	782°C
K_2SO_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 (Concen-tration)	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.

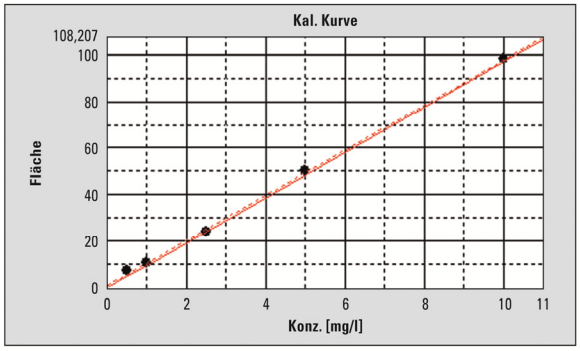


Fig. Multi-point calibration with dilution function

■ Result

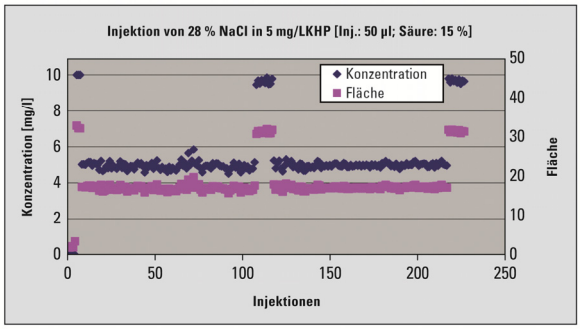
The duplicate determination of the TOC analysis yielded the following results:

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

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Application News

No. SCA-130-305

Sum parameter – Total Organic Carbon

TOC – Determination in sodium hydroxide solution

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 CO_2 from the environment. As air contains approximately 400 ppm CO_2, 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 (Concen-tration)	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.

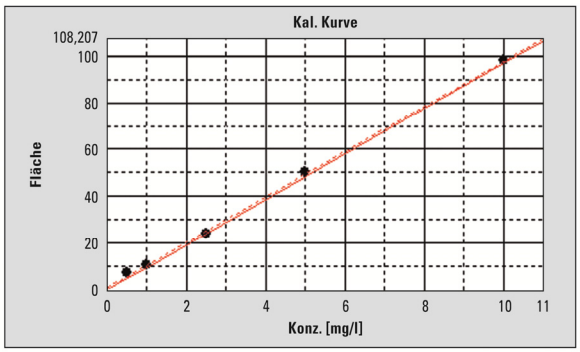
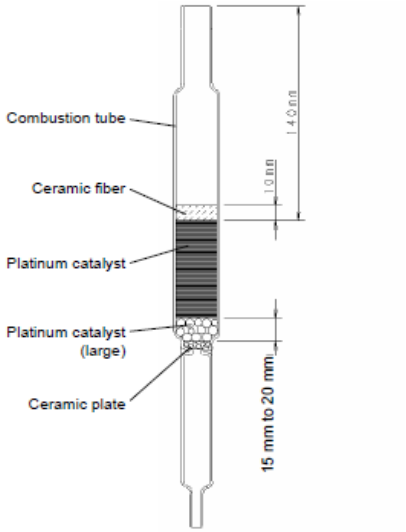


Fig. Multi-point calibration with dilution function

■ 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 $NaSO_4$ 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.

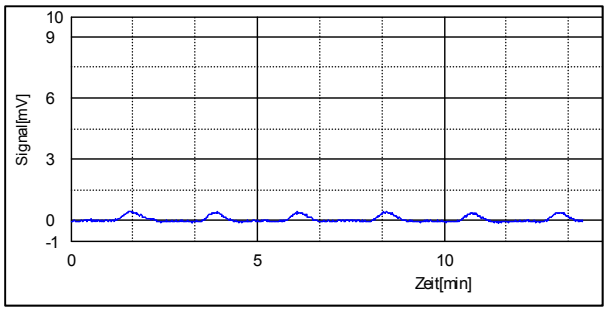


Fig. Example peaks of 50% sodium hydroxide solution

■ Recommended Analyzer / Configuration

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

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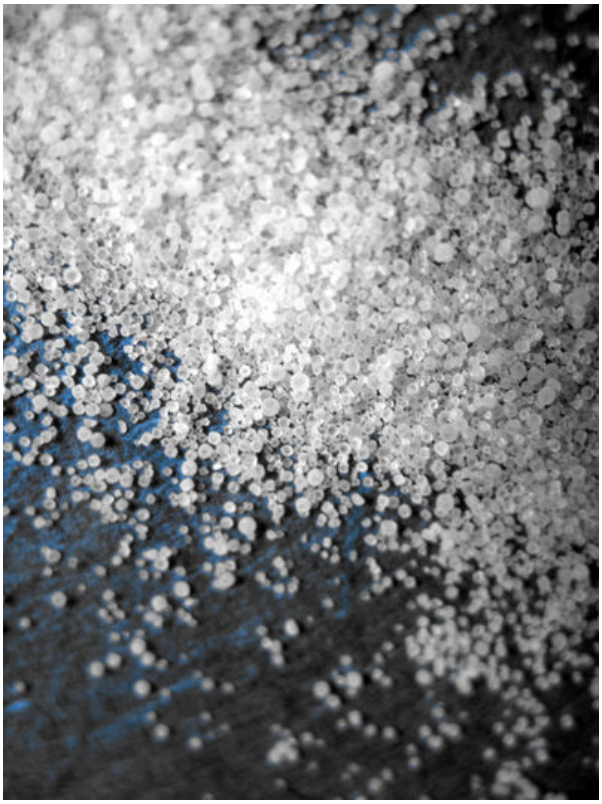
Application News

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 (Concen-tration)	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.

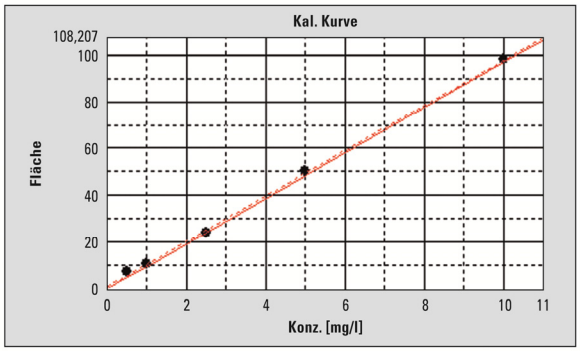
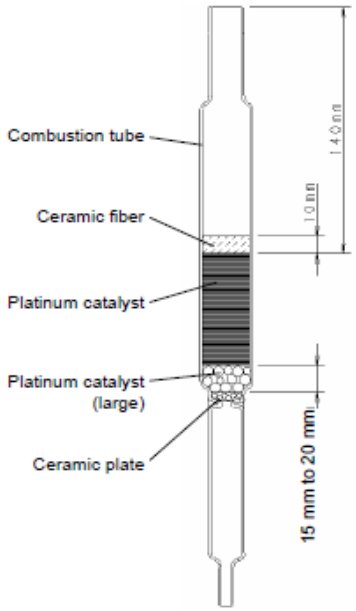


Fig. Multi-point calibration with dilution function

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 $NaSO_4$ (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

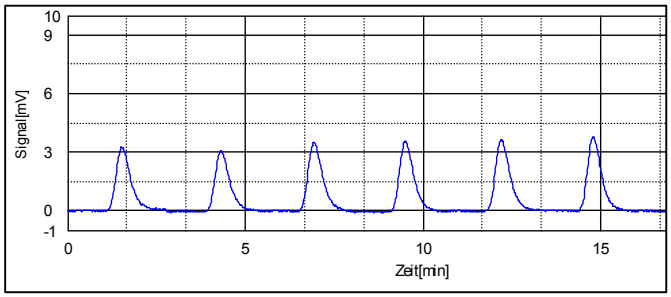


Fig. Peak graphs of a diluted soda solution (ca.5%)

■ Recommended Analyzer / Configuration

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

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Application News

No. SCA-130-307

Sum parameter – Total Organic Carbon

TOC – Determination in ammonia or ammonium salt solutions

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 (Concen-tration)	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.

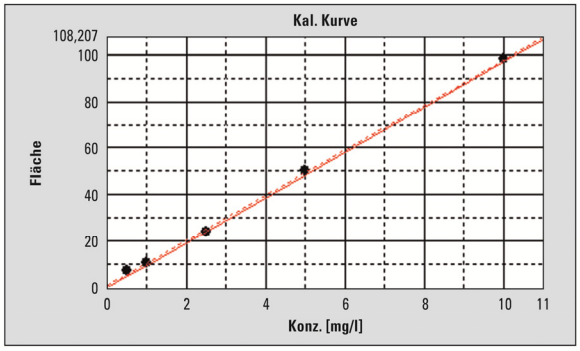

Fig. Multi-point calibration with dilution function

■ Interferences

In addition to CO_2 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 N_2O (nitrous oxide). 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 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

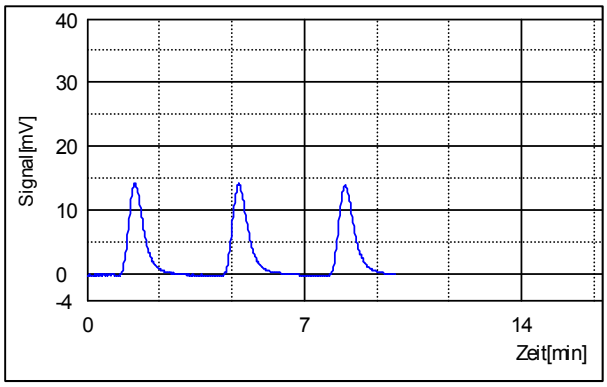

Fig. Example peaks of 40% ammonium nitrate solution

■ Recommended analyzer / Configuration

TOC-L $_{CPH}$

OCT-L (8-port sampler)

B-Type- Scrubber

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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 (Concen-tration)	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.

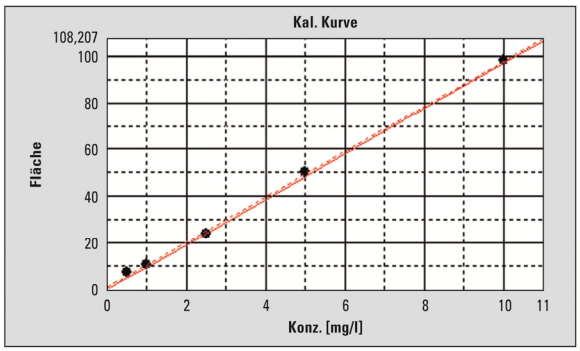
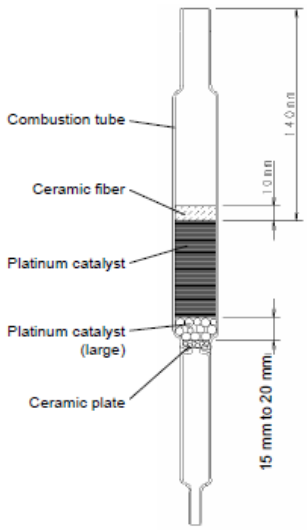


Fig. Multi-point calibration with dilution function

■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

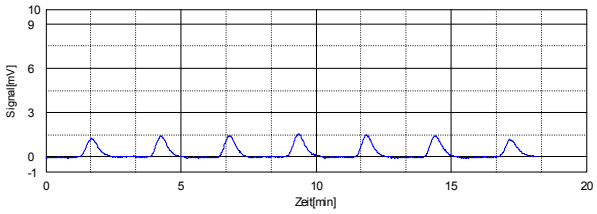


Fig. Example peaks: Sodium nitrate

■ Recommended Analyzer / Configuration

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

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Application News

No. SCA-130-603

Sum parameter – Total Organic Carbon

Continuous TOC determination in the chemical industry

The high demand for many different products from the chemical industry and the required efficiency of the manufacturing processes often requires around-the-clock production. This results in huge amounts of wastewater. This water mostly originates from flowing water bodies.

Industrial wastewaters must be pretreated before being discharged into public sewage treatment plants. Direct discharge into water bodies requires an extensive cleaning process. This is why many large companies or industrial parks operate their own wastewater treatment plants.

■ TOC determination in industrial wastewater

The TOC content (Total Organic Carbon) is a measure of the concentration of organically bound carbon and is an indication of the pollution level by organic compounds in wastewater. This is why the TOC is often used in sewage treatment plants as measuring parameter to monitor and optimize the treatment process and to calculate pollution levels. The matrix in industrial effluents can vary greatly and can – prior to sewage treatment – be polluted with high salt loads. For TOC determination in wastewater, catalytic combustion has become the method of choice based on its higher oxidation potential, especially for particles.

■ Are high salt loads a problem?

During thermal catalytic combustion of the test sample, the dissolved salts crystallize. High salt loads can lead to pollution of the catalyst, or even clogging of the system. Maintenance measures (for instance exchanging the catalyst) would then be required in order to render the instrument operational again. Of course, it is desirable to keep the maintenance intervals as long as possible.

■TOC-4200

The TOC-4200 offers various possibilities to keep the maintenance needs for highly polluted samples at a minimum. The TOC-4200 with catalytic combustion at 680 °C is a high-performance analyzer. This temperature is lower than the melting point of sodium chloride and will, therefore, prevent deactivation of the active centers of the catalyst by a melt. The use of a platinum catalyst ensures the complete conversion of the organic compounds to CO_2. The highly sensitive NDIR detector allows small injection volumes (typically 20 - 50 µL) that reduce the absolute sample input onto the catalyst. A further reduction can be achieved using the integrated dilution function.

This can take place when measurement values are exceeded or can be applied permanently. In this case, the user specifies the desired dilution factor in the selected method.

■ Kit for high-salt samples

For the continuous TOC determination of samples with high salt loads (> 10 g/L), Shimadzu has developed a salt kit. The combustion tube has a special shape and uses two different catalyst beads. This combination prevents crystallization that can lead to clogging of the system.

■ TOC-4200 in daily practice

To verify the robustness and the reliability of the TOC-4200 during practical operation, the analyzer has been subjected to an endurance test in a German chemical park. For three months, the TOC-4200 had to stand the test under the most difficult conditions at one measuring station. The wastewater under investigation was alkaline (pH ≥ 12) and highly saline (conductivity 4 ≥ mS/cm).

Fig. TOC-4200 on site

This is why the instrument was equipped with a kit for salt-containing samples. In addition, the automatic dilution function was used to dilute the samples (including the matrix).

The software enables planning of various automatic maintenance and calibration tasks. This way, automatic calibration of the measuring method was programmed to take place every 48 hours and automatic regeneration of the catalyst twice a week. Sampling took place in the counterflow mode with backflushing in order to prevent clogging.

■ Results of the practice test

As described in the test, a sample was collected every 4 minutes over a period of three months, and subsequently diluted, acidified and analyzed. After three months a total of approximately 27,000 measurements was achieved. . Within this period, the instrument was automatically calibrated 45 times and the catalyst was regenerated nearly 25 times. These functions can be easily programmed via a calendar on the touch screen. The calibration function gradients remained stable over the entire time period.

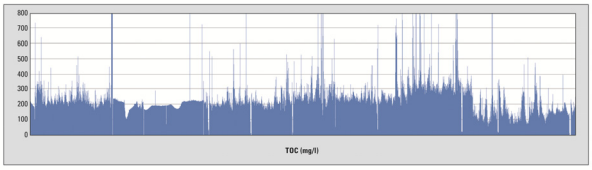

Fig. Diagram of 27.000 Measurement results (three months)

The test did not require any catalyst exchange or a single maintenance operation. There was also no instrument or software failure or any other component failure. In short: the TOC-4200 has successfully passed the endurance test.

■ Recommended analyzer / Configuration

TOC-4200
Kit for high-salt samples

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