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Application News

Total Organic Carbon Analyzer TOC-L

TOC and TIC Analysis in Hydroxide Solutions Using High-Temperature Catalytic Combustion

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User Benefits

- TOC and TIC of hydroxide solutions such as NaOH and KOH can be determined using a TOC-L analyzer
- The internal acidification function minimizes the volume of acid required and reduces the time spent on sample preparation.
- The High salt combustion tube kit prolongs the service life of the combustion catalyst

■ Introduction

Hydroxide solutions, especially sodium hydroxide (NaOH) and potassium hydroxide (KOH), are commonly used in chemical, industrial, and environmental processes. These solutions neutralize acids to form water and salts, a process that is essential in various reactions. As strong bases, NaOH and KOH play a significant role in the production of a variety of goods, including soap, through the saponification process (Figure 1), in which they react with oils and fats. However, organic contaminants in these chemicals can lead to impurities, necessitating quality control of the reactants to ensure product integrity.

Fig. 1 Hydroxide and other ingredients are mixed to create soap.

Furthermore, hydroxides are potent CO_2 absorbers. They form carbonate and bicarbonate ions when they bind CO_2. Their solutions are used for various purposes, including sequestering fossil fuel emissions, which can be quantified by measuring total inorganic carbon (TIC).

KOH is an essential electrolyte in the alkaline electrolysis of green hydrogen. Total organic carbon (TOC) limits must be maintained to ensure the smooth operation of this sensitive technology. Analytical quality control of hydroxide solutions is therefore necessary to ensure product quality and uphold process efficiency of alkaline electrolyzers.

■ TOC analysis of hydroxide solutions

Analyzing TOC in hydroxide solutions presents challenges that necessitate proper method design and system configuration. The "difference method" (TOC = TC − TIC) and the "direct method" (TOC = NPOC) are commonly used for TOC determination. However, using the difference method, direct total carbon (TC) determination of hydroxide can lead to the rapid degradation of the TOC analyzer's catalyst and combustion tube leading to rapidly decreasing sensitivity and poor reproducibility. Therefore, using the difference method is not advisable.

In the direct method, acid is added to the sample to reach a pH value of 2 or less. With hydroxide solutions, this results in the production of large quantities of salts. At the same time, however, the TIC, in the form of carbonates and bicarbonates, is converted into CO_2, which can easily be purged from the sample prior to TOC determination. The goal is to analyze highly saline samples with potentially high acid content successfully and reliably using the NPOC method. Depending on the solution's concentration, the sample may need to be manually diluted beforehand so that the final hydroxide ion concentration is approximately 6 g/l (see Table 1). Manual dilution factors can be entered into the analysis software for concentration calculation.

Table 1 Maximum concentration of hydroxide solutions for TOC and TIC analysis using modified TOC-L

Hydroxide solution	Molar conc.	Mass conc.	Dilution required
KOH 2 %	0,36 mol/l	20 g/l	Not required
KOH 31 % (H_2 electrolysis)	7,1 mol/l	400 g/l	1:20 with pure water
KOH 45 %	11,6 mol/l	650 g/l	1:32 with pure water
NaOH 1,5 %	0,35 mol/l	14,1 g/l	Not required
NaOH 4 %	1,04 mol/l	41,7 g/l	1:3 with pure water
NaOH 33 %	11,2 mol/l	448 g/l	1:32 with pure water
NaOH 45 %	16,6 mol/l	665 g/l	1:48 with pure water
NaOH 50 %	19 mol/l	763 g/l	1:54 with pure water

To acidify highly saline samples in the TOC-L analyzer, 4 mol/l sulfuric acid (H_2SO_4) is used. When analyzing hydroxide solutions, a high acidification factor must be selected to lower the pH to the value of less than 2 required for NPOC determination. For this purpose, an internal acidification factor of 12% was determined. Alternatively, prior manual acidification with sulfuric acid to 0,6 mol/l is possible. However, internal acidification offers advantages. Because the same acidification is used for calibration, the TOC blank values in the acid are automatically included in the concentration calculation. Additionally, since the sample aliquot is acidified prior to injection, the overall acid consumption is significantly reduced. Finally, due to the small volumes, heat generation is negligible.

■ TOC measurement conditions

A TOC-L CPH analyzer was calibrated for NPOC analysis using the automatic dilution function, establishing five calibration points spaced evenly within the 1-10 mg/l carbon range. For the calibration, the high acidification factor used for sample measurement was also set to 12%, ensuring that the TOC blank values from the acid were considered in the final concentration calculation. Figure 2 shows the result of the NPOC calibration, and Table 2 shows the detailed measurement settings for the calibration and sample measurement methods.

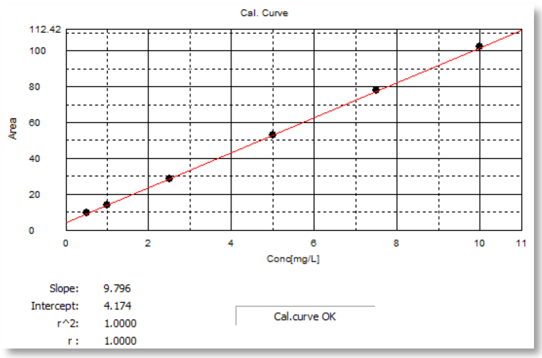

Fig. 2 Multi-point NPOC calibration with dilution function

The “multiple injections” function was activated to reduce the number of internal sample preparation steps required. To facilitate automatic measurement range extension for unknown samples, the function “correction of dilution” was activated in the sample measurement method. In case the measured value is higher than the calibration curve span, the instrument will automatically re-sample and increase the internal dilution factor accordingly.

Table 2 Measurement conditions TOC analysis

Analyzer	: TOC-L CxH (CxN possible for NPOC analysis only)
Catalyst	: Saline
Meas. Parameter	: NPOC (Direct method TOC=NPOC)
Calibration curve	: 5-point NPOC calibration using automatic dilution function in the range of 0,1 - 10 mg/l, 10 mgC/l KHP standard solution
Acidification	: H_2SO_4 4mol/l, acid addition 12 %
Sparge settings	: 5 min. (internal). 80 ml/min
Injection settings	: 150 µl, 3 / max. 5 injections Multiple injections ON
Other settings	: Correction of dilution ON

■ TOC analysis results

The analysis of KOH and NaOH solutions using the NPOC method produced the results shown in Table 3. To control the catalytic oxidation system, KOH samples were spiked with 2 and 8 mg/l TOC as KHP, respectively. The results demonstrate the method's good recovery and robustness.

The limit of quantification (LOQ) of the method was determined to as ten times the standard deviation of a sixfold injected pure water blank sample.

NPOC LOQ: 10 x 0,025 mg/l = 0,25 mg/l.

The LOQ increases with higher concentrations of hydroxide solutions, depending on the dilution factor used. For example, KOH for hydrogen electrolysis would be diluted by a factor of 20 prior to analysis, according to Table 1. In turn, the LOQ would approximately increase by a factor of 20.

Decreasing the injection volume and/or increasing the dilution factor can extend the catalyst's lifetime if a higher method LOQ is sufficient.

Table 3 TOC analysis results of KOH and NaOH samples

Sample	NPOC [mg/l]	SD
Pure water blank (6 injections)	0,037	±0,025 mg/l
QC KOH 2 % + 2 mg/l TOC	2,078	±0,002 mg/l
QC KOH 2 % + 8 mg/l TOC	8,334	±0,074 mg/l
KOH 2 % sample 1	0,673	±0,019 mg/l
KOH 2 % sample 2	0,666	±0,008 mg/l
QC KOH 2 % + 2 mg/l TOC	2,056	±0,003 mg/l
QC KOH 2 % + 8 mg/l TOC	8,414	±0,169 mg/l
NaOH 2 % sample 1	0,118 (< LOQ)	±0,032 mg/l
NaOH 2 % sample 2	0,094 (< LOQ)	±0,011 mg/l
QC KOH 2 % + 2 mg/l TOC	2,069	±0,020 mg/l
QC KOH 2 % + 8 mg/l TOC	8,307	±0,094 mg/l

■ TIC analysis of hydroxide solutions

The TOC-L CPH’s “IC reactor” was used for the TIC determination. An aliquot of the sample was injected into a vessel filled with phosphoric acid. The inorganic carbon in the sample is converted to CO_2, which is expelled using carrier gas and then quantified by an NDIR detector. During this process, salts are formed from the hydroxide. When analyzing the TIC of hydroxide solutions, the resulting phosphate salts should be considered in terms of their solubility. Non-soluble salts could potentially lead to deposits and blockages in the reactor. In this case, potassium phosphate is formed from KOH and sodium phosphate is formed from NaOH. Both are easily soluble and do not tend to cause blockages in the IC reactor. They are also easily removed during the analyzer’s automatic regeneration of the IC acid solution.

■ TIC measurement conditions

A TOC-L CPH analyzer was calibrated for IC analysis using the automatic dilution function, establishing five calibration points spaced evenly within the 1-10 mg/l carbon range. As calibration stock solution, a 50:50 mixture of sodium carbonate (Na_2CO_3) and sodium bicarbonate ($NaHCO_3$) was used. This solution must be tightly sealed from the surrounding atmosphere; otherwise, it will absorb CO_2, which will subsequently increase its TIC content. This may lead to false low TIC analysis results after calibration. In doubt a fresh calibration solution should be created for each new calibration. Figure 3 shows the result of the TIC calibration, and Table 4 shows the detailed measurement settings for the calibration and sample measurement methods.

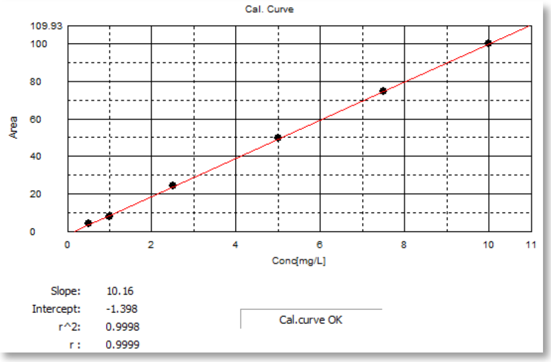

Fig. 3 Multi-point TIC calibration with dilution function

Table 4 Measurement conditions TIC analysis

Analyzer	: TOC-L CxH
Meas. Parameter	: TIC (IC)
Calibration curve	: 5-point IC calibration using automatic dilution function in the range of 0,1 - 10 mg/l, 10 mgC/l Na_2CO_3, $NaHCO_3$ standard solution
Injection settings	: 150 µl, 3 / max. 5 injections Multiple injections ON
Other settings	: Correction of dilution ON

■ TIC analysis results

The results of the analysis of the KOH and NaOH solutions using the TIC method are shown in Table 5. The calibration stock solution with a TIC concentration of 10 mg/l was used as the control standard as well. Since the TIC concentrations of the KOH and NaOH samples were higher than the calibration span, the instrument automatically re-sampled and re-measured the samples with an increased internal dilution factor using the "correction of dilution" function. These results demonstrate the method's good recovery and robustness.

The limit of quantification (LOQ) of the method was determined to as ten times the standard deviation of a sixfold injected pure water blank sample.

TIC LOQ: 10 x 0,006 mg/l = 0,06 mg/l.

The LOQ increases with higher concentrations of hydroxide solutions depending on the dilution factor used. For instance, 400 g/l of KOH for hydrogen electrolysis is diluted by a factor of 20 according to Table 1. Consequently, the LOQ would increase by a factor of approximately 20.

Decreasing the injection volume and/or increasing the dilution factor can reduce maintenance if a higher method LOQ is sufficient.

Table 5 TIC analysis results of KOH and NaOH samples

Sample	TIC [mg/l]	SD	Bound CO_2 [mg/l]
Pure water blank	0,219	±0,006 mg/l	
KOH 2 % sample 1	12,43	±0,026 mg/l	45,54
KOH 2 % sample 2	12,47	±0,059 mg/l	45,69
NaOH 2 % sample 1	35,01	±0,181 mg/l	128,28
NaOH 2 % sample 2	35,28	±0,131 mg/l	129,27
QC 10 mg/l TIC	10,20	±0,056 mg/l	

If needed, the TIC result can be automatically converted to the bound CO_2 content using the "measurement result conversion" function in the PC software. To convert TIC to CO_2, multiply the TIC result by the molar mass factor 3,664.

($CO_2/C = 44{,}01$ g/mol / 12,01 g/mol = 3,664).

■ TOC-L system configuration

For the analysis, a TOC-L CPH was retrofitted with a combustion tube for high-salt samples, operating at 680° C. As a precautionary measure, an SO_3 mist catcher was also installed (see Fig. 4). Combusting at temperatures below the melting points of common salts (particularly sulfates) mitigates blockages caused by molten salt. Instead, the salt precipitates as a powder on the catalyst. The High Salt Kit also includes a catalyst tube with an increased diameter, a mixture of catalyst beads of various sizes, and ceramic mesh to replace the standard platinum nets. This increases the catalyst replacement interval at high salt loads.

The combustion of excess sulfuric acid produces sulfur dioxide (SO_2), which then catalytically produces sulfur trioxide (SO_3) in an oxygen atmosphere. This can lead to interference in the CO_2 detection flow line, potentially resulting in false high TOC readings and peak tailing. Furthermore, the combustion products of large amounts of H_2SO_4 are corrosive and can damage the NDIR detector over time. The optional SO_3 mist catcher removes these unwanted combustion products from the sample gas. It is installed after the dehumidifier and before the halogen scrubber in the TOC-L flow path.

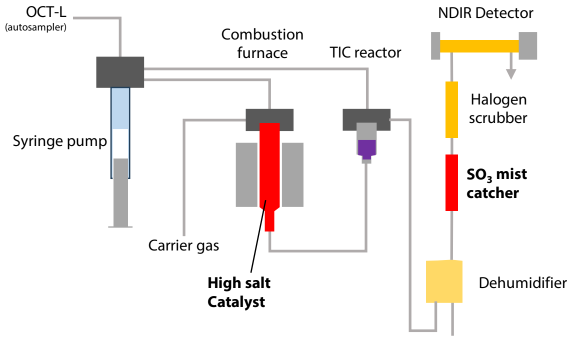

Fig. 4 TOC-L CPH modified for the analysis of hydroxide solutions

To ensure that corrosive solutions have been removed from the system, it is recommended to rinse the instrument with ultrapure water after analyzing hydroxide solutions. This helps prevent salt deposits from forming. For this purpose, ultrapure water can be measured as an NPOC and IC sample. As part of periodic maintenance, regularly check the injection sliders and syringe for salt deposits. If necessary, carefully remove the deposits with a soft, damp cloth, taking care not to scratch the surfaces.

The OCT-L 8-port sampler was used for sample handling. Its consistent use of inert material for the sample flow path makes it a good choice for TOC analysis of aggressive chemicals. The OCT-L allows for automatic sampling from up to eight bottles of any size, eliminating the need to transfer hydroxide solutions from their original bottles into smaller vials. Up to two OCT-L units can be connected to a TOC-L, providing a total of 16 sampling positions. Alternatively, the single-position offline sampling tube can be used for analysis when only a small number of samples are expected. Between samples, the analyzer flushes the OCT-L sampling tube with clean air from the flow line. Since it cannot clean the outside of the sampling tube, it should be carefully wiped of any residues before placing another sample bottle, with personal protection in mind.

■ Recommended analyzer configuration

TOC-L CPH or CSH
LabSolutions TOC software
High salt combustion tube kit
SO_3 mist catcher
OCT-L

Fig. 5 TOC-L CSH with OCT-L 8-port autosampler

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