Challenge

High-temperature TOC analysis in seawater samples places high demands on the analyzer in terms of sensitivity, matrix tolerance, and the durability of the consumables

Solution

With a special salt kit the multi N/C 3300 enables the reliable determination of TOC in seawater samples

Intended audience

Seawater desalination plants, water laboratories, monitoring authorities for environmental protection and nature conservation, laboratories for environmental analysis, contract labs

TOC Determination in Seawater in Accordance with DIN EN ISO 20236

Introduction

Water that is open and unbound on the earth's surface is referred to as surface water. This includes inland waters such as lakes, rivers, streams, ponds, reservoirs as well as coastal waters and seawater. Around 71% of the earth's surface is covered with water, of which 97% is salt water and only around 3% is fresh water. The distribution of fresh water varies greatly from region to region on our planet. In countries with limited access to fresh water, the desalination of seawater is the main source of drinking and industrial water. Different, but mostly energy-intensive processes are used to desalinate seawater.

Seawater and coastal waters are subject to special protection not only as an important resource for drinking and industrial water production, but above all because of their influence on our global climate. It is particularly important to avoid polluting the world's oceans with microplastics and other harmful substances, also with the aim of not permanently damaging the oceans' carbon dioxide storage function. Therefore, there are numerous country-specific laws and monitoring programs in place around the world that serve to protect the oceans and coastal waters. Among other things, these regulations also specify which biological, physical, and chemical parameters and pollutants must be regularly monitored. Standardized methods are usually used to determine individual pollutants in order to ensure the comparability of results. So-called sum parameters such as TOC (total organic carbon) are often used to assess the quality of surface waters. The international standard DIN EN ISO 20236[1] describes a method for determining this parameter. The particular challenge in determining TOC in seawater lies in the high salt load that seawater samples carry with them. Analyzers for the determination of TOC in environmental samples typically work with high-temperature digestion using quartz combustion tubes and catalysts. Salts contained in the sample crystallize during combustion in the analyzer and can form melts above specific temperatures (NaCl as the main component of sea salt at 801 °C). Salt crystals and melts lead to rapid wear of the catalyst and the combustion tube as well as to blockages of the carrier gas flow. Routine analysis of high saline samples is therefore

usually associated with high maintenance costs for the analyzers used. In addition, salt deposits in the combustion tube very quickly affect the accuracy and precision of the measurement results. Excessive salt contamination of the combustion tube is often associated with reduced recovery and increased scattering of results.
This paper demonstrates how a special salt kit can be used in combination with the multi N/C 3300 TOC analyzer to reliably and economically determine TOC in seawater samples over a long period of time.

Materials and Methods

The determination of TOC in seawater was carried out using the NPOC method on the multi N/C 3300 in combination with a salt kit. The salt kit consists of an optimized combustion tube including a special injection head and needle as well as a special catalyst filling and a salt trap. The NPOC (non-purgeable organic carbon) method is preferred when no volatile or purgeable organic compounds are expected in the sample and the expected TIC (total inorganic carbon) content is higher than the expected TOC content. In NPOC determination, the samples are first acidified manually or automatically using an autosampler and then purged with an auxiliary gas. The carbon dioxide formed from carbonates and hydrogen carbonates during acidification as well as the CO_2 dissolved in the sample are expelled in this way, thus the TIC is removed. The completeness of the TIC removal can be checked automatically by activating the TIC control measurement in an NPOC method. After TIC removal, the sample is injected directly into the combustion tube of the salt kit, which is filled with catalyst and a special salt trap. The organic compounds remaining in the sample are completely oxidized there at high temperatures and the carbon dioxide formed in the process is fed to the FR-NDIR (focus radiation non-dispersive infrared) detector. For the automated TOC determination, the AS vario sampler was used in combination with a tray for 72 samples of 40 mL each.

Samples and reagents

- Synthetic seawater with 35 g/L salt (NaCl, $MgSO_4$, $MgCl_2$) in ultrapure water
- 2 mol/L HCl for acidifying seawater and standards
- Stock solution 1000 mg/L TOC (potassium hydrogen phthalate in ultrapure water) for preparing the calibration solutions and for spiking the synthetic seawater samples
- Calibration standard solutions with concentrations from 0.5 mg/L to 100 mg/L TOC (potassium hydrogen phthalate in ultrapure water)
- Synthetic seawater samples spiked with different concentrations of TOC (0.5 mg/L to 100 mg/L)

Sample preparation

First, the synthetic seawater was analyzed (200 injections) in order to introduce a basic load of salt into the multi N/C 3300. For this purpose, the seawater was filled into 40 mL sample vials and placed on the tray of the autosampler. The samples were acidified automatically. The seawater samples spiked with TOC, which had concentrations of 0.5 mg/L to 100 mg/L TOC, were then analyzed. These samples were also filled into 40 mL sample containers, placed on the autosampler and automatically acidified with 2 mol/L HCl.

Calibration

The multi N/C 3300 was calibrated for NPOC measurement in the range from 0.5 to 100 mg/L C with standard solutions (potassium hydrogen phthalate in ultrapure water). A multi-point calibration was used. The calibration curve is shown in Figure 1.

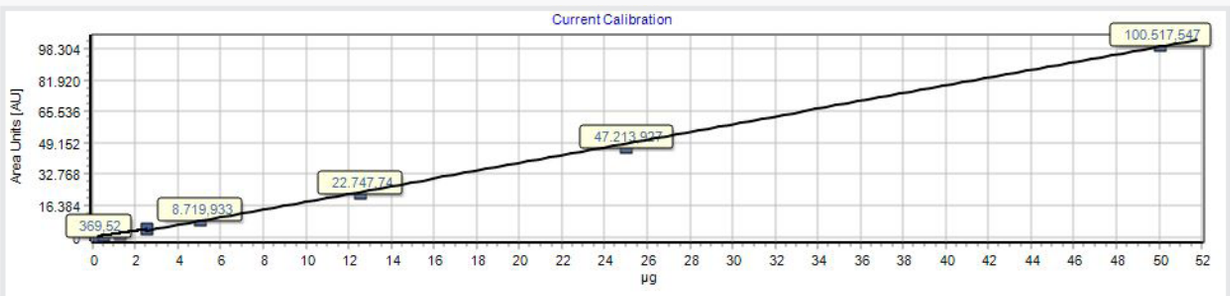

Figure 1: Calibration curve 0.5–100 mg/L TOC

Instrument settings and method parameters

Table 1: Instrument and method settings for seawater samples

Parameter	Setting
Method of determination	NPOC with TIC control
Sample digestion	High-temperature combustion (in presence of a platinum catalyst)
Digestion temperature	680 °C
Carrier gas	Synthetic air (free od CO_2 and hydrocarbons)
Number of replicates from one sample vial	min. 2, max. 3
Autosampler, rack and vial size	AS vario, rack with 72 positions, 40 mL sample vials
Number of rinses with the sample before the first injection	3
Number of reverse rinse cycles (with pure water)	0
Injection volume of sample	500 µL
Purge time (removal of TIC)	180 s

Results and Discussion

First, the sea salt solution was injected 200 times with the aim of accumulating a high amount of salt in the combustion tube. The seawater samples spiked with TOC were then measured individually to check the stability of the measurement performance. For this purpose, the recovery rates and the relative standard deviation of the measured values were observed. The results are summarized in Table 2.

Table 2: TOC results

Sample description	Mean value TOC ± SD [mg/L]	RSD [%]	Recovery of TOC in spiked samples after subtraction of blank [%]	Number of replicate measurements
Seawater (blank), 35 g/L salt	1.19 ± 0.02	1.7	-	200
Seawater spiked with 0.5 mg/L TOC	1.68 ± 0.02	1.2	98	3
Seawater spiked with 1 mg/L TOC	2.21 ± 0.02	0.9	102	2
Seawater spiked with 2.5 mg/L TOC	3.72 ± 0.03	0.8	101	2
Seawater spiked with 5 mg/L TOC	6.17 ± 0.09	1.5	100	2
Seawater spiked with 10 mg/L TOC	11.6 ± 0.07	0.6	104	3
Seawater spiked with 25 mg/L TOC	26.4 ± 0.08	0.3	101	3
Seawater spiked with 50 mg/L TOC	50.8 ± 0.71	1.4	99	2
Seawater spiked with 100 mg/L TOC	102 ± 1.74	1.7	101	2

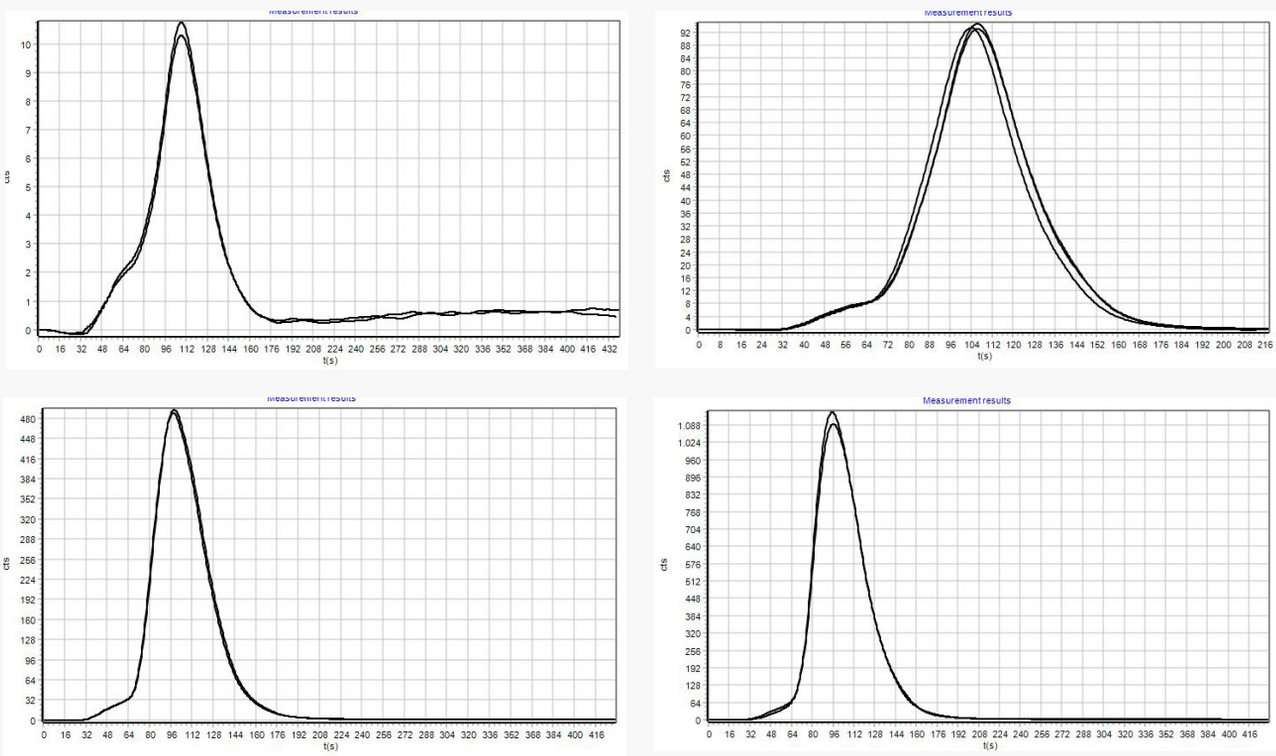

Figure 2–5: Measuring curves of spiked seawater samples, TOC concentrations 1 g/L, 10 mg/L, 50 mg/L, and 100 mg/L

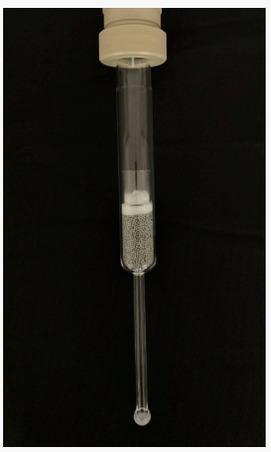

Figure 6: Salt kit, filled

The results of the spiked seawater samples show that the TOC in this matrix can be determined with very good accuracy and precision even after a high salt load has been added to the analyzer. The recovery of the individual spiked samples is in a range of 98 to 104%, the relative standard deviation is very low at < 2% for all sea salt samples. Figure 6 shows the salt kit. The quartz crucible above the catalyst serves as a salt trap. The salt introduced collects there almost completely and the surface of the catalyst is thus protected from salt deposits. At the same time, this prevents blockages in the carrier gas flow and the devitrification of the combustion tube also progresses much slower. The salt trap can be emptied or replaced quickly when the combustion tube has cooled down, as it also serves as a sacrificial material. Even after a high number of sea salt injections, the devitrification of the combustion tube itself is extremely low, so that a very long service life can be assumed for the tube and the catalyst. The salt kit gives the multi N/C 3300 a high matrix tolerance and ensures reliable measurement results.

Summary

Together with the salt kit, the multi N/C 3300 is ideally suited for determining both low and high TOC concentrations in seawater and related matrices. The salt kit effectively prevents premature wear of critical consumables such as the combustion tube and catalyst and thus also ensures very stable and reproducible measurement results. This ensures reliable and economical routine analysis for the determination of TOC in high saline matrices at all times

Figure 7: multi N/C 3300 with AS vario

Recommended device configuration

Table 3: Overview of devices, accessories, and consumables

Article	Article number	Description
multi N/C 3300	450-500.500-2	Flow injection TOC analyzer
AS vario	450-900.140	Autosampler for multi N/C 3300
Sample rack 72 positions	450-900.141	Accessory for AS vario
Salt kit	450-500.550	Combustion tube including head and filling material

References

[1] DIN EN ISO 20236 Water quality — Determination of total organic carbon (TOC), dissolved organic carbon (DOC) total bound nitrogen (TN_b) and dissolved bound nitrogen (DNb) after high temperature catalytic oxidative combustion

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