### Challenge

High-temperature TOC analysis in samples with high salt content is a challenge for the analyzer in terms of its matrix tolerance and the longevity of the consumables

### Solution

The multi N/C 3300 high-temperature TOC analyzer in combination with a salt kit enables routine analysis of highly saline samples with reduced maintenance requirements

### Intended audience

Desalination plants, food industry (meat processing), road salt manufacturer, contract labs

# TOC Determination in Brine Samples coming from Desalting Process of Crude Oil

## Introduction

Crude oil always contains salt, either dissolved in water droplets or in form of crystalline salt. Since salt contents can cause problems by forming precipitates, accelerating corrosion processes or catalyst degradation during the refining process, crude oil is undergoing a desalting process. By-product of this process is water of high salt concentrations up to 26% of mostly NaCl (smaller amounts of $CaCl_2$ and $MgCl_2$), so-called brine. Brine, as a product of petrochemical industry, is a starting material in other industries, e.g. as refrigerating/freezing agent in food industry or in de-icing processes. One of the quality criteria for the further use of brine is its TOC content. Analysis of brine for TOC content is an important, however challenging task. Quartz components of the TOC analyzer as well as the platinum catalyst are exposed to the destructive influence of this heavily salt loaded water sample.

The common TOC analysis technique uses an oxidation process at 800 °C and above.
At this temperature the melting of NaCl takes place. Salt deposits inside the combustion tube lead to a devitrification of quartz, a fast consumption of the platinum catalyst and gas flow blockages, thus causing high maintenance costs.
To overcome these difficulties, the use of a so-called salt kit can clearly increase the service life of the most affected parts of the analyzer. 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.
In combination with a lower combustion temperature, the salt kit has been proven to deliver reliable analysis results, improve long-term stability and significantly reduce maintenance.

# Materials and Methods

The determination of TOC was carried out using the NPOC method on the multi N/C 3300. The NPOC (non-purgeable organic carbon) method is preferably used if no volatile or purgeable organic compounds are to be expected in the sample. For the determination of NPOC, the samples are first acidified manually or automatically by an autosampler and then purged with an auxiliary gas. This process removes the TIC (total inorganic carbon in the form of carbonates/hydrogen carbonates) from the samples. The completeness of the TIC removal can be checked automatically by activating the TIC control measurement in an NPOC method. After removal of the TIC the sample is then 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 this process is transferred to the FR-NDIR (focus radiation non-dispersive infrared) detector. For the automated determination of TOC, the sampler AS vario was used in combination with a tray for 72 samples of 40 mL each.

## Samples and reagents

- 2 brine samples
- 2 mol/L HCl for acidifying samples and standards
- Stock solution 1000 mg/L TOC (potassium hydrogen phthalate in ultrapure water) for preparing the calibration solutions and for spiking the synthetic brine
- Calibration standard solutions with concentrations from 0.5 mg/L to 10 mg/L TOC (potassium hydrogen phthalate in ultrapure water)
- Synthetic brine (140 g/L sodium chloride in ultrapure water)

## Sample preparation

The two brine samples were stored in the refrigerator at approx. 4 °C until they were measured. After warming to room temperature, the samples were diluted 1:10 with ultrapure water, filled into 40 mL sample vials and placed on the tray of the autosampler. The samples were acidified during the dilution step. For this purpose, 0.5 mL 2 mol/L HCL was added to 10 mL of the original sample and made up to 100 mL with ultrapure water. For a large number of samples, automatic dilution and acidification using the AS vario autosampler is recommended. To test the long-term stability of the analyzer for samples with a high salt load, the synthetic brine was also diluted 1:10, acidified and spiked with 2 mL of the TOC stock solution. The TOC concentration in this solution was 2 mg/L.

## Calibration

The multi N/C 3300 was calibrated for NPOC measurement in the range from 0.5 to 10 mg/L C with standard solutions of potassium hydrogen phthalate in ultrapure water. A multi-point calibration type was used. The calibration curve and its characteristics are presented in Figure 1.

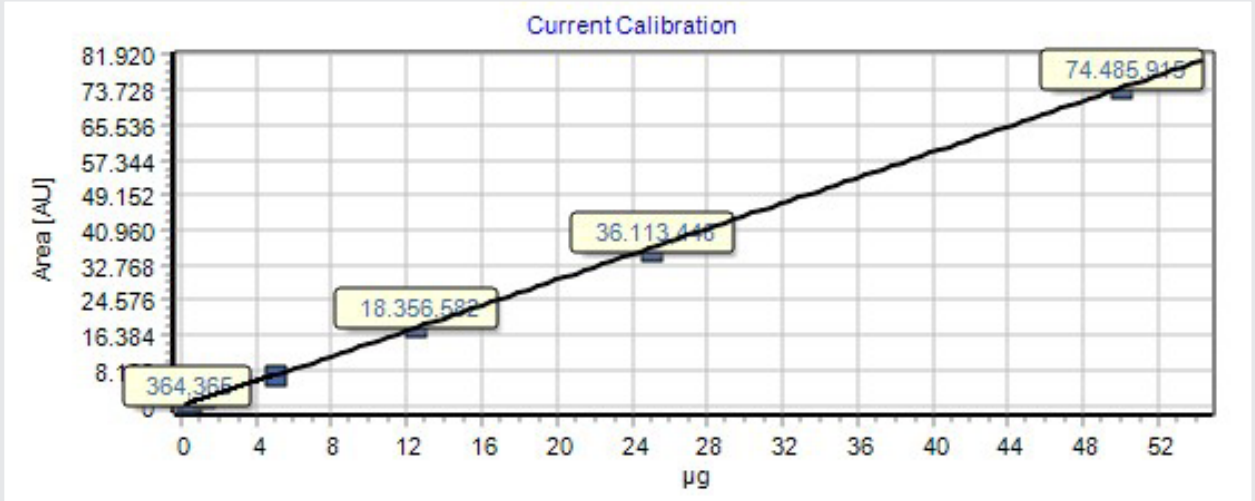


Figure 1: Calibration curve 0.5 – 10 mg/L TOC and characteristics of calibration: LOD = 0,026 mg/L, LOQ = 0,103 mg/L, $R^2$ = 0,99997

### Instrumentation and method settings

Table 1: Instrument and method settings for brine samples

| Parameter | Settings on multi N/C 3300 |
|---|---|
| Method of determination | NPOC with TIC control |
| Sample digestion | Catalyst-assisted high-temperature combustion (Pt) |
| Digestion temperature | 680 °C |
| Carrier gas | Synthetic air (free od $CO_2$ and hydrocarbons) |
| Number of replicates from one sample vial | min. 3, max. 4 |
| 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 |
| NPOC purge time (removal of TIC) | 180 s |

These settings were used to measure the two brine samples.
Since the spiked synthetic brine was used to show the long-term stability of the measurement performance and of specific analyzer components, the method settings were adopted as shown in table 2.

Table 2: Method settings for synthetic brine spiked with 2 mg/L TOC

| Parameter | Settings on multi N/C 3300 |
|---|---|
| Number of replicates from one sample vial | min. 10, max. 10 |
| Number of rinses with the sample before the first injection | 1 |

## Results and Discussion

The two brine samples from the oil desalination plant were each measured in triplicate from one sample vessel. The synthetic brine spiked with TOC was injected and analyzed 1000 times in a long-term test. The blank value of the synthetic brine (without TOC spiking) was determined beforehand in order to determine the proportion of TOC contributed by the salt solution. This blank value was stored in the software as a so-called eluate blank value. When measuring the spiked synthetic brine, the eluate blank value was automatically taken into account and subtracted from the measured TOC value.
The results are summarized in Table 3.

Table 3: TOC results

| Sample Description | Mean value TOC ± SD [mg/L] | Number of replicate measurements | RSD [%] |
|---|---|---|---|
| Brine Sample A from crude oil desalination | 23.7 ± 0.31 | 3 | 1.3 |
| Brine Sample B from crude oil desalination | 7.9 ± 0.14 | 3 | 1.8 |
| Blank value of synthetic brine | 0.55 ± 0.02 | 3 | 3.6 |
| Synthetic brine, spiked with 2 mg/L TOC | 2.01 ± 0.04 | 1000 | 2.0 |

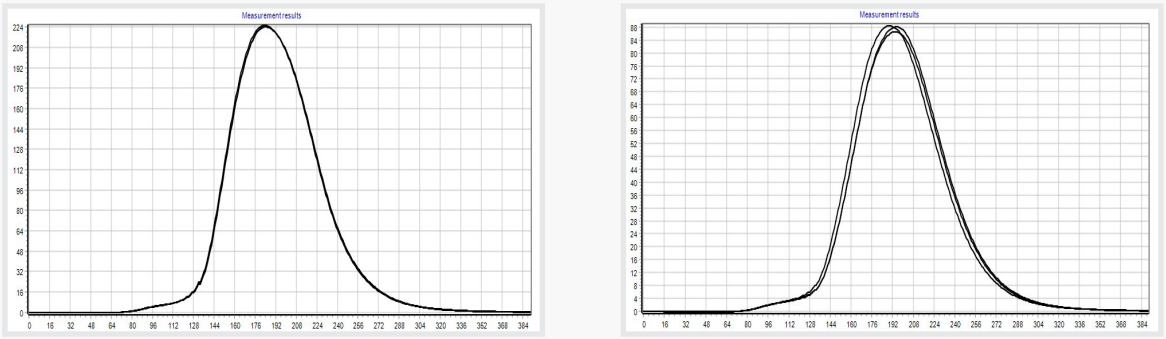


Figure 2: Measuring curves of brine sample A and B

The results prove that the TOC in brine samples can be determined with very good reproducibility. The long-term measurement of the spiked synthetic brine shows that the analysis system delivers very stable TOC values with low scatter over a long period of time, even with a high salt load. This is illustrated by the diagram in Figure 3, where 50 consecutive measuring values were combined to form a TOC mean value, from which the standard deviation was calculated and both values were shown as points in the graph. The highest standard deviation determined was 0.03 mg/L (n=50), which corresponds to a maximum RSD of 1.5%. The RSD calculated over all 1000 measured values was 2%, which underlines the excellent stability of the analysis system.

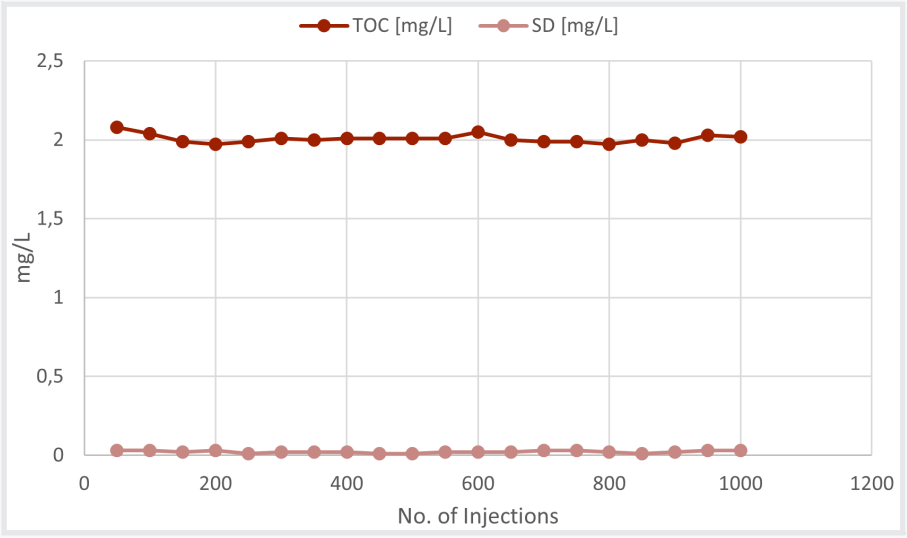


Figure 3: TOC values and standard deviation of the synthetic brine spiked with 2 mg/L over 1000 injections of 0.5 mL each

Figures 4 and 5 show the salt kit before and after loading with more than seven grams of salt. The salt introduced collects almost completely in the quartz crucible above the catalyst and thus prevents the catalyst from becoming clogged and the associated loss of performance, such as decreasing recovery rates and increased scattering of results. On the other hand, blockage of the gas flow and premature devitrification of the combustion tube is avoided. The salt trap can be emptied and cleaned in a few simple steps when the combustion tube has cooled down. At the same time, the catalyst and combustion tube can be rinsed with ultrapure water and then dried. Even after a high number of brine injections, the devitrification on the tube itself is extremely low, so that a very long service life can be assumed.

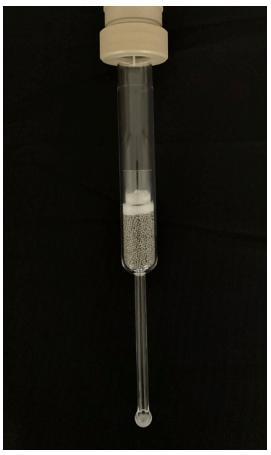

Figure 4: Salt kit, freshly filled

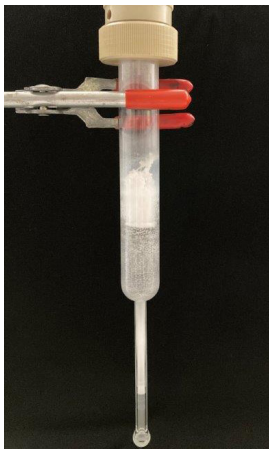

Figure 5: Salt kit, after loading with > 7 g salt

Figure 6: Salt trap new and after emptying the salt

## Summary

In combination with the salt kit, the multi N/C 3300 is ideally suited for analyzing the TOC content of saline samples such as brines or seawater. The stability of the measured values is ensured even when high salt loads are introduced. Long service lives of the catalyst and the combustion tube are achieved. Cleaning or changing the salt trap is quick and easy. This ensures reliable and economical routine analysis for the determination of TOC in difficult, saline matrices at all times.

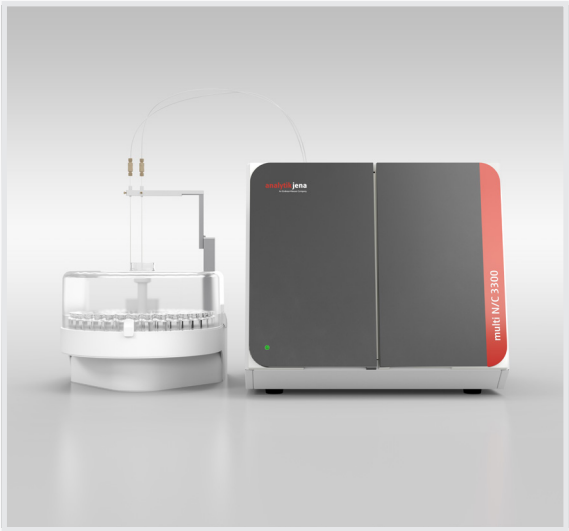


Figure 7: multi N/C 3300

## Recommended device configuration

Table 4: 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 |



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