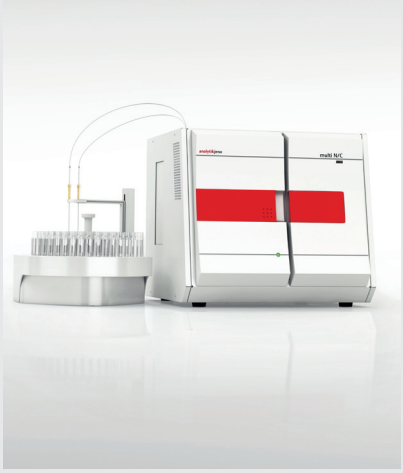

Challenge

To improve stability of results and prolong maintenance cycles for TOC analysis in high saline samples.

Solution

Reduction of maintenance issues by optimization of the combustion process, TOC method settings and sequence setup.

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 fluid, in water purification or 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 expensive 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. 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 common technique and method have been improved. An optimized construction of the combustion tube, the use of a special catalyst filling and a reduced combustion temperature (750 °C) proved to deliver reliable analysis results, improve long-term stability and prolong the lifetime of the components.

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Instrumentation

The analysis has been run with the multi N/C® 3100 TOC analyzer using the non purgeable organic carbon mode (NPOC). The samples have been diluted 1:10 to achieve best analytical performance for this sample matrix.

Table 1: Analyzer specifications: multi N/C® 2100S and mutli N/C® 3100

Parameter	Specification Analyzer
Parameter	TC, TOC, NPOC, POC, TIC and TN_b
Norm	DIN EN 1484, DIN EN 12260
Detection	Focus Radiation NDIR, Chemolumineszenz Detection (CLD) or electrochemical detection (ChD)
Digestion	Thermocatalytic up to 950 ° C
Sample feeding	Direct injection/ flow injection
User confidence and comfort	multiWin® control and evaluation software, VITA® technology, self-check system, etc.
Measuring range	multi N/C® 2100S: Carbon: 50 ppb-30000 ppm, multi N/C® 3100 Carbon: 4 ppb-30000 ppm Nitrogen: 5 ppb-200 ppm (CLD) or 50 ppb-100 ppm (ChD)
Injection volume	multi N/C® 2100: 50- 500 µl multi N/C® 3100: 100-1000 µl
Measuring time	appr. 3-5 min
Autosampler	AS 60 (8 ml or 2 ml vials) or AS Vario (40 ml, 20 ml or 12 ml vials)
Gas supply	Oxygen 4.5 or better, alternatively: HC- and CO_2-free synthetic air

Method settings

The following method settings were used to determine the TOC content:

Table 2: Method settings

Parameter	multi N/C® 2100S, multi N/C® 3100
Measurement parameters	NPOC
Digestion	High temperature digestion at 750 ° C with platinum catalyst
Number of single repetitions	min.2, max. 3
Rinse with sample before injection	3 times
Injektion volume	200 µl
Dilution	1:10

Samples and Reagents

Prior to analysis the sample is automatically acidified with 2 M HCl and subsequently purged with synthetic air/pure oxygen. This ensures a complete removal of the TIC. The subsequent NPOC measurement is carried out with the aid of an autosampler, as described in table 1.

The method setup was optimized by reduction of the sample injection volume to max. 200 µl (instead of 500 µl for standard applications). This reduces the salt load onto the combustion tube siginificantly, while maintaining a very good TOC measurement sensitivity. During the oxidation process all carbon compounds are quantitatively converted to CO_2.

The wide-range Focus Radiation NDIR detector is used for the determination of the carbon content.

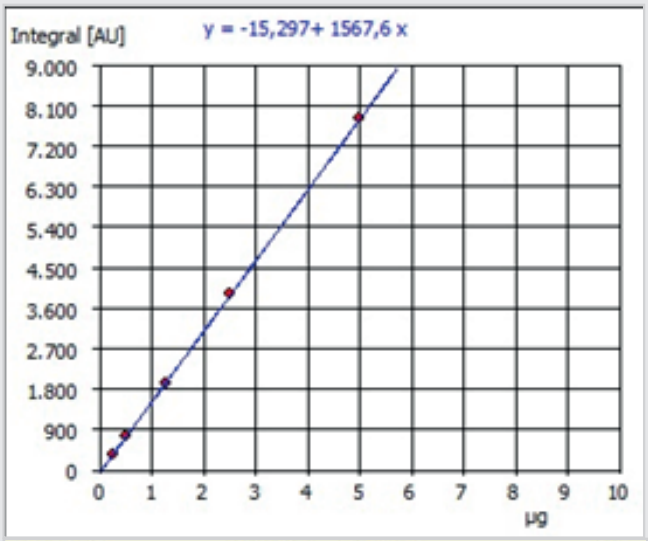
The measurement sequence was supported with the auto sampler AS Vario, which provides parallel purge and analyzing for highest sample throughput and operation comfort.

This application can be performed in the same way using a multi N/C® 2100S with autosampler AS 60 in sequential purge and analyzing mode.

Calibration

The multi N/C® analyzer was calibrated for NPOC measurement in the range 0.5 - 10 mg/l C with standard solutions of potassium hydrogen phthalate. A multi-point calibration type was used. The calibration curve and its characteristics are presented in the figure 1 below.

Calibration Curves



Residual SD:	26,657AU	Linearity:	OK
Method SD:	34,01µg/l	Variance homogeneity:	OK
Method VC:	0,89497%	Detection limit:	70,35µg/l
Qual. of rep.:	0,99994	Identification limit:	140,7µg/l
Correl. coeff.:	0,99997	Quantification limit:	280,6µg/l

Figure 1: NPOC calibration curve and characteristics, range 0.5-10 mg/L

Results and Discussion

Two samples and one NPOC standard were measured for carbon content. The sequence was set up to have an ultra pure water sample after every 5th sample measured to regularly clean the combustion tube from excessive salt deposits. Each sample has been measured at minimum by triplicate injection. The analysis results are summarized in table 3. Examples of the measured curves are shown in figure 2 and 3 below.

Table 3: Results

Sample ID	Dilution ratio	Mean value NPOC [mg/L]	NPOC RSD [%]
Sample A	1:10	23.7	1.3
Sample B	1:10	7.9	1.8
TOC control 2.0 mg/l	no	2.1	0.7

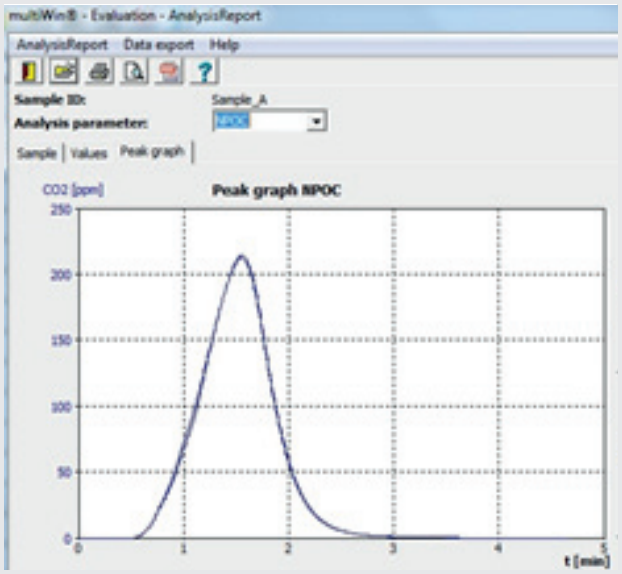


Figure 2: Sample A – Example of analysis curve

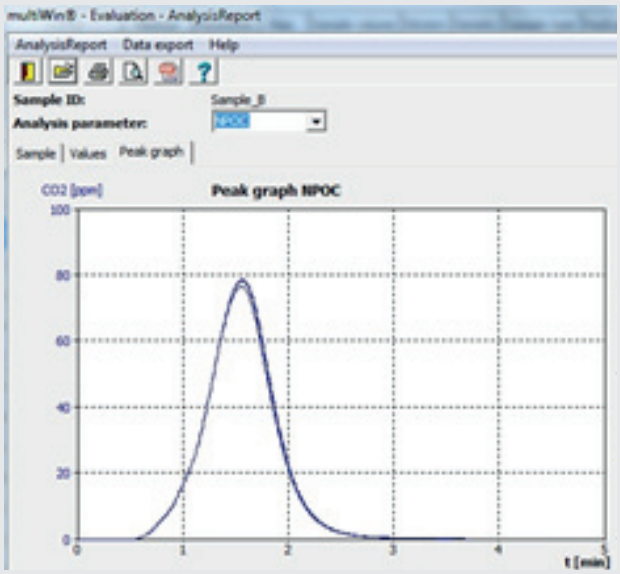


Figure 3: Sample B – Example of analysis curve

The long term stability for the method applied – crucial for extreme matrices with high salt loads – was evaluated as well. A synthetic brine solution, prepared from sodium chloride and ultra-pure water, was spiked with an NPOC standard to have a 2.0 mg/l TOC concentration in the 1:10 dilution. After every 5th brine sample ultra-pure water was inserted into the sequence for rinsing purpose. Almost 800 injections have been run without loss in recovery rates, see figure 4, and without any maintenance. The results have been within the normally expected range of ± 5 % deviation from the nominal concentration.

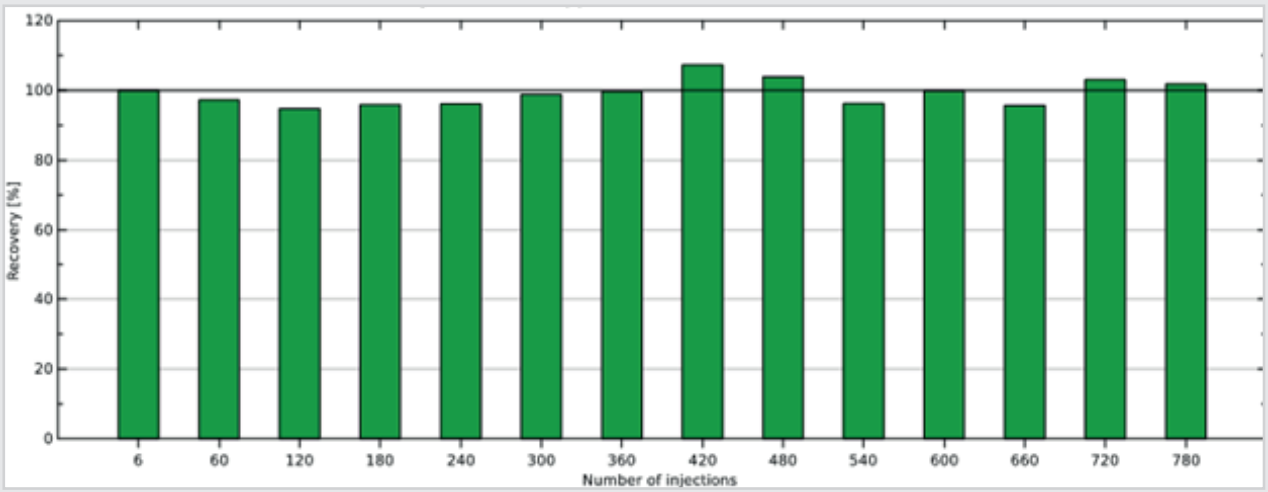


Figure 4: Recovery rates of the 2.0 mg/l NPOC standard material

Figure 5: New filling of the combustion tube (high temperature mat, Pt-catalyst and Pt-grid on the bottom)

Figure 6: Combustion tube after 800 brine injections (salt deposits on the colder exit part of the tube)

Figure 7: Re-dissolving the salt crystals by immersion into ultra-pure water

The above pictures 5-7 show the salt throughput capability of the combustion tube used. Salt aerosols are effectively transported through the combustion tube filling to be condensed and washed off partially at the colder exit part of the combustion tube. This effectively avoids gas blockages due to salt deposits piling up inside the filling, thus providing long maintenance cycles.

Conclusion

The multi N/C® 3100 and multi N/C® 2100S with specially optimized method settings and sequence setup can be applied for the TOC measurement of most challenging brine samples. This application successfully demonstrates that high salt loads do not compromise analysis results or the long term stability.

The use of an autosampler, AS Vario enables a high sample throughput and provides comfortable and fast measurements in NPOC mode with automatic acidification and sample purge in “parallel purge & analysis mode”.

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