Challenge
How to overcome difficulties to analyze brine samples on combustion-based TOC analyzers regarding high wear and tear on consumables as well as high sample variance and poor recoveries.

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
Salt and lithium mining industry, contract labs, or high saline sample testing.

Analysis of the Total Organic Carbon Content in Reinjected Brines from a Direct Lithium Extraction Process Utilizing the multi N/C 3300

Introduction

Lithium's exceptional conductivity properties have made it indispensable across a wide range of applications. Extracted lithium products are used in heat-resistant materials, as components in pharmaceutical drugs, and, most notably, in the production of batteries for electric vehicles, consumer electronics, and other devices. The widespread adoption of lithium-ion batteries (LIBs) is primarily due to their superior energy storage capabilities compared to other rechargeable battery technologies. However, with the increasing demand for sustainable energy solutions, the global lithium supply is under significant strain as existing reserves are depleted at an accelerated pace. Lithium mining offers a pathway to meet this growing demand through various extraction techniques, the most prominent being solar extraction and direct lithium extraction (DLE). Solar extraction, a traditional method, involves harvesting lithium from salt-lake brine through a lengthy evaporation process. Alternatively, DLE employs advanced selective adsorption materials to extract lithium more efficiently from brine water.

At our customer, a proprietary resin is used for lithium extraction. This resin undergoes a series of processing steps, including washing with process water, concentration using recycled oil, and secondary washing. The resulting compound, lithium chloride, can then be converted into lithium hydroxide or lithium carbonate. Lithium carbonate, produced through a precipitation process, is widely used in ceramics and as a key component in battery cathodes. Lithium hydroxide, another essential material for battery production, is obtained from lithium chloride through membrane technology. This process splits water into hydrogen and hydroxide ions, which then combine with lithium ions.

A key advantage of the DLE process is its potential for environmental sustainability. Unlike traditional methods, DLE allows for the reinjection of treated brine into the original underground reservoirs, mitigating long-term environmental impacts. However, one of the primary concerns with expanding lithium mining operations is the significant water consumption and land use required for these processes. To address these challenges, DLE operations have developed filtration methods to improve the quality of spent brine before reinjection. The effectiveness of this filtration process is often measured by the total organic carbon (TOC) content in the treated brine.

In the scope of this work, TOC analysis by high-temperature combustion according to EPA 9060A[1]) was utilized. For this analytical method, brine samples pose unique challenges due to their high total dissolved solids (TDS) content, which can reduce the lifespan of consumables, cause clogs, and result in salt precipitation that impacts recovery rates. To overcome these issues, a robust system designed for high-TDS samples and capable of particle handling is essential. Furthermore, to ensure the reinjected process water meets environmental standards, the system must achieve reliable quantification of TOC at lower ppm levels.

Materials and Methods

Samples and reagents

- DI water for the preparation of standards and samples, ASTM Type 2
- 1000 mg/L KHP (ACS, RICCA®) stock solution
- QC 10: 10 mg/L control solution (KHP)
- QC 1: 1.0 mg/L control solution (KHP)
- 36% HCl (ACS, VWR BDH®)
- 21 pre- and post-treatment process samples

Sample preparation

Our customer provided pre- and post- treatment samples from their organic carbon removal process. The pH of samples was adjusted by acidification with HCl to pH <2. This was done to preserve the samples and ensure no bacterial growth took place.
Samples were diluted 1:4 in DI water inside 40 mL vials. A stirring bar was placed inside of the vial to ensure homogeneity during analysis. Then, the vials were sealed by aluminum septa to prevent contamination from the environment.

Calibration

Calibration standards were prepared from a 1000 mg/L Potassium Hydrogen Phthalate stock solution using DI water. The calibration range extended from 0.5-500 mg/L. This is to accommodate the large variance in concentrations from the pre- and post-treatment samples. Standards were transferred to 40 mL vials, which were covered with aluminum septa as well and placed on the autosampler tray.

One of the functions of the multiWin pro software, outlined in Figure 2, is allowing the calibration to split into multiple ranges. This assists with maintaining linearity over a wide working range and to run the pre- and post-treatment samples with their different concentration levels by the same method without additional dilution. This splitting function also ensures that it is possible to quantify samples at the lowest end of the calibration range with confidence, allowing for the detection limit of 40.95 µg/L seen here. For all three ranges, strong linearity was achieved (r^2 >0.9999).

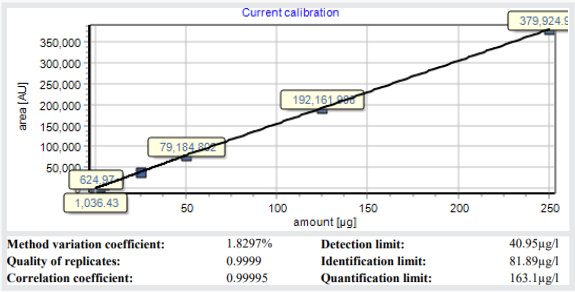

Figure 1: Full calibration curve with calibration characterisitcs from 0.5- 500 mg/L, prepared from KHP standard. Curve was split into three ranges.

Instrumentation

For this analysis, the multi N/C 3300 was selected as the optimal solution. The multi N/C 3300 is a flow injection TOC/TN_b analyzer utilizing catalyst-assisted high-temperature combustion for complete organic carbon oxidation to carbon dioxide. Quantitative CO_2 detection is done by the wide range Focus Radiation NDIR detector. With its 0.8 mm inner diameter tubing, the multi N/C 3300 can handle samples with larger particle sizes. To reduce down-time between runs and prevent carry-over risks, the analyzer is also equipped with reverse-rinse capabilities that wash the sample tubing during analysis. In the case of salt applications, the reverse rinse has the added benefit of preventing salt crystallization in the lines. For sample introduction the AS vario ER autosampler was used. Its external needle rinse function cleans the outside of the sample uptake needles, which come in direct contact with the brine samples, with DI water, preventing salt crystallization.

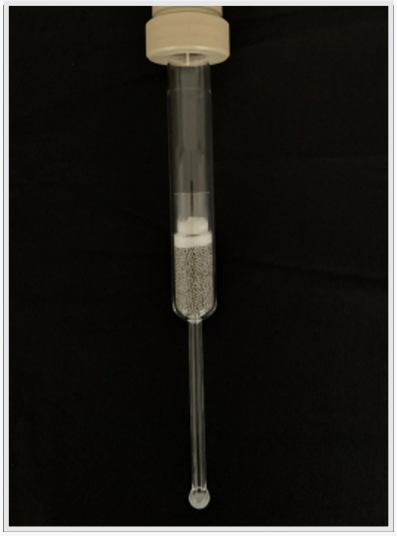

Figure 2: Image of the salt combustion tube, part of the salt kit.

For this application the multi N/C 3300 was upgraded with a salt kit, shown in Figure 2, to aid in the longevity of consumables. It is composed of a 26 mm quartz combustion tube, a quartz crucible to collect salt precipitates, corrosion-free furnace head and injection needle, high temperature mat, platinum net, and platinum catalyst. This kit is designed to prevent clogging caused by salt deposits over daily runs, ensuring longer, uninterrupted analysis. There is the added benefit of being able to inject larger volumes, ensuring it is possible to reach lower limits of detection, in accordance with EPA 9060A, which requires a method detection limit of 1 mg/L.

Instrument settings and method parameters

This analysis was performed on the multi N/C 3300 utilizing the NPOC method, also known as the direct method. This entails the automatic acidification of samples with HCl, followed by the purging of the sample, with gas, to remove inorganic carbon compounds. This NPOC method was chosen over the differential method (TC-TIC), due to the high inorganic carbon content in the customer's samples. A TIC control was taken before the first determination to ensure the inorganic content was successfully purged. An expectation was set that the TIC control should be <1% of the sample's TOC reading. Since the pre-treated samples often had visible particles, automatic sample homogenization by a magnetic stir bar was used to ensure representative sample uptake occurred.
When analyzing brine samples, it is widespread practice to utilize lower furnace temperatures, compared to standard aqueous samples, to prevent clogging caused by salt melts. Due to this, a furnace temperature of 680 °C was chosen.

Table 1: Instrument and method parameters used for the analysis of customer-provided samples by multi N/C 3300.

Parameter	Specification	Parameter	Specification
Analysis type	NPOC	Furnace temperature	680 °C
Reverse rinse Counts	2 (DI water)	Max integration time	350 s
Rinse volume	2000 µL	Determinations	3-5
Sample volume	500 µL	Purge Time	900 s
TIC control	active	Stir Level	3

Results and Discussion

For the calculation of TOC content, the area unit of the peaks is used to correlate the content to the total concentration within the sample. Three representative samples of varying concentrations were chosen that highlight this in Figures 3, 4, and 5 below, with each TOC figure containing 5 replicates. In Figures 4 and 5, the TOC peaks from pre- and post-treated samples are seen. In Figure 6 the TIC control measurement peak of a pre-treated sample with high expected concentration of inorganic carbon is shown. It has a noticeably reduced area compared to the previous TOC peaks, which represents the effectiveness of the purging process used in the NPOC method. The repeatability of the TOC peaks, through multiple determinations, indicates minimal variance between runs, even for the lower concentration in Figure 5.

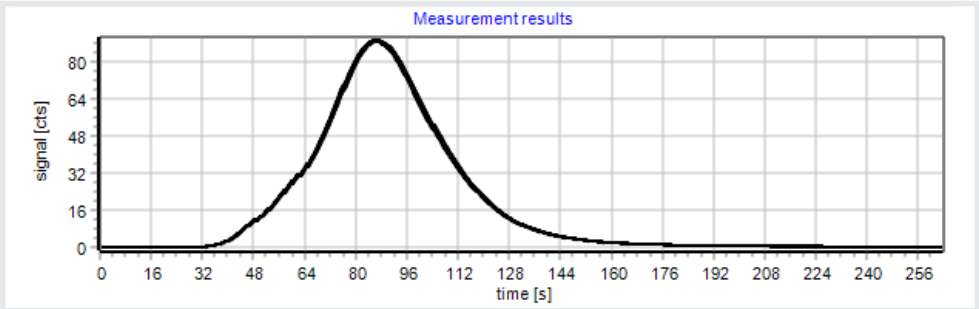

Figure 3: TOC graph for a 10 mg/L KHP QC. This showcases a representative peak, characteristic of this application and combustion tube.

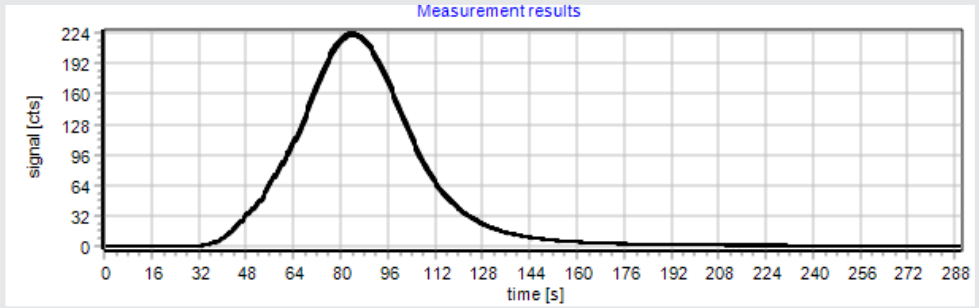

Figure 4: Representative TOC graph from a pre-treatment sample. Concentration is 33.0 mg/L.

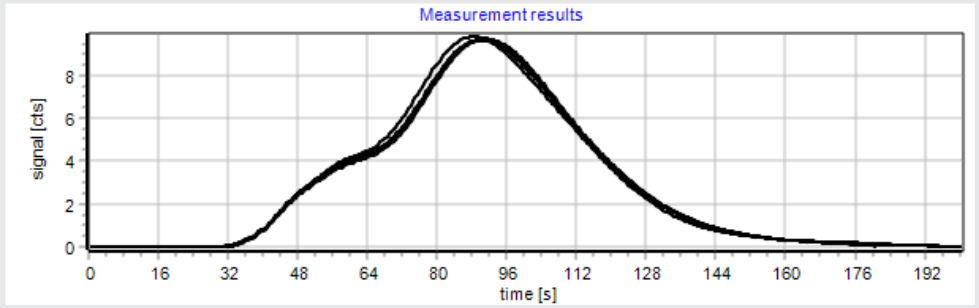

Figure 5: Representative TOC graph from a post-treatment sample. The concentration is 2.05 mg/L.

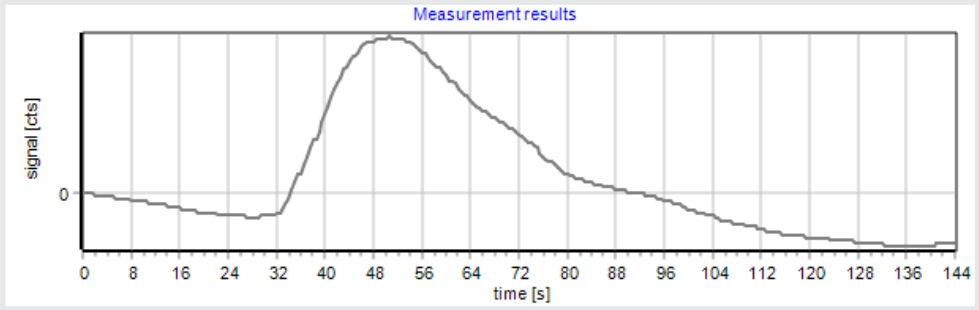

Figure 6: Representative TIC control peak from a pre-treatment sample.

The resulting concentrations of the pre- and post-treatment samples are in Table 2 and 3 below. The range was between 0-500 mg/L, depending on sampling location and treatment. For all samples a TIC control was run, which all showed <1% TIC content, compared to the TOC content of the sample. This indicated that sufficient purging had occurred at the start of the NPOC measurement. Recorded NPOC RSDs were <3% throughout the entirety of the run, showcasing the stability of the system. Since the concentrations of each sample were unknown, samples can switch from a higher to lower concentration during the analysis sequence, which might cause higher RSDs and worse QC recoveries. The low RSDs achieved, therefore proof a lack of noticeable carry-over between runs, showing the success of the reverse rinse, salt kit, and sample digestion working together.

To ensure the system was at optimal performance throughout the analysis, and the calibration was valid, high (10 mg/L) and low (1 mg/L) QCs were run between every 5-6 samples. For both the 1 mg/L and 10 mg/L KHP QC, it can be observed that the recoveries remained at +/- 5% of their expected value. Additionally, the recoveries of these measurements are indicative of the long-term stability of the system as there was very little variance observed during the run. An additional graphical representation of the stability of the QCs, over an 8-hour run, can be viewed below in Figure 7.

Table 2 and 3: The NPOC results of the samples are shown in the below tables, along with RSD and QC recoveries for the relevant standards.

Sample	Results NPOC (mg/L)	RSD (%)	Recovery (%)
QC 10	10.16	0.64	101.6
QC 1	1.00	0.18	100.0
S1	9.68	0.54	-
S2	10.30	2.06	-
S3	22.44	0.93	-
S4	33.00	1.42	-
S5	17.47	1.45	-
S6	16.69	0.37	-
QC 10	9.62	0.58	96.2
QC 1	0.962	1.50	96.2
S7	183.4	0.65	
S8	131	0.78	

Sample	Results NPOC (mg/L)	RSD (%)	Recovery (%)
QC 10	9.68	0.72	96.8
QC 1	0.958	2.46	95.8
S12	233.5	0.17	
S13	97.25	1.35	
S14	108.4	0.27	
S15	458.1	0.39	
S16	150.4	1.25	
QC 10	10.30	0.30	103.0
QC 1	0.989	1.47	98.9
S17	7.42	1.44	-
S18	<Cal	NA	-
S19	2.05	2.84	-

Sample	Results NPOC (mg/L)	RSD (%)	Recovery (%)
S9	74.22	1.85	
S10	197.4	0.12	
S11	36.08	0.92	

Sample	Results NPOC (mg/L)	RSD (%)	Recovery (%)
S20	3.41	2.34	-
S21	7.43	2.27	-
QC 10	10.17	0.33	101.7
QC 1	1.00	0.18	100.0

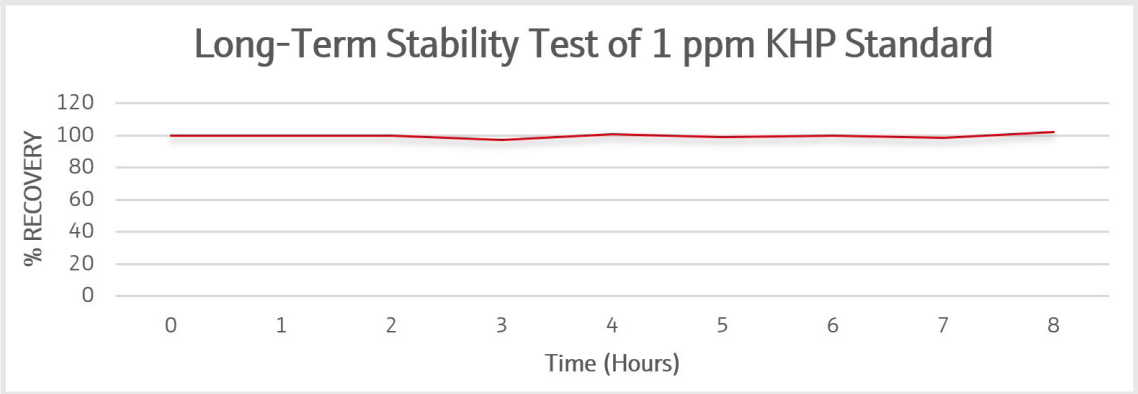

Figure 7: Graphical NPOC representation composed of 9 standards of the 1 mg/L QC, interspersed throughout the high brine analysis over the duration of an 8-hour sample run.

As a method validation test, matrix spiked samples were produced for the lower concentrations to ensure the method was suitably sensitive for the needs of our customer. In Table 4, the results of this testing can be seen. Our customer provided a low-level spike, while the other spikes were prepared in the Analytik Jena application lab, using a KHP standard. The spike recoveries were between 90-100%, validating the method's accuracy and showcasing the system's ability to adequately quantify to low ppm levels even in difficult brine matrices.

Table 4: Representative customer samples were spiked with various concentrations as a method validation step. Recoveries were within +/- 10% of the expected value.

Sample name	Spike concentration (mg/L)			Spike recoveries (%)		
	Conc. 1	Conc. 2	Conc. 3	Recovery 1	Recovery 2	Recovery 3
Customer spike	0.25	-	-	99.0	-	-
S17	5.0	-	-	90.0	-	-
S20	1.0	-	-	108	-	-
S19	1.0	2.5	5.0	92.0	108	103.4
S21	5.0	-	-	95.8	-	-

Summary

Traditionally, brines have presented difficulties for catalytic high-temperature combustion TOC analyzers due to wear on instrument consumables, leading to instrument instability. However, with the multi N/C 3300 and the salt kit, these obstacles can be overcome. The system's ability to handle the high-salt matrix can be seen in the low RSDs (<3%) achieved throughout the run, proving that strong precision is possible. This is further evident when switching from high to low concentrations. Furthermore, the addition of the salt kit, reverse rinse function, and low furnace temperature prevented the formation of salt melts and clogs, allowing for higher injection volumes to achieve the necessary low LODs. These features also allowed for excellent recoveries over the course of 8 hours, showcasing the impressive matrix-handling capabilities.

To validate the method, matrix spikes were performed, with recoveries +/- 10% of the expected values, meaning that this instrument can provide accurate results at the low levels. The system's robustness, sensitivity, and wide-linear range make it ideal for the routine analysis of process brines to be reinjected underground after direct lithium extraction. The used salt kit with the high TDS combustion tube for this application can also be upgraded to older multi N/C 3100 analyzers, see order number in the table below.

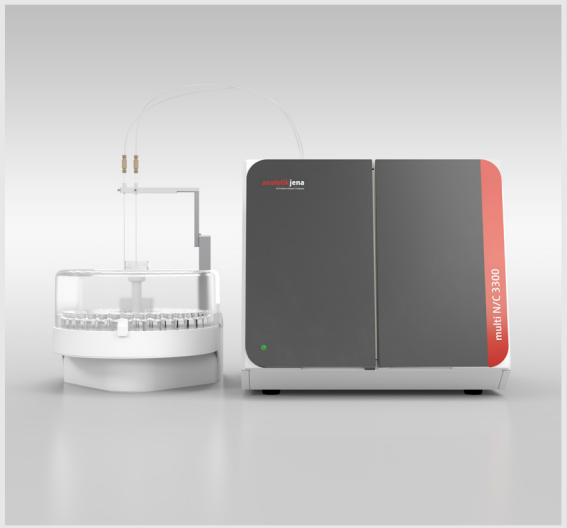

Figure 8: multi N/C 3300 with AS vario ER.

Recommended device configuration

Table 5: Overview of devices, accessories, and consumables.

Article	Article number	Description
multi N/C 3300	450-500.500-2	TOC analyzer with flow injection technique
AS vario ER autosampler	450-900.148	Autosampler for multi N/C 3300 with external needle cleaning
Salt kit for multi N/C 3300	450-500.550	High TDS kit, containing 26 mm combustion tube, salt collection crucible, corrosion-free furnace head and injection needle. Also upgradeable at multi N/C 3100.

References

[1] U.S. Environmental Protection Agency. (1994). Method 9060A: Total Organic Carbon (TOC) (Rev. 1). Washington, DC: EPA. Retrieved January 24, 2025, from https://www.epa.gov/sites/default/files/2015-12/documents/9060a.pdf.

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