



Challenge

The high-temperature determination of low TOC concentrations in high-salt matrices places high demands on the analytical system used regarding its detection strength and matrix tolerance

Solution

The high-temperature TOC analyzer multi N/C 3300 allows the routine analysis of lowest TOC concentrations in high salt samples

Intended audience

Manufacturers of raw materials (salts) for cathode materials for LIB, cathode manufacturers, LIB manufacturers, battery recycling companies

Determination of Organic Impurities (TOC) In Raw Materials for Cathode Production in Lithium-Ion Batteries (LIB)

Introduction

Lithium-ion batteries (LIB) consist of a cathode, an anode, a separator, the electrolyte and finally the cell housing. The main cost factor in the production of battery cells are the raw materials used. The cathode material is usually the most expensive component of the entire battery. For cathode production, active material, which is used to store the lithium ions, is applied to aluminum foil. The composition of the active material can vary and is the subject of current cathode research to make LIB even more powerful and energy rich. So far, the following cathode materials are established in the market: NMC (lithium nickel manganese cobalt oxides), NCA (lithium nickel cobalt aluminum oxide), LFP (lithium iron phosphate) and LMO (lithium manganese oxide). The production of the active materials is usually a multi-stage process, the starting materials of which are usually salts of the characteristic metals. For example, nickel sulfate, manganese sulfate, cobalt sulfate, and lithium carbonate (or lithium hydroxide) are used for NMC production. These salts

must be "battery-compatible", i.e., they must have a certain purity. The lower the degree of impurity of the raw materials, the lower the risk that electrochemically inert phases can form. These can impede the transport of the Li ions and thus reduce the reversible capacity and thus the performance of the battery. For this reason, these salts are often offered in "battery grade" quality. The contamination of the salts with trace amounts of undesirable metals (such as Ca, Mg, Na, Fe, Cu, Zn, etc.) and with organic substances is lower here than with salts of other purity grades such as "technical grade". Like laboratory chemicals, the exact specifications of the "battery grade" quality are defined and specified by the manufacturers and may therefore differ. While trace concentrations of metal impurities are usually determined using ICP-OES, the sum parameter TOC (total organic carbon) is suitable for the analysis of organic impurities. For this purpose, the salt to be analyzed is simply dissolved in distilled water and then analyzed using a TOC analyzer for

aqueous samples. For TOC determination, high-temperature digestion followed by NDIR detection of the carbon dioxide formed from the organic compounds is the method of choice for many applications. However, the salt-rich matrix has an effect on the combustion tube and the catalyst it contains, as higher wear due to oxide formation and deposition of salts must be expected. This paper shows how the wear of the affected components of the analyzer can be significantly

reduced by minimizing the salt load and using a special salt kit. All measurements were carried out with the TOC analyzer multi N/C 3300, which offers the best conditions for the determination of TOC in difficult matrices due to its detection strength and flexibility regarding sample handling and method setting.

Materials and Methods

The determination of TOC was carried out using the NPOC method on the multi N/C 3300. This method for the determination of the TOC 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 with the aid of an autosampler (\leq pH 2, using 2 M HCl) for decomposition of the carbonates/hydrogen carbonates and subsequently the resulting CO_2 and thus TIC (total inorganic carbon) is automatically removed by the purge with an auxiliary gas. The completeness of the removal of the TIC from the sample can automatically be checked by the activation of the TIC control measurement in a NPOC method. A first replicate is then injected to the TIC reactor, where residual CO_2 is released by acid reaction and the gas purge and subsequently detected by the NDIR. Then, the sample is directly injected into the combustion tube of the salt kit filled with catalyst. The organic compounds 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. After a previous calibration of the analyzer, the TOC content of the sample is given in mg/L.

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

- 5 salts: Li_2CO_3 , $\text{CoSO}_4 \times 7 \text{H}_2\text{O}$, $\text{CoCl}_2 \times 6 \text{H}_2\text{O}$, $\text{MnSO}_4 \times \text{H}_2\text{O}$, $\text{NiSO}_4 \times 6 \text{H}_2\text{O}$
- Distilled water for the preparation of the salt solutions
- 2 M HCl for acidifying the salt solutions
- Stock solution 100 mg/L TOC of potassium hydrogen phthalate (KHP) to spike the salt solutions
- Calibration standard solutions with TOC concentrations from 0.5 mg/L to 5 mg/L TOC (KHP)
- Control standard, 1 mg/L TOC (KHP)

Sample preparation

All the salts investigated - except for the lithium carbonate - have a very good water solubility, which is > 300 g/L for all of them. The expected TOC concentration of the salts was < 20 mg/kg. With the aim of keeping the matrix load for the analyzer as low as possible and at the same time obtaining an evaluable signal for the TOC, aqueous solutions of 100g/L salt each were first prepared. Due to the poorer water solubility of lithium carbonate, 2 M HCl was used to prepare the solution, with 20 g/L Li_2CO_3 in solution in the first step. The final HCl concentration in this solution was 1 mol/L. 50 mL of each salt solution was prepared.

The obtained TOC readings (> 2 mg/L) in the 100 g/L salt solutions (20g/L for Li_2CO_3) allowed further reduction of the salt concentrations to 50 g/L resp. 25 g/L. Thus, the matrix load for the combustion tube can be further reduced. An exception to this was nickel sulfate, which at a concentration of 100 g/L had only a very low TOC value. Here, the concentration of the salt solution was increased to 400 g/L to obtain a reliable TOC reading.

Calibration

The TOC analyzer was calibrated prior to measurements using standard solutions of potassium hydrogen phthalate in water in the concentration range of 0.5 mg/L to 5 mg/L TOC.

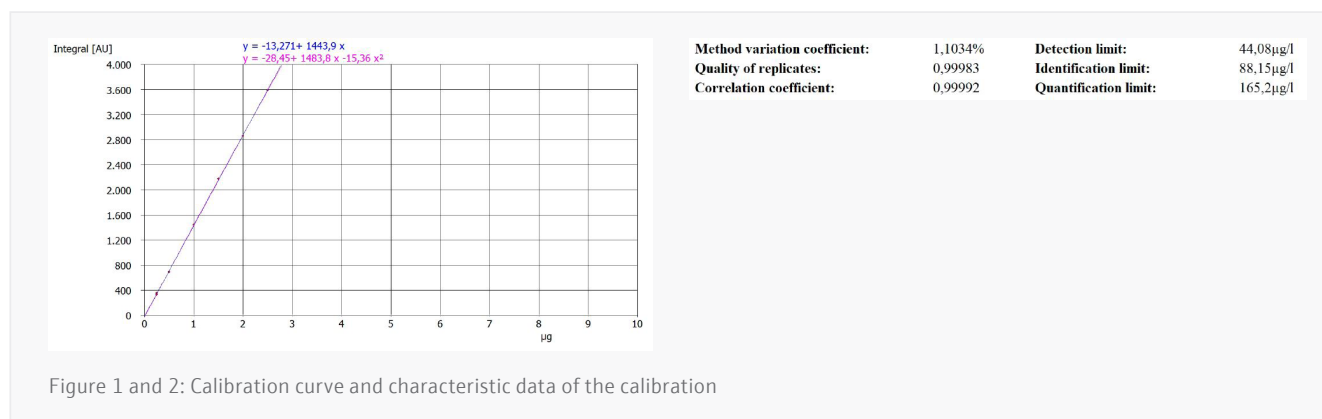


Figure 1 and 2: Calibration curve and characteristic data of the calibration

Instrument settings and method parameters

Table 1: Instrument settings on the TOC analyzer

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
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)	1
Injection volume of sample	500 µL
Purge time (removal of TIC)	180 s (900 s for Li_2CO_3)

In addition to the settings made on the analyzer in the table above, the salt kit was used for this application, which consists of a quartz combustion tube, special filling materials and a special furnace head. The filling materials include a platinum net, platinum catalyst, high-temperature mat and a quartz crucible that serves as a salt trap (see Fig. 3) The combustion temperature was selected in such a way that, on the one hand, complete decomposition of all organic compounds is ensured and, on the other hand, no melts of the formed oxides and salts could form, which would quickly render the combustion tube filling unusable.



Figure 3: Salt kit

Furthermore, a so-called “eluate blank value” was measured before starting the measurements. For this purpose, the TOC value of the distilled water was measured, which was also used to produce the salt solutions. This blank value is later automatically subtracted from the raw TOC signals as an area value from all subsequent sample readings. The TOC result of the salt solution is thus automatically corrected for the TOC contribution of the solvent (water).

Results and Discussion

The analytical results of all salt solutions as well as all spiked solutions are summarized in Table 2. The measurements were each carried out as a triple injection from a sample vessel. The TOC concentrations in the salt were calculated from the results of the aqueous solutions.

Table 2: Results of the TOC determination of the salt solutions

Sample description	TOC \pm SD [mg/L]	CV [%]	TOC \pm SD of the sample spiked with 1 mg/L TOC [mg/L]	Recovery rate of the TOC spike [%]	TOC in the salt [mg/kg]
CoSO ₄ solution, 50 g/L	0.84 \pm 0.03	3.6	1.92 \pm 0.04	108	16.8
CoCl ₂ solution, 25 g/L	1.88 \pm 0.02	1.1	2.82 \pm 0.04	94	75.2
Li ₂ CO ₃ solution, 5g/L	1.07 \pm 0.02	1.5	2.51 \pm 0.07	110	282
MnSO ₄ solution, 50 g/L	0.90 \pm 0.04 (0.003 TIC control)	4.4	1.92 \pm 0.02	102	18.0
NiSO ₄ solution, 400 g/L	1.44 \pm 0.03	2.1	2.45 \pm 0.07	101	3.60
Control standard, 1 mg/L TOC	1.09 \pm 0.02	1.8	-	-	-

The results prove that the TOC in the salt solutions can be determined with very good precision and accuracy. The difference of the measured values in a triplicate determination was less than 5% relative standard deviation in all solutions (output as coefficient of variation [CV] in the analyzer software). Given the low contents around 1 mg/L TOC, this is an excellent value that underlines the detection strength of the analyzer used. The recoveries (all in the range of 94% to 110%) for the TOC content in the spiked salt samples allow the conclusion that the accuracy of the obtained values in the salt solutions is given. Furthermore, a long-term test was carried out in which the CoSO₄ solution was measured alternately with an acidified ultrapure water. The mean TOC value and the standard deviation from 10 x 3 injections of the salt solution here was 0.878 mg/L \pm 0.074 mg/L.

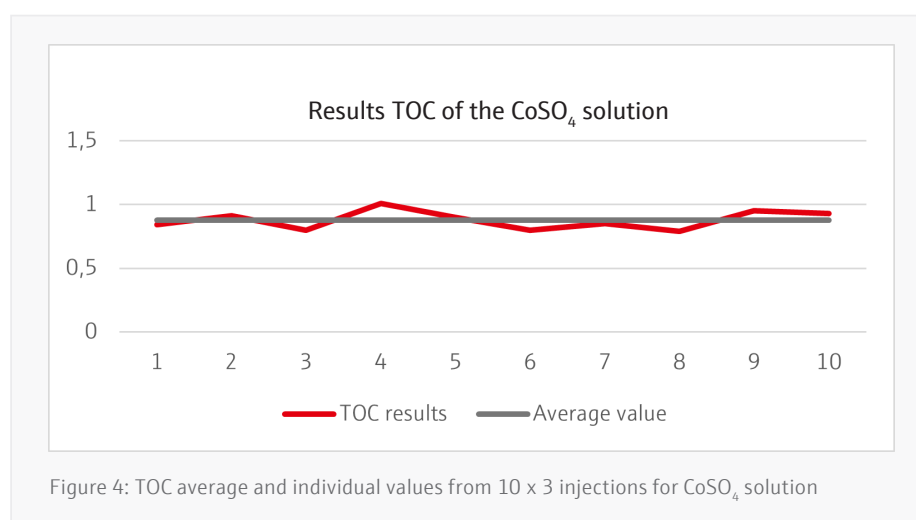
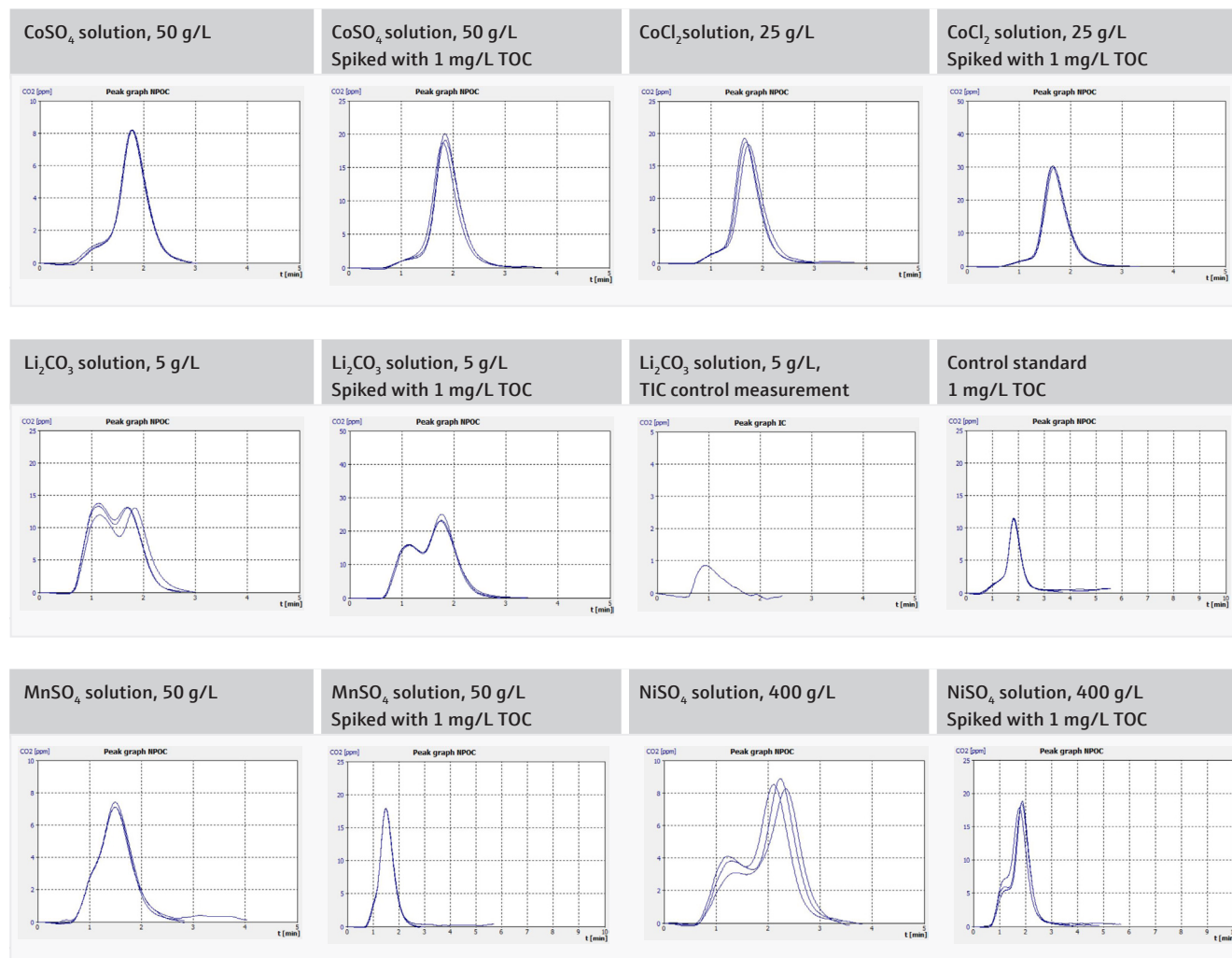


Figure 4: TOC average and individual values from 10 x 3 injections for CoSO₄ solution

It is recommended that the quartz crucible above the catalyst, which acts as a salt trap, is emptied regularly to ensure stable performance of the analyzer for the determination of low TOC concentrations in salt solutions.

This procedure can be performed within a few minutes when the combustion tube is cold. An indication of the need for replacement is the decreasing recovery of the TOC control standard and decreasing reproducibility of the measured values.

Table 3: TOC measuring curves of the salt solutions and spiked salt solutions



Summary

The multi N/C 3300 is a universally applicable TOC analyzer that is ideally suited for the determination of different sample matrices. Due to its high detection strength, the salt solutions to be analyzed can be prepared in very low concentrations, so that the matrix load for the analyzer remains low, while at the same time the TOC content can be determined well. In addition, the analyzer system offers the possibility of setting a lower combustion temperature to avoid the formation of melts that would block the combustion tube. Furthermore, it is advantageous to work with an eluate blank value that takes into account the contribution of the solvent (water) to the TOC result in the salt solution. Furthermore, the TIC control measurement can be used profitably to validate the NPOC results, especially for samples with a high carbonate content, like Li_2CO_3 . Last but not least, the easy accessibility of the salt kit ensures that the salt trap can be changed quickly, thus extending the service life of the combustion tube and the catalyst. Thus, fast and reliable routine analysis in the determination of TOC in salts used as raw materials in cathode production for lithium-ion batteries is guaranteed at all times with the multi N/C 3300.



Figure 5: multi N/C 3300

Recommended device configuration

Table 4: Overview of used devices and possible accessories

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 furnace head and filling materials

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