Application News

Total Organic Carbon Analyzer

TOC and IC Measurements for Lithium Refining Processes

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User Benefits

- By using a TOC-L analyzer, TOC and IC can be analyzed in lithium salt solutions.
- Using the combustion tube kit for high-salt samples can extend the lifespan of the combustion tube and catalyst, and reduce maintenance frequency.
- The automatic dilution function helps reduce the effort required for sample dilution.

■ Introduction

With the expansion of the lithium-ion battery market, lithium consumption is rapidly increasing. As a result, in addition to traditional sources (e.g., salt lakes, mines), new sources of lithium are also being explored. Recently, black mass and oil brine have attracted attention as alternative raw materials and the direct lithium extraction (DLE) method has been developed as a technology for efficiently recovering and refining lithium from those sources.

With the DLE method, lithium is extracted at high concentrations from those new raw materials and the resulting solution is refined to enhance its purity. However, the extracted solutions contain organic substances derived from the raw materials that can interfere with the refining process and reduce both its efficiency and speed. Therefore, the carbon reduction treatments implemented to address those issues have made quantitative quality control of organic substances crucial. The effectiveness of carbon reduction treatments and the quantity of organic substances in the refined solution can be evaluated in terms of the total organic carbon (TOC) content.

In recent years, the demand for lithium hydroxide (LiOH) has been increasing due to its use in the production of high-performance cathode active materials. Lithium hydroxide has the property of absorbing carbon dioxide (CO_2) from the atmosphere and converting it into lithium carbonate (Li_2CO_3). However, the resulting lithium carbonate can adversely affect the performance of cathode active materials, making careful quality control essential. In that context, the carbonate content can be evaluated as inorganic carbon (IC) using a TOC analyzer.

This article describes examples of using a TOC-L total organic carbon analyzer (Fig. 1) to measure TOC and IC levels in lithium solutions refined using the DLE method.

Fig. 1 TOC-L Total Organic Carbon Analyzer

■ Sample Preparation

In this experiment, three types of samples were prepared (Table 1): a lithium hydroxide reagent dissolved in purified water and two lithium extraction solutions from the lithium refining process (one with a carbon reduction treatment and one without).

Table 1 Sample Preparation

	Sample Description	pH
S1	Solution of lithium hydroxide reagent	12-13
S2	Lithium extraction solution with carbon reduction treatment	
S3	Lithium extraction solution without carbon reduction treatment	

■ TOC Analysis

Lithium salt solutions obtained from the lithium refining process are characterized by high alkalinity and high salt concentrations. Therefore, selecting appropriate analytical methods and instrument options is essential.

TOC Analysis Methods

There are two typical methods for TOC analysis.

(1) TC - IC method: TOC is calculated as the difference between total carbon (TC) and inorganic carbon (IC) levels (TOC = TC – IC).

(2) NPOC method: TOC is measured as non-purgeable organic carbon (NPOC). Acid is added to adjust the sample's pH to below 3, IC is subsequently removed by purging, and then TOC is measured as TC. The acidification and purging steps in the NPOC method are performed automatically within the instrument.

For alkaline samples, such as lithium salt solutions, direct TC measurement may lead to rapid sensitivity loss and poor reproducibility. Furthermore, it can accelerate the degradation of the catalyst and combustion tube. Therefore, the NPOC method is recommended.

Combustion Tube for High Salt Samples

When measuring alkaline samples, such as lithium salt solutions, using the NPOC method, acid addition can result in the formation of large amounts of salts. Repeated measurements of samples containing salts may lead to salt accumulation inside the combustion tube, causing issues such as catalyst clogging, reduced sensitivity, and poor reproducibility.

For this analysis, an optional combustion tube for high salt samples, shown in Fig. 2, was used. This combustion tube has a larger diameter than the standard combustion tube and includes larger-sized catalysts to help mitigate salt clogging. Thus, the frequency of combustion tube replacement can be significantly reduced.

Fig. 2 Combustion Tube for High Salt Samples

Acid Solution Used for NPOC Method

For the acidification process in the NPOC method, hydrochloric acid or sulfuric acid is commonly used. However, the salts generated by acid addition should be carefully considered. If hydrochloric acid is used for the lithium extraction solution sample, lithium chloride is produced. Lithium chloride has a melting point of approximately 610 °C, which is lower than the combustion temperature of 680 °C in the TOC-L analyzer. Consequently, salt melting inside the combustion tube may occur. Such molten salts can vaporize and flow downstream into the combustion tube, potentially affecting analytical results and causing devitrification of the combustion tube, which could damage the instrument.

To avoid such issues, sulfuric acid was selected as the acid additive for the NPOC method in this experiment. Lithium sulfate, produced by the addition of sulfuric acid, has a melting point of 859 °C, which is higher than the combustion temperature and thus prevents melting.

Additionally, when measuring alkaline samples using the NPOC method, the acid addition rate should be adjusted according to the sample to ensure the pH is reduced to below 3. In this experiment, the acid addition rate was set relatively high at 2.0 %.

The detailed analytical conditions are indicated in Table 2.

Table 2 TOC Analysis Conditions (NPOC Method)

Instrument	TOC-L_{CPH} + combustion tube for high salt samples + B-type halogen scrubber
Catalyst	TOC catalyst for high salt samples
Substances Measured	TOC (NPOC method)
NPOC Method	Acid addition: 4.5 mol/L sulfuric acid, 2 %
	Purging treatment: 80 mL/min, 90 seconds
Calibration Curves	NPOC: 4-point calibration curve using potassium hydrogen phthalate aqueous solutions at 0, 1, 5, and 20 mgC/L

■ IC Analysis

In alkaline lithium extraction solutions, most of the IC presumably exists as bicarbonate ions (HCO_3^-) or carbonate ions (CO_3^{2-}). IC analysis involves acidifying the sample in a dedicated IC reactor, converting the HCO_3^- and CO_3^{2-} into dissolved CO_2 for extraction. The IC reactor is filled with approximately 25 wt% phosphoric acid solution and carrier gas is bubbled through the solution to facilitate the extraction of CO_2.

During the IC analysis reaction process, lithium salts may be generated. However, lithium phosphate formed during the reaction is soluble in acid, preventing clogging within the IC reactor. Additionally, it can be easily removed using the IC reaction solution regeneration function, which restores the acidity of the phosphoric acid solution by replenishing the acid when consumed, in order to prevent its performance from deteriorating during measurement.

When analyzing alkaline solutions, phosphoric acid may degrade more rapidly than in normal analyses, potentially increasing the frequency of regeneration.

The IC analysis conditions are summarized in Table 3.

Table 3 IC Analysis Conditions

Instrument	TOC-L_{CPH}
Substances Measured	IC
IC Reactor*	Reaction solution: Phosphoric acid (25 wt%) Carrier gas: Continuously bubbled
Calibration Curves	IC: 4-point calibration curve using sodium bicarbonate and sodium carbonate aqueous solutions at 0, 10, 50, and 200 mgC/L

* The IC reactor is only included in the H-type model (high-sensitivity model).

■ Calibration Curves

The 4-point NPOC calibration curve, created using four potassium hydrogen phthalate aqueous solution concentrations (0, 1, 5, and 20 mgC/L), is shown in Fig. 3. The 4-point IC calibration curve, created using four sodium bicarbonate and sodium carbonate aqueous solution concentrations (0, 10, 50, and 200 mgC/L) is shown in Fig. 4.

To correct for carbon components present in the purified water used for preparing the standard solutions, the calibration curves were adjusted by shifting the origin. In both cases, the correlation coefficient (r) was 1.000, indicating excellent linearity.

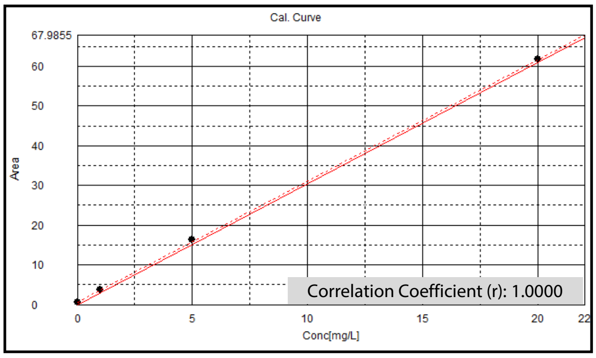


Fig. 3 NPOC Calibration Curve

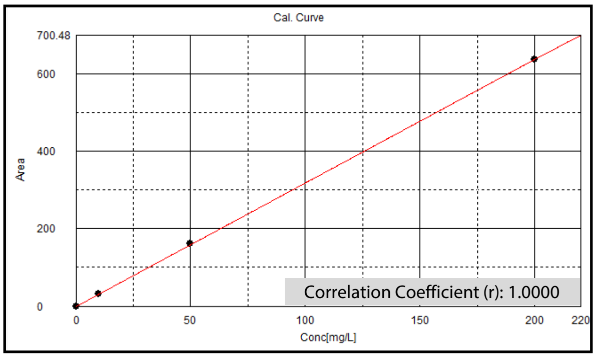


Fig. 4 IC Calibration Curve

■ Results

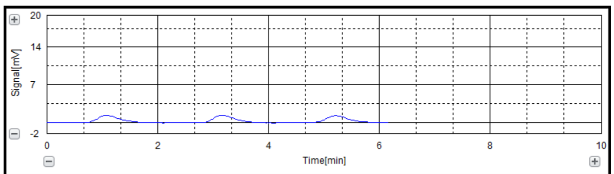
The TOC analysis results are presented in Table 4, with examples of measurement data shown in Figs. 5 and 6.

It was observed that the TOC level of sample S2, which underwent carbon reduction treatment, was comparable to that of sample S1, a solution prepared by dissolving lithium hydroxide reagent in purified water. In contrast, sample S3, which did not undergo carbon reduction treatment, exhibited a higher TOC value than the other samples.

These results confirm the effectiveness of the carbon reduction treatment in the refining process for removing organic substances from lithium extraction solutions.

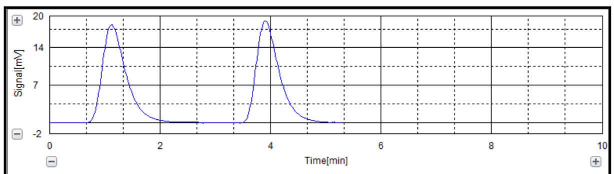
Table 4 TOC Analysis Results

	Sample Description	TOC [mgC/L]
S1	Solution of lithium hydroxide reagent	0.6147
S2	Lithium extraction solution with carbon reduction treatment	0.6301
S3	Lithium extraction solution without carbon reduction treatment	9.174



	Inj. No.	Area	Mean Area	Conc.	Mean Conc.	Result	CV Area	SD Conc.	CV Conc.	Excluded
	1	3.918	3.855	0.6405	0.6301	NPOC:0.6301mg/L	2.33	0.01468	2.33	
	2	4.190		0.6850						E
	3	3.791		0.6198						

Fig. 5 S2 TOC Measurement Data



	Inj. No.	Area	Mean Area	Conc.	Mean Conc.	Result	CV Area	SD Conc.	CV Conc.	Excluded
	1	55.99	56.12	9.153	9.174	NPOC:9.174mg/L	0.32	0.02890	0.32	
	2	56.24		9.194						

Fig. 6 S3 TOC Measurement Data

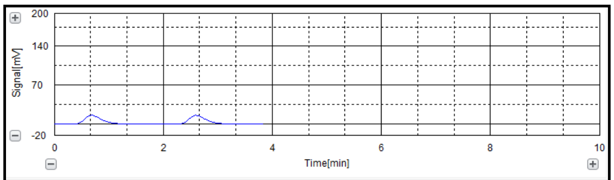
Table 5 summarizes the IC analysis results, with representative measurement data provided in Figs. 7 and 8.

Sample S2, which received carbon reduction treatment, showed a marked decrease in IC content compared to sample S3, which did not undergo such treatment. Furthermore, sample S1, prepared by dissolving lithium hydroxide reagent in purified water, displayed IC levels likely attributable to atmospheric CO_2 absorption, owing to the alkaline properties of the lithium hydroxide solution.

These results indicate that IC analysis serves as an effective tool for evaluating carbonate components in lithium extraction solutions.

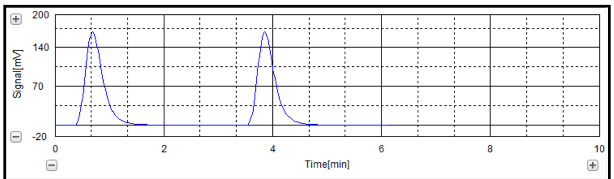
Table 5 IC Analysis Results

	Sample Description	IC [mgC/L]
S1	Solution of lithium hydroxide reagent	5.821
S2	Lithium extraction solution with carbon reduction treatment	11.34
S3	Lithium extraction solution without carbon reduction treatment	119.8



	Inj. No.	Area	Mean Area	Conc.	Mean Conc.	Result	CV Area	SD Conc.	CV Conc.	Excluded
	1	36.24	36.12	11.38	11.34	IC:11.34mg/L	0.47	0.05327	0.47	
	2	36.00		11.30						

Fig. 7 S2 IC Measurement Data



	Inj. No.	Area	Mean Area	Conc.	Mean Conc.	Result	CV Area	SD Conc.	CV Conc.	Excluded
	1	383.7	381.6	120.4	119.8	IC:119.8mg/L	0.80	0.9544	0.80	
	2	379.4		119.1						

Fig. 8 S3 IC Measurement Data

■ Conclusion

This article reports the results of TOC and IC analyses conducted on lithium extraction solutions using a Shimadzu TOC-L total organic carbon analyzer. The results confirm that the carbon reduction process can effectively decrease TOC levels in lithium extraction solutions and verify that carbonate components in the solution can be evaluated using IC analysis.

When analyzing TOC levels in solutions containing lithium salts by the NPOC method, it is essential to consider salt formation during acidification. Accordingly, sulfuric acid is recommended for the process.

Utilizing the optional combustion tube kit for high salt samples helps extend the lifespan of both the combustion tube and catalyst, thereby minimizing maintenance frequency. This is especially beneficial for high-salt samples such as lithium extraction solutions.

Additionally, diluting samples with high salt concentrations can further reduce maintenance requirements during TOC analysis. The TOC-L's automatic dilution function simplifies sample preparation and enhances operational efficiency.

Overall, the TOC-L proves to be a highly effective instrument for TOC and IC analysis in lithium extraction solutions, making it an excellent tool for research and development in lithium refining technologies.

Acknowledgments

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