



### Challenge

A fast and automated method for the determination of  $\text{Li}_2\text{CO}_3$  in recycling waters of the lithium ion battery (LIB) recycling

### Solution

The TIC measurement by multi N/C series offers a fully automated possibility to quickly and accurately determine the carbonate content of the lithium brought into solution

### Intended audience

Battery recycling companies, process developers for lithium recovery in lithium ion battery accumulator recycling

## Benefits of TIC Analysis in Lithium Battery Recycling for Lithium Recovery

### Introduction

The recovery of lithium from lithium ion batteries (LIB) is gaining more and more importance due to the expansion of electrification, especially in the mobility sector. The classification as a critical raw material by the EU<sup>[1]</sup>, rising raw material prices and demand as well as legally defined recycling quotas are currently leading to a high level of research activities and the construction of industrial recycling plants. These projects, besides other valuable components of a battery, focus on the recovery of lithium. A possible target product that could be used as a raw material in battery production is lithium carbonate.

The recovery of lithium in current recycling processes is still very challenging and is either not carried out at all or only with low recovery rates<sup>[2]</sup>. In order to circumvent this problem, the Institute for Metallurgical Process Technology (IME) at RWTH Aachen University is investigating the approach of an early lithium recovery from the so-called active mass<sup>[3][4]</sup>. For this purpose, the battery material to be recycled (whole cells or already shredded batteries) is

subjected to a defined thermal pretreatment. On the one hand, this serves to remove organic substances from the electrolytes, binders, and separators of the battery cells. On the other hand, it is used for phase transformations of the lithium contained in the battery through targeted process parameter adjustment. A target phase for the lithium is lithium carbonate, which is formed by ongoing reduction reactions. Subsequently, for selective recovery of lithium from the active mass a wash-out process with deionized water is carried out. In this process the formed lithium carbonate is dissolved. However, since lithium fluoride is also formed during thermal pretreatment, depending on the selected process parameters, a certain amount of this salt is also brought into solution. The lithium salt product is recovered from the solution, for example, by evaporation of the water. For the evaluation of the process parameters of thermal pretreatment and leaching as well as for the evaluation of the product produced, not only the purity, but also the type of lithium compound present is decisive.

Since the target phase in the case described is lithium carbonate, the TIC (total inorganic carbon) measurement with the multi N/C analyzer provides a reliable and fast way to compare the carbonate contents within a series of tests and to draw conclusions about the ratio of lithium fluoride to lithium carbonate. In addition, the measurement of the TOC value (total organic carbon) provides the possibility to check for unwanted contamination of the sample with organic residues from the thermal treatment process. For this application note, Analytik Jena's multi N/C 2100S\* was used

\*) the multi N/C 2100S is the largely identical predecessor model to the multi N/C 2300

## Materials and Methods

The TIC determination was carried out by the multi N/C 2100 S in combination with the auto sampler AS 60 according to the TIC determination described in DIN EN 1484.

### Samples and reagents

- 4 samples after the water washing process of active mass from 4 different thermal pretreatment processes (610 °C, 1 h holding time, under N<sub>2</sub> atmosphere, N<sub>2</sub> + 2.5 % O<sub>2</sub>, N<sub>2</sub> + 5 % O<sub>2</sub>, resp. CO<sub>2</sub> atmosphere)
- 10 % phosphoric acid for automatic TIC determination
- TIC calibration standard solutions (sodium carbonate and sodium hydrogen carbonate in water)

### Sample preparation and measurement

The liquid samples were diluted 1:8 with deionized water to minimize matrix effects due to metal cations. The samples were filled into sample vials and placed on the sample rack. For direct TIC measurement, a representative sample aliquot of 500 µL was fed by a micro liter syringe into the TIC reactor of the analyzer. An aliquot of 10 % phosphoric acid was automatically dosed into the TIC reactor. By the acid CO<sub>3</sub><sup>2-</sup> is converted to HCO<sub>3</sub><sup>-</sup> (the dissolved form of CO<sub>2</sub>). The dissolved CO<sub>2</sub> is released from the solution by purging with the clean carrier gas (pure oxygen or synthetic air free of hydrocarbon and CO<sub>2</sub>). The measurement gas was transferred to the detector after appropriate drying and purification. Quantification was performed by non-dispersive infrared spectrometry using a focus radiation NDIR detector.

to measure carbonate concentrations. The measurements were carried out on aqueous samples from a series of tests at IME<sup>[3]</sup>. They originate from the water-washing process of four active compounds that have undergone different thermal pretreatments.

In addition, fluorine measurements were performed for verification purposes and XRD images of the precipitated salts were recorded. These also allow qualitative conclusions to be drawn about the phase fractions of lithium fluoride and lithium carbonate.

### Calibration

The multi N/C analyzer was calibrated with sodium carbonate and sodium hydrogen carbonate (50:50 mix) standard solutions for the concentration range of 0.25 - 25 mg/L TIC.

All calibration solutions were prepared according to DIN EN1484. A linear calibration function was used.

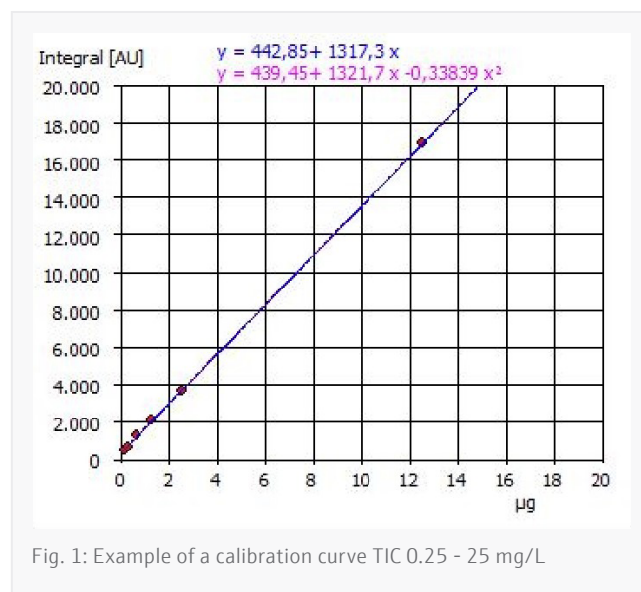


Fig. 1: Example of a calibration curve TIC 0.25 - 25 mg/L

## Method Settings

Table 1: Method parameters for multi N/C 2100S, resp. multi N/C 2300

Parameter	multi N/C 2300
Method of determination	TIC
Sample digestion	10 % H <sub>3</sub> PO <sub>4</sub>
Number of replicates	min. 2, max. 3
Autosampler, rack, and vial size	AS 60, 60 position rack, 8 mL sample vials
Rinse cycles with sample	3
Injection volume	500 µL
Integration time	240 s

## Results and Discussion

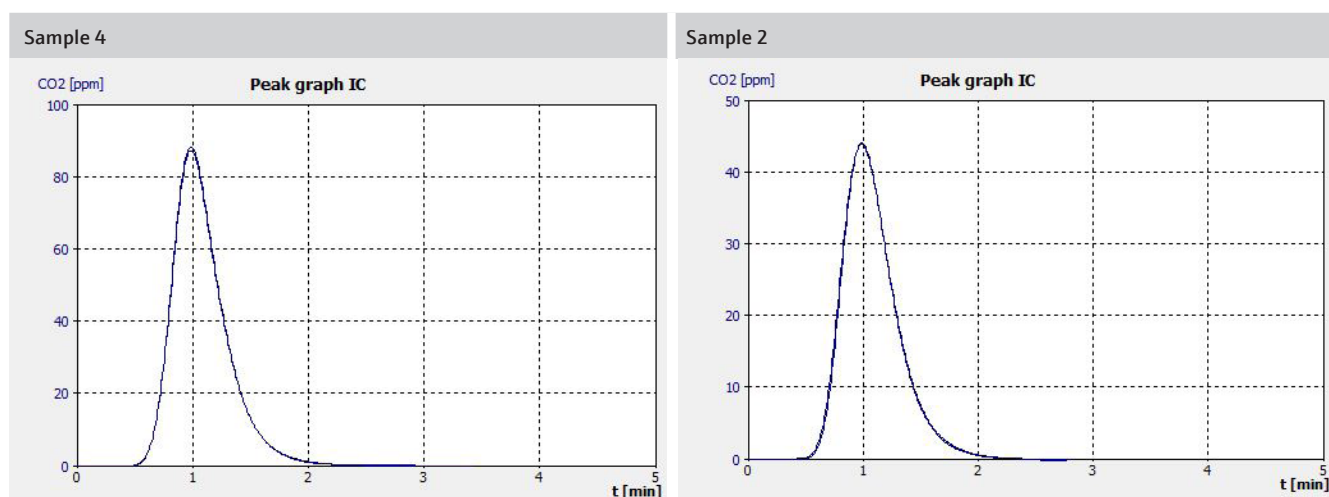
Examples of analytical results are given in table 2 and figure 2. TIC measurements were carried out as multiple injections from a sample vessel.

For comparison of the qualitative statement, additional fluorine analyses with ion-selective electrode as well as semi-quantitative determinations of the lithium carbonate and lithium fluoride fractions from the precipitated lithium salt were carried out by means of XRD measurement. The determination of the carbonate content by XRD measurement, however, has some disadvantages. On the one hand, it is much more time-consuming since an additional process step is required to precipitate the lithium salt. In addition, an XRD measurement including sample preparation takes much longer than the TIC determination from solution. Furthermore, phase fraction determination by XRD is a semi-quantitative methodology. Here, the TIC measurement from solution offers the advantage of being a very accurate measurement method with low standard deviation and short measurement times.

Table 2: Comparison of the results of TIC and fluorine determination based on undiluted original sample and semiquantitative XRD evaluation of the precipitation product

Sample ID	Atmosphere for thermal pretreatment	Results TIC ± SD [mg/L]	F determination [mg/L]	Li <sub>2</sub> CO <sub>3</sub> in precipitated salt [%-wt] (XRD)	LiF in precipitated salt [%-wt] (XRD)
1	N <sub>2</sub>	47.5±0.46	36.6	81.5	18.5
2	CO <sub>2</sub>	60.2±0.54	27.9	86.4	13.6
3	N <sub>2</sub> + 2.5 % O <sub>2</sub>	38.4±0.01	34.8	73.3	26.7
4	N <sub>2</sub> + 5 % O <sub>2</sub>	29.5±0.26	30.0	79.2	20.8

Fig. 2: Examples of measurement curves of samples with different content of carbonates



The example measurement curves in fig. 2 illustrate the excellent reproducibility of the measured values within a multiple injection from a sample vessel. As a result, the lithium recovery rate in the aqueous eluate solution can be quantitatively determined by the TIC analysis. In comparison with the semi-quantitative XRD determination of the proportions of lithium fluoride and lithium carbonate in the subsequent precipitate product, the following relationship can be clearly demonstrated: Samples with higher lithium carbonate content in the salt product show higher TIC readings in solution than samples with lower carbonate content. For the comparison of the samples with each other and for the estimation of the process success regarding the yield of lithium carbonate during thermal pretreatment and the corresponding lithium recovery in the elution step, the TIC measurement thus offers a suitable and time-saving alternative in comparison to the semi-quantitative phase determination by means of XRD.

## Conclusion

TIC determination with the multi N/C x300 series is a suitable method for comparing lithium carbonate generation in the context of battery recycling. As the measurement data show, this method reliably enables the qualitative comparison of lithium carbonate recovery. At the same time, the measurement offers a high time saving to the semi-quantitative phase analysis by means of XRD from the salt precipitation product. The multi N/C 2300 TOC analyzer with direct injection technique and the AS 60 autosampler offers the advantage of very low sample consumption per analysis. Less than 5 mL of sample is usually sufficient for a triplicate determination of the TIC parameter. An additional added value is the possibility to analyze the sample for organic residues (TOC) brought into solution, which in turn would negatively influence the product quality of the lithium salt.



Fig. 3: multi N/C 2300

## Recommended device configuration

Table 3: Overview of devices, accessories and consumables

Article	Article number	Description
multi N/C 2300	450-500.100-2	TOC analyzer with direct injection technique
AS 60	450-126.682	Autosampler for multi N/C 2300
<b>Alternative:</b>		
multi N/C 3300	450-500.500-2	TOC analyzer with flow injection technique
AS vario	450-900.140	Autosampler for multi N/C 3300
Rack 72 positions	450-900.141	Accessory for AS vario

## References

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