Challenge
Reproducible, reliable determination of elemental and organically bound carbon in black mass, which is generated and processed during recycling of lithium-ion batteries

Solution
Safe and fully automated differentiation of carbon species by pyrolysis method

Intended audience
Recycling sector of the battery industry and related contract labs

Recycling of Lithium Ion Batteries (LIB) - Determination of the Elemental and Organically Bound Carbon in Black Mass by Pyrolysis Method

Introduction

Do you remember the days when low-power batteries stood in the way of carefree everyday life? The nickel metal hydride batteries in the first digital cameras lasted for what felt like 20 pictures, the GAME BOY™ was discharged after about 3 hours. Over the last 20 years, energy-dense rechargeable batteries have become a cornerstone of our mobile society. Without them, mobile work and leisure would be unthinkable. From smartwatches, cell phones and laptops to e-bikes and e-cars, rechargeable lithium-based batteries provide electrical energy everywhere. They have a longer lifespan, are designed for significantly more charging cycles and store more energy than any other battery type for a comparable weight and size. Lithium-ion batteries can be classified based on their composition into different types, such as lithium iron phosphate based (LFP) or based on a combination of lithium, nickel, cobalt and manganese (NCM). Due to the drastically increasing amount of used batteries, especially in view of e-mobility, the need for effective recycling processes is growing. In the future, up to 65% by mass of lithium-based batteries will be recycled in the European Union[1].

During the recycling process of spent batteries, their disassembly, crushing, and thermal treatment produces a granular or powdery dark mixture, the so-called "black mass". Depending on the battery type, it consists of various metals (e.g., lithium, cobalt, copper, nickel, manganese), as well as elemental carbon, such as graphite, which is a typical component of every battery as anode material. However, depending on the reprocessing step in the recycling process, organic carbon compounds (OC) may also be contained in the black mass, e.g., from plastic components, such as the separators, or from solvents, which are also contained in rechargeable batteries.

The multi EA 4000 is well suited for the monitoring of the various carbon parameters in black mass samples generated during the recycling process.

The analyzer is designed for the separate determination of different carbon species with a high degree of automation according to VGB pyrolysis method[2] and DIN EN 15936 solids TOC method[3]. For the determination of elemental carbon (EC), a so called pyrolysis step – a treatment where the sample is exposed to high temperatures in the absence of oxygen, is applied. During this, the organic carbon components, which undergo thermal decomposition, are released from the sample, and only elemental carbon (EC) remains. The EC is converted to CO_2 during subsequent combustion in a pure oxygen atmosphere. The total carbon (TC) is measured in addition. The amount of organic carbon (OC) can be calculated afterwards as difference between TC and EC. These parameters can be used to infer the effectiveness of the large-scale thermal treatment and pyrolysis processes used to generate the black mass when recycling lithium-ion batteries.

Materials and Methods

The determination of organically bound carbon (OC) by pyrolysis method was carried out according to a differential method:

OC = TC - EC

For this purpose, two sample aliquots were weighed into ceramic boats for each determination. For the EC measurement, the furnace temperature of the multi EA 4000 was set to 850 °C, the combustion tube was purged with a constant argon flow. The ceramic boats filled with samples were transferred into the furnace using the FPG 48 solids sampler. After a pyrolysis time of 360 seconds, the system automatically switches from argon to oxygen. The hot sample reacts immediately with the oxygen. During this process, the present EC is completely converted to CO_2 and detected by NDIR spectrometry after appropriate purification and drying. A second sample aliquot was transferred directly to the hot furnace for the determination of TC. Without a previous pyrolysis step, all contained carbon compounds are converted to CO_2 in a pure oxygen stream. The determination of the EC and TC contents is carried out fully automatically by the control and evaluation software. The organic carbon (OC) is then calculated externally on basis of the EC and TC measurement results.

Samples and reagents

Pyrolyzed black mass (LFP) of different particle sizes:

- Sample 1: LFP black mass, filter fraction
- Sample 2: LFP black mass, fine (particle size 0–0.25 mm), V1
- Sample 3: LFP black mass, coarse (particle size 0.25–0.5 mm)
- Sample 4: LFP black mass, fine (particle size 0–0.25 mm), V3
- Glassy carbon, powder, 99.95% C (Sigma-Aldrich) – calibration and system test

Sample preparation

The analyzed samples were homogeneous, fine black powders of different grain size. Due to this a special sample preparation was not required.

Method settings

For analysis of samples and standards a method for combined EC/TC determination was applied. The settings for the process and detection parameters are summarized in table 1 and 2.

Table 1: Method parameters multi EA 4000

Parameter	Setting
FPG	EC/TC_inorg_without_TIC_auto
Furnace temperature	850 °C
EC – Purge time	360 s
Oxygen	2.5 L/min
Argon (pyrolysis)	1.5 L/min
Suction flow (pump)	1.7 L/min

Table 2: Detection parameters – Carbon determination (NDIR)

Parameter	Specification
Max. integration time	1800 s
Start	0.12 ppm
Threshold	3 ppm
Stability	3

Calibration

The multi EA 4000 was calibrated with pure glassy carbon (99.95% C) before analysis. The applied quantities and calibrated range are summarized in table 3. Figure 1 and 2 show the related calibration curves. The quality of calibrations was checked by another carbon standard.

Table 3: Calibration standard and ranges

Parameter	Standard	C content (%)	Quantity (mg)	Calibrated range
EC	Carbon	99.95	13–110	13–110 mg C abs.
TC	Carbon	99.95	11–125	11–125 mg C abs.

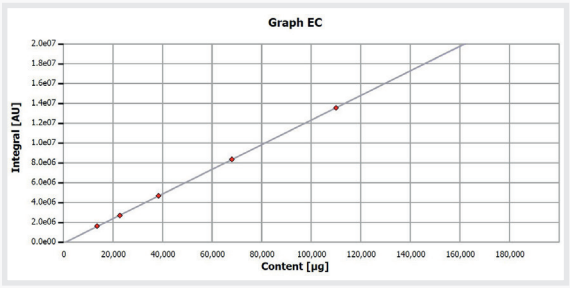

Figure 1: calibration curve EC determination

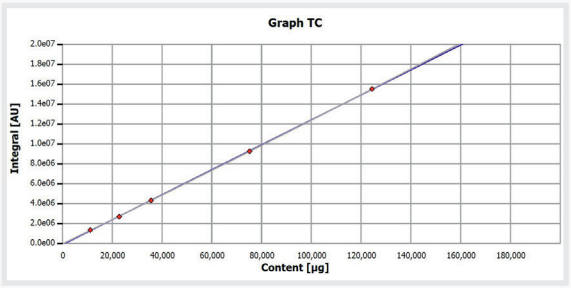

Figure 2: calibration curve TC determination

Results and Discussion

Samples were measured as triplicates, standard as duplicate analysis. The resulting EC and TC curves are shown exemplarily in figure 3–10, the measured results given in table 4 are average values of the replicate analysis. Exemplary measuring curves of the EC/TC measurements are given in the following figures. The results are summarized in Table 3. Prior to the measurements all samples were tested for the carbonate content, the total inorganic carbon (TIC). No significant contributions of TIC were found.

Table 4: Results of EC, TC, and OC determination

Sample ID	EC ± SD (g/kg)	TC ± SD (g/kg)	OC* (g/kg)
Sample 1 (filter fraction)	758.7 ± 5.06	772.8 ± 6.39	14.1
Sample 2 (0–0.25 mm), V1	512.8 ± 3.61	522.4 ± 12.8	9.61
Sample 3 (0.25–0.5 mm)	241.9 ± 1.74	237.3 ± 0.39	0*
Sample 4 (0–0.25 mm), V3	223.3 ± 1.70	232.6 ± 4.48	9.32
Standard, 99.95% C	998.3 ± 0.54	985.2 ± 17.1	0*

* calculated values, negative values set to 0

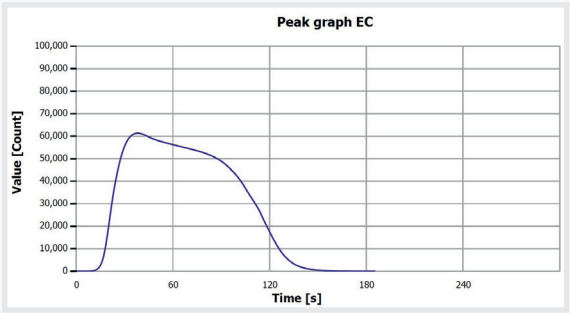

Figure 3: EC determination sample 1 (filter fraction)

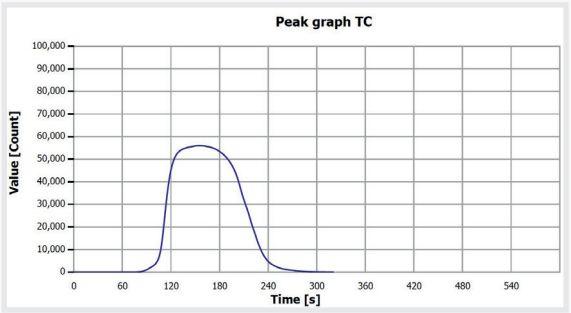

Figure 4: TC determination sample 1 (filter fraction)

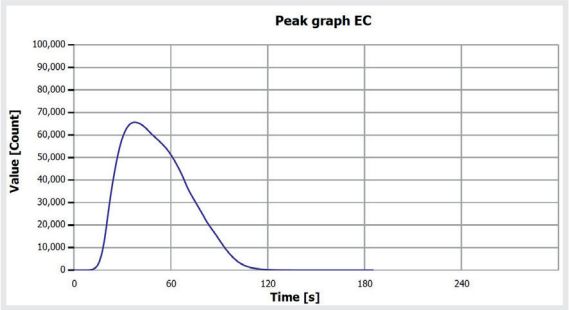

Figure 5: EC determination sample 2 (0–0.25 mm), V

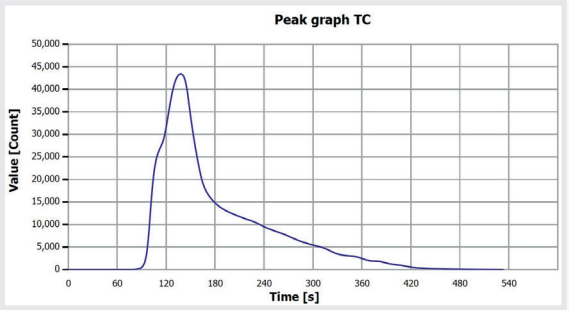

Figure 6: TC determination sample 2 (0–0.25 mm), V1

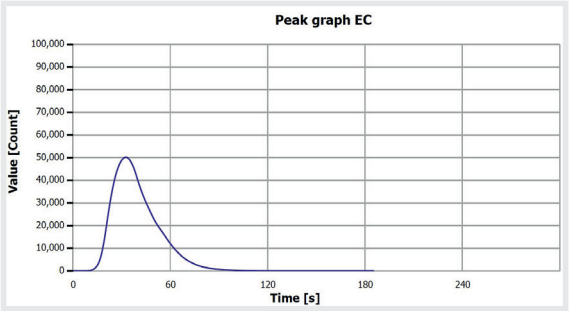

Figure 7: EC determination sample 3 (0.25–0.5 mm)

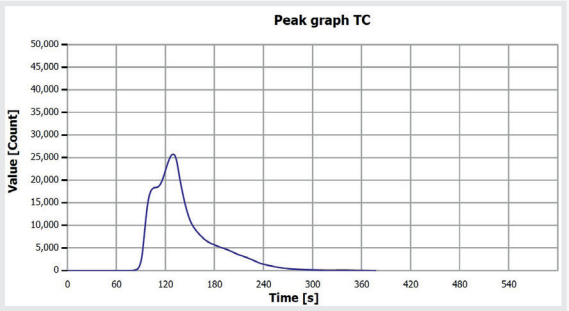

Figure 8: TC determination sample 3 (0.25–0.5 mm)

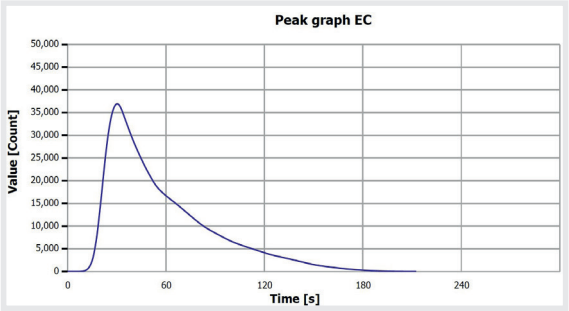

Figure 9: EC determination sample 4 (0-0.25 mm), V3

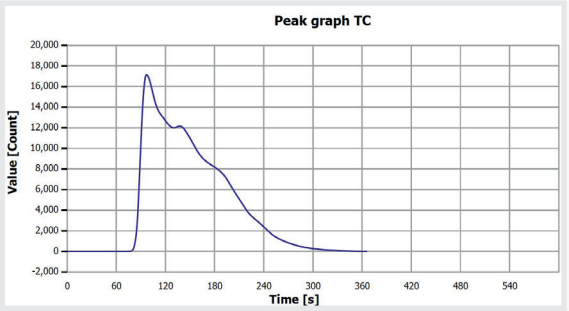

Figure 10: TC determination sample 4 (0-0.25 mm), V3

Summary

The black mass samples from a lithium battery recycling process were analyzed quickly and easily with the elemental analyzer type multi EA 4000 (see table 5 for configuration) for their content of elemental and organically bound carbon. The reproducibility of the EC/TC measurements of the samples is very good. Due to their partly very high contents, the scattering (SD) of the measurement values can have a remarkable influence on the OC contents calculated on their basis by means of difference method. The scattering of the results can be improved by running more replicates and utilization of an outlier selection. This has a positive effect on the calculated OC values.
The fully automated measurement procedure allows separate determination of the different carbon parameters with minimum effort for the operator. Thanks to the wide measuring range of the NDIR detector, both very low (LOD: 10 µg abs.) and very high contents (≤ 500 mg C abs.) can be detected quickly and quantitatively. Besides, multi EA 4000 can be extended by optional accessories for other interesting application tasks, such as automated TIC determination or the determination of total sulfur (TS) and total halogens (TX).

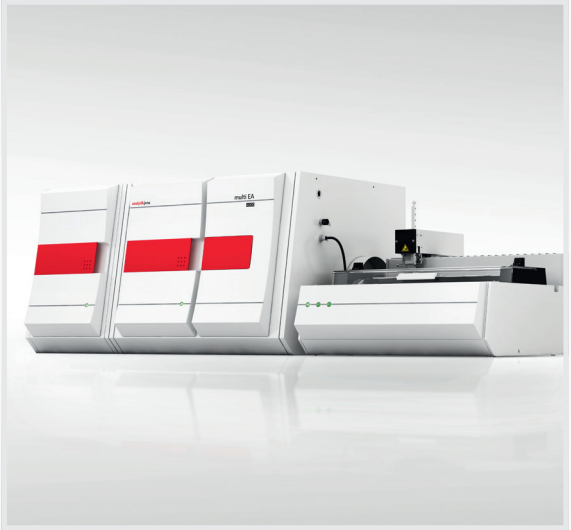

Figure 11: multi EA 4000 with pyrolysis function and FPG 48 solids sampler

Recommended device configuration

Table 5: Overview of devices, accessories, and consumables

Component	Article number	Description
multi EA 4000 with pyrolysis option	450-126.568	Elemental analyzer for carbon determination with pyrolysis option
Solid autosampler FPG 48	450-126.574	Autosampler for 48 solid samples

References

[1] European Commission; Proposal for a REGULATION OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL concerning batteries and waste batteries, repealing Directive 2006/66/EC and amending Regulation (EU) No 2019/1020, 2020, page 9.

[2] VGB PowerTech is an international interest group of companies from the electricity and heat supply industry, more information on www.vgbe.energy

[3] DIN EN 15936 Sludge, treated biowaste, soil and waste - Determination of total organic carbon (TOC) by dry combustion

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Version 1.0 · Author: SJ
en · 09/2023