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Innovatives Analysenverfahren für Recyclate aus LIB's

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PHYSIKALISCHE CHEMIE
INNOVATION DURCH ANALYTIK

Neue analytische Ansätze zur direkten Charakterisierung komplexer Recyclate

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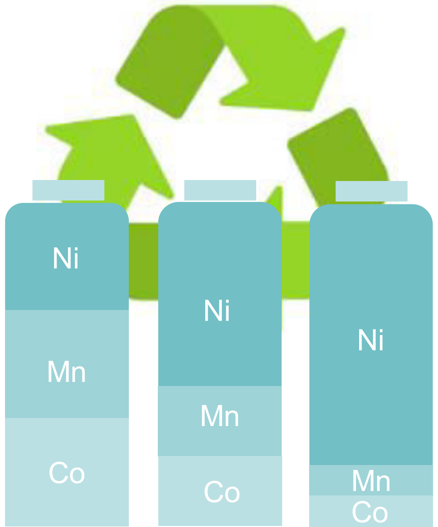
Entwicklung einer Methode zur direkten Bestimmung von Hauptkomponenten in NMC-Recyclaten mittels Feststoff-AAS

Ziel:
zuverlässige und hinreichend präzise Methode,
unabhängig von sonstiger Zusammensetzung des Recyclats und Stöchiometrie des NMC



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Lithium-ion batteries: direct solid sampling for characterisation of black mass recyclates using graphite furnace atomic absorption spectrometry†

Maria Dommaschk,* Tim Sieber and Jörg Acker

In this work, the potential for direct major component analysis of lithium–nickel–manganese–cobalt oxide variants in solid samples by graphite furnace atomic absorption spectrometry (SS-GF AAS) was critically evaluated, always with the aim of developing a simple and rapid method that relies only on the use of aqueous standards for calibration. The accuracy of the developed method was evaluated against an established wet chemical acid digestion method using an inductively coupled plasma optical emission spectrometer (ICP-OES). The most challenging aspect was the selection and use of suitable standards, ...ria of liquid standards, single oxide solid standards and multi-... ...ined. With the result that multi-element liquid standards can be ...ent with the certified reference values and with the values ... cases. The precision of the method was better than 12% with ... The results show that not only the major components in pure ... can be reliably analysed, but also the cathode coatings made from recycled battery materials. This demonstrates the range of applications of the methods and their suitability under industrial conditions, for example in the analysis of recyclates. The technology is almost predestined for use in industrial laboratories in order to quickly and accurately determine the stoichiometric composition of cathode coatings from aged lithium batteries and to ensure battery shredding by type.

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Introduction

Electromobility makes a significant contribution to sustainability and to reducing the environmental impact of the transport sector. It enables a reduction in the consumption of limited resources such as crude oil, thereby reducing dependency on fossil fuel imports. E-mobility helps to reduce local air pollution, as no harmful exhaust gases such as nitrogen oxides or particulate matter are emitted. This is particularly important in urban areas, where air pollution is a serious health problem. As electric vehicles are also quieter in operation than combustion vehicles, they also reduce noise pollution in urban areas and thus improve the quality of life for residents along transport routes.

A key component of electric vehicles is the energy storage system – the battery. Lithium-ion technology is the most favoured technology for batteries in electric vehicles. Currently, variants of lithium–nickel–manganese–cobalt oxide compounds are the most powerful and widely used battery materials for electric mobility. The research field for this technology is constantly growing, as the number of used batteries is also increasing enormously with their use in electric vehicles. Spent lithium-ion batteries are an important resource as they contain enormous quantities of the complex oxides of the elements lithium, nickel, manganese and cobalt. These compounds are generally referred to as NMC (N – nickel, M – manganese, C – cobalt), whereby a suffixed number indicates the stoichiometry of the compound, for example NMC111 stands for $Li_1Ni_{0.33}Mn_{0.33}Co_{0.33}O_2$ and NMC622 for $Li_1Ni_{0.60}Mn_{0.20}Co_{0.20}O_2$. The complex oxides have a high commercial value, which is determined in particular by the global market price of cobalt. Numerous thermal, mechanical and chemical processes have therefore been developed specifically for the recovery of the cathode material (NMC), resulting in the so-called black mass, a powdery mixture of NMC, graphite and binder (typically PVDF), which may contain significant impurities of aluminium, copper and iron as well as residues of plastics (separator residues) and electrolyte (organic solvent with dissolved lithium salts).[1-9] However, these recycling processes (e.g. shredding processes) were not developed specifically for energy storage systems from electric vehicles, but for various types of rechargeable batteries. These can also include cylindrical batteries, such as nickel-metal hydride batteries.[10] However, this unsorted shredding results in lower recycling efficiency. From an

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J. Anal. At. Spectrom.

Architecture of a Lithium-Ion Battery Pouch Cell

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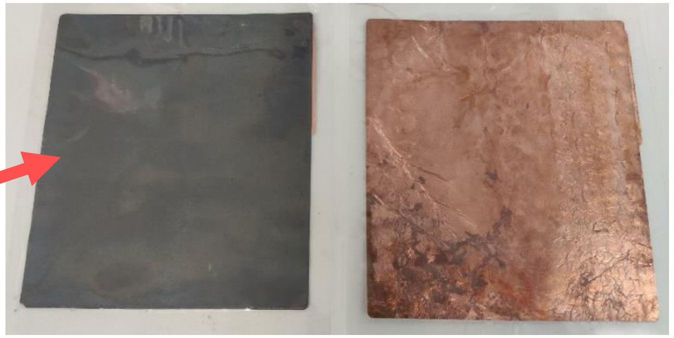
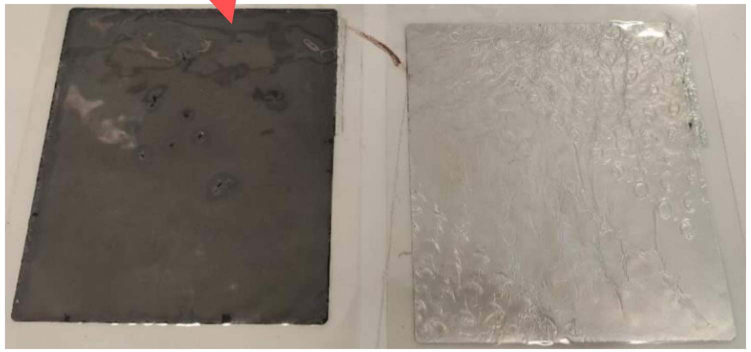


Anode
copper sheet coated with carbon black and binder

Separator
polymer sheet coated with a ceramic material

Elektrolyte
liquid organic solvents with fluorine- and sulfur- containing lithium salts

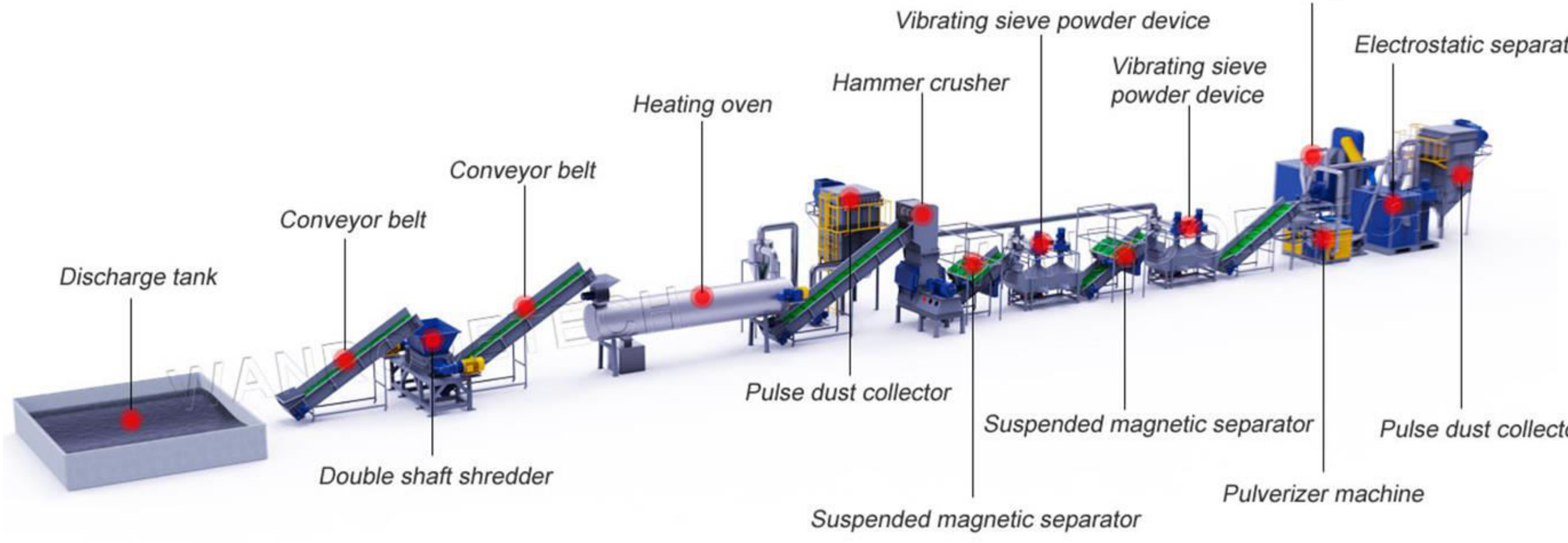


Cathode
aluminum sheet coated with NMC particles, carbon black and binder

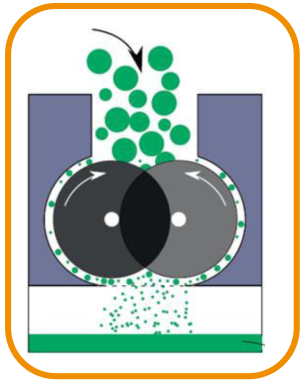
source: Department of Physical Chemistry, BTU Cottbus-Senftenberg

State-of-the-Art: Mechanical-Thermal Recycling

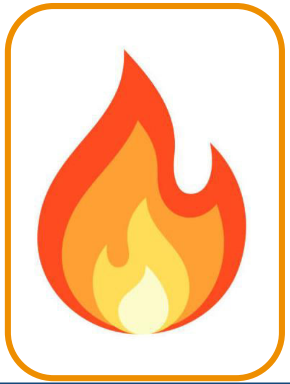
source: https://www.wanrooerecycle.com/solution/lithium-ion-battery-recycling/



shredder

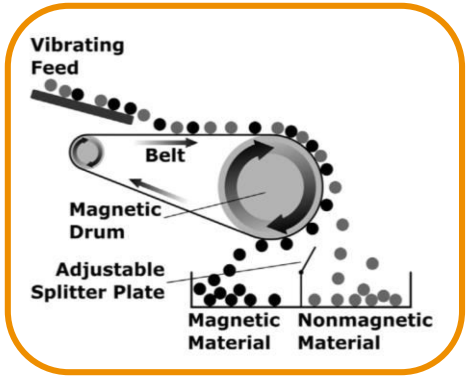


thermal treatment

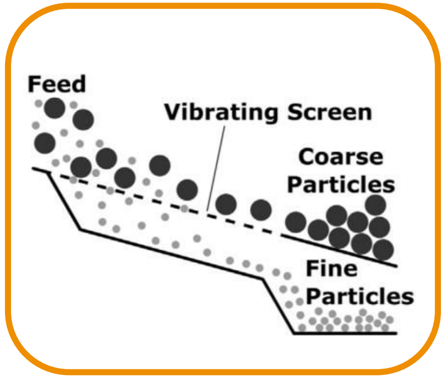


hammer mill

magnetic separation of iron particles



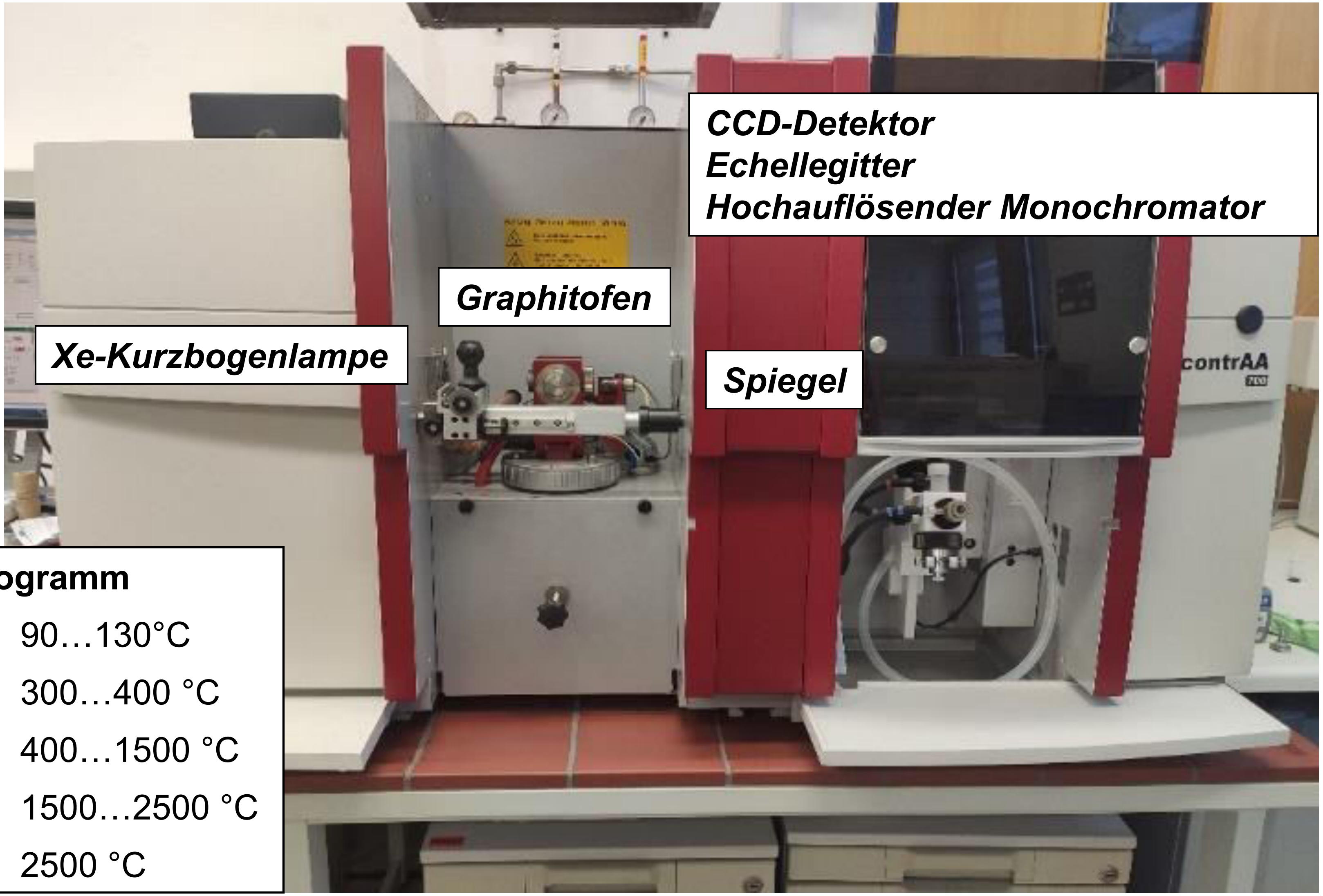
vibrating sieve



source: Sommerville et al., Sustainable Materials and Technologies 25 (2020) e00197

source: https://www.youtube.com/watch?v=hETeeN4yFqU

HIGH-RESOLUTION CONTINUUM SOURCE GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY



Ofenprogramm	
Trocknung 1	90…130°C
Trocknung 2	300…400 °C
Pyrolyse	400…1500 °C
Atomisierung	1500…2500 °C
Ausheizen	2500 °C

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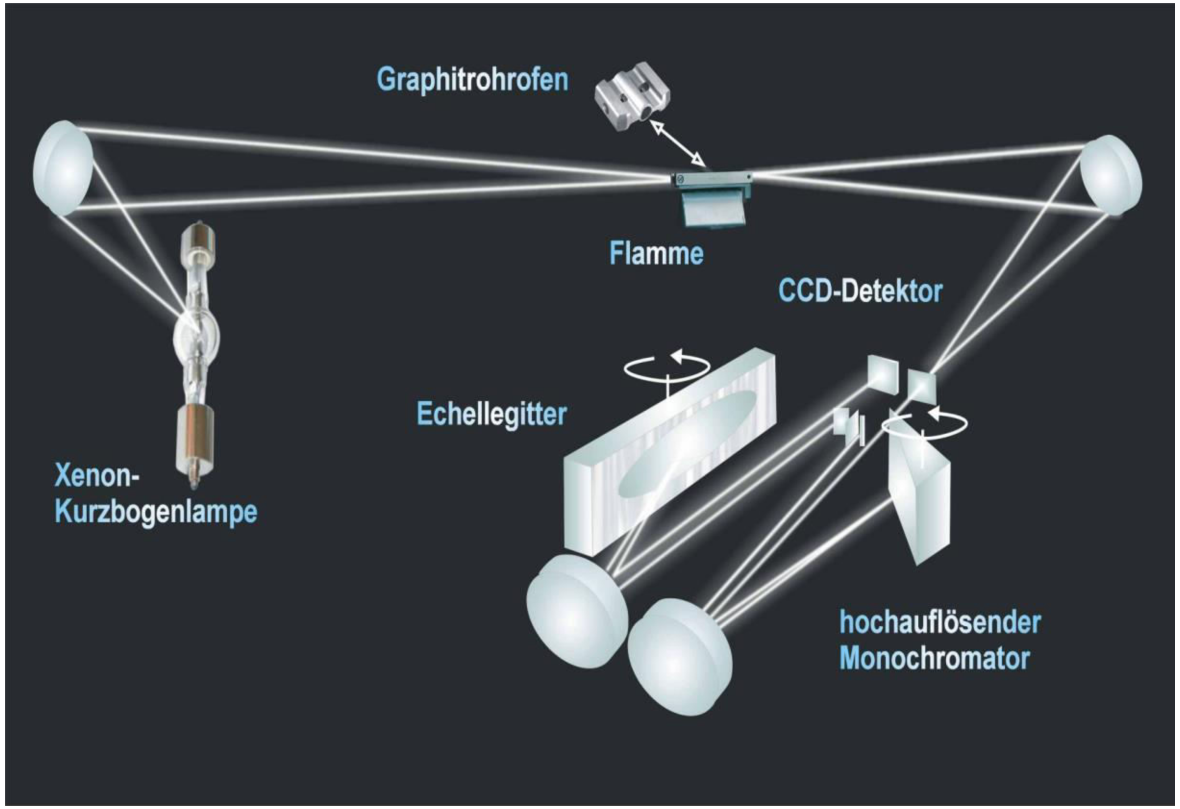
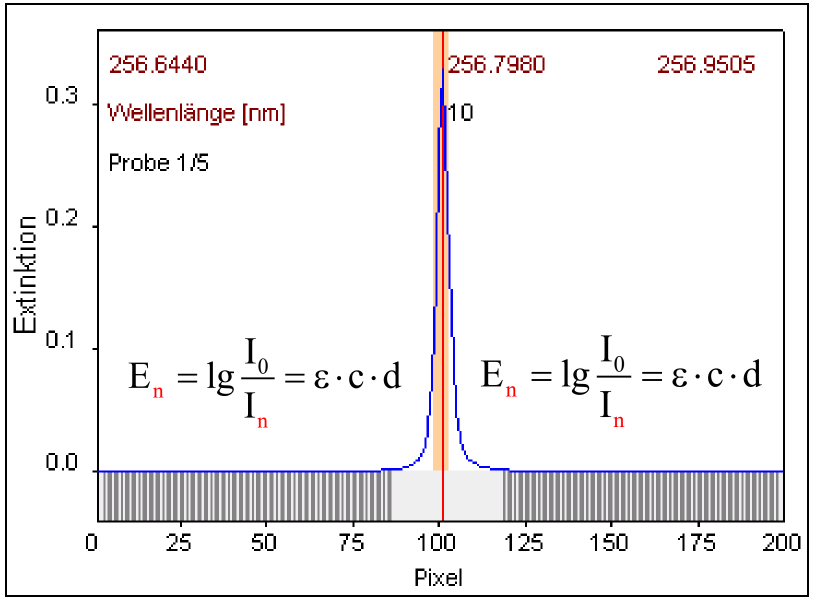
Lambert-Beer

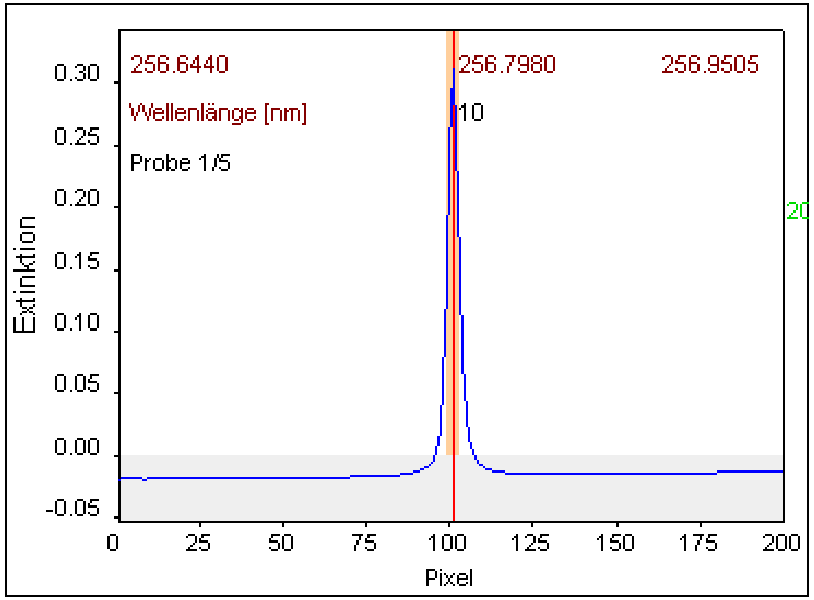
$$E_\lambda = \log_{10}\left(\frac{I_0}{I}\right) = \varepsilon_\lambda c\, d$$



source: Analytik Jena AG

Background correction

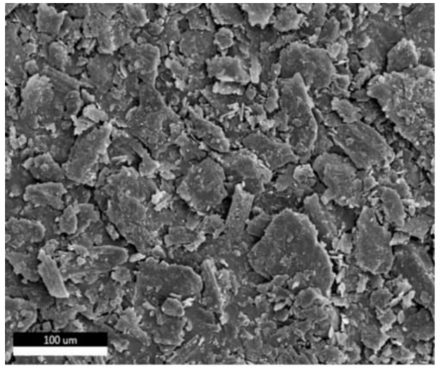


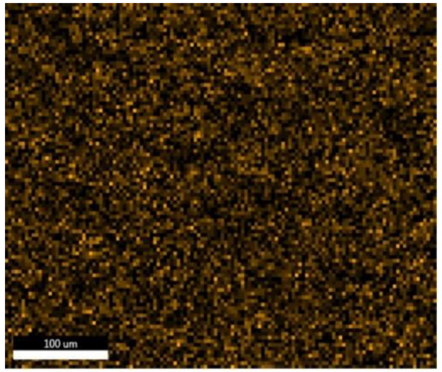


High-Resolution Continuum Source Graphite Furnace Atomic Absorption Spectrometry

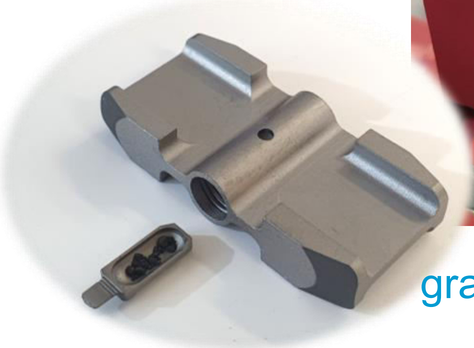
grinding with ultra-pure carbon:
preparation of diluted NMC samples

NMC111 1000fold diluted by carbon:
(a) SEM micrograph (magn. 264x)
(b) EDX element mapping for Ni indicated by yellow color





Sample mass



graphite boat and furnace

High-Resolution Continuum Source Graphite Furnace Atomic Absorption Spectrometry

Physikalische Chemie
Innovation durch Analytik

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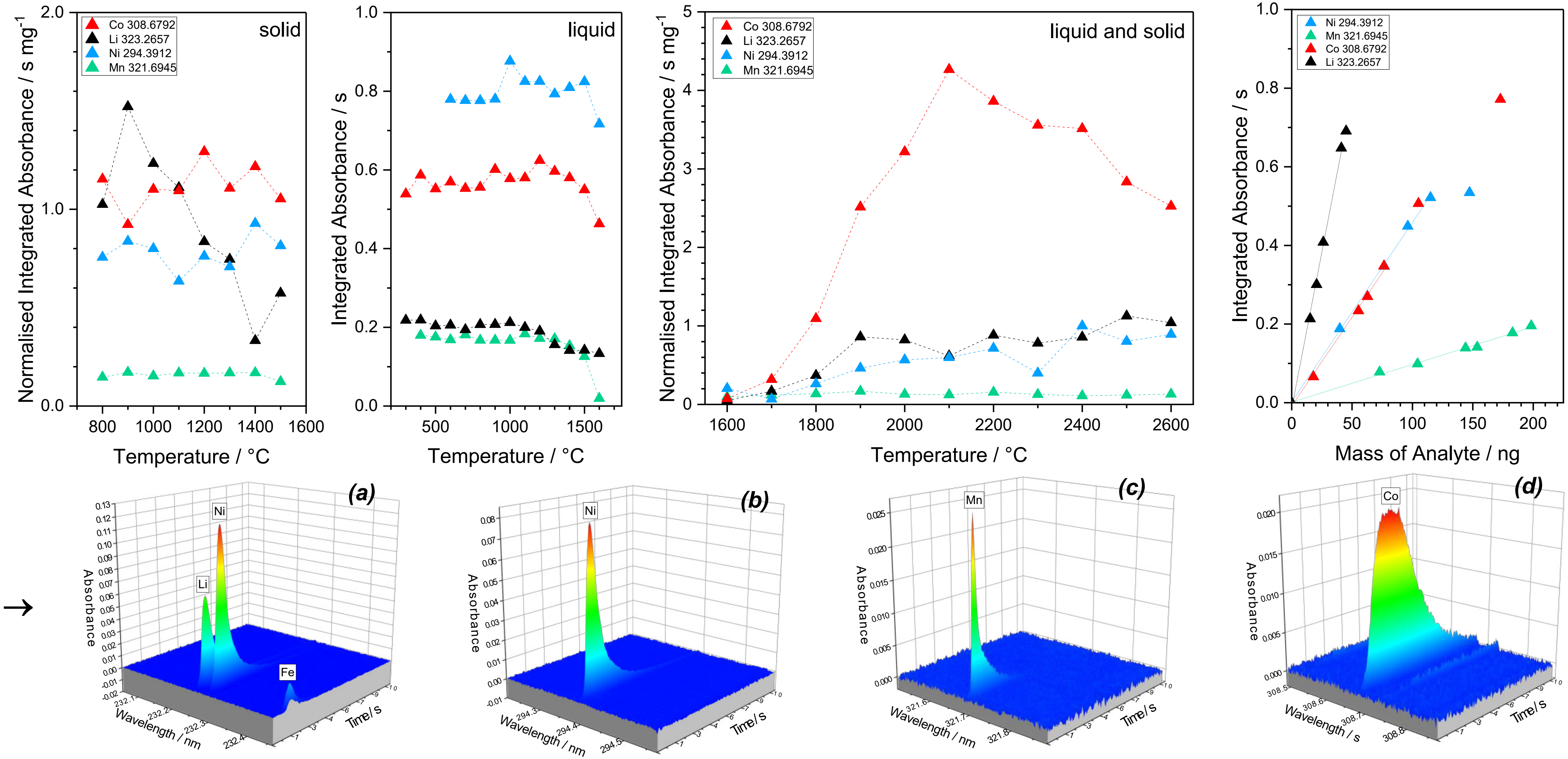

Time- and wavelength-resolved absorption spectra of
(a) Li at 323.2657 nm, **(b)** Ni at 294.3912 nm, **(c)** Mn at 321.6945 nm and **(d)** Co at 308.6792 nm

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High-Resolution Continuum Source Graphite Furnace Atomic Absorption Spectrometry

Physikalische Chemie – Innovation durch Analytik

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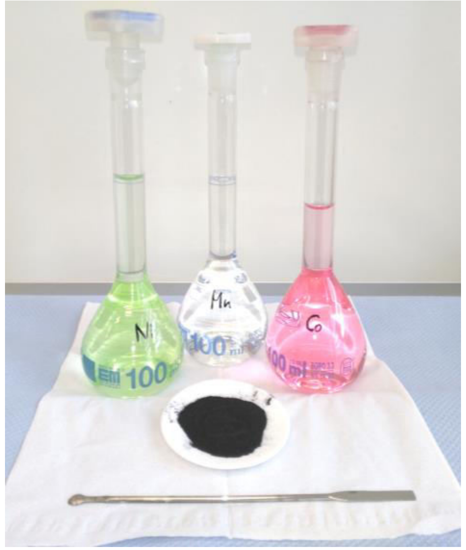
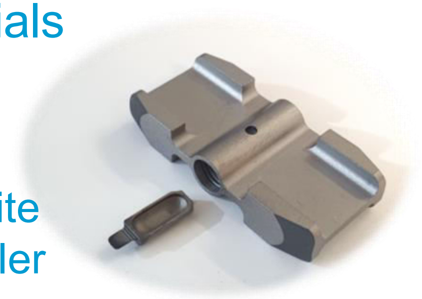
calibration against aqueous standard solutions

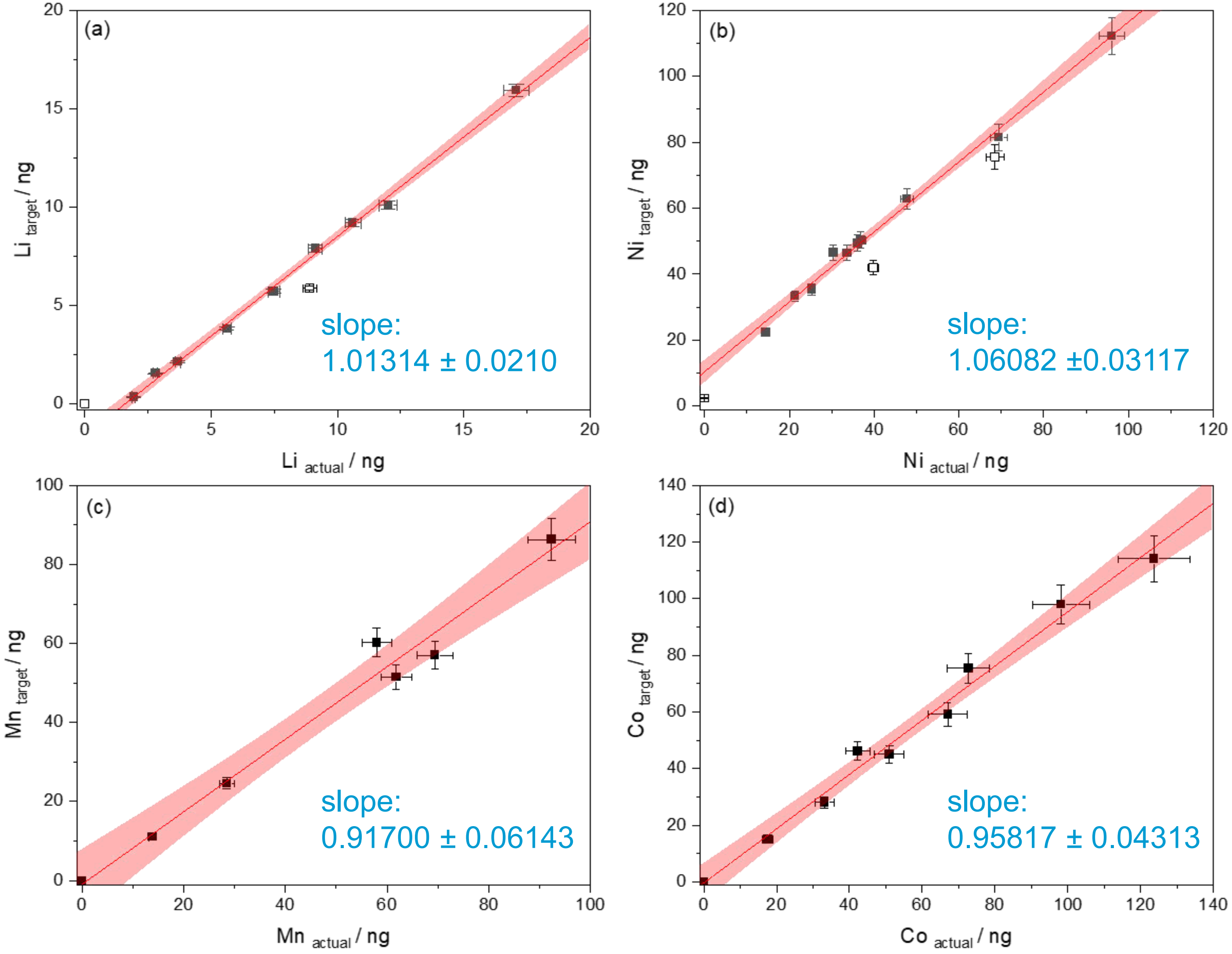


multi-element standard solution of lithium, nickel, manganese and cobalt were prepared in approximation to the stoichiometric ratios of typical NMC materials

liquid standards were transferred to the graphite furnace using autosampler



same graphite tube, the same graphite boat and the same atomisation programme can be used for solid and liquid sample measurements



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HIGH-RESOLUTION CONTINUUM SOURCE GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY

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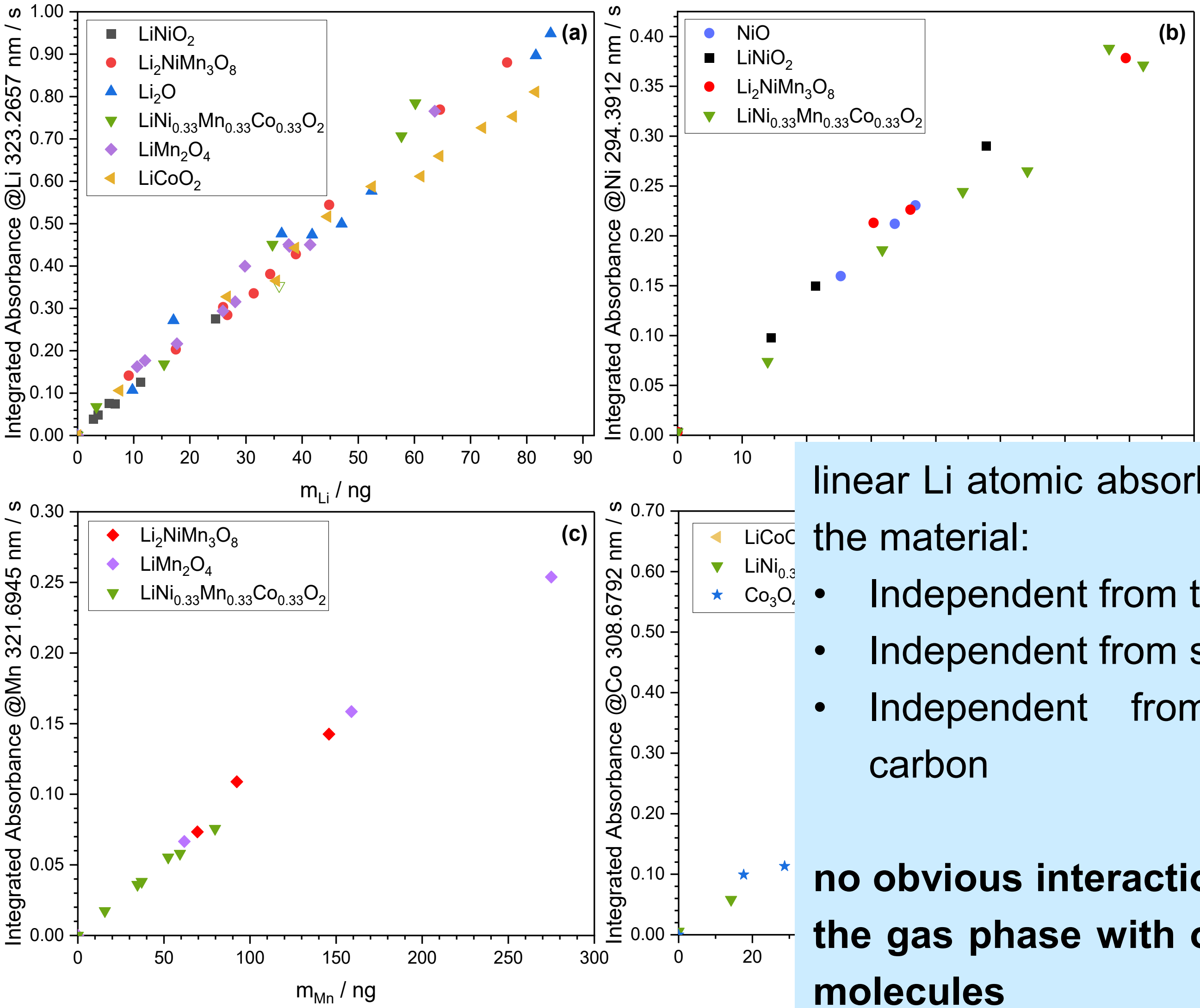
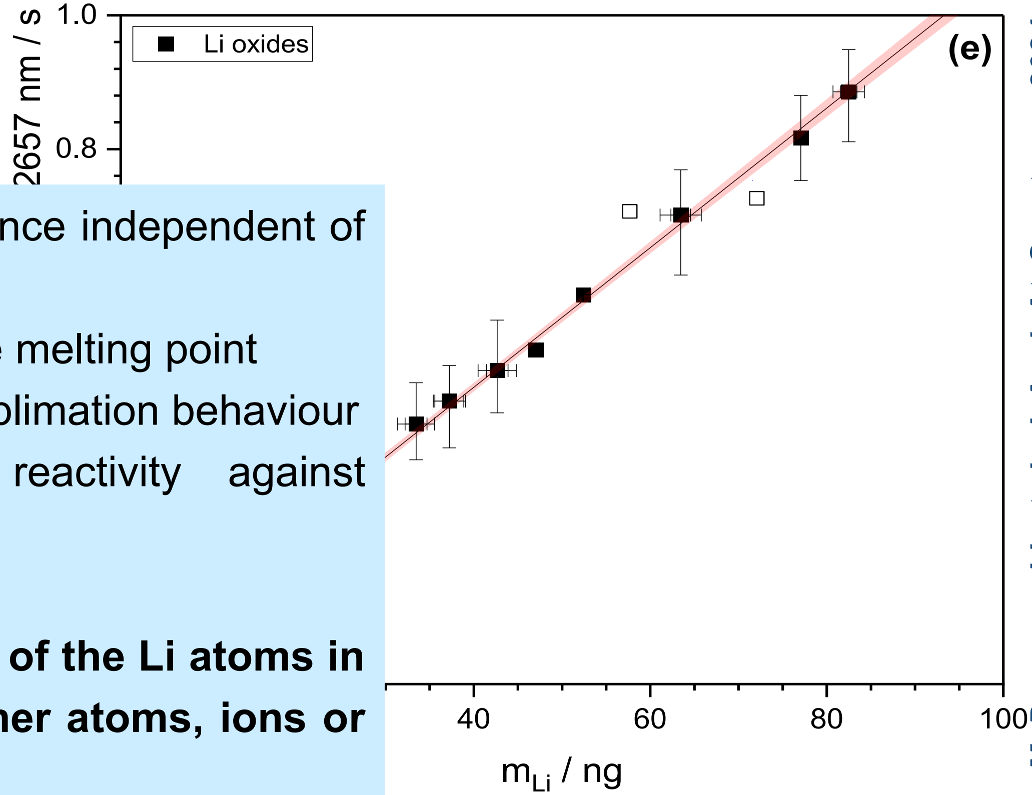


Calibration function based on Li-containing binary and ternary oxides:
Li_2O, $LiNiO_2$, $LiMn_2O_4$, $LiCoO_2$, $Li_2NiMn_3O_8$, NMC111.
Empty symbols represent statistical outliers.



linear Li atomic absorbance independent of the material:

- Independent from the melting point
- Independent from sublimation behaviour
- Independent from reactivity against carbon

no obvious interaction of the Li atoms in the gas phase with other atoms, ions or molecules

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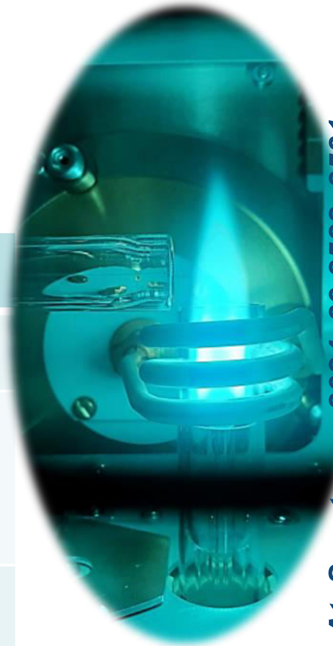
Validation of ICP-OES and SS-GF-CS AAS analytical procedures against Certified Reference Material „BAM-S014 Li-NMC 111 cathode material“

		Concentration / mg g^{-1}				
Sample		Li	Ni	Mn	Co	**NMC type**
CRM BAM-S014 Li-NMC 111	Found ICP-OES Certified	85.5 ± 11.5 78.0 ± 0.4 76.2 ± 1.6	183.7 ± 11.6 197.4 ± 0.5 197.6 ± 1.3	185.9 ± 5.9 184.7 ± 1.8 182.2 ± 1.4	196.7 ± 7.1 199.9 ± 0.5 198.0 ± 1.2	**111**
Recyclate 1	Found ICP-OES	55.65 ± 7.61 61.99 ± 0.43	213.12 ± 9.25 224.65 ± 1.71	150.67 ± 4.32 151.37 ± 1.29	151.19 ± 13.28 163.85 ± 1.29	**433**
Recyclate 2	Found ICP-OES	33.77 ± 4.00 40.71 ± 0.32	202.06 ± 8.67 222.94 ± 0.70	148.98 ± 9.07 149.21 ± 0.85	158.99 ± 8.91 162.25 ± 0.73	**433**
Recyclate 3	Found ICP-OES	51.45 ± 1.71 54.50 ± 0.36	215.03 ± 1.43 224.94 ± 0.93	147.42 ± 2.75 150.89 ± 0.82	186.89 ± 1.98 163.78 ± 0.69	**433**
Recyclate 4	Found ICP-OES	56.77 ± 6.29 69.57 ± 1.36	322.89 ± 13.35 330.33 ± 3.00	121.27 ± 0.96 104.14 ± 2.03	112.54 ± 14.02 100.84 ± 1.29	**622**



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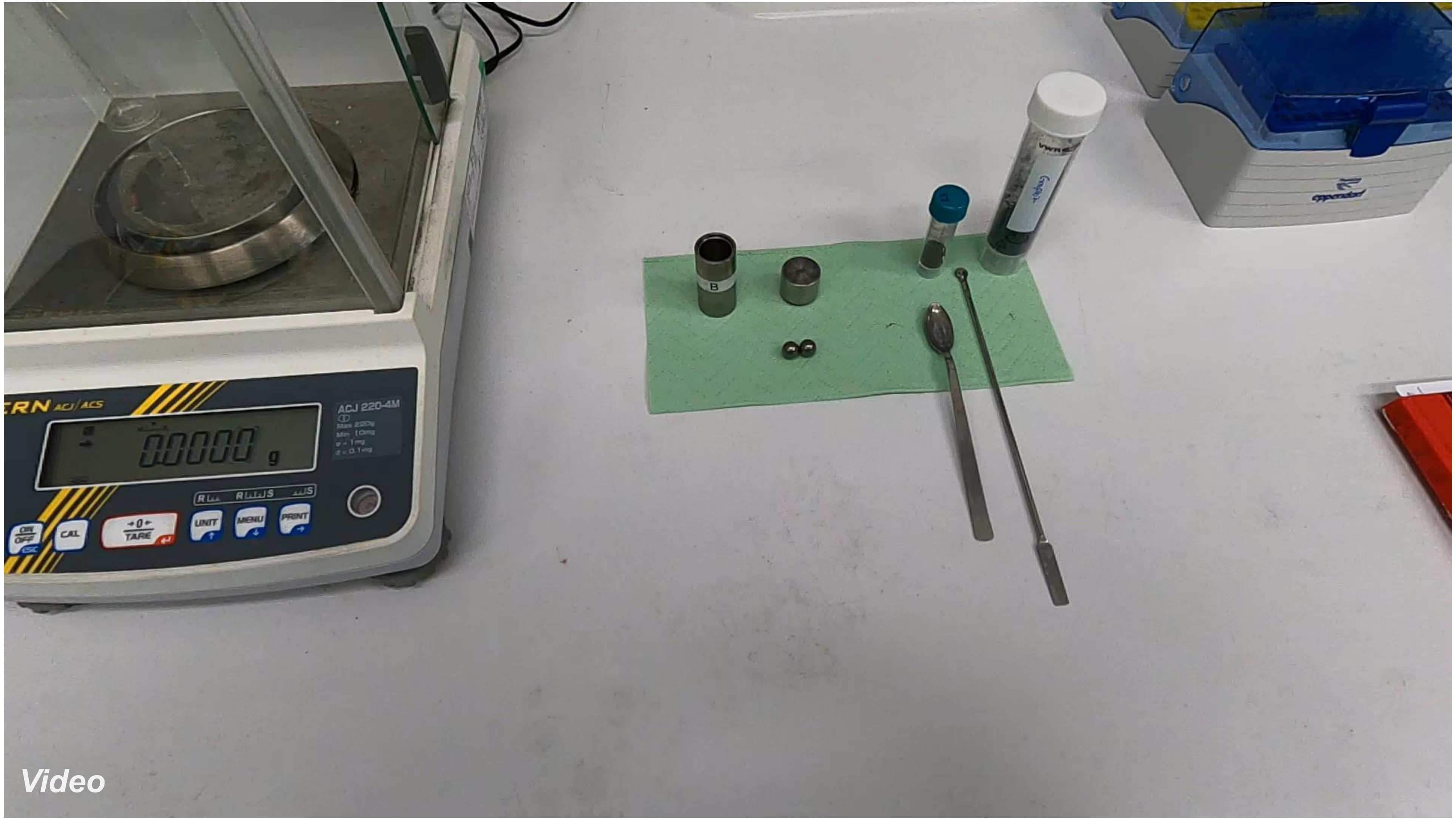
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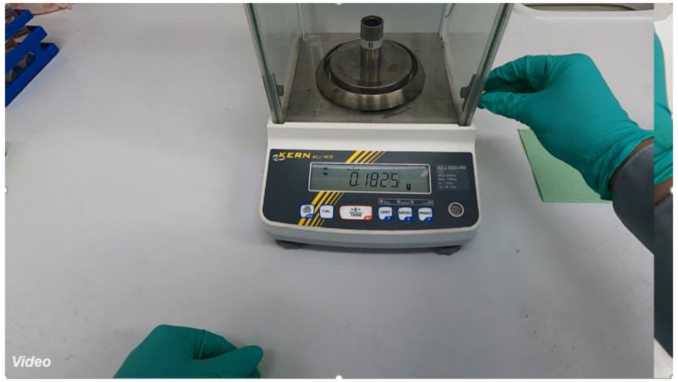

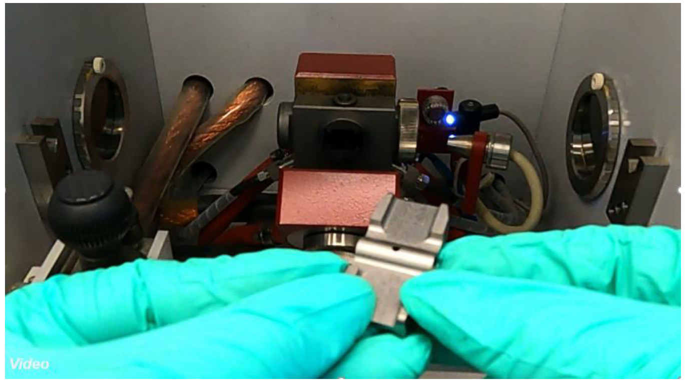

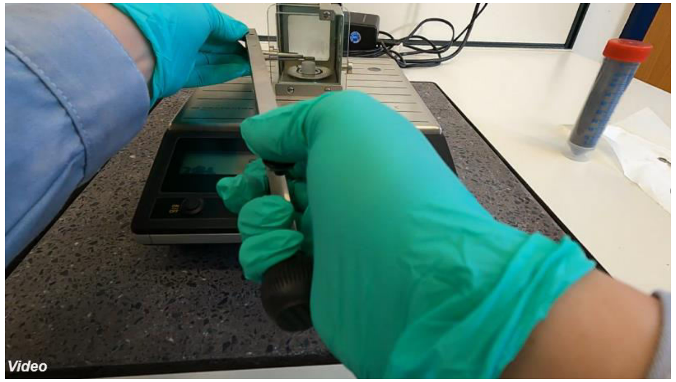

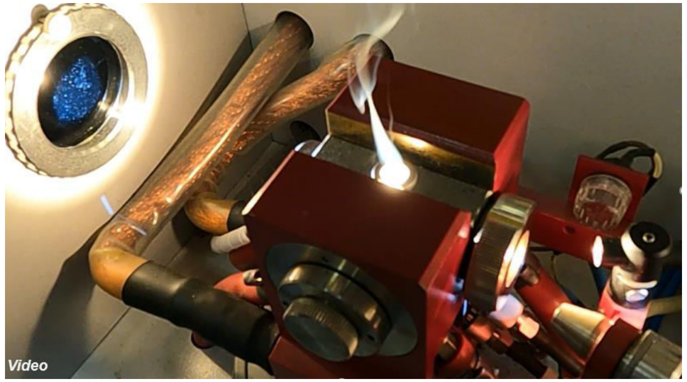

Video

High-Resolution Continuum Source Graphite Furnace Atomic Absorption Spectrometry

Vergleich zu ICP-OES

X Mikrowellengestützter Säureaufschluss
X Analyse über mehrere Tage
X Hoher Chemikalien- und Gasverbrauch

✔ direkte Feststoffanalyse
✔ Schnelle Analyseergebnisse
✔ minimaler Verbrauch

AAS – Prozess- und Qualitätskontrolle

- Kontrolle von Lebensmitteln auf giftige Metalle
- Spurenanalyse toxischer Elemente in Trinkwasser
- Schwermetallbestimmung in Klärschlämmen und Böden
- chemische Industrie, Bergbau oder Umweltanalytik

Recyclingunternehmen

→ stöchiometrische Zusammensetzung von Kathodenbeschichtungen aus gealterten und zu recycelnden Lithiumbatterien
→ sortenreines Batterie Schreddern
→ Bestimmung der Zusammensetzung von Schwarzmasse

Prüfen, ob Batterieabfälle rein sind | Aus Lithiumionenbatterien werden Cobalt, Lithium, Nickel oder Mangan zurückgewonnen. Um zu prüfen, ob diese Metalle rein sind, schließen Recyclingunternehmen sie erst mit Mikrowellen auf und untersuchen dann die Elementzusammensetzung per Spektroskopie mit induktiv gekoppeltem Plasma (ICP-OES oder ICP-MS).

Eine Methode von Domaschk und Kollegen überspringt die Probenvorbereitung, was die Analyse beschleunigt. Dazu nutzen die Forschenden der BTU Cottbus-Senftenberg Atomabsorptionsspektroskopie (AAS) mit Feststoffprobeneintrag. So lassen sich die Batteriematerialien direkt analysieren. BM

Nachrichten aus der Chemie, Oktober 2024, S. 48-51

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Innovatives Analysenverfahren für Recyclate aus LIB’s

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