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Application News

Energy Dispersive X-Ray Fluorescence Spectrometer EDX-7200
Inductively Coupled Plasma Optical Emission Spectrometer ICPE-9800 Series

Fast and Accurate Analysis of Black Mass Using EDX-7200 Facilitated by Using ICPE-9820

Alexander Nellessen
Shimadzu Europa GmbH

User Benefits

- EDX-7200 Series represents a very fast tool for on-site process control with little sample preparation.
- ICPE-9800 Series allows in-depth analysis of black mass samples for calibration of EDX-7200 and investigation of out-of-the-ordinary samples identified in process-control.
- Both instruments complement another and provide any user with a full set of capabilities for their endeavors.

■ Introduction

In the recycling process of lithium-ion batteries (LIB) black mass is an intermediate product from which, through various processes, precious metals like nickel, manganese and cobalt may be extracted (compare Fig. 2). The coarser fractions obtained in the mechanical recycling process typically contain metals like Al and Cu, which can negatively affect the smelting process, while essential metals for cathode materials, Co and Ni, are found mostly in the finer fractions. Any company trying to economically recover these valuable components requires information on the elemental composition of the black mass to be used as the input material to their processes. At the same time, the producers of black mass strive to control their mechanical stage of the recycling process to assure a constant quality of their product. Both parties require instrumentation allowing fast and accurate elemental analysis for quality control.

Difficulties associated with direct analysis of solids

Direct analysis of solid samples, as possible with EDX-7200, allows for obtaining results fast and effortless. In the absence of certified reference materials (CRM), it may however be difficult to validate the accuracy of the obtained results. In case of black mass, no CRM matching real samples is known to us. There are CRMs of the cathode material of LIBs[1)], but these neither contain the large amounts of graphite of the anode material nor the significant amounts of Al and Cu fragments of the separator foils. In the absence of CRMs, the analysis of samples by different means to produce reference values for validation can be useful. In case of black mass, ICPE-9820 represents a suitable analysis technique as outlined in a previously released Application News[2)]. Analysis using ICP-OES necessitates liquid samples which can be obtained by extensive sample preparation. This effort pays off, as this method allows to investigate the plausibility of the obtained results in many ways. Furthermore, liquid samples can easily be measured against certified calibration standards traceable to SI units.

With this Application News we demonstrate how reference values obtained with ICPE-9820 may be used to enhance the measurement results obtained by EDX-7200 allowing fast and accurate measurements on-site and in-time. The determination of reference values using ICPE-9800 Series is described in another publicly available Application News[3)].

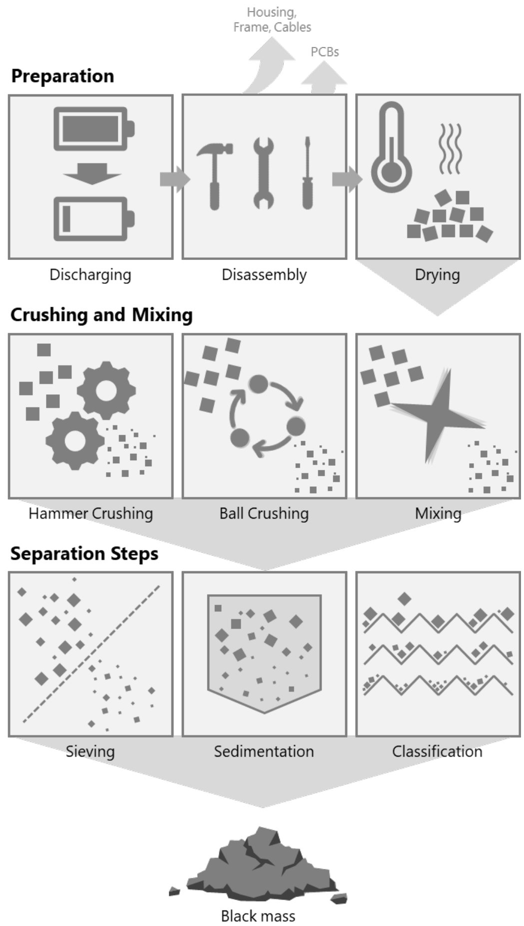

Fig. 2 Schematic depiction of the mechanical recycling process of LIB. The batteries are discharged, disassembled and the electrolyte evaporated. Black mass is obtained by varying crushing, mixing and separation steps.

Fig. 1 Shimadzu EDX-7200 Series and ICPE-9800 Series

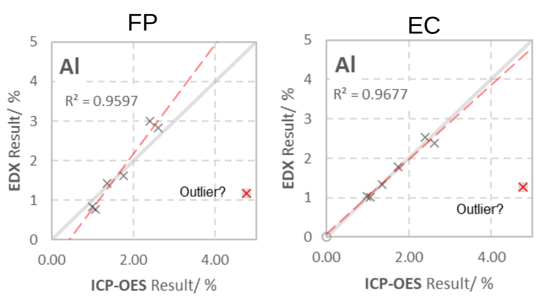

Fig. 3 Correlation of results obtained using EDX-7200 with Fundamental Parameters (FP) method and Empirical calibration (EC) method.
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■ Sample and Standard Preparation

Eight samples of black mass were provided by different European producers. The samples have been first analyzed using ICPE-9820[3]. For analysis using EDX-7200, the samples were transferred to ED-XRF cups prepared using Ultralene® thin film.

Samples A-E stem from an established process used routinely for producing black mass from different NMC type batteries. Samples F-H have been obtained by different and not yet established processes and from different discharges but with the same type of NMC622 battery.

■ Configuration & Measurement Condition

For direct analysis of the samples EDX-7200 equipped with a sample turret for automatic sample changing and the He option for replacement of the atmosphere was used. Depending on the humidity of the samples, it may be difficult to obtain a vacuum. For dry samples however, vacuum option would be suitable as well. The instrument configuration and analytical conditions are stated in Table 1.

Table 1 ED-XRF Instrument and analytical conditions

Instrument	: EDX-7200
X-ray tube	: Rh target
Detector	: SDD
Tube Voltage	: 50 kV (Ni, Mn, Co, Cu, Zn), 15 kV (Al, P, S)
Tube current	: Auto
Primary Filter	: None (Al, P), #2 (S), #3 (Ni, Mn, Co), #4 (Cu, Zn)
Collimator	: 10 mm
Atmosphere	: He
Live Time	: 60 sec (Al, P, S, Cu, Zn), 10 sec (Ni, Mn, Co)
Dead time	: 30 %

The energy of the Li Kα line's energy is too low to be detected by ED-XRF systems. However, Li is a major element in black mass, and its content is of interest. A calculation channel was added to the method to calculate the Li concentration based on the results of Ni, Mn and Co. The coefficients required for this calculation have been empirically determined based on the reference values obtained using ICPE-9820[3].

■ Results and Discussion

Fundamental Parameters Method (Quan-FP)

First all samples have been measured using a Quan-FP method. This method assumes the compounds of Ni, Mn and Co to be $LiNiO_2$, Li_2MnO_3 and $LiCoO_2$ respectively. The carbon content that was determined as the loss on ignition was entered to the calculation. The carbon content is a relevant information that will be determined by any producer of black mass with specialized equipment. Table 2 states the quantitative results thus obtained as well as the recovery of the ICP-OES reference values. These results can be obtained without any prior measurement of calibration standards. For all elements good correlation of the results obtained with EDX-7200 and ICPE-9820 could be observed as demonstrated by the coefficient of determination R^2 in the left column of Figure 3, however the results do not align 1:1 in all cases.

Calibration Curve (Quan-EC)

To improve the accuracy of ED-XRF measurement results, calibration of the instrument is recommended. Due to the absence of suitable CRMs, well-defined real samples have been used for calibration of the Quan-EC method.

Figure 4 displays the calibration functions for all elements both with and without matrix correction. Based on the coefficient of determination R^2 the linearity is greatly improved by applying the correction based on Ni, Mn and Co content in most cases. With matrix correction applied the recovery of the reference values is greatly improved as displayed in Table 3. The right column of Figure 3 displays the correlation of EDX-7200 and ICPE-9820 obtained results and demonstrates vastly improved correlation compared to the results obtained with Quan-FP method as displayed in the left column of Figure 3. In Figure 5 the overall recovery for each element in all eight samples is displayed as a boxplot. Generally, the recovery is close to 100%. In case of Al and Cu larger variation and even outliers can be observed. These elements occur in the coarser fractions of black mass which cannot always be completely removed in the sieving and classification steps of the mechanical recycling process.

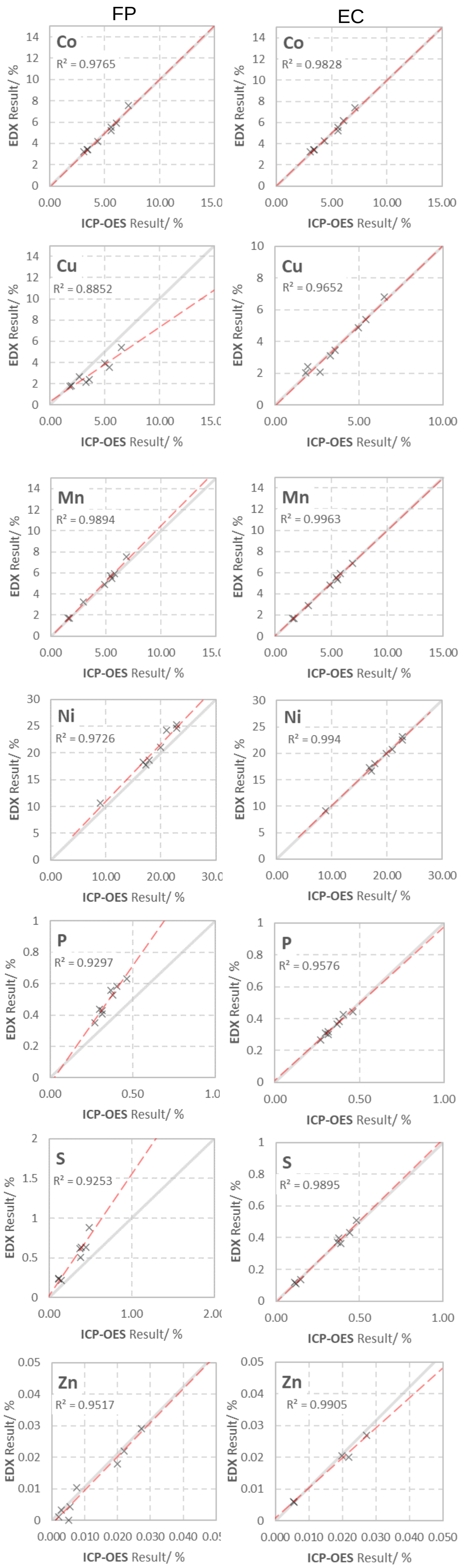

Fig. 3 Correlation of results obtained using EDX-7200 with Fundamental Parameters (FP) method and Empirical calibration (EC) method.

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■ Conclusion

As can be seen from Figure 5, EDX-7200 can generate results that correspond very well to results obtained using ICPE-9820. Compared to the ICP-OES measurements, sample preparation is barely existent, all that needs to be done is preparing a ED-XRF cup and filling it with sample. The possibility to skip time-consuming and error-prone steps like combustion with subsequent microwave digestion for routine analysis, makes EDX-7200 ideally suited for fast and accurate on-site analysis of black mass. The measurement time was below 6 minutes per sample.

<References>

1) BAM-S014, Li-NMC 111 Cathode Material, Bundesanstalt für Materialforschung und –prüfung (BAM)
2) Determination of Essential Metals and Trace Elements in Black Mass using ICPE-9820. Zhen Hao, Qi An, Shimadzu (Asia Pacific) Pte Ltd, Singapore
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3) Analysis of Black Mass using ICPE-9800 Series for enhancing accuracy of EDX-7200 results, Nellessen, Shimadzu Europa GmbH, Germany
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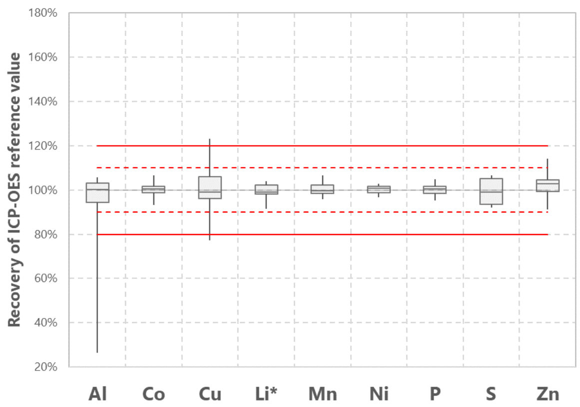

Fig. 5 Boxplot indicating the maximum and minimum recovery for all eight samples obtained using EDX-7200 and Quan-EC method (whiskers). The box indicates 50% of the samples, the horizontal line within each box is the median recovery of the ICPE-9820 reference values (compare Table 3).

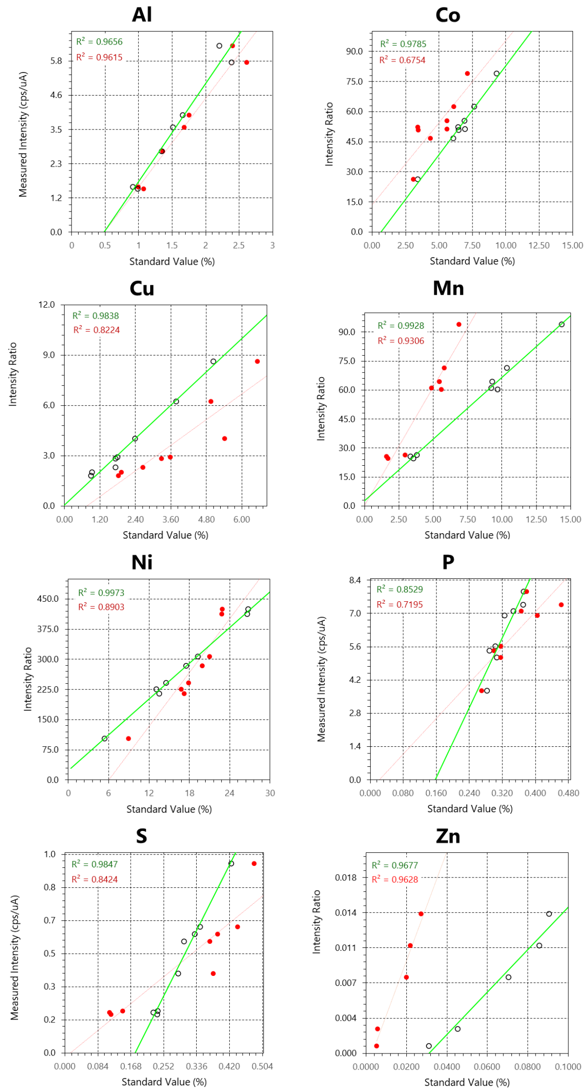

Fig. 4 Calibration functions obtained by measuring well defined reference samples. Red: calibration without matrix correction. Green: calibration with matrix correction employed.

Table 2 Measurement results obtained using EDX-7200 with Fundamental Parameters (Quan-FP) method. The recovery of the ICP-OES generated reference values are displayed. Lithium was not actually measured but calculated based on the Ni, Mn and Co content.

	Al		Co		Cu		Li (calc)		Mn		Ni		P		S		Zn	
Elem.	%	Recovery	%	Recovery	%	Recovery	%	Recovery	%	Recovery	%	Recovery	%	Recovery	%	Recovery	%	Recovery
Sample A	3.01	125%	5.23	93%	1.75	96%	3.22	100%	5.50	99%	17.72	103%	0.407	129%	0.636	163%	0.0179	90%
Sample B	2.84	109%	5.50	98%	2.41	67%	3.33	104%	5.75	106%	18.21	108%	0.436	146%	0.617	167%	0.0292	107%
Sample C	1.42	105%	4.19	97%	2.14	65%	3.45	100%	4.91	101%	21.11	106%	0.559	153%	0.219	149%	0.0000	0%
Sample D	0.83	84%	3.39	99%	3.95	80%	3.44	122%	1.68	99%	24.57	108%	0.584	144%	0.237	210%	0.0012	59%
Sample E	0.76	71%	3.39	100%	5.44	83%	3.53	114%	1.74	109%	25.30	111%	0.632	137%	0.229	195%	0.0032	110%
Sample F	1.62	93%	3.21	105%	2.66	100%	1.93	101%	3.27	111%	10.57	118%	0.527	139%	0.877	182%	0.0103	136%
Sample G	1.18	25%	7.54	106%	3.57	66%	4.44	112%	7.55	110%	24.20	115%	0.351	130%	0.504	133%	0.0044	78%
Sample H	1.63	97%	5.88	97%	1.83	94%	3.44	97%	5.92	102%	18.68	105%	0.430	136%	0.635	144%	0.0220	100%

Table 3 Measurement results obtained using EDX-7200 with external calibration (Quan-EC) method. The recovery of the ICP-OES generated reference values are displayed. Lithium was not actually measured but calculated based on the Ni, Mn and Co content.

	Al		Co		Cu		Li (calc)		Mn		Ni		P		S		Zn	
Elem.	%	Recovery	%	Recovery	%	Recovery	%	Recovery	%	Recovery	%	Recovery	%	Recovery	%	Recovery	%	Recovery
Sample A	2.53	105%	5.22	93%	2.04	112%	3.18	99%	5.34	96%	16.68	97%	0.301	95%	0.364	94%	0.0205	103%
Sample B	2.38	91%	5.55	99%	3.45	96%	3.30	103%	5.55	102%	17.26	103%	0.311	104%	0.371	100%	0.0270	99%
Sample C	1.33	98%	4.24	98%	3.11	95%	3.41	99%	4.83	99%	19.97	100%	0.367	100%	0.137	93%	0.0060	114%
Sample D	1.05	106%	3.43	100%	4.87	98%	2.94	104%	1.67	99%	22.58	99%	0.425	105%	0.120	107%	-	-
Sample E	1.02	95%	3.42	101%	6.80	104%	3.02	98%	1.70	107%	23.21	102%	0.442	96%	0.108	92%	-	-
Sample F	1.79	102%	3.27	107%	2.06	77%	1.74	91%	2.90	98%	9.11	102%	0.381	101%	0.507	105%	-	-
Sample G	1.27	27%	7.39	104%	5.41	100%	4.03	102%	6.89	100%	20.75	99%	0.268	99%	0.398	105%	0.0059	105%
Sample H	1.72	102%	6.16	101%	2.41	123%	3.50	98%	5.93	103%	18.11	101%	0.318	101%	0.432	98%	0.0200	91%

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