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

Application News

Analysis of Black Mass Using ICPE-9800 for Enhancing Accuracy of EDX-7200 Results

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User Benefits

- 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.
- EDX-7200 Series represents a very fast tool for on-site process control with little sample preparation.
- 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. 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.

Strengths and weaknesses of ED-XRF and ICP-OES

A great strength of EDX-7200 is the capability to directly analyze solid samples with little sample preparation. However, it may be difficult to spot interferences and gauge the accuracy of the obtained result. Sample preparation for analysis using ICPE-9820 can be time-consuming and complex, but the obtainable results may be more easily evaluated to spot possible biases due to matrix effects. Preparing calibration standards based on certified reference materials (CRMs) traceable to SI units is easy for liquid samples. This makes ICPE-9820 suitable to be used for preparing reference values on production samples.

The complementary strengths and weaknesses of both techniques make Shimadzu's EDX-7200 Series and ICPE-9800 Series a conclusive solution for the elemental analysis of black mass.

This application shows how to analyze black mass using ICPE-9800 to obtain an accurate reference value for EDX analysis[1)].

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

■ Samples and Standards for ICP-OES

Eight samples of black mass were provided by different European suppliers.

100 mg of sample have been placed in ceramic crucibles and subjected to ashing for 120 minutes at 800 ℃ . The ash was transferred to the PTFE microwave digestion vessel and 6 mL of concentrated HCl and 2 mL of concentrated HNO_3 were added. The microwave digestion program consisted of a 25 minutes ramp to 220 ℃ which was held for 40 minutes. After cooling the digestate was made up to 50 mL. Before analysis, the digestates have been volumetrically diluted by a factor of ten. Since this procedure yielded clear solutions, no filtration was required. Each sample was prepared in triplicate to evaluate variations due to sample preparation and/or sample inhomogeneity. In total 24 analytical portions have been prepared according to the above procedure.

Calibration standards were prepared from commercially available single-element standard solutions (compare Table 1). To each standard and sample Y was added as an internal standard to monitor the instrument's stability over time.

Table 1 Calibration concentration range for target elements

Elements	Min/ mg L^{-1}	Max/ mg L^{-1}
Ni	20	50
Mn, Co, Li, Al, Cu	2.5	20
P, S, Zn	0.25	2
Y internal Standard 1 mg L^{-1}		

■ Configuration & Measurement Condition

Measurement was conducted using standard configuration ICPE-9820 with the optional peristaltic pump for sample introduction. The instrument configuration and analytical conditions are stated in Table 2.

Table 2 ICP-OES Instrument and analytical conditions

Instrument	: ICPE-9820
Radio frequency power	: 1.2 kW
Plasma gas flowrate	: 10.0 L/min
Auxiliary gas flowrate	: 0.60 L/min
Carrier gas flowrate	: 0.70 L/min
Nebulizer	: Nebulizer 10 UES
Spray Chamber	: Cyclone Chamber
Plasma Torch	: Mini-Torch
Peristaltic Pump	: Black-black tubing, 20 r.p.m.
Observation	: Axial (AX)/ Radial (RD)

■ Results and Discussion

Calibration Curve and Detection Limits

Measurement of the calibration standards yielded highly linear functions as judged by the coefficient of correlation. The achieved instrument limits of detection (IDL) and quantitation allow for the precise determination of all elements on interest (compare Table 3).

Table 3 Linear regression, IDL and LOQ

Elem.	View	Wavelength/ nm	Coefficient of Correlation	IDL/ mg L^{-1}	LOQ/ mg L^{-1}
Al	Axial	394.403	0.99999	0.002	0.007
Co	Axial	237.862	0.99994	0.001	0.004
Cu	Axial	327.396	0.99999	0.007	0.03
Li	Radial	670.784	1.00000	0.02	0.07
Mn	Radial	259.373	0.99996	0.005	0.02
Ni	Radial	231.604	0.99968	0.02	0.06
P	Axial	178.287	0.99990	0.02	0.06
S	Axial	180.731	0.99997	0.01	0.04
Zn	Axial	206.200	0.99956	0.001	0.004

IDL = 3 x σ / slope of the calibration curve
LOQ = 10 x σ / slope of the calibration curve

Ensuring the absence of matrix effects

A big benefit of working with ICP-OES and liquid samples is the possibility to check for matrix effects easily. If standards and samples exhibit a different behavior in the plasma, biased results are obtained. To confirm the absence of *non-spectral interference*, one sample was diluted by a factor of two and three to check the dilution recovery. The results displayed in Table 4 indicate the absence of non-spectral interferences.

Table 4 Analysis results at different dilution levels of sample A #1 with dilution factors applied. The recovery is within 100 +/- 10 % in all cases.

Elem.	Undiluted Sample	Dilution Factor 2	Rec.	Dilution Factor 3	Rec.
Al/ %	2.43	2.39	98%	2.38	98%
Co/ %	5.59	5.54	99%	5.55	99%
Cu/ %	1.85	1.83	99%	1.82	98%
Li/ %	3.20	3.19	100%	3.14	98%
Mn/ %	5.56	5.51	99%	5.43	98%
Ni/ %	17.2	17.0	99%	16.8	98%
P/ %	0.315	0.290	92%	0.295	94%
S/ %	0.387	0.375	97%	0.396	102%
Zn/ %	0.0194	0.0197	102%	0.0200	103%

To further validate our measurement results, we checked the absence of *spectral interferences* due to overlapping emission lines. A common and quick procedure is to compare the results of different analysis lines. Spectral interference is unlikely to affect all lines at once and to the same degree. If multiple lines yield similar results, the absence of spectral interference is likely. The results of three different analysis lines per element are depicted in Table 5. In case of P and Zn not all analysis lines yield the same result. We should pay closer attention to these elements next.

In case of phosphorous the profile of the emission line at 213.618 nm indicates a possible, partial, overlap with Cu or Fe as indicated by the software (compare Figure 2). The significant interference by Cu could be confirmed by measuring a 100 mg/L Cu standard and overlapping the spectrum with the measurement of a 7 mg/L P standard (compare Figure 3). A similar, however much less severe, interference can be spotted for the analysis line at 177.499 nm. At line 178.287 nm no significant interference of the major components, Ni, Mn, Co, Al or Cu could be observed. Due to this reason, we selected this line for the analysis. In case of Zn there is no line in agreement with another, as with phosphorous, closer investigation is required. By aspirating single-element solutions, spectral interference due to Cu and Ni could be observed on lines 202.548 nm and 213.856 nm. No spectral interference on line 206.200 nm could be observed for any of the major components of black mass (Al, Cu, Mn, Ni, P, S and Zn). For this reason, the analysis result obtained at 206.200 nm is accepted as the best estimate of the Zn content in the sample.

Measurement Stability

Y was added to all samples as an internal standard. The relative internal standard (ISTD) intensity over the course of the measurement indicates the measurement stability. The relative ISTD intensity did not exceed 100% +/- 10% which shows very good stability. The validity of the calibration was repeatedly confirmed throughout the measurement sequence by measuring a calibration standard in fixed intervals. The recovery of this continuing calibration verification (CCV) standard did not exceed 100% +/- 5% over the course of about 3.5 hours. The measurement sequence in total consisted of 39 diluted digestates, 4 CCVs, 9 rinse steps and 5 calibration standards. The measurement time per sample was about 3 minutes and 50 seconds which included both axial and radial measurement within a single sample injection.

Table 5 Analysis results at different analysis lines for sample A #1 with dilution factors applied.

Elem.	Result Line 1	Result Line 2	Result Line 3
Al/ %	2.95 Al 167.081	2.43 Al 394.403	2.40 Al 396.153
Co/ %	5.53 Co 228.616	5.59 Co 237.862	5.51 Co 238.892
Cu/ %	1.84 Cu 224.700	1.88 Cu 324.754	1.85 Cu 327.396
Li/ %	3.10 Li 323.261	3.15 Li 610.364	3.20 Li 670.784
Mn/ %	5.58 Mn 257.610	5.56 Mn 259.373	5.52 Mn 260.569
Ni/ %	17.4 Ni 221.647	17.2 Ni 231.604	17.4 Ni 341.476
P/ %	0.303 P 177.499	0.315 P 178.287	0.259 P 213.618
S/ %	0.387 S 180.731	0.404 S 182.037	0.399 S 182.625
Zn/ %	0.0310 Zn 202.548	0.0194 Zn 206.200	0.0891 Zn 213.856

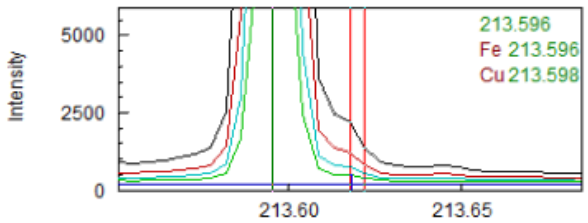

Fig. 2 Line profile of P 213.618. The red vertical lines represent the integration range while the green vertical line indicates the Peak Search function that indicates possible interferences by Fe and Cu.

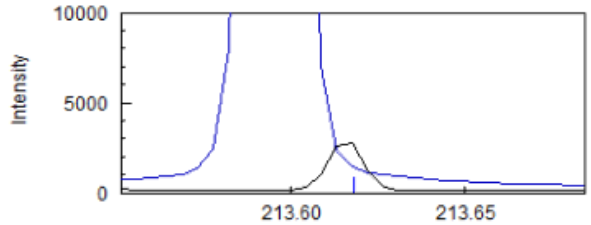

Fig. 3 Overlap of the profiles of single element solutions of 100 mg/L Cu (blue) and 7 mg/L of P (black) at P 213.816.

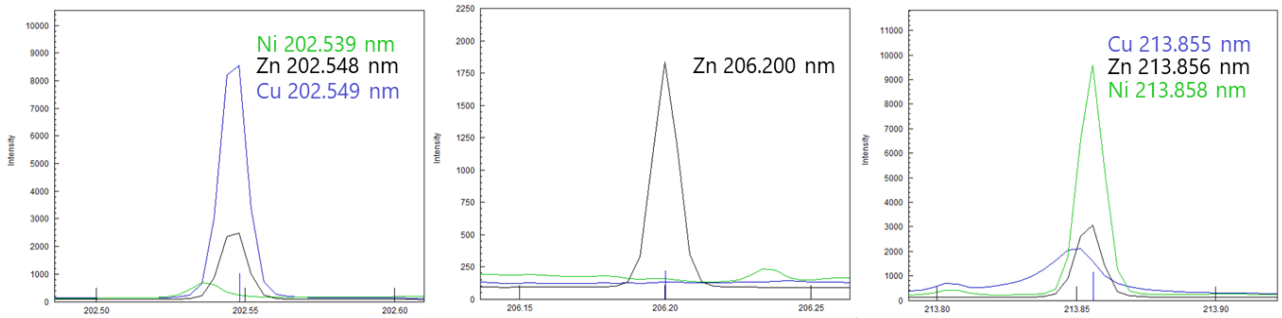

Fig. 4 Profiles of single-element solutions of 100 mg/L Ni (green), 100 mg/L Cu (blue) and 0.270 mg/L Zn (black) demonstrate the spectral interference of the analysis lines 202.548 nm and 213.856 nm. This indicates, that only the result obtained at 206.200 nm is free of interference.

Measurement Results

Table 6 shows the individual analysis results of each independently prepared triplicate with the corresponding dilution factor applied. For each sample, the average of the three triplicates was determined as the best estimate of the elemental composition of the sample.

The relative standard deviation (RSD) of the ICP-OES measurement is stated for each triplicate, also the RSD between the triplicates is stated as a measurement of the sample's homogeneity and reproducibility of the sample preparation and is highlighted for easy identification of very precise values and values suffering from larger variations.

■ Conclusion

Shimadzu's ICPE-9800 Series allows to conveniently validate obtained measurement results due to the ability to compare and add additional analysis lines after measurement. Liquid solutions allow for dilution or spike recovery experiments, that cannot be easily recreated with solid samples. Compared to ED-XRF however, sample preparation is vastly more extensive. That is why both techniques complement another that well. The herewith presented results will serve as reference values for calibration of Shimadzu's EDX-7200 to set up as a fast analysis procedure for on-site analysis of black mass that is equivalent to results obtained using ICPE-9800 Series[2].

Additional Information

The herein used two-step sample preparation is different to the procedure commonly described in other publications[2][3]. There a one-step procedure with subsequent filtration is used. The benefit of the two-step procedure including a combustion step, is the possibility to determine the carbon content based on the loss on ignition. Since no solid residues remain in the digestate, the cleaning of the microwave digestion vessels becomes quicker and easier compared to a one-step sample preparation procedure. Disposable inserts for microwave digestion vessels are not recommended at the high temperatures typically used for digestion of black mass, so facilitating the cleaning of the vessels corresponds to an additional benefit.

<References>

1) Fast and accurate analysis of Black Mass using EDX-7200 facilitated by using ICPE-9820, Nellessen, Shimadzu Europa GmbH, Germany
Application News 05-SCA-125-031-EN

2) Mousa et al. Characterization and Thermal Treatment of the Black Mass from Spent Lithium-Ion Batteries. Sustainability 2023, 15, 15.

3) Determination of Essential Metals and Trace Elements in Black Mass using ICPE-9820. Zhen Hao, Qi An, Shimadzu (Asia Pacific) Pte Ltd, Singapore
Application News 04-AD-0298-en

Table 6 Analysis results of each triplicate of all eight samples. The relative standard deviation (RSD) for each individual sample is based on three repeated measurements and corresponds to the instrument's precision. The RSD of the average value (colored, legend below) refers to the variation of the results of the triplicate and is mostly affected by sample homogeneity and reproducibility of the sample preparation.

	Al		Co		Cu		Li		Mn		Ni		P		S		Zn	
	AVG (%)	RSD	AVG (%)	RSD (%)	AVG (%)	RSD (%)	AVG (%)	RSD (%)	AVG (%)	RSD (%)	AVG (%)	RSD (%)	AVG (%)	RSD (%)	AVG (%)	RSD (%)	AVG (%)	RSD (%)
Sample A																		
#1	2.43	0.6%	5.59	0.2%	1.85	0.3%	3.20	0.7%	5.56	1.0%	17.20	1.0%	0.315	1.2%	0.387	1.3%	0.0194	0.2%
#2	2.40	0.9%	5.58	0.4%	1.75	0.0%	3.15	0.9%	5.52	0.7%	17.10	0.7%	0.311	0.5%	0.388	1.2%	0.0208	0.5%
#3	2.38	1.4%	5.65	0.2%	1.88	0.4%	3.30	0.4%	5.62	0.7%	17.40	0.4%	0.323	2.6%	0.392	0.3%	0.0196	0.4%
Average	2.40	1.05%	5.61	0.68%	1.83	3.73%	3.22	2.37%	5.57	0.90%	17.23	0.89%	0.316	1.93%	0.389	0.68%	0.0199	3.80%
Sample B																		
#1	2.74	2.3%	5.71	0.4%	3.87	0.7%	3.35	0.7%	5.57	0.3%	17.20	0.2%	0.328	1.7%	0.375	0.6%	0.0279	0.5%
#2	2.68	1.3%	5.75	0.3%	3.56	0.9%	3.22	0.4%	5.56	0.4%	17.20	0.2%	0.270	1.5%	0.385	1.6%	0.0273	0.5%
#3	2.42	0.7%	5.33	0.2%	3.30	0.5%	3.02	0.5%	5.18	0.6%	16.00	0.6%	0.300	1.0%	0.349	1.2%	0.0264	0.1%
Average	2.61	6.51%	5.60	4.14%	3.58	7.98%	3.20	5.20%	5.44	4.09%	16.80	4.12%	0.299	9.69%	0.370	5.03%	0.0272	2.78%
Sample C																		
#1	1.45	0.8%	4.38	0.2%	3.08	0.7%	3.31	2.3%	4.93	1.6%	20.10	1.2%	0.334	2.7%	0.154	3.2%	0.0051	0.8%
#2	1.36	2.1%	4.37	0.1%	3.44	0.6%	3.48	0.8%	4.90	0.7%	20.00	0.4%	0.388	1.2%	0.145	3.0%	0.0054	0.4%
#3	1.26	0.4%	4.27	0.1%	3.33	0.4%	3.54	0.9%	4.81	0.9%	19.70	1.0%	0.377	0.9%	0.142	3.5%	0.0053	0.9%
Average	1.36	7.01%	4.34	1.40%	3.28	5.62%	3.44	3.46%	4.88	1.28%	19.93	1.04%	0.366	7.79%	0.147	4.25%	0.0053	2.19%
Sample D																		
#1	1.04	1.7%	3.38	0.2%	4.83	0.5%	2.60	1.6%	1.67	1.2%	22.60	0.9%	0.398	1.6%	0.112	2.3%	0.0023	1.2%
#2	0.97	2.0%	3.43	0.3%	5.02	1.0%	2.82	0.7%	1.69	0.5%	22.80	0.5%	0.408	0.7%	0.111	0.8%	0.0019	1.1%
#3	0.96	0.5%	3.48	0.2%	5.03	0.1%	3.07	0.5%	1.72	0.5%	23.10	0.4%	0.409	1.3%	0.115	5.3%	0.0020	0.8%
Average	0.99	4.43%	3.43	1.46%	4.96	2.27%	2.83	8.31%	1.69	1.49%	22.83	1.10%	0.405	1.50%	0.113	1.85%	0.0021	8.87%
Sample E																		
#1	1.12	0.5%	3.37	0.4%	6.63	0.6%	2.82	1.3%	1.59	1.2%	22.80	0.9%	0.462	1.3%	0.115	3.8%	0.0033	1.5%
#2	0.98	1.0%	3.39	0.2%	6.44	0.6%	3.08	0.6%	1.60	0.2%	23.00	0.0%	0.466	2.0%	0.117	0.7%	0.0018	5.7%
#3	1.11	0.9%	3.41	0.2%	6.50	0.4%	3.37	0.3%	1.59	0.6%	22.80	0.4%	0.458	1.6%	0.120	3.8%	0.0036	1.7%
Average	1.07	7.30%	3.39	0.59%	6.52	1.49%	3.09	8.90%	1.59	0.36%	22.87	0.50%	0.462	0.87%	0.117	2.14%	0.0029	33.70%
Sample F																		
#1	1.76	1.2%	3.05	0.1%	2.71	0.7%	1.87	1.0%	2.93	0.7%	8.87	0.5%	0.390	1.1%	0.474	0.5%	0.0092	0.9%
#2	1.79	0.8%	3.10	0.2%	2.60	0.6%	1.94	1.3%	2.98	0.4%	9.04	0.2%	0.369	1.4%	0.479	0.8%	0.0059	0.7%
#3	1.70	1.1%	3.06	0.1%	2.68	0.4%	1.91	0.7%	2.95	0.3%	8.96	0.1%	0.376	2.0%	0.495	0.7%	0.0076	0.5%
Average	1.75	2.62%	3.07	0.86%	2.66	2.14%	1.91	1.84%	2.95	0.85%	8.96	0.95%	0.378	2.83%	0.483	2.27%	0.0076	21.90%
Sample G																		
#1	4.81	2.4%	7.20	0.2%	5.45	1.0%	3.93	1.3%	6.94	0.9%	21.20	0.8%	0.283	2.1%	0.387	1.2%	0.0056	1.8%
#2	4.69	1.3%	7.23	0.2%	5.47	0.6%	4.12	1.3%	7.00	0.7%	21.40	0.5%	0.255	2.9%	0.381	0.3%	0.0055	0.9%
#3	4.83	0.9%	6.99	0.4%	5.35	0.5%	3.82	1.7%	6.71	1.4%	20.50	1.3%	0.271	0.9%	0.365	1.6%	0.0058	1.4%
Average	4.78	1.59%	7.14	1.83%	5.42	1.19%	3.96	3.84%	6.88	2.22%	21.03	2.25%	0.270	5.21%	0.378	3.01%	0.0056	3.08%
Sample H																		
#1	1.68	2.4%	6.01	0.2%	1.92	0.8%	3.55	0.5%	5.72	0.3%	17.70	0.4%	0.329	0.5%	0.438	0.6%	0.0215	0.4%
#2	1.69	1.3%	6.10	0.2%	1.99	0.5%	3.52	0.7%	5.80	0.8%	17.90	0.5%	0.279	2.3%	0.445	1.5%	0.0217	0.4%
#3	1.67	0.9%	6.15	0.3%	1.96	0.3%	3.62	0.7%	5.83	0.6%	18.00	0.5%	0.341	1.3%	0.441	1.0%	0.0226	0.6%
Average	1.68	0.60%	6.09	1.17%	1.96	1.79%	3.56	1.44%	5.78	0.98%	17.87	0.85%	0.316	10.40%	0.441	0.80%	0.0219	2.67%

Average RSD	>10%	5 - 10%	<5%

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