



X-ray fluorescence

Monitoring metal salt baths for the production and recycling of lithium-ion batteries (LIB) using the ARL QUANT'X EDXRF Spectrometer

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Figure 1. ARL QUANT'X EDXRF Spectrometer.

Introduction

With the growing demand for lithium-ion batteries (LIBs), efficient recycling of these batteries has become essential for sustainability. A key aspect of recycling is the recovery of valuable metals like manganese (Mn), cobalt (Co), and nickel (Ni) from black mass, the by-product of spent batteries. The hydrometallurgical process involves steps such as leaching, purification, and separation to extract these metals, and the accurate measurement of their concentration in solution is critical for optimizing recovery.

Energy-dispersive X-ray fluorescence (EDXRF) has emerged as a powerful analytical technique for this purpose, offering fast, non-destructive, and highly sensitive detection of these metals in aqueous solutions. EDXRF is particularly valuable in both the recycling process and the production of new batteries, ensuring the quality of precursor materials used in cathode fabrication.

For analyzing aqueous samples, ICP-OES is a widely recognized reference technique, particularly effective for detecting element concentrations at ppm or ppb levels. However, when dealing with samples from metal salt baths, where element concentrations are high, significant dilution (1000x to 10000x) is required before ICP-OES analysis. This dilution process increases preparation time and introduces potential errors. In contrast, EDXRF can analyze samples directly, simplifying and speeding up the sample preparation process.

Instrumentation

The Thermo Scientific™ ARL™ QUANT'X EDXRF Spectrometer (e.g., Figure 1) is equipped with a silicon drift detector (SDD) and an air-cooled 50-Watt rhodium (Rh) or Silver (Ag) target X-ray tube, capable of a maximum excitation voltage of 50 kV. It features nine primary beam filters designed to optimize peak-to-background signals for elements from fluorine (F) to americium (Am). The SDD sets the performance benchmark for all energy-dispersive detectors, with its large 30 mm² active area effectively capturing characteristic X-rays emitted by the sample. The optional SDD with graphene window extends light element detection down to carbon (C). The 10-position auto-sampler allows for unattended analysis of multiple samples.

Excitation conditions

To control Mn, Co, and Ni concentrations in metal salt baths used in the hydrometallurgical process for recovering these metals from spent lithium-ion batteries, as well as the production of battery-grade precursors, only one excitation condition is required to excite all three elements of interest.

Table 1 below shows spectra collected on samples for a total live time of 200 s to 300 s. Measurement time can be further fine-tuned according to specific applications. Analysis is conducted in air.

Figure 2 shows a typical spectrum obtained for the type of samples handled in this application note.

Condition	Voltage, kV	Filter	Atmosphere	Live time, s	Elements
Mid Zb	22	Pd medium	Air	200/300	Mn, Co, Ni

Table 1. Analytical condition.

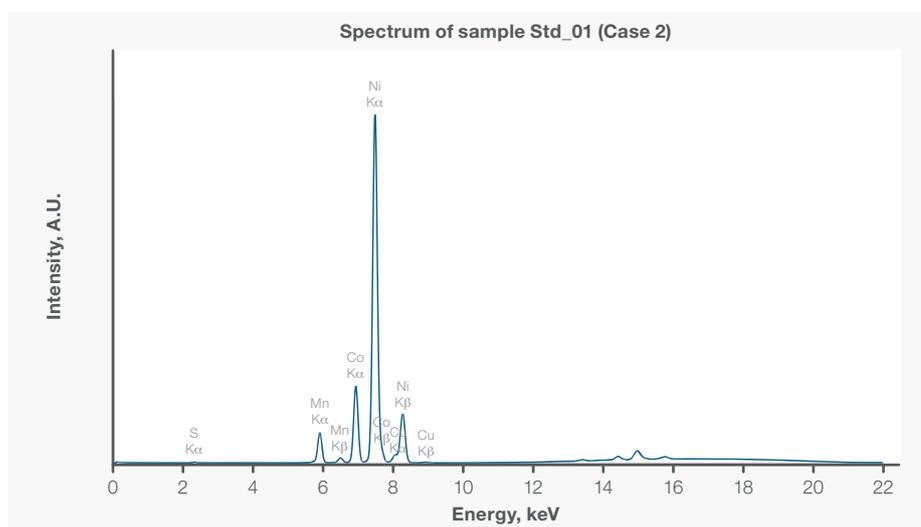


Figure 2. Typical spectrum showing the characteristic lines of Mn, Co, and Ni as well as the contaminant Cu.

Sample Preparation

Samples are prepared for analysis by filling an XRF cup (\varnothing 31 mm) sealed with a 4-micron thick polypropylene film. The typical volume of liquid transferred to the cup equals 4 mL and this volume is kept constant.

	Mn		Co		Ni	
	Given	Calculated	Given	Calculated	Given	Calculated
	g/L	g/L	g/L	g/L	g/L	g/L
Std_01	36.0	35.9	21.0	20.9	38.0	38.0
Std_02	30.0	30.1	17.5	17.6	47.5	47.5
Std_03	24.0	24.0	14.0	14.0	57.0	56.9
Std_04	18.0	18.0	10.5	10.5	66.5	66.6
Std_05	12.0	12.0	7.0	7.0	76.0	76.0
Std_06	6.0	6.0	3.5	3.5	85.5	85.6
Std_07	0.0	0.0	0.0	0.0	95.0	95.0

Table 2. Case study 1 – Calibration results.

Case study 1: Production of precursor materials

Calibration

This first case study focuses on the control of metal salt baths as used in the hydrometallurgical process to produce precursor materials. Standards are aqueous solutions with known compositions of Mn, Co, and Ni sulfates, prepared in the laboratory. A limited set of only 7 standards is used for the calibration of the ARL QUANT'X EDXRF Spectrometer.

Figures 3a, 3b and 3c show plots of the calculated versus given concentrations based on the calibration curves. An empirical calibration model was used (ref. Lucas-Tooth and Price) with one correction per element which is sufficient to correct for matrix effects. Table 2 shows the calibration results in more detail.

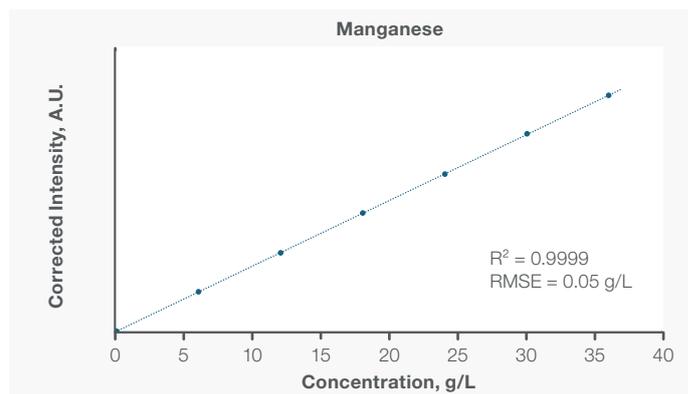


Figure 3a – Case study 1 – Calibration curve for manganese – Matrix corrected intensity versus concentration.

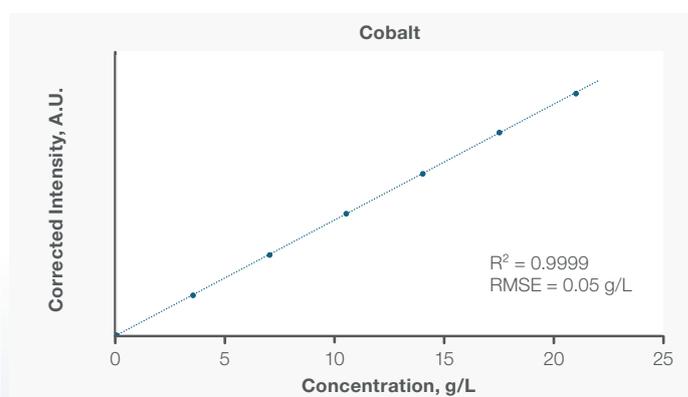


Figure 3b – Case study 1 – Calibration curve for cobalt – Matrix corrected intensity versus concentration.

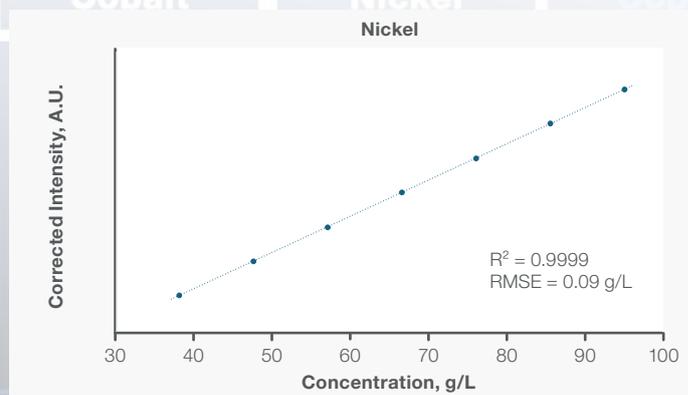


Figure 3c – Case study 1 – Calibration curve for nickel – Matrix corrected intensity versus concentration.

24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper
42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver
74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold

Validation

To validate the calibration, three samples taken from production were analyzed using EDXRF and results are compared with ICP-OES results. Table 3 gives an overview of the results.

	EDXRF			ICP			Delta		
	Mn	Co	Ni	Mn	Co	Ni	Mn	Co	Ni
	g/L	g/L	g/L	g/L	g/L	g/L	g/L	g/L	g/L
Val_A	26.9	19.2	49.1	26.4	19.1	48.0	0.48	0.04	1.08
Val_B	26.7	9.7	57.7	26.5	9.7	57.6	0.14	-0.04	0.06
Val_C	3.7	5.7	85.3	3.6	5.7	85.0	0.05	-0.04	0.30

Table 3. Case study 1 - validation results.

Repeatability

Validation sample Val_A was analyzed 11 times in a row to assess the short-term repeatability of the instrument. Results are shown in Table 4. The relative standard deviation is less than 0.2 % for a measurement live time of 200 s.

	Mn	Co	Ni
	g/L	g/L	g/L
Val_A 01	26.81	19.11	48.90
Val_A 02	26.83	19.14	48.97
Val_A 03	26.85	19.15	49.04
Val_A 04	26.87	19.17	49.04
Val_A 05	26.88	19.19	49.10
Val_A 06	26.92	19.19	49.07
Val_A 07	26.90	19.20	49.11
Val_A 08	26.91	19.20	49.09
Val_A 09	26.96	19.21	49.12
Val_A 10	26.92	19.19	49.14
Val_A 11	26.94	19.19	49.14
Average	26.89	19.18	49.07
1-Sigma	0.05	0.03	0.08
% RSD	0.17	0.16	0.15
Minimum	26.81	19.11	48.90
Maximum	26.96	19.21	49.14

Table 4. Case study 1 - Repeatability results.

	Mn		Co		Ni	
	Given	Calculated	Given	Calculated	Given	Calculated
	g/L	g/L	g/L	g/L	g/L	g/L
Std_01	28.88	28.83	20.66	20.69	58.90	59.19
Std_02	29.17	29.21	20.82	20.83	57.49	57.41
Std_03	29.29	29.29	20.45	20.36	62.07	62.00
Std_04	28.88	28.89	20.30	20.22	62.71	62.55
Std_05	29.68	29.67	20.67	20.79	61.21	61.29
Std_06	22.62	22.86	20.22	20.20	102.29	101.94
Std_07	22.61	22.18	20.54	20.58	103.39	103.99
Std_08	21.53	21.71	21.92	22.07	100.37	99.54
Std_09	21.54	21.61	22.63	22.66	99.18	99.08
Std_10	21.27	21.21	22.77	22.57	99.71	100.33

Table 5. Case study 2 - Calibration results.

Case study 2: Recycling black mass to extract Mn, Co, and Ni

Calibration

The second case study focuses on the determination of Mn, Co, and Ni content in metal salt baths used to recover these elements from black mass. The difference with metal salt baths to produce precursor materials is the presence of impurities such as Cu and Zn. While the concentrations of these impurities are usually too low to cause any significant matrix effect, they can cause spectral interference.

A total of 19 samples were taken from the baths and analyzed with ICP-OES. 10 samples were used to calibrate the ARL QUANT'X spectrometer while the 9 remaining samples are used for validation. Care was taken to cover a wide concentration range for every element while making sure concentration varied independently across the three elements of interest.

Figures 4a, 4b and 4c show plots of the calculated versus given concentrations based on the calibration curves. An empirical calibration model was used (ref. Lucas-Tooth and Price) with one correction per element (2 for Ni) which is sufficient to correct for matrix effects. Table 5 shows the calibration results in more detail.

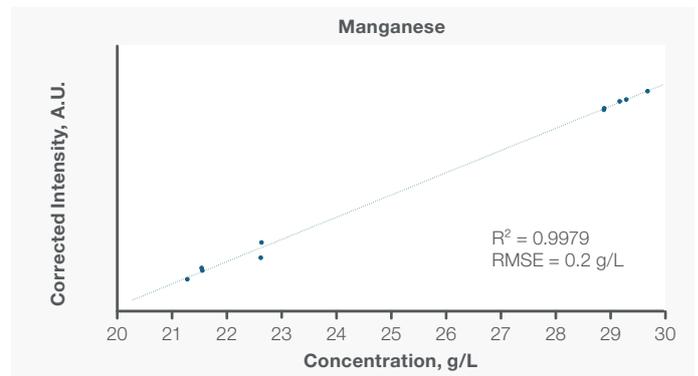


Figure 4a – Case study 2 – Calibration curve for manganese – Matrix corrected intensity versus concentration.

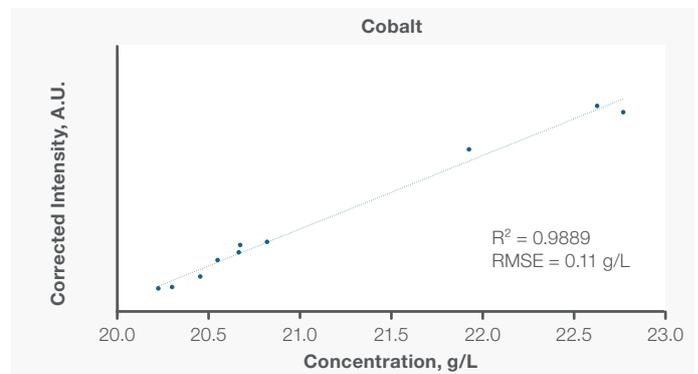


Figure 4b – Case study 2 – Calibration curve for cobalt– Matrix corrected intensity versus concentration.

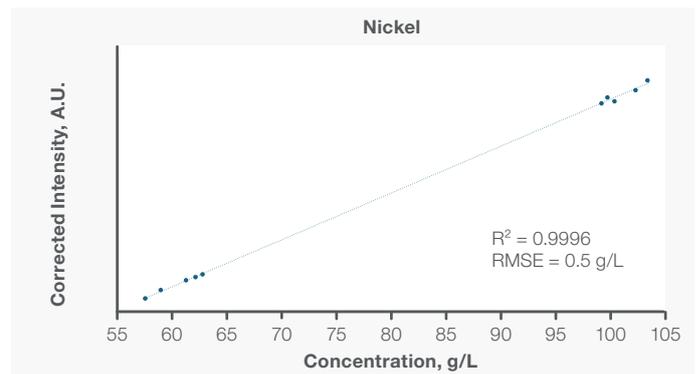


Figure 4c – Case study 2 – Calibration curve for nickel – Matrix corrected intensity versus concentration.

Validation

To validate the calibrations, the 9 remaining samples were analyzed as unknowns and the resulting concentrations are compared to ICP-OES results. Table 6 gives an overview of the results.

	EDXRF			ICP-OES			Delta		
	Mn	Co	Ni	Mn	Co	Ni	Mn	Co	Ni
	g/L	g/L	g/L	g/L	g/L	g/L	g/L	g/L	g/L
Val_01	29.19	21.70	57.74	28.94	21.97	58.15	0.25	-0.27	-0.41
Val_02	29.03	19.87	62.52	29.35	19.77	61.74	-0.32	0.10	0.78
Val_03	29.10	20.50	62.09	29.21	20.43	61.73	-0.11	0.07	0.36
Val_04	28.85	20.09	62.59	29.04	20.06	62.29	-0.19	0.03	0.30
Val_05	22.52	19.73	104.22	22.51	19.58	103.40	0.01	0.15	0.82
Val_06	22.50	20.41	102.28	22.42	20.33	101.90	0.08	0.08	0.38
Val_07	21.71	22.09	100.65	21.54	21.97	101.50	0.17	0.12	-0.85
Val_08	21.65	22.21	98.92	21.46	22.19	99.66	0.19	0.02	-0.74
Val_09	21.71	21.77	101.21	21.58	21.80	101.40	0.13	-0.03	-0.19

Table 6. Case study 2 - Validation results.

Repeatability

Validation sample Val_03 was analyzed 11 times in a row to assess the short-term repeatability of the instrument. Results are shown in Table 7. In this case, the relative standard deviation is less than 0.01 % for a measurement live time of 300 s.

	Mn	Co	Ni
	g/L	g/L	g/L
Val_03 01	29.17	19.63	62.03
Val_03 02	29.17	19.63	61.99
Val_03 03	29.17	19.63	62.02
Val_03 04	29.17	19.63	62.01
Val_03 05	29.16	19.65	62.06
Val_03 06	29.16	19.64	62.05
Val_03 07	29.16	19.67	62.03
Val_03 08	29.16	19.65	62.06
Val_03 09	29.15	19.65	62.09
Val_03 10	29.16	19.66	62.06
Val_03 11	29.15	19.66	62.10
Average	29.16	19.65	62.04
1-Sigma	0.007	0.014	0.032
% RSD	0.03	0.07	0.05
Minimum	29.15	19.63	61.99
Maximum	29.17	19.67	62.10

Table 7. Case study 2 - Repeatability results.

Conclusion

This application note shows the suitability of the ARL QUANT'X EDXRF Spectrometer for the quantitative determination of Mn, Co, and Ni in metal salt baths, typically used in the hydrometallurgical process for battery production or recycling. The compact ARL QUANT'X spectrometer allows for reliable and fast analysis. Accuracy and repeatability data show that satisfactory results are obtainable for an analysis of aqueous solutions in air. This instrument can be placed close to the production line. With simple and fast sample preparation, the time between sampling and reporting is short. While the application note uses measurement times of 200 s to 300 s to ascertain repeatability, the measurement time can be set as short as 30 s to 60 s and still yield satisfactory results.

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