

## ICP - Mass Spectrometry

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## Determination of Elemental Impurities in Lithium Battery Cathode Materials Using NexION 1000 ICP-MS

### Introduction

The quality of the cathode material of a lithium ion (Li-ion) battery, especially the ratio of the primary elements and the concentrations of impurities, has great impact on its charging and discharging performance as well as safety.<sup>1</sup>

For example, in the battery formation process, metal impurities such as Fe, Cu, Cr, Zn, or Pb will be oxidized on the cathode and then reduced and deposited on the anode when the applied power reaches the redox potential of the respective metal. This deposition of impurities has two consequences. First, impurities can block Li ions reducing the coulombic efficiency of the battery, essentially its ability to charge and discharge. Second, impurities can encourage the formation of dendrites, which are microstructures that form on the anode and can pierce the battery's separator leading to a short circuit. Since conventional liquid electrolytes are flammable, a short circuit is a fire hazard and could also cause some electrolytes to decompose exothermically, adding to the safety issues. Therefore, it is particularly important to monitor and address the presence of impurities in cathode materials.

Conventionally, inductively coupled plasma optical emission spectrometry (ICP-OES) has been the method of choice for the battery industry to determine the ratios of primary elements and the concentrations of impurities. However, impurity control is becoming more stringent with the development of new battery technologies, leading to the need for ever-decreasing detection limits for metal impurities. Presently, some detection limits have dropped below what is practical to be detected by ICP-OES, particularly for Cr, Cu, Fe, Zn, and Pb. Most manufacturers set the acceptable limit of these five elements to be < 1 ppm, which can be as low as 10 ppb in the final solution after sample digestion. While this would be challenging for ICP-OES, inductively coupled plasma mass spectrometry (ICP-MS) is an excellent alternative with higher sensitivity and lower detection limits than ICP-OES.

Cathode materials contain high concentrations of primary elements, which can combine in the plasma with elements from the matrix as well as plasma and atmospheric gases to create polyatomic interferences. Additionally, in cases where a mass adjacent to the analyte of interest has a high concentration, the importance of quadrupole length becomes apparent as there is a direct correlation between the quadrupole length and the abundance sensitivity of the instrument. Table 1 summarizes potential interferences in a typical cathode material, using lithium nickel cobalt manganese oxide (LNCM) as a specific example, where the isotopes of the primary element masses (Li, Mn, Co, Ni), represented by M, are combined with various elements in each column ( $^6\text{Li}$ ,  $^7\text{Li}$ ,  $^{14}\text{N}$ ,  $^{16}\text{O}$ ,  $^{35}\text{Cl}$ , and  $^{37}\text{Cl}$ ) and the table's cells show what elemental measurements would be affected by that interference. The columns labeled "M+1" and "M-1" show analytes on adjacent masses that could be affected by the high concentration of these primary elements if the resolution on the mass spectrometer was not adequate to separate them. Fortunately, PerkinElmer's NexION® 1000 and 2000 instruments are designed with full-length transmission

analyzer quadrupoles, providing both excellent stability and abundance sensitivity.

Whenever a sample is diluted, any bias or background signal in the final solution measurement is amplified by that dilution factor once the result is back-calculated to original sample concentrations. To minimize this effect, a dilution in the range of 100x to 200x is recommended for sample preparation in a non-cleanroom environment. With this dilution factor applied, the resulting sample solution has a relatively high concentration of acid(s) and total dissolved solids (TDS), which can cause the analysis of target elements to be challenging. The challenges presented by high matrix and high TDS can be mitigated through the use of on-line gas dilution.

This application brief reports a proof of concept for the determination of Cr, Cu, Fe, Zn, and Pb impurities in lithium battery cathode materials, namely lithium nickel cobalt manganese oxide (LNCM), as well as two precursor materials, lithium cobalt oxide (LCO) and lithium manganese oxide (LMO), using a NexION 1000 ICP-MS.

Table 1: Possible Interferences in LNCM Samples.

Main Element		M-1	M+1	M+6	M+7	M+14	M+16	M+35	M+37
Li	6	5 /	7 /	12 /	13 /	20 /	22 /	41 K	43 Ca
	7	6 Li	8 /	13 /	14 /	21 /	23 Na	42 Ca	44 Ca
Mn	55	54 Fe	56 Fe	61 /	62 /	69 Ga	71 Ga	90 Zr	92 Zr, Mo
Co	59	58 Fe	60 /	65 Cu	66 Zn	73 Ge	75 As	94 Zr, Mo	96 Mo
Ni	58	57 Fe	59 /	64 Zn	65 Cu	72 Ge	74 Ge, Se	93 Nb	95 Mo
	60	59 /	61 /	66 Zn	67 Zn	74 Ge, Se	76 Ge, Se	95 Mo	97 Mo
	61	60 /	62 /	67 Zn	68 Zn	75 As	77 Se	96 Zr, Mo	98 Mo, Ru
	62	61 /	63 Cu	68 Zn	69 Ga	76 Ge, Se	78 Se	97 Ru	99 Ru
	64	63 Cu	65 Cu	70 Zn, Ge	71 Ga	78 Se	80 Se	99 Ru	101 Ru

## Experimental

### Sample and Standard Preparation

The cathode material and its precursor samples (ca. 0.4 g) were accurately weighed into 50 mL centrifuge tubes, to which 4 mL of aqua regia solution was added. Each tube was gently agitated to mix the sample and acid solution and then placed into PerkinElmer's SPB sample digestion blocks with the cap loosely fitted. The samples were digested at 120°C for two hours. At the end of digestion, the samples were allowed to cool down, then diluted with ultrapure water to 50 mL and analyzed. In this work, the method of standard addition (MSA) was used to correct for matrix effects and analytical accuracy was verified by using sample spikes.

### Instrumentation

The analysis was performed on a NexION 1000 ICP-MS equipped with the All Matrix Solution (AMS) on-line gas dilution feature.<sup>2</sup> The instrument configuration and operating conditions are shown in

Table 2. The method described within this application brief is not limited to the NexION 1000 ICP-MS, but is instead transferable and can be performed using any PerkinElmer NexION model.

Table 2: Instrument Configuration and Operating Conditions.

Parameter	Value
RF power	1600 W
Nebulizer gas flow	0.94 L/min
AMS gas flow	0.4 L/min
Nebulizer	PFA ST3 Nebulizer
Spray chamber	Glass cyclonic with AMS port
Torch	One-piece quartz torch with 2 mm injector
Cones	Sampler: Nickel 1.1 mm Ø Skimmer: Nickel 0.9 mm Ø Hyper-skimmer: Aluminum 1.0 mm Ø
Sample uptake	0.3 mL/min
KED collision gas	Helium

NexION models are equipped with Universal Cell Technology (UCT), which allows effective elimination/removal of interferences when operating in Collision (KED) and/or Reaction (DRC) modes. In this work, helium gas was used in Collision mode for all analytes to remove polyatomic interferences.

Additionally, all NexION models are equipped with a Quadrupole Ion Deflector (QID), which deflects the positive ions by 90 degrees into the Universal Cell and diverts negative and neutral species to waste, thus effectively reducing space charge effects, lowering the background, and decreasing interferences for a high matrix sample, which in turn leads to increased accuracy.

## Results and Discussion

### Method Development

Spectral interferences for Li-ion battery cathode material analysis can be divided into two groups. The first group is polyatomic interferences, often formed from elements in the matrix. One example of this is when chlorine from aqua regia combines with oxygen and hydrogen from water and forms  $^{35}\text{Cl}^{16}\text{O}^1\text{H}^+$ , which has the same mass as the analyte  $^{52}\text{Cr}^+$ . These types of interferences can be easily addressed using Collision mode with KED. If much lower analyte detection than presented here is needed, the Universal Cell can also be operated in Reaction mode for interference removal with the ultimate analyte sensitivity.

The other group of interferences is caused by a large peak of high-concentration matrix element on the adjacent mass.

For example, for the analysis of Fe in the cathode material LNCM,  $^{54}\text{Fe}$  and  $^{57}\text{Fe}$  can be affected by interferences from  $^{55}\text{Mn}$  and  $^{58}\text{Ni}$  respectively. However, with the NexION 1000 ICP-MS,  $^{56}\text{Fe}$  is fully resolved and can be used for quantitation.

Table 3 shows the results for  $^{54}\text{Fe}$ ,  $^{56}\text{Fe}$  and  $^{57}\text{Fe}$ , as well as  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  in four nickel cobalt manganese (NCM) samples, which contained no lithium, represented as NCM-X (1, 2, 3, 4). Sample NCM-1 was digested in triplicate to assess repeatability. As spectral interferences are cumulative, the higher concentrations obtained using  $^{54}\text{Fe}$ ,  $^{57}\text{Fe}$  and  $^{63}\text{Cu}$  indicate the influence of spectral interferences on the analytes. It is not necessarily true, however, that the isotope with the highest result has the most interference, so further investigation of the data is required. Through careful data analysis including varying the monitored mass, comparison of blank data with results that contained matrix and, in the case of Fe, comparison with ICP-OES results,  $^{56}\text{Fe}$  and  $^{65}\text{Cu}$  were shown to be the least affected by interferences, so those isotopes were chosen for final sample analysis in this work.

Table 4 shows the testing results of  $^{66}\text{Zn}$  and  $^{68}\text{Zn}$  in the battery material of lithium nickel cobalt manganese oxide (LNCM), and two precursor materials of lithium cobalt oxide (LCO) and lithium manganese oxide (LMO). As  $^{66}\text{Zn}$  was interfered by the polyatomic interference from  $^{60}\text{Ni}^6\text{Li}$  and  $^{59}\text{Co}^7\text{Li}$ , higher concentrations were obtained from measuring  $^{66}\text{Zn}$  than from  $^{68}\text{Zn}$  in LNCM and LCO that contain Ni and/or Co. The difference was not obvious in LMO, which does not contain Ni or Co. Therefore,  $^{68}\text{Zn}$  was chosen for the final sample analysis.

Table 3: Testing Results for Fe and Cu Analysis using Different Isotopes in the NCM Samples.

Sample ID	$^{56}\text{Fe}$ (µg/L)	$^{54}\text{Fe}$ (µg/L)	$^{57}\text{Fe}$ (µg/L)	$^{63}\text{Cu}$ (µg/L)	$^{65}\text{Cu}$ (µg/L)
NCM-1-1	20.1	83	2293	3.73	2.07
NCM-1-2	19.9	80.1	2065	3.48	1.9
NCM-1-3	19.2	77.5	2061	3.6	2.03
NCM-2	13.8	57.6	1829	4.59	3.14
NCM-3	13.8	57.5	1846	3.19	1.75
NCM-4	13.4	52.2	1719	2.51	1.21

Note: Concentrations shown in this table were for the analytical solution.

Table 4: Results for Zn in Various Li-ion Battery Cathode Materials.

Sample ID	$^{68}\text{Zn}$ (µg/L)	$^{66}\text{Zn}$ (µg/L)	Percentage Difference (%)
LMO-1	34.0	33.5	1%
LMO-2	33.7	34.2	-1%
LCO-1	3.10	3.60	-16%
LCO-2	4.02	4.74	-18%
LNCM	9.54	10.1	-6%

Note: Concentrations shown in this table were for the analytical solution.

## Sample Analysis Results

As mentioned previously, the method of standard addition (MSA) was used to correct for matrix effects. Figure 1 shows the calibration curves obtained using MSA. A coefficient of correlation (R) higher than 0.9998 was obtained for all measured isotopes. The average concentrations of two digestions for each sample after blank subtraction and dilution factor correction are listed in Table 5.

A digestion of sample LNCM-2 was also used for a standard spike recovery test in order to verify the analytical accuracy of the method. The results are shown in Table 6. Excellent spike recoveries in the range of 100-101% were achieved for all measured elements.

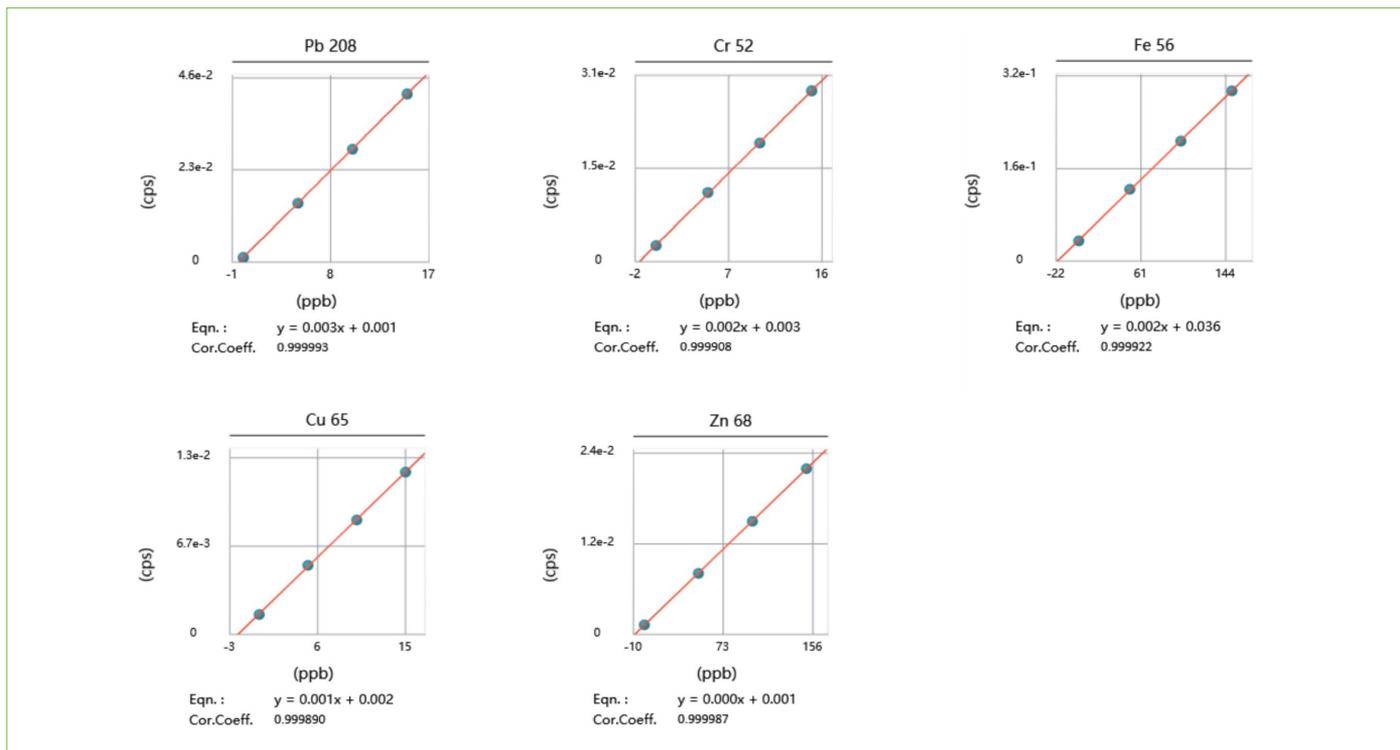


Figure 1: Standard addition calibration curves for all measured isotopes.

Table 5: Measured Concentrations of the LNCM Samples.

Sample ID	<sup>65</sup> Cu (µg/kg)	<sup>68</sup> Zn (µg/kg)	<sup>208</sup> Pb (µg/kg)	<sup>52</sup> Cr (µg/kg)	<sup>56</sup> Fe (µg/kg)
LNCM-1	425	4372	136	924	8845
LNCM-2	269	1133	50.8	186	2533
LNCM-3	380	1367	89.2	1355	4387

Table 6: Matrix Spike Recovery Results (LNCM).

Sample ID	<sup>65</sup> Cu (µg/L)	<sup>68</sup> Zn (µg/L)	<sup>208</sup> Pb (µg/L)	<sup>52</sup> Cr (µg/L)	<sup>56</sup> Fe (µg/L)
LNCM-2-1	2.21	9.25	0.42	1.61	21.4
LNCM-2-1 with spike	7.26	59.9	5.4	6.65	71.5
<b>Spike Recovery</b>	<b>101%</b>	<b>101%</b>	<b>100%</b>	<b>101%</b>	<b>100%</b>

Note: Added standard concentrations were: 5 µg/L for Cu, Pb and Cr; and 50 µg/L for Zn and Fe.

## Conclusions

Equipped with the All Matrix Solution on-line gas dilution feature, Quadrupole Ion Deflector, and Universal Cell Technology with Collision mode, the NexION 1000 ICP-MS provides excellent matrix tolerance and interference removal as required by the battery industry. This work has demonstrated the instrument's ability to accurately measure trace metal impurities in high matrix Li-ion battery materials through the appropriate selection of isotopes and instrumental conditions. For the Li-ion battery industry, ICP-MS technology has proven to be a useful alternative to ICP-OES where more stringent impurity monitoring and quality control is required.

## References

1. Olimpia A. Nasser and Martina Petranikova, "Review of Achieved Purities after Li-ion Batteries Hydrometallurgical Treatment and Impurities Effects on the Cathode Performance", *Batteries*, 2021, 7(3), 60.
2. "All Matrix Solution System for NexION ICP-MS Platforms", PerkinElmer Technical Note, 2017.
3. Tak Shun Cheung, Cindy Wong and Hamid R. Badiei, "Advantages of a Novel Plasma Generator for the NexION 1000/2000/5000 ICP-MS Systems", PerkinElmer Technical Note, 2020.
4. Hamid R. Badiei, William Fisher, Serguei Savtchenko, Ewa Pruszkowski and Andrew Icasiano, "Advantages of a Novel Interface Design for NexION 5000 ICP-MS", PerkinElmer Technical Note, 2020.

## Consumables Used

Component	Description	Part Number
Nebulizer	PFA ST3 MicroFlow	N8152378
	PFA-ST Nebulizer Internal Standard Addition Tee	N8152423
Spray Chamber	Glass Cyclonic with AMS Port	N8152389
Cones	Ni Sampler	W1033612
	Ni Skimmer	W1026356
	Al Hyper-skimmer	W1033995
Torch	One-piece Quartz, 2 mm Injector	N8152472
Peripump Tubing	Sample: 0.44 mm i.d.	N8152404
	Internal Standard: 0.38 mm i.d.	N8152403