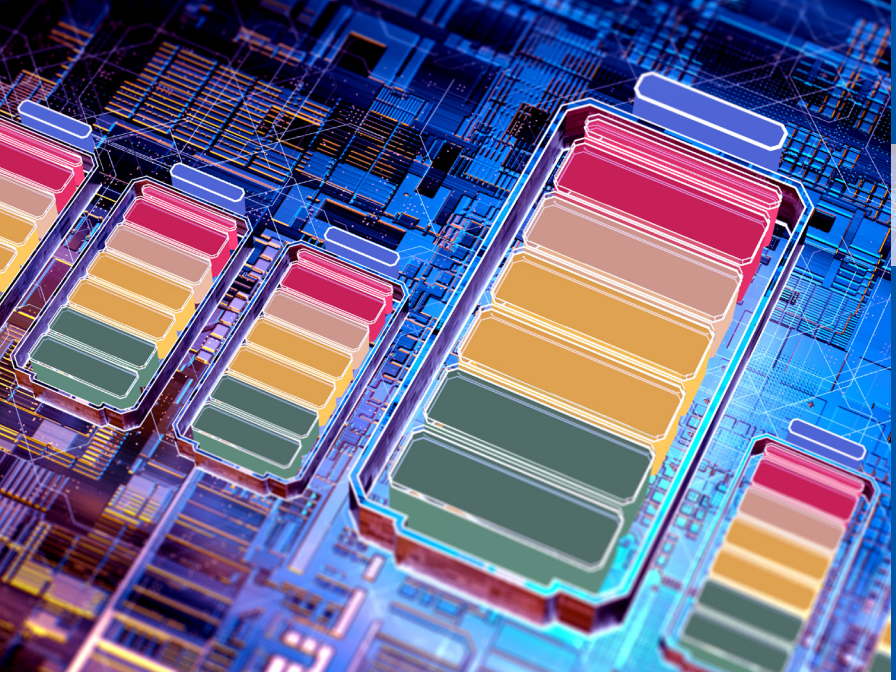

APPLICATION BRIEF

ICP - Mass Spectrometry

AUTHOR

Guan-Yu Chen
PerkinElmer
Shanghai, China

Determination of Chloride in Cathode Materials Using the NexION 1100 ICP-MS

Introduction

Lithium nickel cobalt manganese oxide (LNCM) is the key cathode material for ternary lithium batteries which have a higher electric capacity and are less costly than lithium iron phosphate batteries. Chloride (Cl) is a type of impurity that may affect the efficiency and storage capacity of the battery. Therefore, as regulated by the People's Republic of China Nonferrous Metals Industry Standard (YS/T928.1-2013), the presence of Cl in LNCM needs to be monitored for the purpose of quality control.

Although regular testing methods for this material include a silver nitrate turbidimetric method and an ion-selective electrode method, both of these techniques have poor detection limits of ca. 0.01%. Inductively coupled plasma mass spectrometry (ICP-MS), in contrast, is a powerful elemental analysis technique with excellent detection limits as well as very high sensitivity and is well suited for the determination of Cl in cathode materials and their precursor materials.

There are a few challenges associated with the characterization of Cl in cathode and precursor materials using ICP-MS, such as the poor ionization efficiency of this element and the high total dissolved solids (TDS) of such matrices, where the latter issue can be effectively addressed via dilution. Unlike liquid dilution methods which require additional solvent and may take up a considerable amount of time, online gas dilution offered by some ICP-MS systems can be greatly beneficial in these applications by reducing the chances for analytical error, contamination, and sample preparation time.

This work discusses the characterization of Cl in LNCM using PerkinElmer's NexION® 1100 ICP-MS[1] equipped with the All Matrix Solution (AMS)[2] online gas dilution feature.

PerkinElmer®
Science with Purpose

Experimental Conditions

Sample Preparation

Cathode and precursor materials (ca. 0.5 g of each) were accurately weighed into a 50 mL centrifuge tube, and 4 mL of concentrated nitric acid was added. The cap was loosely closed, and the sample was allowed to digest at room temperature for one hour. At the end of digestion, the sample was allowed to cool down, then diluted with ultrapure water to 50 mL, followed by analysis.

Standards and Quality Control

Matrix-matched Cl calibration standards (n=3) were prepared with germanium (Ge) as an internal standard. In the absence of certified reference materials, the accuracy of the method was verified by spiking the cathode and precursor materials with 1 ppm Cl and the spike recoveries determined.

Instrument Parameters

The total dissolved solids in the sample solution used in this method were calculated to be about 1%, which would be challenging for regular ICP-MS analysis due to serious matrix effects. PerkinElmer's NexION ICP-MS series is uniquely equipped with wide-aperture sampler and skimmer cones as well as the AMS gaseous dilution system, allowing the analysis of high TDS samples with accuracy and precision. All analyses were performed with the NexION 1100 ICP-MS using the method setup described in Table 1 and the conditions and hardware described in Table 2.

Results and Discussion

The calibrations were found to have excellent linearity over the measured concentrations as can be seen in Figure 1.

In this test, the recoveries of the internal standard and matrix spiked samples were all within ± 25% (Table 3), meeting the industry's requirements. The method detection limit is 3.2 mg/kg with dilution factor considered. Therefore, this method is well suited for the determination of Cl in lithium battery materials.

Table 1. Method Setup.

	Element	Mass	Mode	Gas Flow	Dwell Time	RPq
Analyte	Cl	35	He KED	3.5	400	0.25
Internal Standard	Ge	72	He KED	3.5	100	0.25

Table 2. Conditions and Hardware.

Parameter	Value
RF Power	1600 W
Nebulizer Gas Flow	0.92 L/min
AMS Gas Flow	0.4
Nebulizer	PFA-ST3 MicroFlow
Spray Chamber	Glass Cyclonic with AMS Port
Cones	Ni Sampler Ni Skimmer Al Hyper-Skimmer
Torch	One-piece Quartz, 2 mm Injector
Peripump Tubing	Sample: 0.38 mm i.d. Internal Standard: 0.38 mm i.d.
Sample Uptake	0.25 mL/min

Table 3. Spike Recovery Results

Sample ID	Cl35 in Solution (mg/L)	Cl35 in Sample (mg/kg)	Ge72 (Internal Standard)
LNCM	0.932	93.2	80.9%
LNCM + 1 ppm	2.06		78.8%
Recovery	113%		
NCM	0.756	75.6	91.0%
NCM + 1 ppm	1.75		93.6%
Recovery	99%		

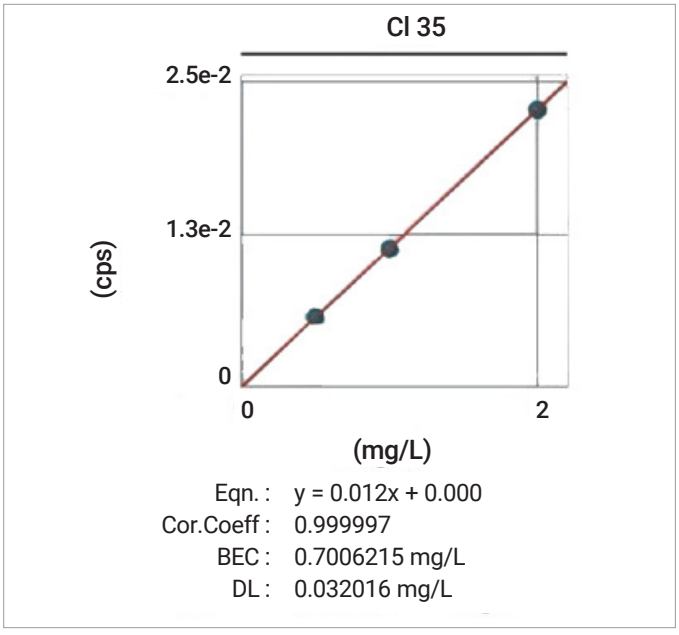

Figure 1. External standard calibration curve for Cl.

Conclusion

This work has demonstrated the ability of PerkinElmer's NexION 1100 ICP-MS to accurately measure the chloride content in cathode materials and their precursor materials, ideal for QC laboratories performing impurities testing of lithium batteries. The instrument's proprietary Triple Cone Interface with wide-aperture cones and the All Matrix Solution gaseous dilution system allowed analysis of high TDS samples with accuracy and precision.

References

1. NexION 1100 ICP Mass Spectrometer, PerkinElmer Interactive Brochure, 2024.
2. All Matrix Solution System for NexION ICP-MS Platforms, PerkinElmer Product Note, 2023.

Consumables Used

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

PerkinElmer U.S. LLC
710 Bridgeport Ave.
Shelton, CT 06484-4794 USA
(+1) 855-726-9377
www.perkinelmer.com

87069 (486023)