



### Challenge

Precise determination of impurities despite matrix effects, interference from organic solvents, sample deterioration and difficulties in detecting certain elements such as phosphorus and fluoride.

### Solution

The PlasmaQuant 9100 Elite offers unrivaled measurement results with difficult matrices thanks to the unique HF generation and intelligent interference management.

### Intended audience

Electrolyte Manufacturers for lithium- and sodium-ion batteries, battery manufacturers, specialized laboratories.

## Analysis of Impurities in Lithium Hexafluorophosphate Electrolyte (Lithium-Ion Battery)

### Introduction

Elemental analysis of lithium battery electrolytes plays a critical role in ensuring the quality and performance of modern energy storage systems. Lithium batteries are integral components of numerous technical applications, ranging from portable electronic devices to electric vehicles. Their efficiency and longevity are heavily dependent on the purity and precise composition of the electrolytes used. In batteries, the electrolyte's primary function is to facilitate ion flow between the electrodes, making it essential for battery performance. Thus, thorough and reliable quality control of the electrolyte solution is necessary to ensure optimal performance. The Chinese standard HG/T 4067-2015<sup>[1]</sup> sets forth detailed procedures and requirements for the chemical analysis of electrolytes in lithium batteries. This standard ensures that all relevant elements in the electrolytes are accurately identified and quantified to maximize battery performance and safety. It provides a standardized method that facilitates result comparability and compliance with

international quality standards. In lithium-ion batteries, lithium hexafluorophosphate ( $\text{LiPF}_6$ ) is utilized due to its excellent conductive properties. The Chinese industrial standard HG/T 4067-2015<sup>[1]</sup> describes a methodology for the analysis of lithium hexafluorophosphate electrolyte, specifying that a mixture of methyl ethyl carbonate, ethanol, and water (1:4:5) is used to prepare calibration and sample solutions.

This application note elucidates the practical implementation of the standard HG/T 4067-2015<sup>[1]</sup>, with a particular focus on the analytical techniques and procedures for determining various elements in lithium battery electrolytes. In this study, three electrolyte samples were analyzed for 14 elements each using the high-resolution ICP-OES PlasmaQuant 9100 Elite in accordance with the aforementioned standard. Since lithium hexafluorophosphate leads to the formation of hydrofluoric

acid, the measurement system was additionally equipped with a hydrofluoric acid resistant sample introduction kit (HF kit). The carbon-rich matrix generates spectral overlaps on some analytical lines. This effect was corrected using

the CSI software tool (Correction of Spectral Interferences), which resulted in an improved baseline without spectral disturbances, thereby enhancing the reliability of the measurement results.

## Materials and Methods

### Samples and reagents

- Lithium hexafluorophosphate electrolytes
- Multielement standard solution for ICP (100 mg/L Al, As, Ca, Cd, Cr, Cu, Fe, Mg, Na, Ni, Pb, Zn)
- Single element standard solutions for Hg and K (1000 mg/L each)
- Ethanol
- Ethyl methyl carbonate

### Sample preparation

The test samples were diluted by weighing by factor 10. According to standard HG /T 4067-2015 the diluent was prepared with methyl ethyl carbonate, ethanol and deionized water in a ratio of 1:4:5.

### Instrumentation and method parameters

With respect to the low amount of provided sample material, the analysis was performed in manual operation mode (without autosampler) on the high-resolution ICP-OES PlasmaQuant 9100 Elite, equipped with a hydrofluoric acid resistant sample introduction system (HF kit). Individual settings and components are summarized in table 1. Detailed information about the method parameters and settings are listed in table 2.

### Calibration

The standards for the external calibration were prepared using single element and multielement standard solutions with a diluent containing methyl ethyl carbonate, ethanol and deionized water (1:4:5). The concentrations of the calibration standards are listed in table 3 and examples for resulting calibration functions are shown in figure 1.

Table 1: Instrument configuration and settings

Parameter	Specification
Plasma power	1450 W
Plasma gas flow	15 L/min
Auxiliary gas flow	0.5 L/min
Nebulizer gas flow	0.35 L/min
Nebulizer	parallel path, PFA, 1 mL/min
Spray chamber	cyclonic, 50 mL, PTFE
Outer tube / inner tube	ceramic/ceramic (alumina)
Injector	alumina, 2 mm id
Pump tubing	PU (sample: black/black, waste: red/red)
Pump rate	0.2 mL/min
Fast pump	0.2 mL/min
Delay time/rinse time	100 s/100 s
Torch position	0 mm

Table 2: Method parameters

Element	Line [nm]	Plasma view	Integration	Read time [s]	Evaluation			
					Pixel	Baseline fit	Poly. deg.	Correction
Al	308.215	axial	Spectrum	3	3	ABC	auto	-
As	193.698	axial	Spectrum	3	3	ABC	auto	CSI
Ca	317.933	axial	Spectrum	3	3	ABC	auto	-
Cd	228.802	axial	Spectrum	3	3	ABC	auto	CSI
Cr	205.552	axial	Spectrum	3	3	ABC	auto	CSI
Cu	324.754	axial	Spectrum	3	3	ABC	auto	-
Fe	259.940	axial	Spectrum	3	3	ABC	auto	-

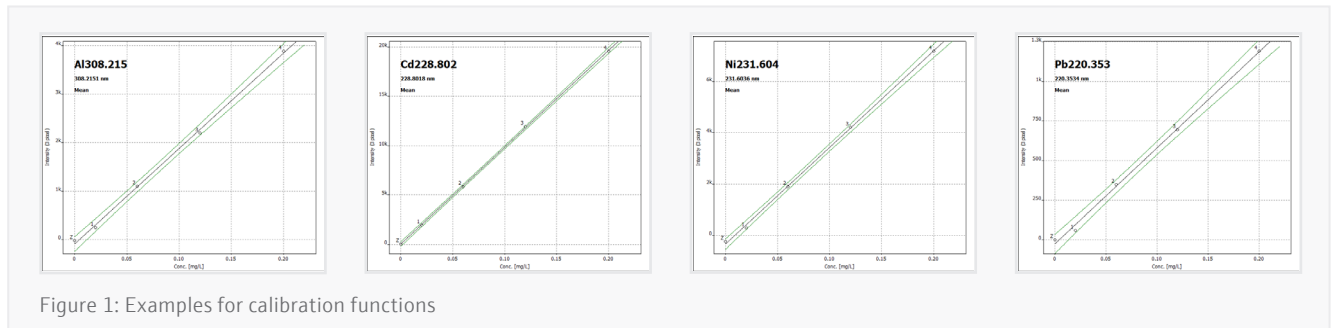
Continuation of table 2

Element	Line [nm]	Plasma view	Integration	Read time [s]	Evaluation			
					Pixel	Baseline fit	Poly. deg.	Correction
Hg	184.886	axial	Spectrum	3	3	ABC	auto	CSI
K	769.897	axial	Spectrum	3	3	ABC	auto	-
Mg	285.312	axial	Spectrum	3	3	ABC	auto	-
Na	589.592	axial	Spectrum	3	3	ABC	auto	-
Ni	231.604	axial	Spectrum	3	3	ABC	auto	-
Pb	220.353	axial	Spectrum	3	3	ABC	auto	CSI
Zn	213.856	axial	Spectrum	3	3	ABC	auto	-

ABC: Automatic Baseline Correction, CSI: Correction of Spectral Interferences

Table 3: Concentrations of the calibration standards

Element	Concentration [mg/L]				
	Cal. 0	Std. 1	Std. 2	Std. 3	Std. 4
Al, As, Cd, Cr, Cu, Hg, K, Mg, Ni, Pb, Zn	0	0.02	0.06	0.12	0.2
Ca, Fe, Na	0	0.2	0.6	1.2	2.0



## Results and Discussion

The results for the three electrolyte samples are listed in table 4. An independent QC standard of 0.12 mg/L was additionally prepared and measured after the sample analysis. The recovery is listed in the results table as well.

The method specific detection limits (MDL) of the analysis are given in table 5. These values were determined by using the reagent blank method (3 times the standard deviation of 11 repeated measurements of the reagent blank). The calculation of the results and the MDL comprises the sample preparation dilution factor of 10.

Table 4: Measuring results and QC standard recovery

Element	Measured values [mg/kg]			QC std. recovery [%]
	Electrolyte 1	Electrolyte 2	Electrolyte 3	
Al	<MDL	< MDL	0.02	103
As	<MDL	<MDL	<MDL	109
Ca	0.61	0.711	0.60	107
Cd	< MDL	< MDL	< MDL	101
Cr	< MDL	< LOQ	< LOQ	101
Cu	< MDL	< MDL	< LOQ	99.0
Fe	0.21	0.477	0.45	103
Hg	< LOQ	< MDL	< LOQ	94.0
K	0.85	1.12	0.80	95.0
Mg	0.04	< LOQ	< LOQ	104
Na	1.36	1.65	0.92	109
Ni	< LOQ	< LOQ	< LOQ	103
Pb	< LOQ	< MDL	< LOQ	96.0
Zn	< MDL	< MDL	< MDL	104

MDL/LOQ: Method specific Detection Limit/Limit Of Quantification (3 or 9 times the standard deviation of 11 reagent blank measurements)

Table 5: Method specific detection limits (MDL)

Element/Line [nm]	MDL [mg/kg]	Element/Line [nm]	MDL [mg/kg]
Al308.215	0.15	Hg184.886	0.11
As193.698	0.13	K769.897	0.02
Ca317.933	0.06	Mg285.312	0.01
Cd228.802	0.01	Na589.592	0.01
Cr205.552	0.07	Ni231.604	0.03
Cu324.754	0.02	Pb220.353	0.11
Fe259.940	0.01	Zn213.856	0.01

MDL: Method specific Detection Limit

## Summary

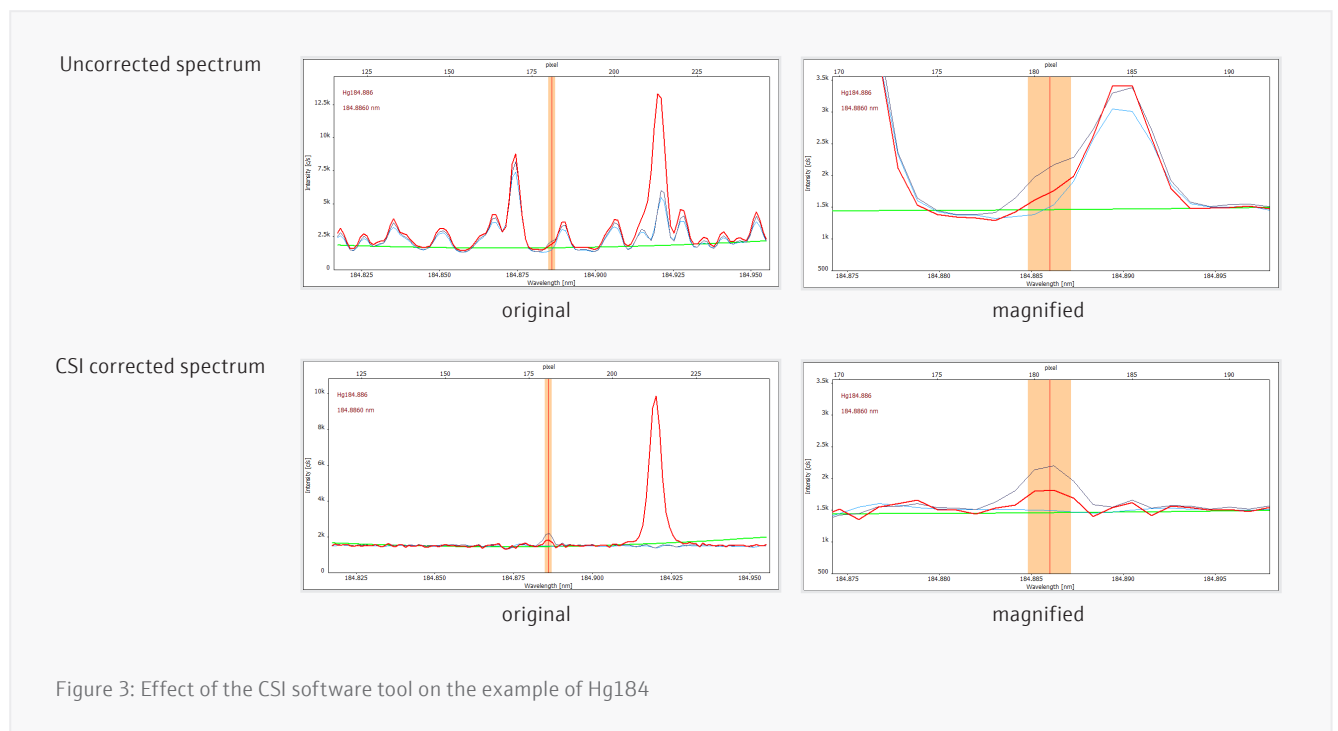
The high matrix tolerance as well as the high resolution and measurement sensitivity of the PlasmaQuant 9100 Elite enable an interference-free and robust analysis of battery electrolytes. Software tools such as automatic baseline correction (ABC) facilitate spectra evaluation and provide reliable results.

Some of the analysis lines show a spectral overlay by matrix related emission bands. To eliminate this structured background, the CSI (Correction of Spectral Interferences) software tool was applied, which is based on a mathematical algorithm ("Least Squares Model", LSM). For this purpose, a spectrum of a pure sample matrix solution (diluent) was recorded at the wavelengths concerned and saved into a database. This correction spectrum is subtracted from the recorded sample spectra.



Figure 2: PlasmaQuant 9100 Elite

The created correction model can be implemented in the method so that it is automatically applied during the routine measurements. Figure 3 demonstrates the high spectral resolution of the PlasmaQuant 9100 Elite (2 pm @ 200 nm) and the effect of using the CSI tool on the example of mercury (184 nm).



## Recommended device configuration

Table 6: Overview of recommended devices, accessories and consumables

Article	Article number	Description
PlasmaQuant 9100 Elite	818-09101-2	High resolution ICP-OES
Teledyne Cetac ASX 560	810-88015-0	Teledyne-Cetac ASX-560 autosampler for ICP-OES and ICP-MS
HF-Kit	810-88007-0	HF resistant sample introduction kit
Consumable set HF Kit	810-88042-0	Consumables Set HF Kit for PlasmaQuant 9x00 series
PU pump tubing (sample)	418-13-410-528	PU pump tubing (black/black) for sample
PU pump tubing (waste)	418-13-410-529	PU tubing (red/red) for waste

## References

[1] Chinese standard Standard HG/T 4067-2015 (<https://www.chinesestandard.net/PDF/English.aspx/HGT4067-2015>)

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