Application Note

Energy and Chemicals

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Rapid Assay of Sodium Hexafluorophosphate for Use in Sodium-Ion Batteries by ICP-OES

Quantification of 26 impurity elements in sodium salt-based electrolytes using ICP-OES

Authors

Feng Wenkun, Neli Drvodelic

Agilent Technologies, Inc.

Introduction

Sodium-ion battery (Na-ion battery, SIB, or NIB) technology is still emerging, although battery packs are already being used in stationary energy storage systems and low-cost electric transport applications, including electric vehicles. China dominates global SIB production, accounting for roughly 95% of the world's capacity. However, interest and development of this technology is also increasing in other regions due to the cost-effectiveness, safety, fast charging times, and long life cycles of SIBs. The production capacity of the batteries worldwide is expected to rise significantly by 2030.[1]

The electrolyte of a battery facilitates the movement of ions between the cathode and anode, making it a key component that affects the charge transfer properties and overall performance of the final device. Many SIBs use a Na-conducting salt as the electrolyte, such as sodium hexafluorophosphate ($NaPF_6$), sodium perchlorate ($NaClO_4$), or sodium bistrifluoromethylsulfonimide (NaTFSI).

$NaPF_6$ is the most widely used salt due to its higher ionic conductivity and electrochemical stability compared to the other salts. However, these properties can be affected by the presence of elemental impurities such as chromium (Cr), copper (Cu), iron (Fe), nickel (Ni), and zinc (Zn) in the electrolyte. Impurities can also lead to side reactions within the electrolyte or can contribute to the formation of passivation layers on electrode surfaces or current collectors, reducing overall battery efficiency, lifespan, and safety. The detection of trace elements in Na salt electrolytes has therefore become an essential part of the quality control (QC) process in Na-ion battery manufacturing.[2]

Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) is a fast, robust analytical technique that is widely used for the simultaneous measurement of multiple trace elements in complex battery-related samples.[3, 4]

However, the presence of many Na and other metal ions in the plasma can affect the analysis of easily ionized elements (EIEs), such as calcium (Ca), lithium (Li), magnesium (Mg), and potassium (K) leading to false high results. To avoid ionization interference by the Na matrix on other elements, ICP-OES is often used in radial view mode. However, radial view mode lacks the sensitivity required for the analysis of trace elements, which is problematic if EIEs are present in the electrolyte at low concentrations. In response to this challenge, an Agilent 5800 Vertical Dual View (VDV) ICP-OES operating in axial view mode was used to determine low-concentration elemental impurities in the Na-based electrolytes. Agilent ICP-OES systems use a resilient, plug-and-play torch configuration to produce a vertical plasma that is especially good at handling challenging matrices, including battery-related samples.[4] The solid-state RF (SSRF) system of the Agilent ICP-OES instruments, operating at 27 MHz, and a Cooled Cone Interface (CCI) produce a reliable, robust, and maintenance-free plasma suitable for high matrix samples, such as Na-salt electrolytes. The CCI deflects the plasma's cooler tail, avoiding interferences that form in that region and enabling measurement of most elements at trace concentration levels in axial view mode. Matrix matched calibration standards were also used to minimize EIE interferences.

The 5800 method, which was used to determine 26 analytes in two $NaPF_6$ electrolyte samples, was evaluated in terms of sensitivity, accuracy, and stability. The elements included aluminum, arsenic, boron, beryllium, calcium, cadmium, cobalt, chromium, copper, iron, potassium, lithium, magnesium, manganese, mercury, molybdenum, niobium, nickel, lead, sulfur, tantalum, titanium, tungsten, vanadium, zinc, and zirconium. While there is currently no standard for sodium hexafluorophosphate, many of these elements are specified in the China standard GB/T 19282-2014 for lithium hexafluorophosphate[2], plus some elements of concern within the industry.

Experimental

Standard preparation

To prepare a 1% (w/v) sodium chloride (NaCl) solution, 5 g of high-purity NaCl (Merck & Co) was weighed into 490 mL of de-ionized (DI) water (Millipore Milli-Q Ultrapure Water System). After the NaCl was fully dissolved, 5 mL of high-purity hydrochloric acid (HCl, CNW, Shanghai Anpu Experimental Technology Co., Ltd., China) was added. The 1% NaCl solution was used as the matrix for preparation of the calibration standards.

Agilent multi-element standards were used to create calibration standards at 0.05, 0.1, 0.2, 0.5 mg/L. Multi-element calibration standard-2A (part number 8500-6940) and multi-element calibration standard-4 (p/n 8500-6942) containing 10 mg/L and 10 µg/L respectively of multiple elements were diluted with 1% NaCl.

Sample preparation

Two commercially available $NaPF_6$ electrolyte samples, A and B, obtained from different lots were used in the study. To produce a 100 mL solution of the sodium salt electrolytes, 2.5 g of each sample was accurately weighed and the volume was adjusted using 1% (v/v) HCl. The samples were prepared under moisture-free conditions in a glovebox since $NaPF_6$ exhibits similar chemical properties and decomposition pathways to lithium hexafluorophosphate ($LiPF_6$), which is the most widely used salt in the electrolytes of commercial rechargeable lithium-ion batteries. Both compounds decompose into their respective fluoride salts (LiF for $LiPF_6$ and NaF for $NaPF_6$) and PF_5. When PF_5 is exposed to moisture, it reacts with water to form POF_3 and hydrogen fluoride (HF), a highly toxic and corrosive gas.[7, 8] These properties pose a significant safety hazard and can accelerate battery degradation, potentially resulting in failure.

A spiked solution of electrolyte sample B was also prepared with all analytes added at 0.025 mg/L.

Instrumentation

Elemental analysis of the electrolyte samples was carried out using the Agilent 5800 VDV ICP-OES fitted with a MiraMist nebulizer, inert double-pass cyclonic spray chamber, and an inert Easy-fit fully demountable VDV torch. The SSRF system of the 5800 produced a robust plasma suitable for high matrix samples, such as $NaPF_6$ electrolytes. Agilent ICP Expert Pro software was used to control the 5800 ICP-OES, optimize and run the method, and to process the data. The software includes smart tools to ensure a robust and reliable method for the analysis of precursor chemicals for SIB production, including IntelliQuant Screening.[5]

Instrument operating conditions are given in Table 1.

Table 1. Agilent 5800 VDV ICP-OES operating conditions.

Parameter	Setting
RF Power (kW)	1.1
Plasma Flow (L/min)	12
Aux Flow (L/min)	1.0
Nebulizer Flow (L/min)	0.7
Pump Speed (rpm)	12
Replicates	3
Rinse Time (s)	15
Read Time (s)	10
Stabilization Time (s)	15
Sample Pump Tubing	Black/black Solvaflex
Waste Pump Tubing	Gray/gray Solvaflex
Viewing Mode	Axial

Method development

IntelliQuant Screening is a unique and powerful method development tool within ICP Expert Pro that enables analysts to know more about each sample. A quick full-spectrum scan of the $NaPF_6$ electrolyte samples provided a summary of the presence and semiquantitative concentration of elements in the samples. The data can be viewed as a pie chart, bar chart, or periodic table 'heat map', as shown in Figure 1. A relatively high concentration of Fe was detected in the sample.

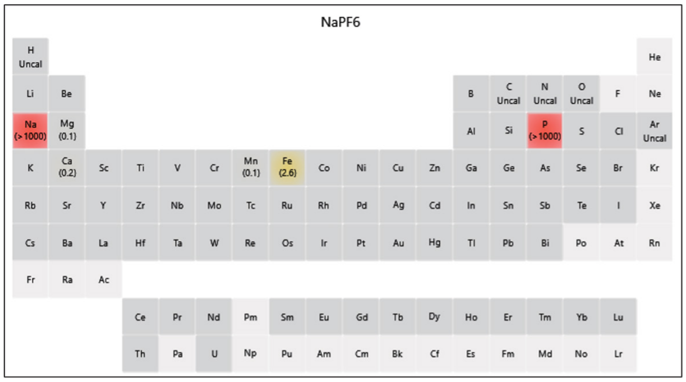
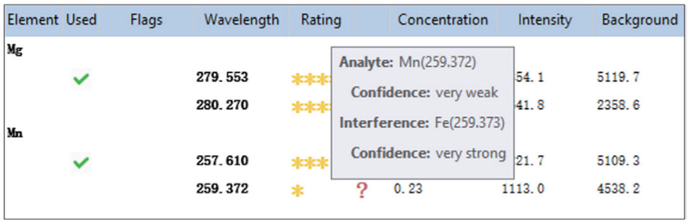


Figure 1. IntelliQuant Screening heat map view showing which elements are present in one of the $NaPF_6$ electrolyte samples. All values are semiquantitative and are reported in ppm.

The analyst can also use the IntelliQuant data to identify or confirm the best element wavelengths to use for the quantitative study. The software identifies any spectral interferences on analyte lines, as shown for Mn in Figure 2. Mn 257.610 is preferred to Mn 259.372 due to an interference on Mn 259.372 by Fe 259.373 nm. Recommendations for interference-free wavelengths for analytes greatly assist wavelength selection.



Element	Used	Flags	Wavelength	Rating		Concentration	Intensity	Background
Mg								
	✓		279. 553	***			54. 1	5119. 7
			280. 270	***			41. 8	2358. 6
Mn								
	✓		257. 610	***			21. 7	5109. 3
			259. 372	*	?	0. 23	1113. 0	4538. 2

Analyte: Mn(259.372)
Confidence: very weak
Interference: Fe(259.373)
Confidence: very strong

Figure 2. IntelliQuant uses a star ranking system to indicate the best analyte wavelengths and which wavelengths to avoid. The information enables the analyst to select the best line for the quantitative method before starting the analysis.

Automatic background correction

The ICP Expert software includes Fitted Background Correction (FBC), which corrects simple and complex background peaks automatically, requiring no input from the analyst.[6] FBC was applied to all elements in this study. In the peak profile spectra shown in Figure 3, the dashed line represents the FBC.

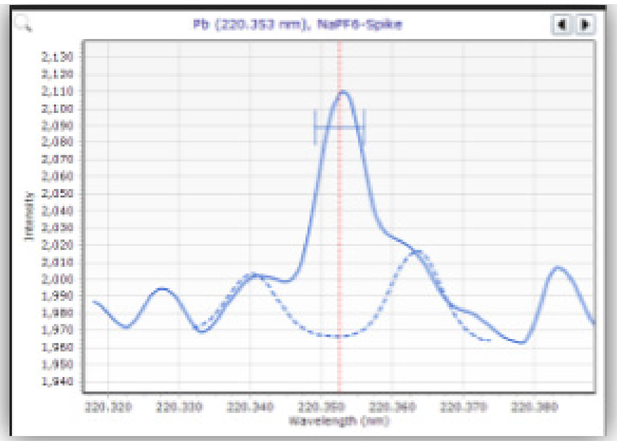
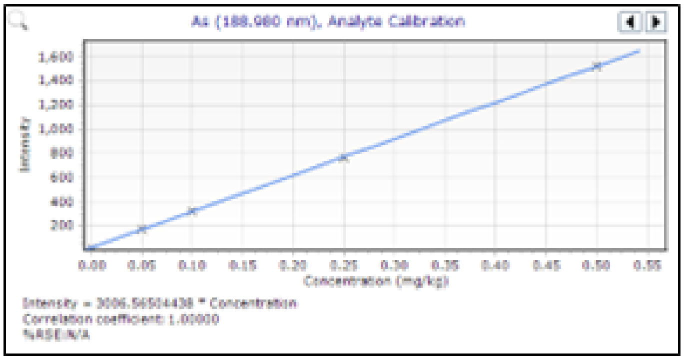


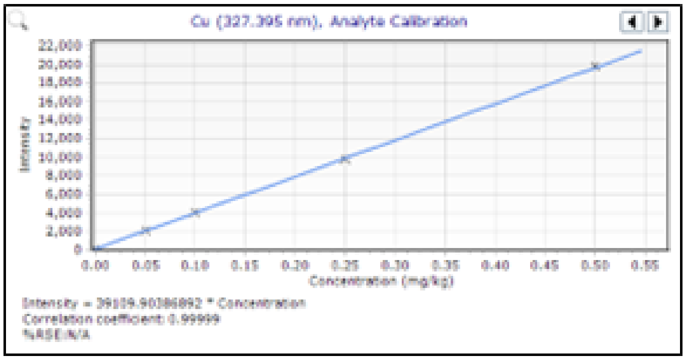
Figure 3. Fitted Background Correction of Pb 220.353.

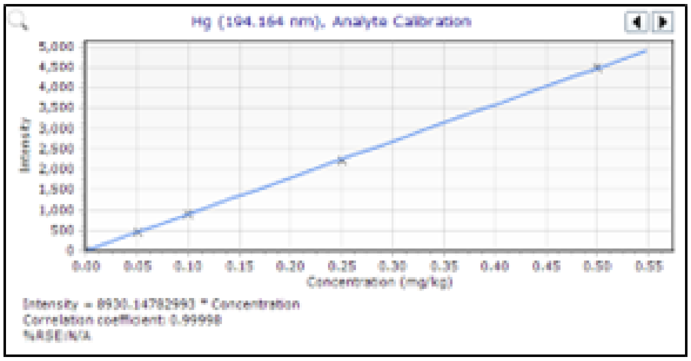
Results and discussion

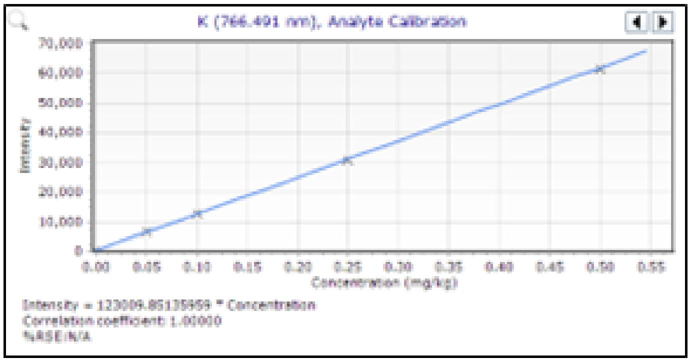
Calibration

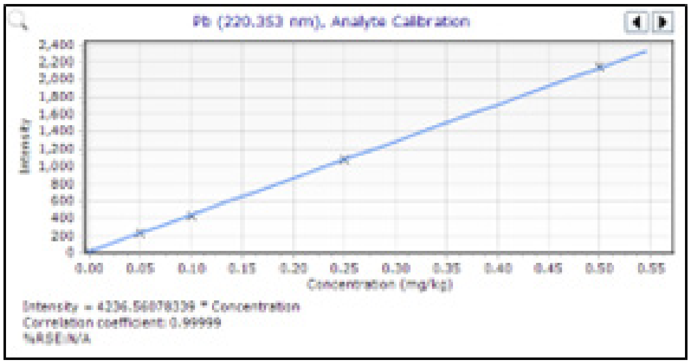
The 26 elements were quantified in the Na salt electrolyte samples against matrix matched calibration standards. The standard curves and linear regression results of representative analytes are shown in Figure 4. Good linearity (R>0.9999) was achieved for all elements across their respective analytical ranges.

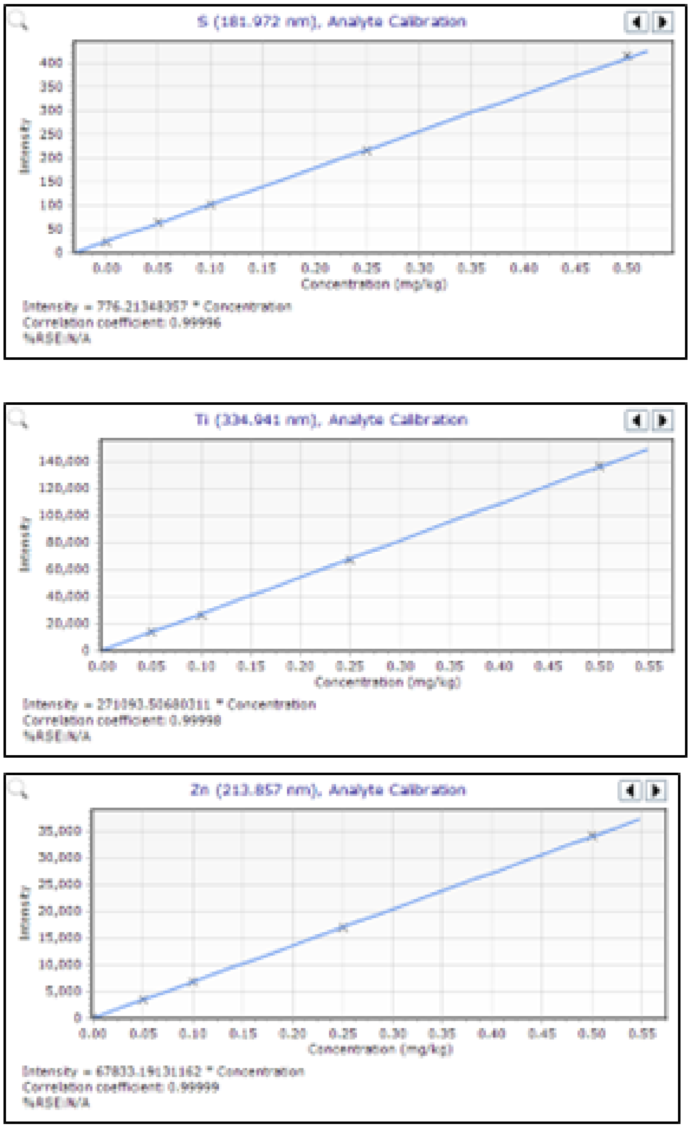












```
Intensity = 776.21348357 * Concentration
Correlation coefficient: 0.99996
%RSE:N/A
```

```
Intensity = 271093.50680311 * Concentration
Correlation coefficient: 0.99998
%RSE:N/A
```

```
Intensity = 67833.19131162 * Concentration
Correlation coefficient: 0.99999
%RSE:N/A
```

Figure 4. Representative ICP-OES matrix-matched calibration curves for As, Cu, Hg, K, Pb, S, Ti, and Zn.

Method detection limit (MDLs)

To obtain MDLs, the 1% (w/v) NaCl matrix blank solution was analyzed 11 times consecutively using the 5800 ICP-OES. The MDLs were calculated as three times the standard deviation of the 11 measurements multiplied by a dilution factor of 40. The high sensitivity of the 5800 is demonstrated by the ppb-level MDLs for all analytes, as shown in Table 2.

Table 2. Analytical wavelengths and method detection limits.

Analyte	Wavelength (nm)	MDL (mg/kg)	Analyte	Wavelength (nm)	MDL (mg/kg)
Al	396.152	0.044	Mg	279.553	0.001
As	188.980	0.078	Mn	257.610	0.002
B	249.772	0.014	Mo	202.032	0.025
Be	234.861	0.002	Nb	295.088	0.032
Ca	396.847	0.002	Ni	216.555	0.049
Cd	214.439	0.006	Pb	220.353	0.060
Co	238.892	0.015	S	181.972	0.135
Cr	206.550	0.054	Ta	263.558	0.080
Cu	327.395	0.036	Ti	334.941	0.006
Fe	238.204	0.016	V	292.401	0.030
Hg	194.164	0.041	W	209.475	0.081
K	766.491	0.030	Zn	213.857	0.009
Li	670.783	0.008	Zr	343.823	0.011

Quantitative data and spike recoveries

Quantitative results for $NaPF_6$ electrolyte samples A and B that were acquired by the 5800 are shown in Table 3. Although the samples were from different lots, the results were similar for all analytes measured above the MDL. All elements except for Fe, Li, and S were measured below 1 mg/kg. Fe was measured at 3.5 mg/kg, while Li and S were measured close to 1 mg/kg.

Electrolyte sample B was spiked at 0.025 mg/L with all analytes. The spike recoveries ranged from 98 to 108% of the expected concentration, demonstrating the accuracy of the method for the analysis of the target analytes in the Na-salt electrolyte solution.

Table 3. Quantitative results for two NaPF$_6$ electrolytes and spike recovery results for commercial electrolyte sample B, spiked at 0.025 mg/L with all analytes. Concentration units: mg/kg.

Elements	NaPF$_6$	NaPF$_6$	NaPF$_6$	Spike Recovery (%)
	Sample A	Sample B	Sample B Spiked	
Al	0.357	0.351	1.429	108
As	0.338	0.321	1.305	98
B	0.087	0.092	1.094	100
Be	0.005	0.005	1.018	101
Ca	0.285	0.284	1.339	106
Cd	<MDL	0.002 (<MDL)	1.001	100
Co	0.028	0.023	1.008	99
Cr	0.367	0.376	1.358	98
Cu	0.122	0.113	1.168	106
Fe	3.471	3.462	4.473	101
Hg	0.049	0.052	1.062	101
K	0.11	0.122	1.171	105
Li	1.133	1.127	2.150	102
Mg	0.201	0.203	1.277	107
Mn	0.165	0.166	1.197	103
Mo	0.045	0.053	1.045	99
Nb	0.061	0.058	1.043	99
Ni	0.262	0.253	1.285	103
Pb	0.094	0.108	1.153	105
S	1.055	1.008	2.018	101
Ta	0.249	0.236	1.292	106
Ti	0.045	0.045	1.051	101
V	0.033	0.044	1.023	98
W	0.309	0.322	1.353	103
Zn	0.065	0.068	1.062	99
Zr	0.030	0.038	1.032	99

Method stability

The robustness of the 5800 method was evaluated by analyzing the spiked NaPF$_6$ electrolyte sample B once every 10 minutes over 90 minutes. As shown in Figure 5, the precision of the measured concentrations of each analyte over 90 minutes was excellent, as indicated by the RSDs < 2.5%. The excellent stability and repeatability of the measurements confirmed the suitability of the 5800 VDV ICP-OES method for the routine analysis of impurity elements in Na salt electrolytes over 1.5 h.

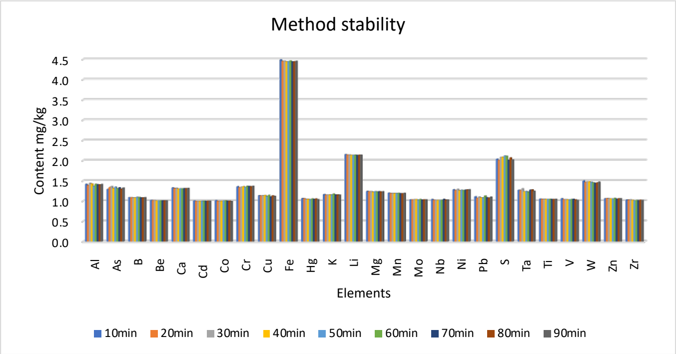


Figure 5. Nine repeated measurements of the spiked NaPF$_6$ electrolyte samples over 1.5 hours.

Conclusion

The Agilent 5800 VDV ICP-OES in axial view mode was used for the quantitative analysis of 26 elemental impurities in sodium hexafluorophosphate (NaPF$_6$)—a common salt used in the electrolytes of sodium-ion batteries.

The IntelliQuant Screening smart tool included in the Agilent ICP Expert Pro software acquired a full-spectrum scan of the NaPF$_6$ samples. The data provided an elemental profile of the electrolytes, identifying a relatively high concentration of iron. It also assisted with selection or confirmation of the best analyte wavelengths for the quantitative method, increasing confidence in the results. Fitted Background Correction (FBC) was used to automatically correct the background structures that arise when analyzing complex samples, improving the accuracy and reliability of all measurements.

The robust vertical plasma, SSRF generator, and Cooled Cone Interface of the 5800 effectively handled the high concentration of Na in the sample matrix, along with the use of matrix matched calibration standards. Excellent calibration linearity (R> 0.9999) and method detection limits ranging between 0.001 and 0.135 mg/L were achieved. The recoveries of low concentration 0.025 mg/kg spikes in one of the electrolyte samples ranged between 98 and 108%, demonstrating the method's accuracy in detecting trace levels of the analytes. The 5800 also maintained excellent stability during the nine repeated measurements of the spiked electrolyte sample over 90 minutes, as indicated by RSDs < 2.5%.

This 5800 ICP-OES method is suitable for the accurate quantification of impurity elements in the electrolyte salts used in SIBs. Only Fe, Li, and S were measured above 1 mg/kg in the two Na-conducting salts.

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