

Improved Analysis for the Lithium Battery Industry: How Pure are your Organic Solvents?

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Introduction

The ability to measure trace element impurities in organic solvents in the Lithium battery industry is critical to achieving the highest-performing systems. While organic solvents are simple in terms of chemistry, their physical characteristics differ greatly, making analysis far from “simple,” as a variety of issues must be addressed. Sample preparation, matrix matching, interference, volatility, calibration, and analytical equipment all need to be considered for proper analysis. A high-performance ICP-OES system, coupled with a high-efficiency spray chamber and the revolutionary Jet Vortex Interface™ (JVI), simplifies the typical issues associated with this application.

Key Objectives

1. Eliminate the need for aqueous digestion of an organic material. This eliminates the mechanical error associated with the sample preparation (i.e. 100-1000x dilution).
2. Calibrate an organic matrix that does not have “matrix-matched” calibration standards.
3. Validate the calibration by using a commercially available material’s certificate of analysis (COA) since there is no CRM available.
4. Utilize system hardware capable of routinely analyzing these materials, even in a production/QC laboratory environment (low maintenance and easily to operate).
5. Reduce the cost associated with analyzing the samples by consolidating instrumentation (ICP-OES as opposed to microwave digestion + ICP/ ICP-MS/GFAA + IC etc).

This work represents cooperation between Glass Expansion and Pure Lithium to evaluate the benefits of an innovative aerosol filtration accessory combined with a low-volume, high-efficiency spray chamber to measure lithium battery electrolytes by ICP-OES without the need to digest the sample. This paper reviews the capabilities of this innovative sample introduction system coupled with an ultra-high-performance ICP-OES system that supplants ICP-MS capabilities, especially concerning one critical element of interest, chlorine.

Experimental

A Spectro Arcos II MV (SPECTRO Analytical Instruments Inc.) was chosen due to its flexibility, offering both Radial (SOP) or Axial (EOP) orientation, in addition to being the only sealed and recirculated simultaneous ICP-OES instrument on the market capable of measuring the halogens (Cl, Br, I) down to 130 nm. For this work, the EOP (axial) orientation was used exclusively, providing superior sensitivity for Na, K, Cl, S, P, Ca, Mg, Fe, Al, Sr, Ba, and Li. The Arcos also supports additional gas options, which was integral for this work due to the preparation of samples in undiluted isopropyl alcohol (IPA), as working with an organic solvent like IPA benefits from the O₂ gas option by improving long-term stability and preventing frequent maintenance of the torch due to carbon build-up.

The higher RF power of 1700 W results in a complete breakdown of the organic matrix. A single-piece quartz torch with 1.2mm ID injector was employed, as a smaller bore is a standard option for volatile organic matrices. A complete list of the ICP-OES operating parameters can be found in Table 1.

Table 1. Instrument Operating Parameters

Plasma Power	1700 W
Coolant Gas Flow Rate	18.5 L/min
Auxiliary Gas Flow Rate	2.5 L/min
Auxiliary Gas Flow Rate O ₂	0.075 L/min
Nebulizer Gas Flow Rate	0.5 L/min
JVI Gas Flow Rate	0.075 L/min
View Type	EOP (Axial)
Stabilization Time	0 seconds
Pre-flush Time	45 seconds
Rinse Time	25 seconds (2.5 mL/min)
Sample Flow Rate	1.5 mL/min
Sample Peristaltic Pump Tubing	Viton – 0.89 mm (Orange/Orange)
Waste Peristaltic Pump Tubing	Viton – 1.65 mm (Blue/Blue)

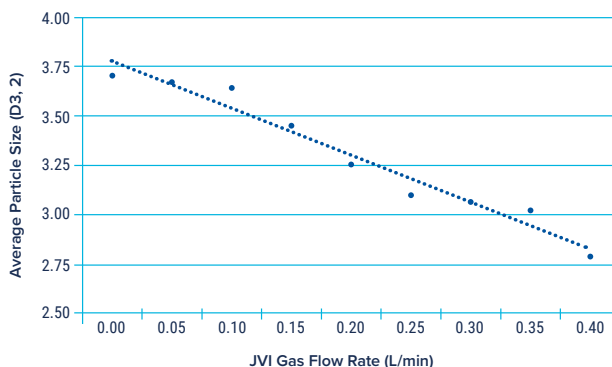
The sample introduction system (Figure 1.) from Glass Expansion consists of the SeaSpray DC nebulizer, Tracey DC cyclonic spray chamber, and patent-pending Jet Vortex Interface (JVI). The SeaSpray DC was chosen due to its ability to handle a complex matrix, while providing outstanding nebulization efficiency that translates to enhanced sensitivity and precision compared to other concentric nebulizers. The Tracey DC cyclonic spray chamber is a brand-new product to Glass Expansion's popular line of cyclonic spray chambers. The Tracey DC is a smaller volume at 30 mL compared to the standard 50 mL, and, in combination with the trademark Helix CT interface, translates to a high-efficiency spray chamber design for improved transport efficiency and faster washout times. The direct connection feature of the Tracey DC design guarantees perfect alignment to the torch and is compatible with the patent-pending JVI, which adds an aerosol filtration accessory to the sample introduction system.

The JVI is essential to this application, as it adds the ability to reduce the average particle size exiting the spray chamber by 3-4% for every 0.05 L/min flow of argon (Figure 2). In this work, the JVI replaces a high-cost temperature-controlled spray chamber that would have been traditionally used to cool the spray chamber temperature to below ambient temperatures to analyze a volatile organic solvent like IPA. The use of the JVI gas to control transport efficiency decreases carbon deposition and dramatically improves the stability and robustness of the plasma.

Figure 1. Glass Expansion SeaSpray DC nebulizer, Tracey DC spray chamber, and JVI.



Figure 2. JVI gas flow rate effect on average particle size.



Calibration Reagents

A multi-element standard solution (Inorganic Ventures) was prepared using 99.5% anhydrous IPA (Sigma Aldrich), in a 1:10 dilution. The stability of aqueous standards in IPA is typically 24 to 78 hours to ensure the accuracy agreement with the COA for the organic solvents. All results are density-corrected (water vs. ethylene carbonate).

Calibration standards were prepared between 0 to 100 ppm, depending on the analytes of interest. Carbon 131 nm was used as a monitor line for sample introduction performance. Because of the closely matched sample matrix (IPA) and the ability to monitor C 131 nm, the use of an artificial internal standard such as Y was not needed.

Table 2. Short-term Precision in IPA for Blank and 100 ppm Li standard

Sample Name		Li 323.261	Ar 420.067	C 131.136
Blank (ETH)	Mean (CPS)	67068	2152751	1781762
	SD	119	16292	735
	RSD	0.178	0.757	0.0412
Li (100ppm STD)	Mean (CPS)	259158	3026940	2180429
	SD	2004	28708	7241
	RSD	0.773	0.948	0.332

Outstanding RSDs of <1 % can be achieved using the JVI setup, even in volatile organic matrices, which often require a Peltier temperature-controlled spray chamber.

Sample Preparation

The samples tested in this study were ethylene carbonate, dimethyl carbonate, and ethyl methyl carbonate. One gram of the sample was weighed in a synthetic polypropylene test tube and brought up to 10 g using the IPA diluent. All samples were density corrected (DI H₂O to organic sample matrix).

Results and Discussion

Table 3 provides the 3-sigma limits of detection (LOD) for an IPA solution, and also includes the background equivalent concentration (BEC) and calibration ranges. As one can see, the setup allows for LODs that are typically in the single-digit ppb level (even sub-ppb in some cases).

Table 3. Detection limits in IPA/Electrolyte Matrix.

Wavelength	LOD (ppm)	BEC	Calibration Range (ppm)
Ag 328.068	0.0008	0.243	0.000752 - 6.00
Al 167.078	0.0018	0.250	0.001753 - 6.00
B 249.773	0.0020	0.098	0.002008 - 6.00
Be 313.107	0.0001	0.013	0.000093 - 6.00
Br 154.065	0.4738	49.796	0.474 - 120
Ca 315.887	0.0032	0.630	0.003178 - 6.00
Ca 396.847	0.0002	0.037	0.000166 - 3.00
Cd 214.438	0.0003	0.052	0.000313 - 6.00
Cl 134.724	0.4501	49.750	0.450 - 120
Co 228.616	0.0013	0.172	0.001254 - 6.00
Cr 267.716	0.0004	0.117	0.000388 - 6.00
Cu 324.754	0.0006	0.164	0.000634 - 6.00
Fe 259.941	0.0005	0.120	0.000538 - 6.00
I 161.760	0.3670	24.872	0.367 - 120
I 183.038	0.1062	28.577	0.106 - 120
K 766.491	0.0228	1.793	0.0228 - 60.0
Li 323.261	0.2496	39.403	0.250 - 1000
Mg 279.553	0.0001	0.003	0.000057 - 6.00
Mn 257.611	0.0001	0.016	0.000119 - 6.00
Mo 202.095	0.0041	0.290	0.004142 - 6.00
Na 589.592	0.0123	1.271	0.0123 - 50.0
Ni 231.604	0.0020	0.362	0.001974 - 6.00
Si 251.612	0.0015	0.282	0.001530 - 3.00
Ti 334.941	0.0004	0.084	0.000427 - 6.00
V 292.464	0.0010	0.285	0.000976 - 6.00
Zn 213.856	0.0005	0.085	0.000520 - 6.00

Table 4 shows the accuracy of the calibration as compared to a commercially available 1 molar Li electrolyte with an expected Li concentration of 6941 ppm. The recovery using this methodology is excellent, at nearly 95% of the expected value.

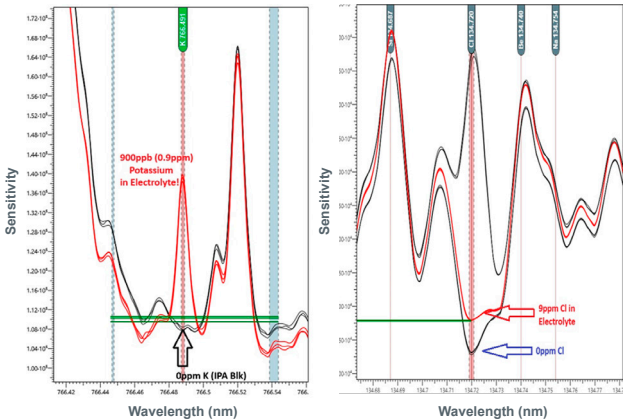
Table 4. Accuracy of Cl and Li Measurement in Electrolyte (EL-102) in IPA Matrix.					
Sample Name		Cl 134.724	Expected Cl Concentration	Li 323.261	Expected Li Concentration
EL-102			< 100 ppm		6941 ppm
	Mean (ppm)	35.9*		6623**	
	SD	3.08		25.2	
	RSD	8.57		0.38	
*Cl in electrolyte measured concentration 35.9 ppm +/- 3 ppm					
**Commercial 1 M Li in electrolyte measured concentration 6623 ppm (95.4% accurate)					

Table 5 displays the detected trace impurities in the electrolyte (along with lithium). Of particular interest is the ability to measure K and Na with excellent precision (< 1 % RSD) as well as Cl at < 100 ppm.

Table 5. Trace Impurities Found in Electrolyte (EL-102) in IPA Matrix.			
Wavelength	Mean (ppm)	SD	RSD
Ca 315.887	6.01	0.0367	0.612
Ca 396.847	5.66	0.0382	0.674
Cl 134.724	35.9	3.08	8.57
K 766.491	8.57	0.0443	0.516
Li 323.261	6623	25.2	0.38
Mg 279.553	0.002978	0.000294	9.86
Mn 257.611	0.0121	0.001563	12.9
Na 589.592	24.2	0.0869	0.36
Si 251.612	0.199	0.003539	1.78
Note: Ag, Al, B, Be, Br, Cd, Co, Cr, Cu, Fe, I, Mo, Ni, Ti, V, and Zn are all < LOD (not detected)			

The spectral scans shown in Figure 3 were taken from electrolyte sample “EL-102” in an IPA matrix. It is important to note that K and Cl are measured at 900 ppb and 3.7 ppm, respectively. This calculates to be 8.57 ppm K and 35.0 ppm Cl in the electrolyte sample.

Figure 3. Spectral scan of ethyl carbonate electrolyte for K 766 nm and Cl 134 nm in IPA.



The ability to measure chlorine in the electrolyte allows one to eliminate this highly reactive elemental concern from the Li metal battery manufacturing process. Since there is no sample preparation other than a basic wt/wt dilution in IPA, the mechanical error is greatly reduced. However, the true benefit is the JVI’s ability to filter the aerosol in-line, allowing for the ultimate optimization of sample delivery into the plasma.

This benefit, along with the O₂ bleed, makes it possible to measure all elements of interest in only one integration at ppb levels (in solution), especially for the alkali elements (K, Na, etc.). The aerosol filtering ability of the JVI, along with oxygen, allows for the use of an AXIAL view ICP-OES without any of the usual maintenance concerns (i.e. carbon buildup in the torch). This greatly reduces the need to use multiple analytical techniques, such as ICP-OES, ICP-MS, GFAA, and IC, saving the laboratory added overhead.

Conclusion

The ability to measure electrolyte organic materials in a matrix-matched IPA solvent, without the need for aqueous digestion, allows for lower detection limits and better accuracy. The JVI system further helps improve solvent “sample delivery” to the plasma while providing better short-term precision and accuracy. This system setup avoids carbon build-up on the torch and allows for axial viewing without any added maintenance. The benefit of being able to use axial view exclusively for these samples due to the JVI accessory translates into superior sensitivity (even surpassing ICP-MS), particularly for Na, K, Cl, S, P, Ca, Mg, Fe, Al, Sr, Ba and Li.