Application Note

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Solvents and Additives Analysis in Lithium Battery Electrolytes Using the Agilent 8850 GC System and Applying It to Real Samples

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Abstract

The electrolyte is a key component in lithium-ion batteries, playing a vital role in transferring and conducting current between the positive and negative electrodes. The selection and optimization of electrolyte components are important in improving battery performance. Therefore, the analysis of electrolyte composition is an essential task in the lithium battery industry. This application note introduces an analytical method for determining carbonate solvents and additives in lithium battery electrolytes based on the Agilent 8850 gas chromatography (GC) system with a flame-ionization detector (FID). In this study, standard samples were used for method evaluation, and excellent performance results in terms of linearity, reproducibility, and detection limits were obtained. Real samples were run to investigate the impact of high acid and high salt samples on the performance of the entire GC system. Compared to undiluted samples, diluted samples can significantly extend the lifespan of the liner and column.

Introduction

The lithium battery industry is a rapidly growing sector, largely driven by the increasing demand for electric vehicles and renewable energy storage systems. Lithium batteries are known for their high energy density and long cycle life. One of the four key materials in lithium batteries, the electrolyte, has main components including organic solvents, lithium salts, and a small amount of additives. The solvents in the electrolyte, such as ethylene carbonate (EC) or dimethyl carbonate (DMC), determine its ionic conductivity and stability. An optimal blend of solvents can enhance the battery's efficiency and lifespan. Additives are also crucial, as they can improve the electrolyte's performance and safety. For instance, they can suppress the formation of harmful byproducts, enhance the stability of the electrolyte, and improve the interface between the electrolyte and electrode. Therefore, analyzing and identifying the composition of carbonate compounds and additives in the electrolyte of lithium batteries is of great significance for performance study and quality control in the lithium battery industry.

An earlier Agilent application note demonstrated the use of the Agilent 5977B single quadrupole gas chromatography/mass selective detector (GC/MSD) system to measure carbonate solvents and additives in the electrolyte. The note detailed the accurate quantification of target compounds and the qualitative analysis of unknown additives or impurities.[1] In 2023, another application note was published describing the determination of carbonate and additive compounds in the electrolyte with the Agilent 8860 GC/FID system.[2] Compared with GC/MSD, the GC/FID configuration is easier to use and more cost-effective for users. It is very suitable for laboratories that only need to quantify target compounds and do not need to detect unknown substances. This application note was developed based on the latest small-size, high-performance 8850 GC/FID system. With an effective analytical method established, the impact of running a large number of real samples on the overall GC system performance was examined, particularly the effects of the consumables on the GC inlet and the lifespan of the column.

Experimental

This study was performed on an 8850 GC system equipped with a split/splitless inlet and FID. Table 1 shows the details of the operating conditions, using helium as the carrier gas. Data acquisition was performed using Agilent OpenLab CDS, version 2.7.

Chemicals, standards, and samples

Single standards of 13 analytes (> 97% purity) and dichloromethane (HPLC grade) were purchased from ANPEL Laboratory Technologies (Shanghai) Inc. Two electrolyte samples were sourced from an industry laboratory.

Preparation of mixed standard stock solutions: Standards were prepared by weighing 50 mg of each single standard into a 5 mL volumetric flask and diluting to the mark with dichloromethane, yielding a composite standard stock mixture concentration of 10,000 mg/L.

Preparation of calibration curve solutions: Calibration standards containing 13 target compounds were prepared in dichloromethane at concentrations of 10, 25, 50, 100, 250, and 500 mg/L.

The real electrolyte samples were diluted to different concentrations with dichloromethane, ranging from 5x to 1,000x.

Results and discussion

The electrolyte is typically formulated from high-purity organic solvents, electrolytic lithium salts, and essential additives, among other raw materials. Under specific conditions, these components are mixed in a certain proportion. For companies that manufacture and use electrolytes, solvent purity analysis, solvent composition analysis, and additive analysis are essential for their routine checks. This study targeted 13 carbonate solvents and certain additives, exploring the establishment of calibration curves, instrument stability tests, determination of limits of detection, and performed a quantitative analysis of real samples obtained from customers. After completing the quantitative analysis, this study also examined the impact on the GC inlet and column by directly injecting real samples without dilution.

Table 1. Agilent 8850 GC system conditions.

Parameter	Value
GC	Agilent 8850 GC system
Inlet	Split/splitless; 250 °C; split ratio 20:1
Liner	Ultra Inert, split, low pressure drop, glass wool (p/n 5190-2295)
Column	Agilent J&W DB-1701, 30 m × 0.25 mm, 0.25 µm (p/n 122-0732E)
Carrier	Helium, 1.2 mL/min, constant flow
Oven	40 °C (3 min), 10 °C/min to 160 °C (5 min), 20 °C/min to 240 °C (3 min), Post run: 250 °C for 4 min
FID	250 °C; hydrogen: 30 mL/min; air: 400 mL/min; makeup gas (nitrogen): 25 mL/min
Injection Volume	1 µL

Evaluation of the analytical method

Figure 1 is the chromatogram of the 13 target compounds at a concentration of 100 mg/L. In this study, helium was used as the carrier gas and separation was carried out with a J&W DB-1701 column. As shown in Figure 1, all compounds were baseline-separated and the peak shapes were symmetrical.

The mixed standard solutions of electrolyte with concentrations of 10, 25, 50, 100, 250, 500 mg/L were prepared and analyzed, and a six-point calibration curve was plotted for each compound. Excellent linearity was obtained within the concentration range, with correlation coefficients (R^2) all exceeding or equal to 0.999, as shown in Table 2.

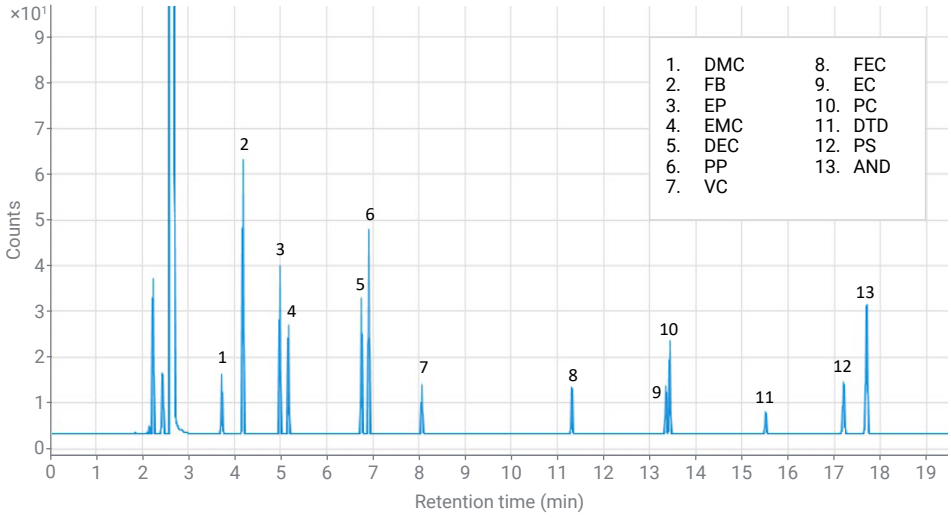

Figure 1. Chromatogram of the 13 target compounds at a concentration of 100 mg/L.

Table 2. Performance results for 13 analytes.

No.	Compound Name	Abbreviation	R^2	Area %RSD			Limit of Detection (LOD) (mg/L)	Limit of Quantification (LOQ) (mg/L)
				10 mg/L	50 mg/L	500 mg/L		
1	Dimethyl carbonate	DMC	0.9993	1.538	0.527	0.365	0.21	0.72
2	Fluorobenzene	FB	0.9994	0.483	0.523	0.237	0.04	0.12
3	Ethyl propionate	EP	0.9993	0.784	0.569	0.329	0.06	0.20
4	Ethyl methyl carbonate	EMC	0.9993	0.792	0.666	0.323	0.10	0.33
5	Diethyl carbonate	DEC	0.9993	0.631	0.619	0.371	0.07	0.25
6	Propyl propionate	PP	0.9993	0.486	0.593	0.361	0.05	0.16
7	Vinylene carbonate	VC	0.9992	0.975	0.522	0.378	0.26	0.87
8	Fluoroethylene carbonate	FEC	0.9994	1.548	0.594	0.433	0.23	0.76
9	Ethylene carbonate	EC	0.9993	1.02	0.652	0.433	0.24	0.80
10	Propylene carbonate	PC	0.9995	0.647	0.682	0.429	0.11	0.35
11	Vinyl sulfate	DTD	0.999	2.19	0.953	0.675	0.43	1.43
12	1,3-Propanesultone	PS	0.999	0.492	0.718	0.437	0.18	0.60
13	Adiponitrile	AND	0.9994	0.574	0.706	0.43	0.07	0.24

Repeatability was evaluated by eight replicates at low, middle, and high concentrations of calibration standard (10, 50, and 500 mg/L). Table 2 and Figure 2 illustrate the excellent performance results based on this system. The area %RSD was between 0.24% and 2.19%, and the RT %RSD was between 0.001% and 0.014%.

A concentration of 4 mg/L standard solution was used to test the LOD and LOQ, which were calculated based on a signal-to-noise ratio of 3 and 10, respectively. The LOD values are listed in Table 2 and ranged from 0.04 to 0.43 mg/L, which shows the excellent sensitivity of this GC/FID system.

Real sample analysis

quantification of the target substance in the samples: Two real samples (samples 1 and 2) obtained from an industry laboratory were tested with pH strips, yielding a pH value of approximately 1. The linear range established by the calibration curve was between 10 and 500 mg/L. Some of the target analytes exceeded the range boundary when the samples were initially analyzed. To improve quantitation, dilutions were applied to the sample to bring the amount on the column to levels supported by the calibrated range.

In addition, the concentrations of some compounds in the real samples were already in the linear range even if they were not diluted, but the undiluted samples will cause damage to the column (discussed in detail in the following paragraph), so the real samples were diluted when quantifying. Table 3 lists the dilution ratios needed for different compounds in the original real sample. Then, the concentrations were calculated through the calibration curve for each compound, and finally, the actual concentrations of the analytes in the original real sample were calculated by incorporating the dilution ratios. Figure 3 presents the chromatogram of sample 1 after dilution.

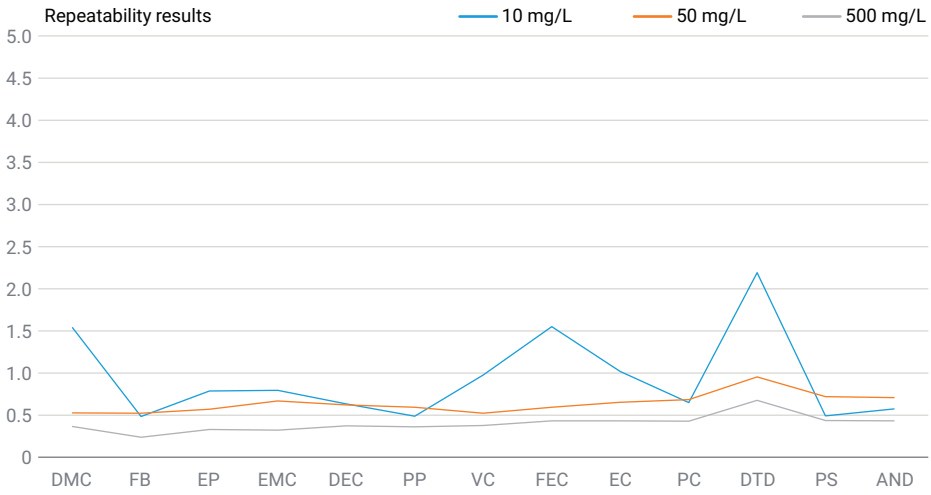

Figure 2. Repeatability results at low, middle, and high concentrations of calibration standards.

Table 3. The quantitative results of the real samples.

Compound Name	Sample 1			Sample 2		
	Dilution Ratio	Calculated Concentration (mg/L)	Original Concentration (mg/L)	Dilution Ratio	Calculated Concentration (mg/L)	Original Concentration (mg/L)
DMC	10	5.298	52.98	1,000	789.132	789,132
FB	–	–	–	–	–	–
EP	10	10.529	105.29	–	–	–
EMC	10	6.142	61.42	1,000	88.4	88,400
DEC	1,000	279.867	279,867	5	21.118	105.59
PP	1,000	626.437	626,437	–	–	–
VC	50	43.676	2,183.8	–	–	–
FEC	1,000	195.574	195,574	500	91.143	45,571.5
EC	1,000	229.14	229,140	1,000	326.574	326,574
PC	1,000	295.434	295,434	–	–	–
DTD	50	109.976	5,498.8	5	102.943	514.715
PS	100	174.026	17,402.6	–	–	–
AND	100	115.605	11,560.5	–	–	–

Note: "–" means no target analyte was detected.

Real sample analysis without dilution: When the objective is to identify trace components within an electrolyte sample, the sample would be directly injected without any sample preparation, as any form of sample preparation could potentially result in the loss of some trace components of interest. Therefore, users will directly inject the sample into the GC inlet without any dilution. However, such analysis work is carried out at the expense of the inlet consumables and the lifespan of the column, because the electrolyte sample is usually highly acidic and has high salt content. These high concentrations of acid and salt can cause significant harm to the column.

This study investigated the direct injection of undiluted samples. Prior to the test, a new septum, liner, and gold seal were installed, and a new DB-1701 GC column was installed onto the 8850 GC system. In the beginning, to maximize the lifetime of the column, a 0.5 m, 0.25 mm restrictor was installed between the inlet and the analytical column acting as the guard column using an Agilent Ultra Inert Ultimate union (part number G3182-60581). The sequence table is shown in Figure 4. First, the dichloromethane solvent blank was injected, followed by the 100 mg/L standard sample. Then, the undiluted sample was analyzed, and finally, the solvent blank and the 100 mg/L standard sample were analyzed again. Here, the 100 mg/L standard sample acts as a quality control sample, used to monitor changes in system performance after running the undiluted sample.

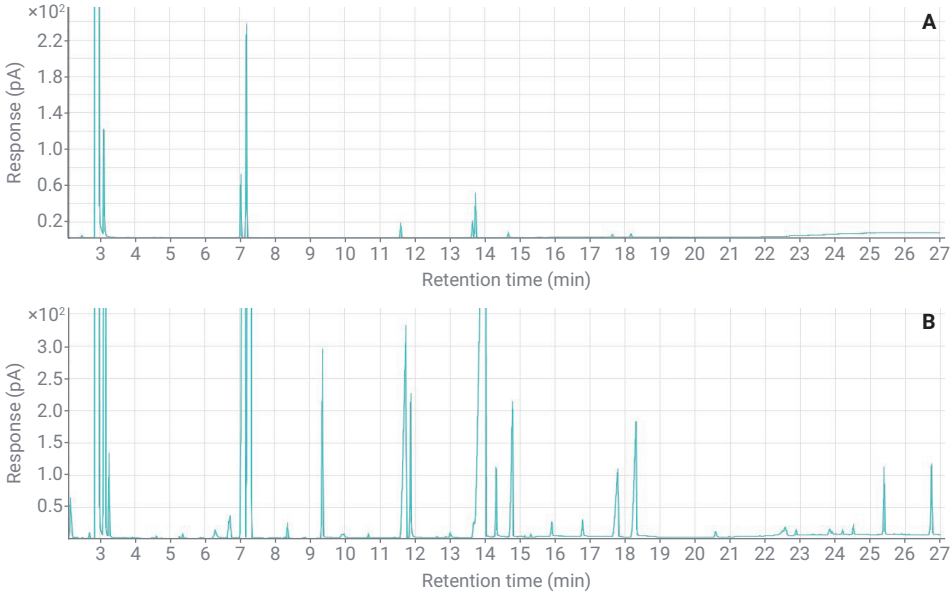

Figure 3. (A) The chromatogram of sample 1 after 1,000-fold dilution with dichloromethane and (B) the chromatogram of sample 1 after 10-fold dilution with dichloromethane.

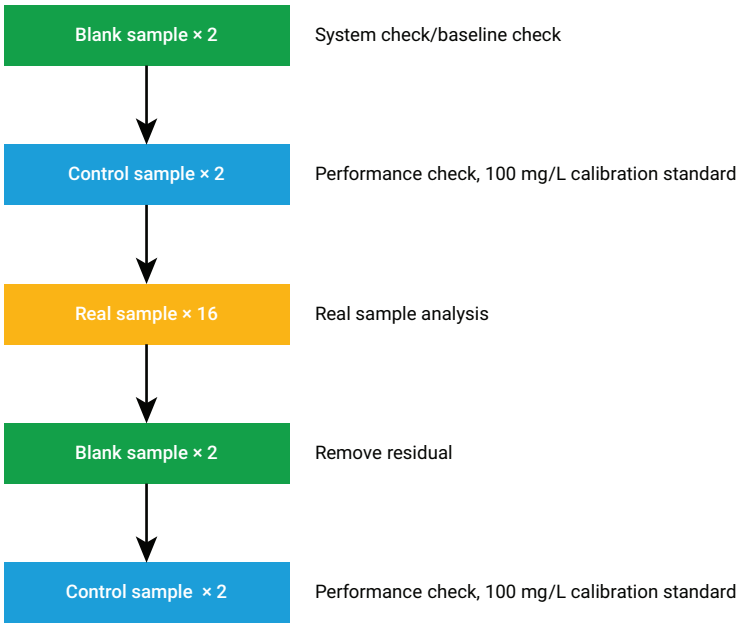

Figure 4. Typical sequence table.

As shown in Figure 5, before running the real samples without dilution, the chromatogram of the 100 mg/L control sample was perfectly symmetrical, with each compound achieving baseline separation. However, after running the real samples, tailing began to appear in the peak shapes, especially in the late-eluting compounds where the tailing was more pronounced. Moreover, the retention times began to shift forward and the separation became worse.

The two compounds, EC and PC, which were initially able to achieve baseline separation, subsequently had poorer separation. Additionally, as the number of injections of the real samples increased, phenomena such as peak tailing, retention time shift, and separation issue became more pronounced. After the inlet consumables, such as the septum, liner, and gold seal were replaced, the 0.5 m restrictor was also replaced, and the head of the column was trimmed by 50 cm, the chromatographic behavior slightly improved. However, it was challenging to restore the chromatographic performance (stable retention time, symmetrical peak shape) to its initial state. This indicates that the damage to the column caused by high acidity and high salinity is irreversible, and the protective capability of the guard column is very limited. Thus, the guard column was removed from the system, and it was not installed when standard samples and diluted real samples were tested.

In the process of directly injecting undiluted samples, due to the particularity of the samples, the injection syringe was found to be prone to blockage, and especially the plunger was prone to bending. Therefore, choosing the right syringe-washing solvent was very important. In this experiment,

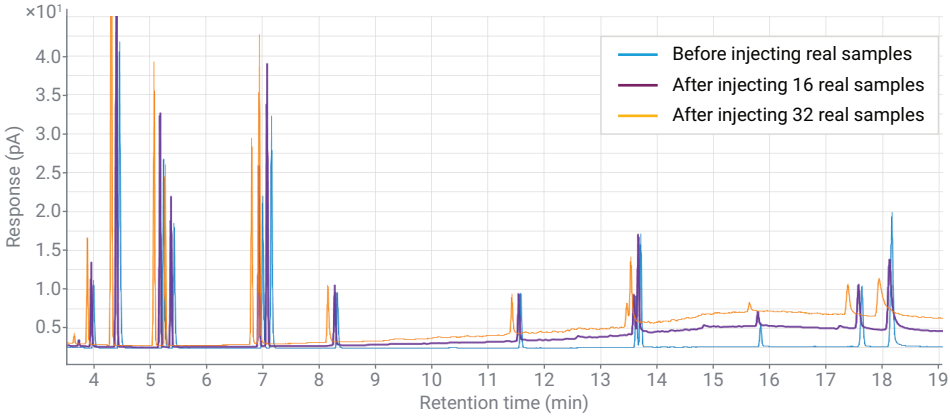

Figure 5. The performance comparison of 100 mg/L calibration standard before and after injecting real samples without dilution. The decreasing retention time and rising baselines indicate column damage.

using dichloromethane as the dilution solvent for the sample could solve the problem of high salt and high acidity. However, it was not suitable to use dichloromethane as the syringe-washing solvent, because the syringe plunger bent after a few real samples were injected. When the syringe-washing solvent was changed to acetonitrile, this problem was solved. Therefore, for different electrolyte samples, when it is found that the plunger of the syringe is easily bent, it is necessary to try different syringe-washing solvents until a suitable one is found.

Long-term stability study on the diluted samples: If users are concerned about the main composition of the electrolyte solvent, or they are not concerned about the analysis of trace components, it is recommended to dilute the real samples before injection, as previously discussed.

The damage to the system caused by direct injection of undiluted samples is significant. To maximize the lifetime of consumables such as the liner and column, and to enhance the detection of low-concentration compounds, real samples were diluted 100x for long-term stability research on a new column with new inlet consumables. After the samples were diluted, the pH value rose from 1 to approximately 6, and it was visibly apparent that many lithium salts had precipitated and settled.

Uninterrupted sample analyses were performed over several consecutive days according to the sequence table shown in Figure 4. Taking sample 1 as an example, a total of 414 real samples were run with 100-fold dilution without changing the septum and liner of the inlet, nor maintaining the column. Trend changes were observed in the peak area and retention time of DEC, PP, VC, FEC, EC, PC, DTD, PS, and AND, which were detected in sample 1 with 100-fold dilution. The RSD values of peak area and retention time were calculated every 16 injections, and the RSD value of peak area was less than 2.5%, while the RSD value of retention time was less than 0.03%. If all 414 injections were calculated together, then the RSD value of peak area was less than 5%, and the retention time was less than 0.03%.

Figure 6 shows the trend of peak area changes for the three representative compounds DEC, EC, and PS detected from sample 1, plotted over 414 injections. Compared to undiluted sample direct injection, the retention time and peak area repeatability of the samples diluted 100x with dichloromethane were very good. This indicates that the dilution process not only effectively addresses the issues of high salt and high acidity but also ensures the long-term high performance of the whole system, thereby greatly extending the lifespan of the consumables used.

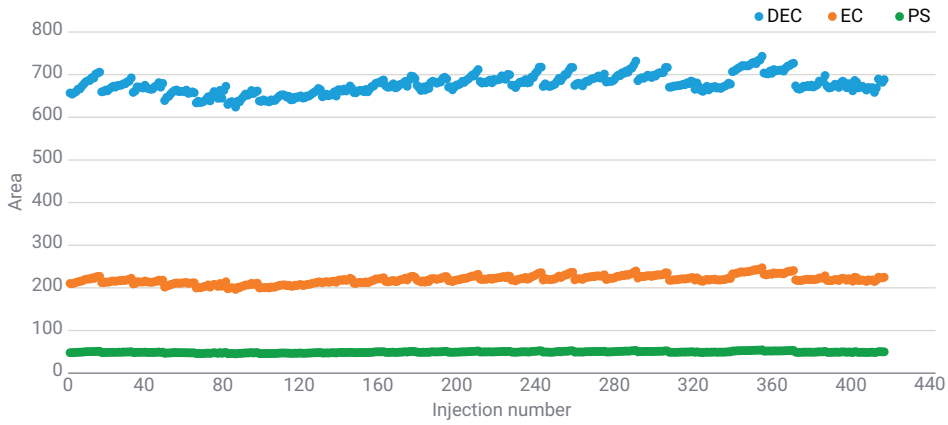

Figure 6. The peak area variation of the three representative compounds in 414 runs after sample 1 was diluted 100x.

Conclusion

This application note introduces an analytical method for determining carbonate solvent and some additive compounds in lithium battery electrolytes based on an Agilent 8850 GC system with FID. The performance results for the linearity, repeatability, and detection limit of 13 target compounds indicate the outstanding sensitivity and reliability of this system. By running undiluted real samples, the impact of high-salt, high-acid samples on the entire system was explored. This study also demonstrates that even after more than 400 runs, the whole system can still maintain excellent stability after the real samples have been diluted 100x. Injecting diluted samples can ensure that the system operates at its best performance and greatly extend the life of consumables. In summary, this method using the 8850 GC system with FID provides an easy-to-use, cost-effective, and stable platform for electrolyte analysis.

References

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