Application Note

Energy & Chemicals

Quality Control of Lithium-Ion Battery Electrolytes and Solvents by UV-Vis Spectroscopy

Color measurements and safe chemical handling using an Agilent Cary 3500 Flexible UV-Vis with Cary Sipper pump

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Abstract

Ensuring the quality of electrolytes used in lithium-ion batteries (LIBs) is crucial for maintaining the safety, performance, and longevity of these energy storage devices. LIB electrolytes consist of lithium salts dissolved in organic solvents. Any discoloration (yellowness) of these near-clear solutions can indicate contamination or degradation. Industry methods such as ASTM D5386-16 Standard Test Method for Color of Liquids Using Tristimulus Colorimetry can be applied to assess the quality of electrolytes by conducting instrumental color measurements using UV-Vis spectroscopy. Given the low absorbance of colorless-to-near-colorless liquid samples like LIB electrolytes and solvents, a highly accurate and sensitive UV-Vis spectrophotometer is essential.

This study demonstrates an effective quality assessment method for LIB electrolytes and solvents using the Agilent Cary 3500 Flexible UV-Vis spectrophotometer fitted with the optional Agilent Cary Sipper flow cell pump. The method is suitable for production quality control of hazardous samples, ensuring safe sample handling, high throughput, and high quality results for production-critical chemicals.

Introduction

The American Public Health Association (APHA) color scale, also known as the platinum-cobalt (Pt-Co) or Hazen color scale, is a widely used standard for measuring the color of liquids as gradient values of yellowness. Ranging from 0 to 500 Pt-Co units, where 0 represents distilled water and 500 units indicate a yellow liquid, the scale is effective for assessing the yellowness of water and other near-colorless substances. The APHA color scale is used in diverse industries, including chemical, energy, environmental, and pharmaceutical sectors. Common uses involve assessing wastewater purity, detecting impurities or contaminants, and ensuring quality control of reagents and products.

There are two primary ASTM standards that govern color measurements of samples based on the APHA color scale, including:

1. ASTM D1209: This standard relies on the visual comparison of clear liquids to the APHA/Pt-Co/Hazen color scale.[1]
2. ASTM D5386: This standard employs Commission International de l'Eclairage (CIE) tristimulus colorimetry using advanced spectrophotometers for precise and consistent color measurements.[2]

In the lithium-ion battery (LIB) sector, quality control (QC) testing of raw materials is essential to prevent defects, ensure safety, and maintain the overall quality of the final batteries. Discoloration (yellowness) of electrolytes or solvent can indicate contamination or degradation. As a preventive measure, LIB manufacturers often perform color tests on materials before use, relying on APHA-related measurements. Since the color change of the materials may not be discernible to the human eye, sensitive instrumental color measurements are typically used, as specified in the ASTM D5386 standard method.

The ASTM D5386 method measures the color of liquids in the visible region (400 to 700 nm) as outlined in the following three steps:

1. Calculate the tristimulus values X, Y, and Z for the sample. To obtain these values, normalizing and weighing factors must first be calculated from the values provided in ASTM E-308,[3] based on the CIE C illuminant and a 2° observer.
2. Calculate the tristimulus values X, Y, and Z by multiplying the sum of W_x, W_y, and W_z by the sample transmission value, as described in equations provided in ASTM D5386. Convert X, Y, Z tristimulus values into yellowness index (YI) values according to ASTM E-313.[4]
3. The correlation between measured YI values and the Pt-Co units color standard solutions is then used to yield an equivalent instrumental Pt-Co rating for the liquid samples.

Experimental

Preparation of color standards

Six standards were prepared from NIST SRM 930e traceable Platinum-Cobalt Color Standard Solution (HAZEN 500), which was bought from Merck (product number 1.00246). Different volumes of the Pt-Co (HAZEN 500) calibration standard were diluted with ultrapure water (Milli-Q, Millipore, Burlington, MA, USA) to 100 mL in volumetric flasks, as detailed in Table 1.

Table 1. Preparation details of the six color standards.

Color Standard Pt-Co Unit	Pt-Co (HAZEN 500) Standard (mL)	Milli-Q Water (mL)
1	0.20	99.80
2	0.40	99.60
3	0.60	99.40
4	0.80	99.20
5	1.00	99.00
10	2.00	98.00

Samples

Two types of battery-grade LIB electrolyte and two organic solvents were bought from Merck. The electrolytes comprised 1.0 M lithium hexafluorophosphate ($LiPF_6$) in ethylene carbonate/dimethyl carbonate (EC/DMC) 50/50 (v/v) and 1.0 M $LiPF_6$ in EC/ethyl methyl carbonate (EC/EMC) 50/50 (v/v). The electrolytes were kept under different conditions before direct measurement by UV-Vis, as detailed in Table 4. Two used bottles of LIB organic solvents, DMC and EMC, were also analyzed.

Instrumentation

A Cary 3500 Flexible UV-Vis spectrophotometer (Figure 1) was used for this study. The Cary 3500 Flexible model includes variable-pathlength cell holders that enhance measurements of diluted samples and allow accurate measurement of low-concentration samples. The cell holders support various pathlengths (2, 4, 5, and 10 cm) and accommodate both rectangular and cylindrical cuvettes.

To avoid direct contact and handling of the hazardous samples, the instrument was fitted with the Cary Sipper three-channel peristaltic pump accessory. The Sipper can pump sample solutions through flow cells that are situated inside the instrument large sample compartment. This setup can be used with a glovebox or fume hood if the chemicals require such handling conditions.

As shown in Figure 1, measurements were performed by inserting the Sipper inlet tube into the sample being analyzed. The solution was then pumped into a single 10 mm pathlength, 390 µL quartz flow cell (Agilent part number 5061-3398) using yellow PVC solvent flexible (Solvaflex) tubing. Milli-Q water was used for rinsing the flow cell between scans to avoid cross contamination. The measurement of each standard and sample was repeated three times.

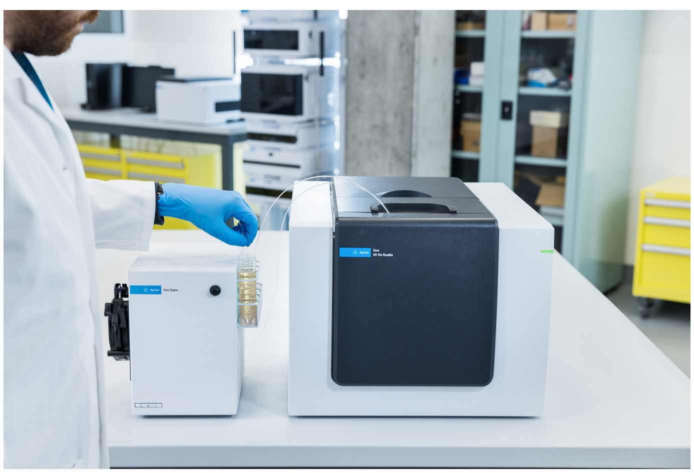

Figure 1. The Agilent Cary 3500 Flexible UV-Vis spectrophotometer fitted with the Agilent Cary Sipper pump accessory (left) and flow cell (located inside the Cary 3500 sample compartment) is ideal for hazardous liquid analysis. This setup ensures operator safety while maximizing sample throughput and achieving significant time savings.

Agilent offers multiple types of easy-fit chemical resistance tubing that can handle corrosive chemicals. The correct tubing must be selected based on the sample matrix and application (see the peristaltic pump tubing chemical resistance chart).

The Cary Sipper pump operates at a fixed speed of 80 rpm. The length of time required to pump the solutions through the flow cell before measurement is called the 'Fill' time. The subsequent period of no pumping (to allow the solution to settle) is called the 'Hold' time. The final setting of the Sipper is the length of time for the rinse solution to be pumped through the cell ('Rinse' time). All three times are set within the Agilent Cary UV Workstation software and can be saved as part of a stored method. To prevent any interference with water, the sample fill time was sufficiently long to ensure that all water had been completely removed from the cell. Instrument operating parameters are listed in Table 2.

Table 2. Operating parameters of the Agilent Cary 3500 Flexible UV-Vis with Agilent Cary Sipper pump.

Parameter	Setting
Wavelength Range	400 to 700 nm
Spectral Bandwidth	2 nm
Data Interval	5 nm
Signal Averaging Time	0.1 s
Replicates	3
Path Length	10 mm flow cell
Fill Time	30 s
Hold Time	5 s
Rinse Time	30 s
Baseline	Water

Results and discussion

Calibration curve of color standards

The color calibration standards were prepared in the 1 to 10 Pt-Co unit range, which covers the lowest color levels needed to determine color in liquid samples that range from colorless to nearly colorless. The excellent sensitivity and detection limit capability of the Cary 3500 Flexible UV-Vis allowed the standards in the absorbance range of 0.0003 to 0.0028 to be measured, as shown in Figure 2.

The Agilent Cary WinUV Color application is an optional software package that expands the Cary WinUV Workstation software and allows users to perform color calculations on data collected by Cary spectrophotometers.[5] Users can select from multiple calculation options within the Color application. Once selected, any calculations are performed automatically and a report can be generated and exported, displaying all the values of the selected calculations, as shown in Figure 3.

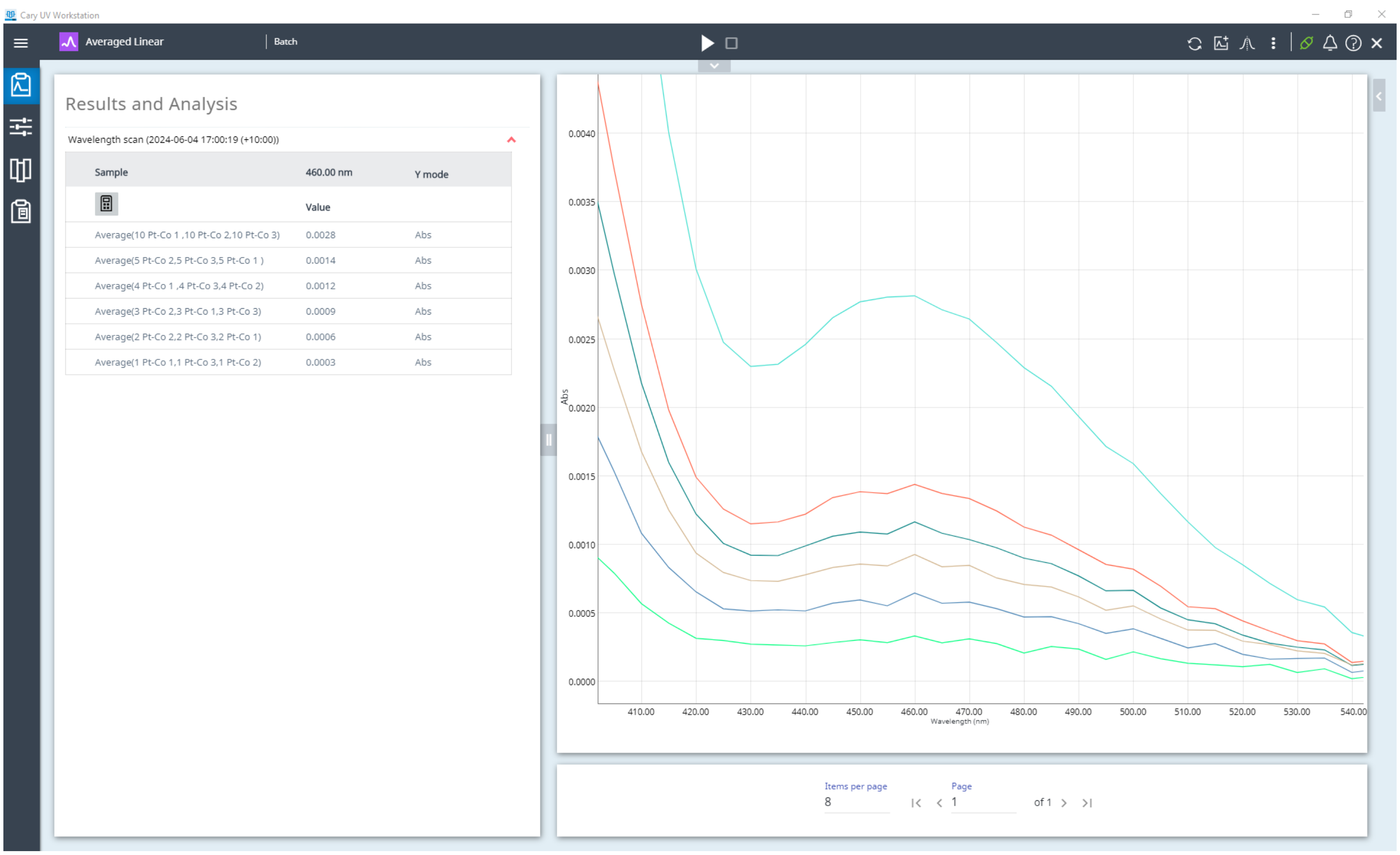

Figure 2. Right: wavelength scans of each of the six color standard solutions (1, 2, 3, 4, 5, and 10 Pt-Co unit). Left: absorbance values at 460 nm for all standards, ranging from 0.0003 to 0.0028.

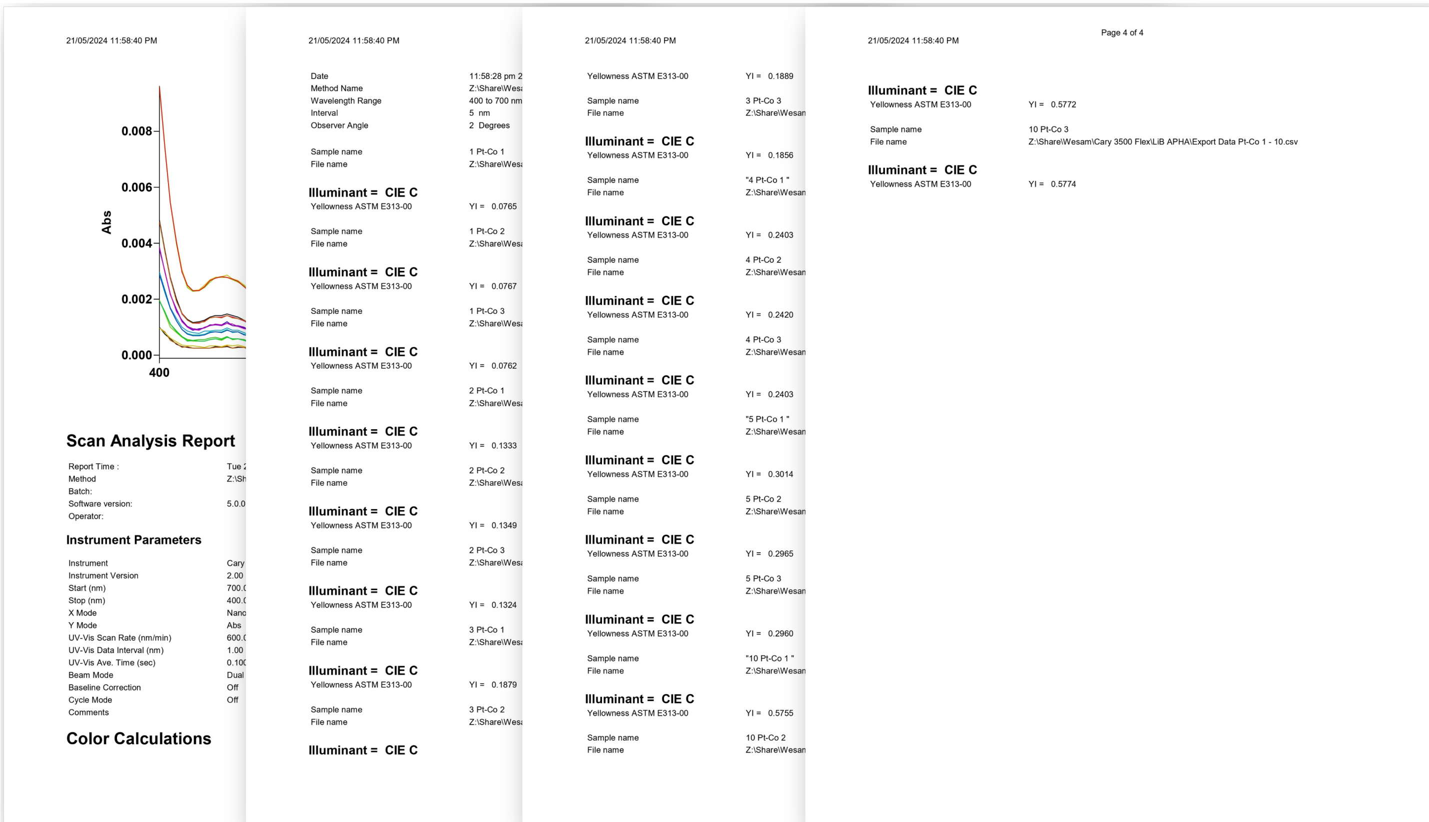

Figure 3. Report generated by the Agilent Cary WinUV Color application after the automatic calculation of the YI.

In this study, the color standards data acquired using the Cary 3500 Flexible and Cary UV Workstation software was exported to the Cary WinUV Color application to obtain the YI data. A calibration curve was then generated based on the measured YI values and the Pt-Co unit color standards.

The calibration curve generated from the measurement of six standards using the Cary 3500 Flexible UV-Vis and the Sipper achieved an R^2 value of 1 (Figure 4). The instrument's excellent photometric linearity for very light liquid samples enables accurate photometric measurements of highly diluted solutions.

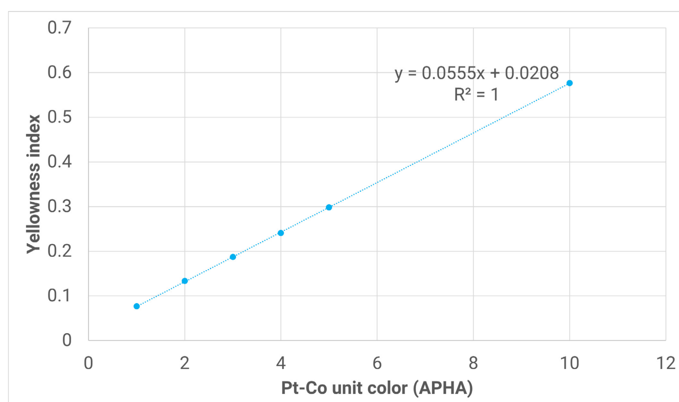

Figure 4. Yellowness index versus Pt-Co unit color calibration curve generated using the Agilent Cary 3500 Flexible UV-Vis spectrophotometer with the Agilent Cary Sipper.

Color measurements of LIB electrolytes and solvents

The calibration curve was used to determine an equivalent instrumental Pt-Co rating for the two LIB electrolytes and two solvents. After data collection, the YI of the samples was obtained using the Cary Color software. The YI was then easily converted to Pt-Co units (APHA) using the equation derived from the calibration curve.

Measuring Pt-Co color (APHA) units is an effective method for assessing the quality of LIB electrolytes. As shown in Table 4, lower Pt-Co (APHA) values were obtained for new bottles of the electrolytes compared to the used (opened) bottles.

The higher Pt-Co values suggest color changes that were not visible to the human eye (Figure 5) and potential degradation over time once a bottle has been opened. The Pt-Co (APHA) value for 1.0 M $LiPF_6$ in EC/EMC increased from 2.8318 (new) to 5.4138 (used) (Table 4).

Similarly, the quality of colorless to near-colorless LIB solvents DC and EMC was also assessed using Pt-Co color (APHA) measurements. Used bottles of these solvents produced Pt-Co color (APHA) values of 3.5272 and 3.5661, respectively, reflecting their quality levels.

Overall, higher Pt-Co color (APHA) values indicated decreased quality due to color changes. The results emphasize the importance of UV-Vis measurements in maintaining the reliability and effectiveness of LIB electrolytes and solvents in both manufacturing QC settings and research and development (R&D) laboratories.

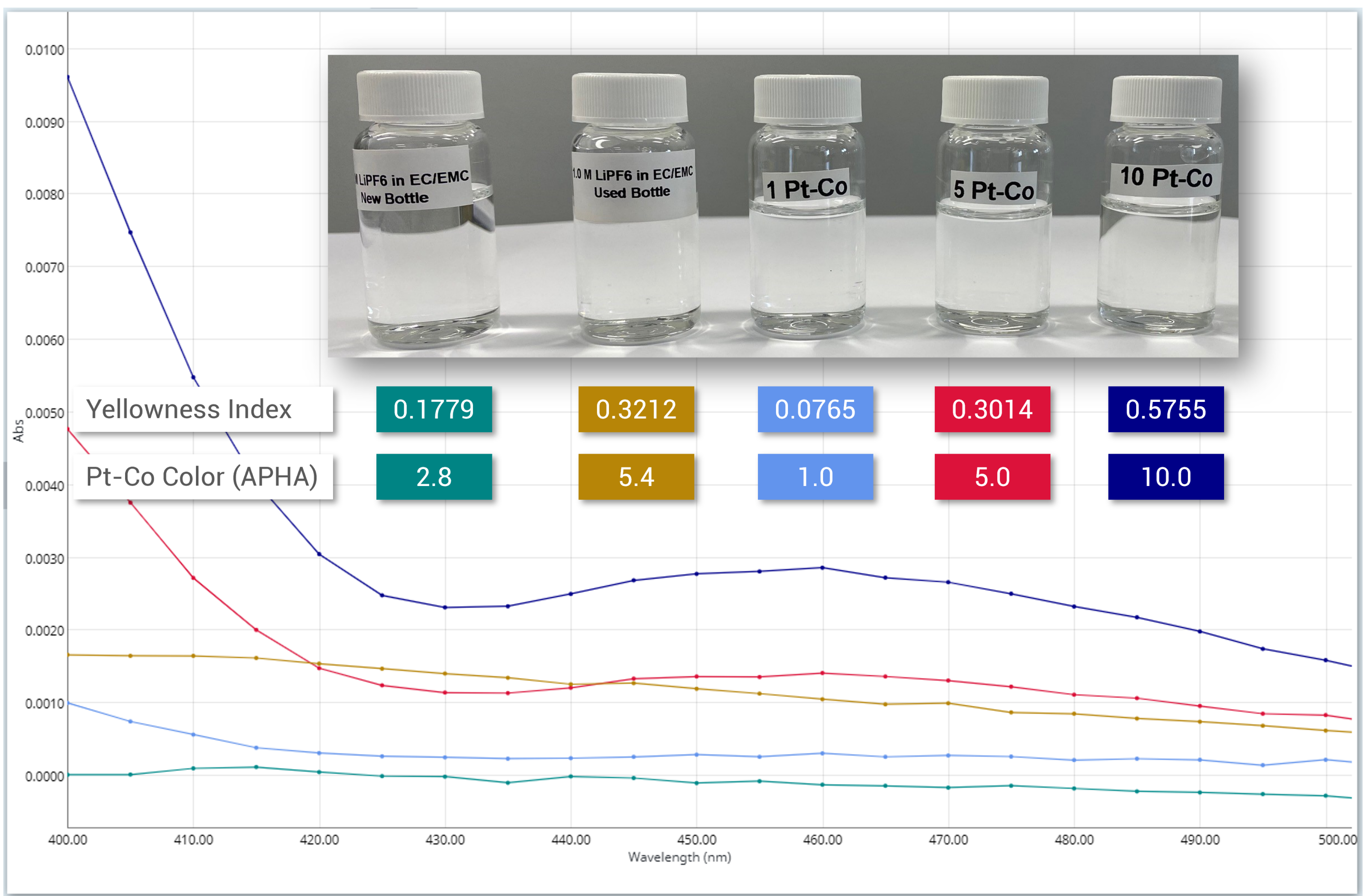

Figure 5. UV-Vis absorbance spectra of 1, 5, and 10 Pt-Co standard solutions, and new and used bottles of 1.0 M $LiPF_6$ in EC/EMC showing the correlation between the yellowness index, Pt-Co color (APHA) values and visual appearance of the samples in the clear bottles.

Table 4. YI and Pt-Co Color (APHA) values of LIB electrolytes and solvents measured using the Agilent Cary 3500 Flexible UV-Vis spectrophotometer with the Agilent Cary Sipper.

Sample	Product Number	Status	YI (n = 3)	Pt-Co Color (APHA) (n = 3)
1.0 M $LiPF_6$ in EC/DMC = 50/50 (v/v)	746711	New bottle	0.2078	3.3699
1.0 M $LiPF_6$ in EC/EMC = 50/50 (v/v)	746738	New bottle	0.1779	2.8318
1.0 M $LiPF_6$ in EC/DMC = 50/50 (v/v)	746711	Used bottle	0.2884	4.8228
1.0 M $LiPF_6$ in EC/EMC = 50/50 (v/v)	746738	Used bottle	0.3212	5.4138
Dimethyl Carbonate	D152927	Used bottle	0.2165	3.5272
Ethyl Methyl Carbonate	754935	Used bottle	0.2187	3.5661

Conclusion

The Agilent Cary 3500 Flexible UV-Vis spectrophotometer provided accurate and precise color measurements for colorless to near-colorless LIB electrolytes and solvents in accordance with the ASTM D5386 standard method. Advantages of the Cary 3500 Flexible method and findings based on the data set include:

- Hazardous samples were introduced directly into a 10 mm path length flow cell using the Cary Sipper pump, ensuring user safety and high sample throughput without compromising data quality.
- The superior sensitivity (high signal-to-noise ratio) of the Cary 3500 combined with Agilent Cary WinUV Color application software enabled the reliable monitoring and control of electrolyte properties by analyzing light absorption in the visible spectrum.
- Higher Pt-Co color (APHA) values of the used LIB electrolytes compared to fresh samples suggested a deterioration in quality due to the color changes.
- Color measurements could be used to improve the quality control of LIB electrolytes and solvents by identifying discoloration—an indication of contamination or degradation that could affect battery performance.
- This effective method could be implemented in both manufacturing QC settings and R&D laboratories.

QC color measurements using the Cary 3500 Flexible UV-Vis would ensure that only high-quality electrolytes are used in the production of LIBs, enhancing their safety, efficiency, and durability.

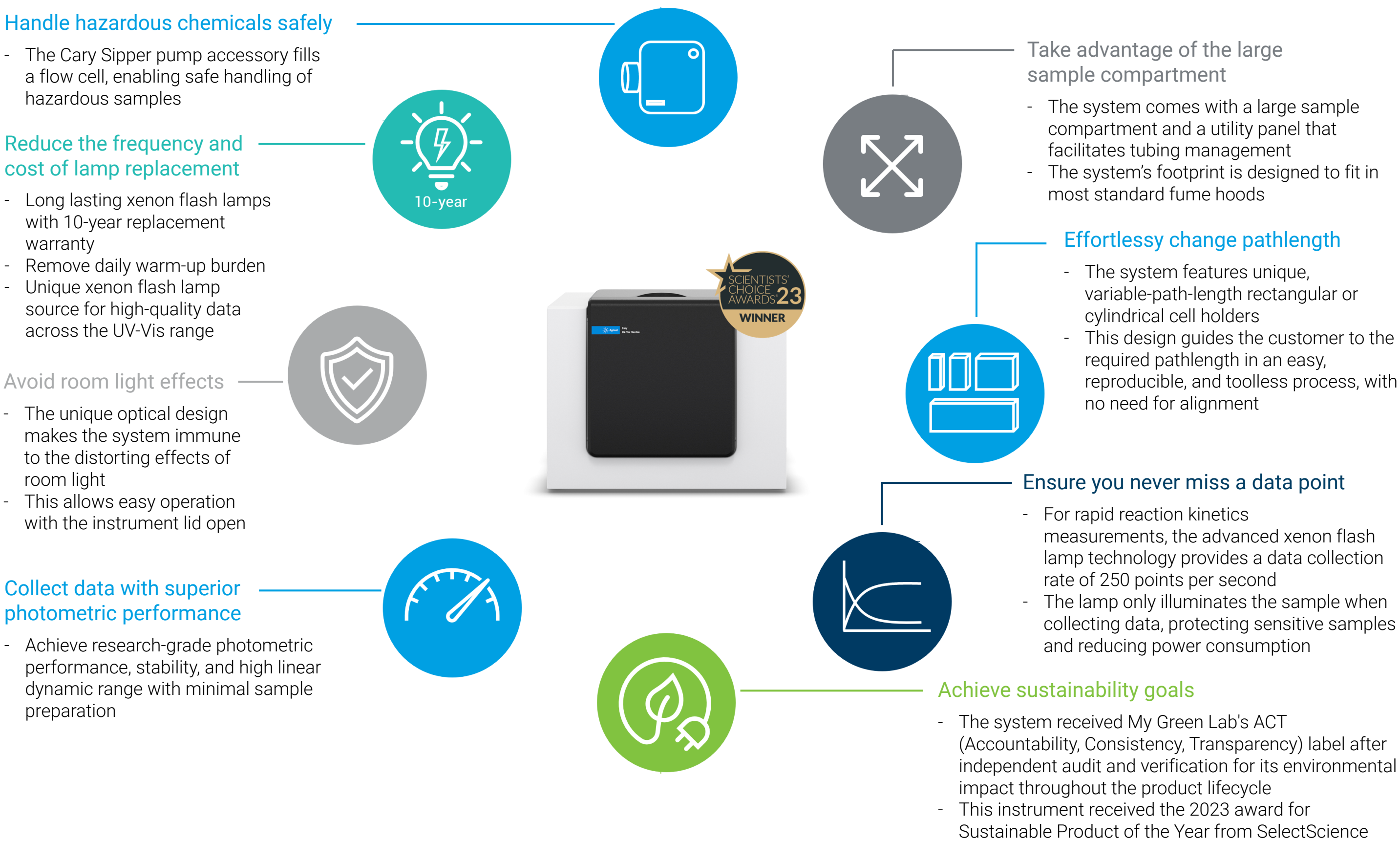

Figure 6. Overview of the advantages of the Agilent Cary 3500 Flexible UV-Vis for the production and R&D needs of the chemicals and energy sector.

References

1. ASTM D1209 (**2019**) Standard Test Method for Color of Clear Liquids (Platinum Cobalt Scale) (accessed July 2024).
2. ASTM D5386 Standard Test Method for Color of Liquids Using Tristimulus Colorimetry, https://www.astm.org/d5386-16.html (accessed July 2024).
3. ASTM E-308 Standard Practice for Computing the Colors of Objects by Using the CIE System, https://www.astm.org/e0308-22.html (accessed July 2024).
4. ASTM E313-20 Standard Practice for Calculating Yellowness and Whiteness Indices from Instrumentally Measured Color Coordinates, https://www.astm.org/e0313-20.html (accessed July 2024).
5. Color Measurements by Agilent UV-Vis and UV-Vis-NIR Spectrophotometers, *Agilent Technologies white paper*, publication number 5994-6792EN, **2023**.

Further information

- Agilent Cary 3500 Flexible UV-Vis Spectrophotometer
- Agilent Cary UV Workstation software
- UV-Vis Spectroscopy and Spectrophotometer FAQs

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