

# Exploration of Lithium-Thorin Complex Formation Using UV-Vis Spectroscopy

Advantages of the Agilent Cary 3500 Multizone UV-Vis for efficient metal-complex kinetic studies



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## Abstract

Lithium-ion batteries (LIBs) play an essential role in growth sectors such as electric vehicles, energy storage systems, and portable electronic devices. The rising demand for LIBs requires cost-effective methods to accurately quantify lithium (Li) in various matrices. This application note investigates the formation of Li-thorin complexes under different conditions using an **Agilent Cary 3500 Multicell UV-Vis spectrophotometer**. Different experimental conditions were investigated based on the technique's ability to monitor color changes resulting from the binding of Li to a chromogenic reagent. The Cary 3500 system's multizone capability, built-in cuvette stirring, and temperature control streamlined data collection, enabled the identification of optimal reaction conditions, and ensured consistent results.

## Introduction

Li is used in numerous sectors, most notably in the manufacture of LIBs, ceramics, glass, and lubricants. The rising demand for LIBs to power electric vehicles and portable electronic devices has required the development of reliable analytical methods to accurately measure Li concentrations in various matrices. For example, at mining and production sites, Li levels must be monitored in industrial and wastewater samples before treatment and discharge.

UV-Vis spectroscopy is used extensively in analytical chemistry due to its simplicity, cost-effectiveness, and fast analysis capabilities. The technique enables the detection and quantification

of elements such as Li, cobalt (Co), nickel (Ni), and others by forming complexes with chromogenic reagents.<sup>1-4</sup>

Thomason outlined a UV-Vis spectrophotometric method for the determination of Li using thorin as a chromogenic agent in a potassium hydroxide (KOH) solution.<sup>1</sup> Thorin was used to form a complex with Li, as it causes a color change that can be quantitatively analyzed through UV-Vis spectroscopy. However, interferences and stability of the Li-thorin complex may cause inconsistencies in the results. Therefore, it is important to monitor reaction kinetics under varying conditions to understand any influencing factors on the formation of the complex and to ensure accurate Li quantification.

This study demonstrates the benefits of the Cary 3500 Multicell UV-Vis spectrophotometer (Figure 1) to monitor the formation of Li-thorin complexes under different conditions.

The capability of the Cary 3500 Multicell UV-Vis to measure multiple samples simultaneously makes spectrophotometric measurements highly efficient, while maintaining consistent measurement conditions. With eight cell positions available, the Cary 3500 can perform analyses on samples in a single zone (eight cuvettes), two zones (four cuvettes in each zone), or four zones (two cuvettes in each zone). Each zone has its own reference channel.



**Figure 1.** The Agilent Cary 3500 Multicell UV-Vis spectrophotometer fitted with a temperature-controlled Multizone module.

## Experimental

### Reagents and materials

- **De-ionized (DI) water:** fresh DI water was obtained from a Milli-Q Integral system (Millipak, Merck-Millipore, Billerica, MA, USA) equipped with a 0.22 µm membrane point-of-use cartridge.
- **Lithium chloride (LiCl) stock solution (1,000 ppm):** 142.54 mg of lithium chloride monohydrate was transferred into a 100 mL volumetric flask, dissolved in 50 mL of DI water, and diluted to 100 mL with DI water.
- **LiCl standards:** 1 mL of a 1,000 mg/L stock solution was diluted in a 100 mL volumetric flask with DI water to achieve a 10 ppm solution. Serial dilutions were then performed to create 10 mL solutions of 0.3125, 0.625, 1.25, 2.5, and 5 ppm.
- **10% KOH solution:** 10 g of KOH was dissolved in 50 mL of DI water in a 100 mL volumetric flask and made up to volume with DI water.
- **0.2% Thorin indicator:** 200 mg of thorin indicator (thorin, 1-(2-arsenophenylazo)-2-hydroxy-3,6-naphthalene-disulfonic acid sodium salt, 2-(2-hydroxy-3,6-disulfo-1-naphthylazo)-benzene-arsonic acid sodium salt (Merck, product number 1082940005)) was dissolved in a 100 mL volumetric flask. The 0.2% thorin solution was further diluted to concentrations of 0.01, 0.05, and 0.10% using DI water.

### Experiments

In a previous study, Thomason outlined a spectrophotometric method for determining Li using a 0.2% thorin indicator as the chromogenic agent in an alkaline medium (10% KOH) within a solvent mixture of 30% water and 70% acetone.<sup>1</sup> This study focused on evaluating two key aspects of the published method to further optimize the formation of Li-thorin complexes conditions:

- **The impact of varying the concentration of the thorin indicator:** In a 10 mL volumetric flask, 3 mL of a 5 ppm Li standard was introduced, followed by the addition of 0.5 mL of 10% KOH, then 0.3 mL of either 0.01, 0.05, 0.10, or 0.20% of the thorin indicator. The volume was made up to 10 mL with acetone.
- **The effects of different solvent systems:** In a 10 mL volumetric flask, 3 mL of the 5 ppm Li standard was introduced, followed by the addition of 0.5 mL of 10% KOH, then 0.3 mL of 0.20% thorin indicator. The volume was made up to 10 mL with either acetone, acetonitrile, ethanol, or water.

All flasks were shaken to mix the contents, and any gases produced were allowed to escape. Then, 3 mL of each solution was transferred into a standard 3.5 mL quartz cuvette equipped with a magnetic stir bar, ready for analysis.

Blanks were prepared in the same way as the standard solutions, but with 3 mL of DI water instead of the Li standard.

The linearity of the calibration curves generated using the LiCl standards with different solvent systems and 0.2% thorin was evaluated at specific stability time points, as described in the results section.

The 3500 Multicell UV-Vis operated by Agilent Cary UV Workstation software performed data collection using the parameters listed in Table 1.

**Table 1.** Data collection parameters using an Agilent Cary 3500 Multicell UV-Vis spectrophotometer.

Parameter	Value
Wavelength Range	325 to 700 nm
Signal Averaging Time	0.1 s
Data Interval	1 nm
Spectral Bandwidth	2 nm
Stirring Speed	500 rpm
Temperature	25 °C
Temperature Control	Block
Stop Time	180 min
Cycle Time	1 min

## Results and discussion

### Identification of the Li-thorin complex peak

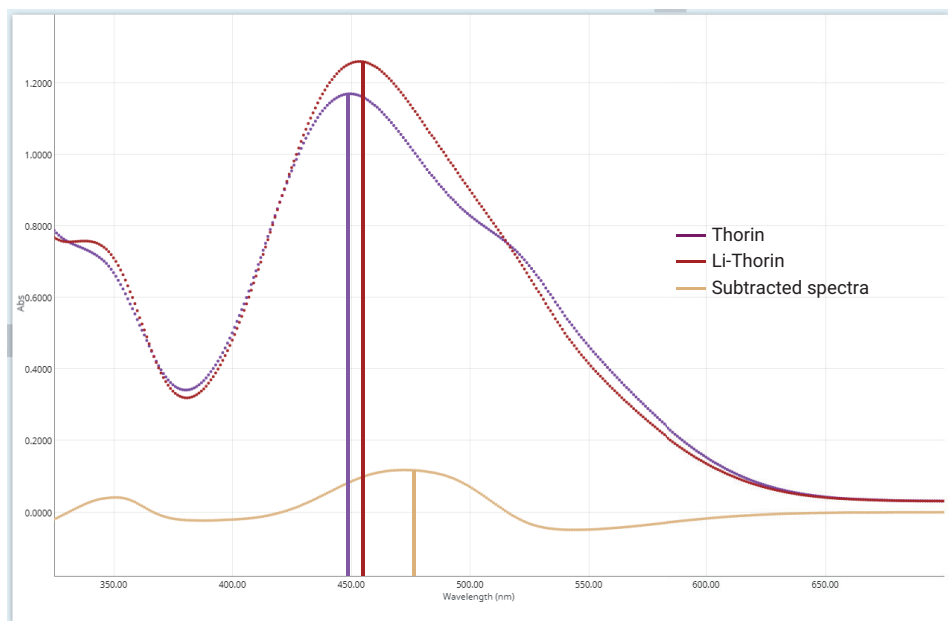
To better understand the Li-thorin complex and its characteristic absorbance peak, a LiCl solution (in DI water) was scanned at three different concentrations (5, 10, and 1,000 ppm). As shown in Figure 2, no absorbance peak was observed for LiCl within the 325 to 700 nm range, regardless of concentration.

This finding highlights the necessity of identifying a suitable chromogenic reagent that can bind to Li and produce an absorbance peak at a specific wavelength.

Figure 3 shows the spectrum of the thorin reagent (purple trace with a  $\lambda_{\text{max}}$  at 450 nm) and illustrates how the spectrum changes in the presence of Li (red trace). When the Li-thorin sample was measured after 40 minutes (time for the complex to stabilize), the  $\lambda_{\text{max}}$  had shifted to 460 nm and the absorbance had increased. By subtracting the thorin spectrum from the Li-thorin spectrum, a distinct peak at 480 nm emerged, indicating the presence of Li in the sample (formation of a Li-thorin complex). This peak was used in all subsequent analyses.



**Figure 2.** UV-Vis spectra of LiCl solution in water (5, 10, and 1,000 ppm) measured using an Agilent Cary 3500 Multicell UV-Vis spectrophotometer. The samples were baseline-corrected against air.



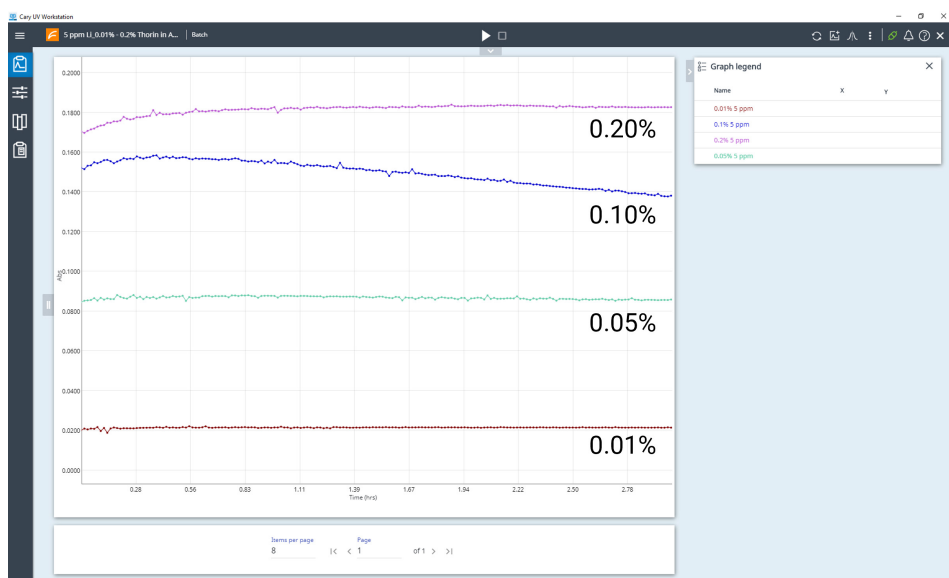
**Figure 3.** UV-Vis spectra of 0.2% thorin reagent (purple), thorin plus 4 ppm Li (red), and subtraction of thorin and thorin-Li 4 ppm spectra (yellow), revealing a distinct peak at 480 nm.

## The impact of varying thorin indicator concentrations

Four Li standard samples, each with a concentration of 5 ppm Li, were prepared in a water-acetone system with varying thorin concentrations, as detailed in the experimental section.

The multizone capability of the Cary 3500 enabled simultaneous monitoring of all four samples and their respective blanks at 480 nm with instant blank correction. The instrument's xenon flash lamp, which captures 250 data points per second, streamlines data collection, enabling the efficient study of reaction kinetics. For equivalent monitoring experiments of four samples, the multizone method took three hours, compared to 12 hours using a single-cuvette UV-Vis spectrophotometer.

As illustrated in Figure 4, a thorin concentration of 0.2% was required to achieve an appropriate absorbance response and facilitate formation of the metal complex. The reaction stabilized after 40 minutes. Lower thorin concentrations resulted in reduced absorbance at 480 nm, highlighting the necessity of using an excess of the indicator to effectively form the complex and detect Li using UV-Vis spectroscopy.



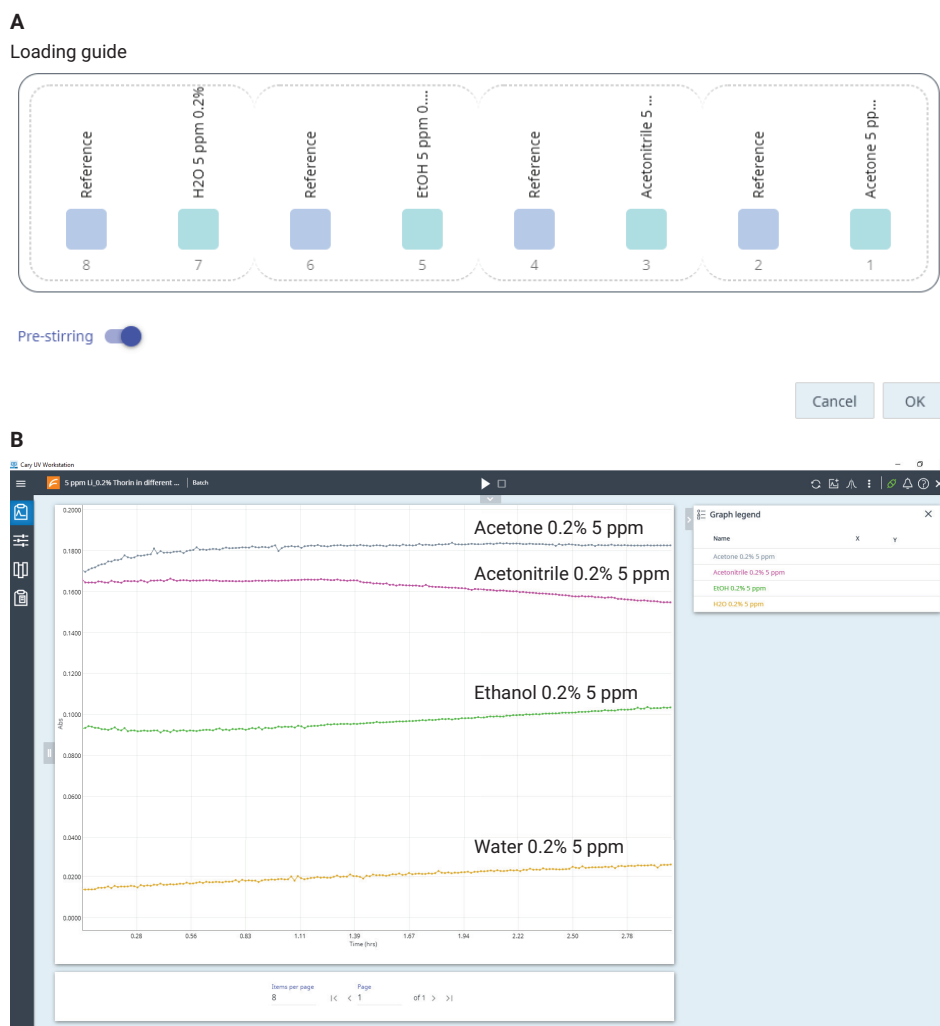
**Figure 4.** Four 5 ppm Li standards prepared in acetone with varying thorin concentrations (0.01 to 0.2%). Absorbance at 480 nm was monitored simultaneously using the multizone capabilities of an Agilent Cary 3500 Multicell UV-Vis spectrophotometer.

## The effects of different solvent systems

The use of different solvents was examined in this study using the Cary 3500 system's ability to divide into four independently controlled zones, each with its own blank (reference). Using this configuration, the system enables the simultaneous monitoring of reaction kinetics of up to four samples. As shown in Figure 5A, the four samples were located in positions 1, 3, 5, and 7, with four corresponding reference beams (in positions 2, 4, 6, and 8) providing instant correction for the measurements.

The multizone system allows independent temperature control for each zone, which, along with built-in cuvette stirring, ensures homogeneity of the reaction mixture. The temperature for each zone was set to 25 °C to ensure consistent temperatures across all eight cuvettes and to minimize evaporation. Based on previous results, a 0.2% thorin concentration was maintained while varying the solvent systems.

As shown in Figure 5A, for the Li-thorin complex in acetone, reaction stability was achieved and maintained after 40 minutes and the highest absorbance at 480 nm (0.1825) was measured. In contrast, the Li-thorin reaction reached stability after five minutes with an absorbance of 0.1650 in acetonitrile but began to degrade after 90 minutes. With ethanol and water (absorbance readings of 0.0940 and 0.0140, respectively), the reaction fluctuated and did not stabilize after three hours of monitoring.

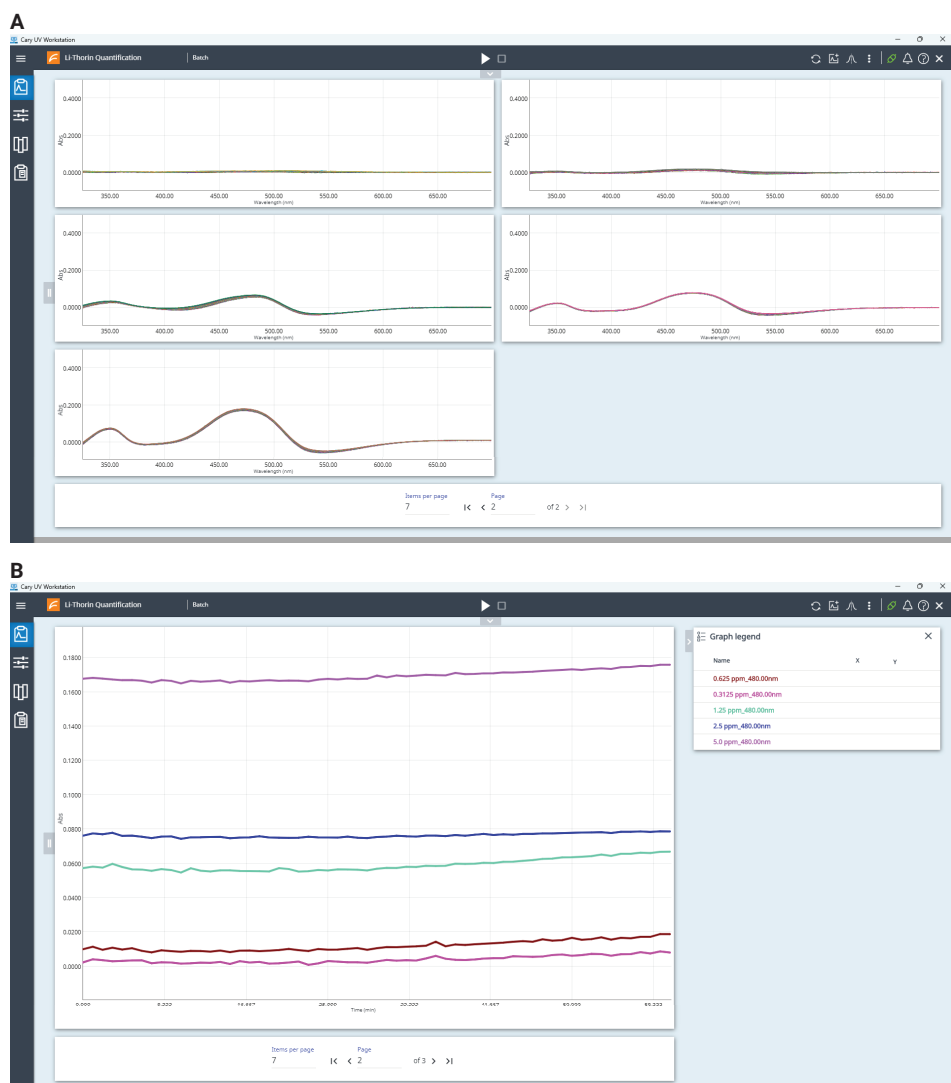


**Figure 5.** Absorbance at 480 nm for 5 ppm Li standards prepared in acetone, acetonitrile, ethanol, and water, with 0.2% thorin added to each standard.

## Linearity with different solvents

The linearity of the LiCl standards at 0.3125, 0.625, 1.25, 2.5, and 5 ppm in acetone and acetonitrile solvent systems with 0.2% thorin was assessed using the Cary UV Workstation (Figure 6). The Cary 3500 system enables the simultaneous monitoring of reaction kinetics for up to seven samples, with a single blank providing instant correction for samples in positions 1 to 7.

Based on the stability results obtained in Figure 5, absorbance values recorded at 40 minutes for acetone and 5 minutes for acetonitrile were used to construct calibration curves for Li-thorin complexes. The calibrations were based on concentrations of LiCl ranging from 0.3215 to 5 ppm with 0.2% thorin.



**Figure 6.** Kinetics of five LiCl standards (prepared in acetonitrile and 0.2% thorin) were monitored over 60 minutes: (A) wavelength range scan and (B) 480 nm single wavelength scan. The Agilent Cary 3500 Multicell UV-Vis allows up to seven samples to be monitored simultaneously.

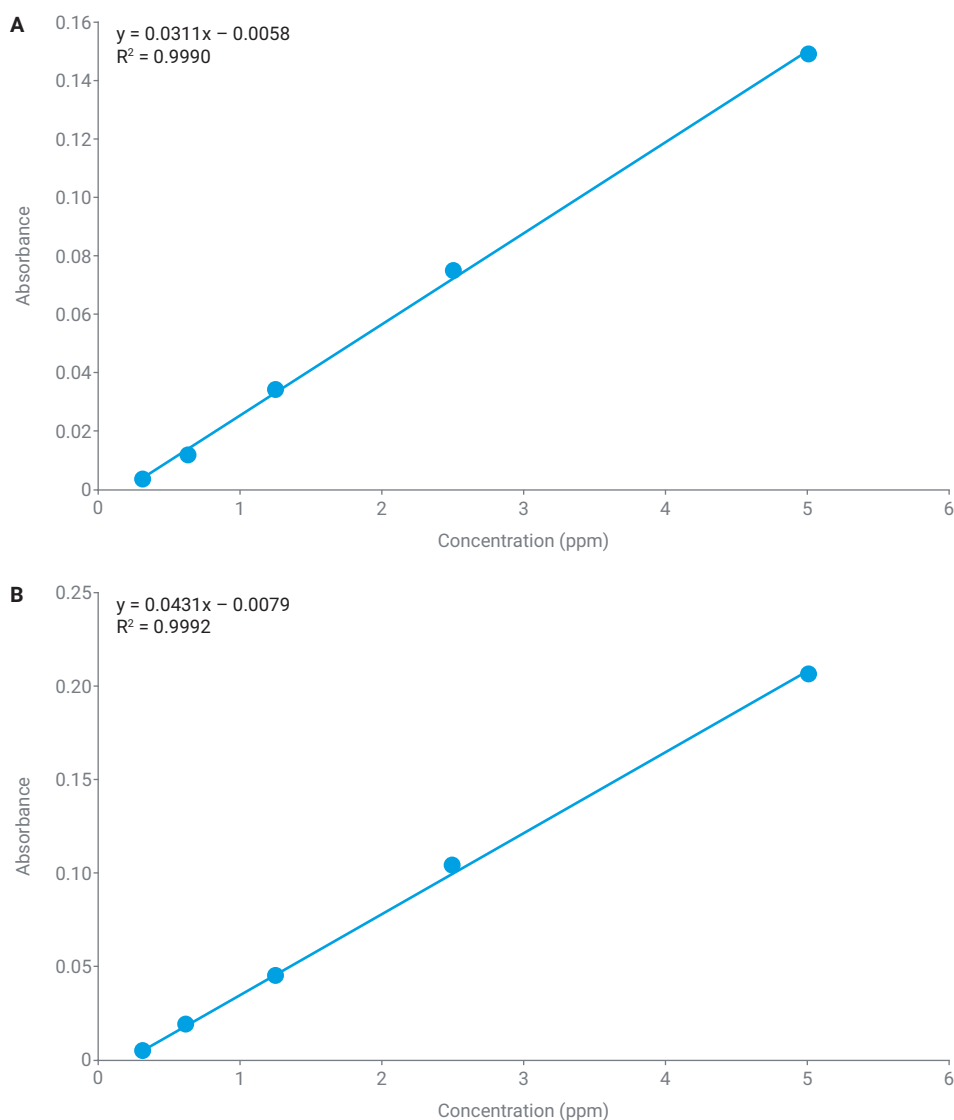
As shown in Figure 7, both calibration curves demonstrated excellent linearity, with a correlation coefficient of 0.9992 and 0.9990 for acetone and acetonitrile, respectively.

## Conclusion

This study demonstrated the feasibility of using UV-Vis spectroscopy with a thorin indicator for the quantification of lithium in various sample matrices. The method used the formation of a Li-thorin complex, which exhibits a distinct absorbance peak at 480 nm, allowing Li detection. The calibration curve developed for Li concentrations ranging from 0.3125 to 5 ppm showed excellent linearity with both acetone and acetonitrile as solvent systems, confirming the method's potential for quantifying Li containing samples.

The Agilent Cary 3500 Multicell UV-Vis spectrophotometer with Agilent Cary UV Workstation enabled the thorough study of reaction kinetics, offering benefits such as:

- A "multizone" capability that streamlined data collection, allowing faster and more efficient analysis compared to single-cuvette instruments
- A simplified experimental design enabled by the identification of optimal conditions and timings of complex formation
- Increased data collection speed using the xenon flash lamp, which captures 250 data points per second, boosting throughput
- Built-in cuvette stirring capability that ensured uniform reaction conditions
- The maintenance of a stable temperature across the eight cell positions within four zones, ensuring consistent results



**Figure 7.** Calibration curve of the Li-thorin complex across a concentration range of 0.3125 to 5 ppm LiCl standards and 0.2 % thorin in (A) acetone at 40 minutes and (B) acetonitrile at five minutes.



## References

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## Further information

- Cary 3500 Multicell UV-Vis Spectrophotometer
- Cary UV Workstation software
- UV-Vis Spectroscopy & Spectrophotometer FAQs

[www.agilent.com/chem/cary3500uv-vis](http://www.agilent.com/chem/cary3500uv-vis)

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