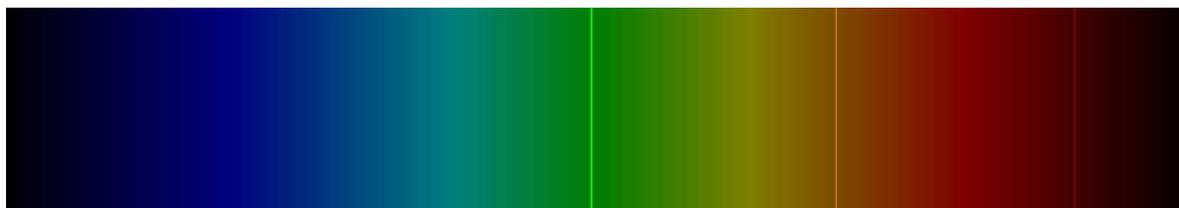




Lithium (Li) Analysis that Meets the Requirements of the United States Environmental Protection Agency Fifth Unregulated Contaminant Monitoring Rule (US EPA UCMR 5) and EPA Method 200.7.

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Spectral Lines of Lithium

Introduction

The US EPA has a specific program designed to monitor for unregulated contaminants in drinking water. In the latest version lithium was added primarily due to its use as a pharmaceutical. The following ACT NOTE presents an analytical method that meets and exceeds the requirements for testing via EPA 200.7, Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). UCMR 5 specifically requires use of this technology in monitoring for lithium in drinking water. A reporting limit of 9 ug/L is required.

Contaminant	Chemical Abstract Service Registry Number (CASRN)	Minimum Reporting Level	Sample Point Location ¹	Analytical Methods
Lithium	7439-93-2	9 µg/L	EPTDS	EPA Method 200.7; SM 3120 B (2017); SM 3120 B-99 (1999); ASTM D1976-20



Experimental

All measurements were performed using an Agilent 5110 ICP-OES fitted with an AVS-7 advanced valve system as well as an SPS-4 autosampler. The sample introduction included a OneNeb Series 2 nebulizer and a double pass glass cyclonic spray chamber. Sample / carrier tubing was white / white with an internal standard tubing of blue / orange. Yttrium (Y) was used as an internal standard.

While 200.7 allows for a 2-point calibration, UCMR 5 specifically requires a multi-point calibration for this application. The concern is that lithium is very easily ionized and can be non-linear if method conditions are not properly optimized. For this ACT NOTE, nine levels were used (0, 8, 40, 80, 160, 500, 1000, 2000, and 4000 ug/L) to demonstrate linearity across a wide range. In a production setting, one could use as few as 4 levels: a blank plus 3 non-zero standard levels.

Lithium was measured at 670.783 nm while the internal standard, Yttrium, was measured at 488.368 nm. To meet the requirements of EPA 200.7, 4 replicate readings were taken.

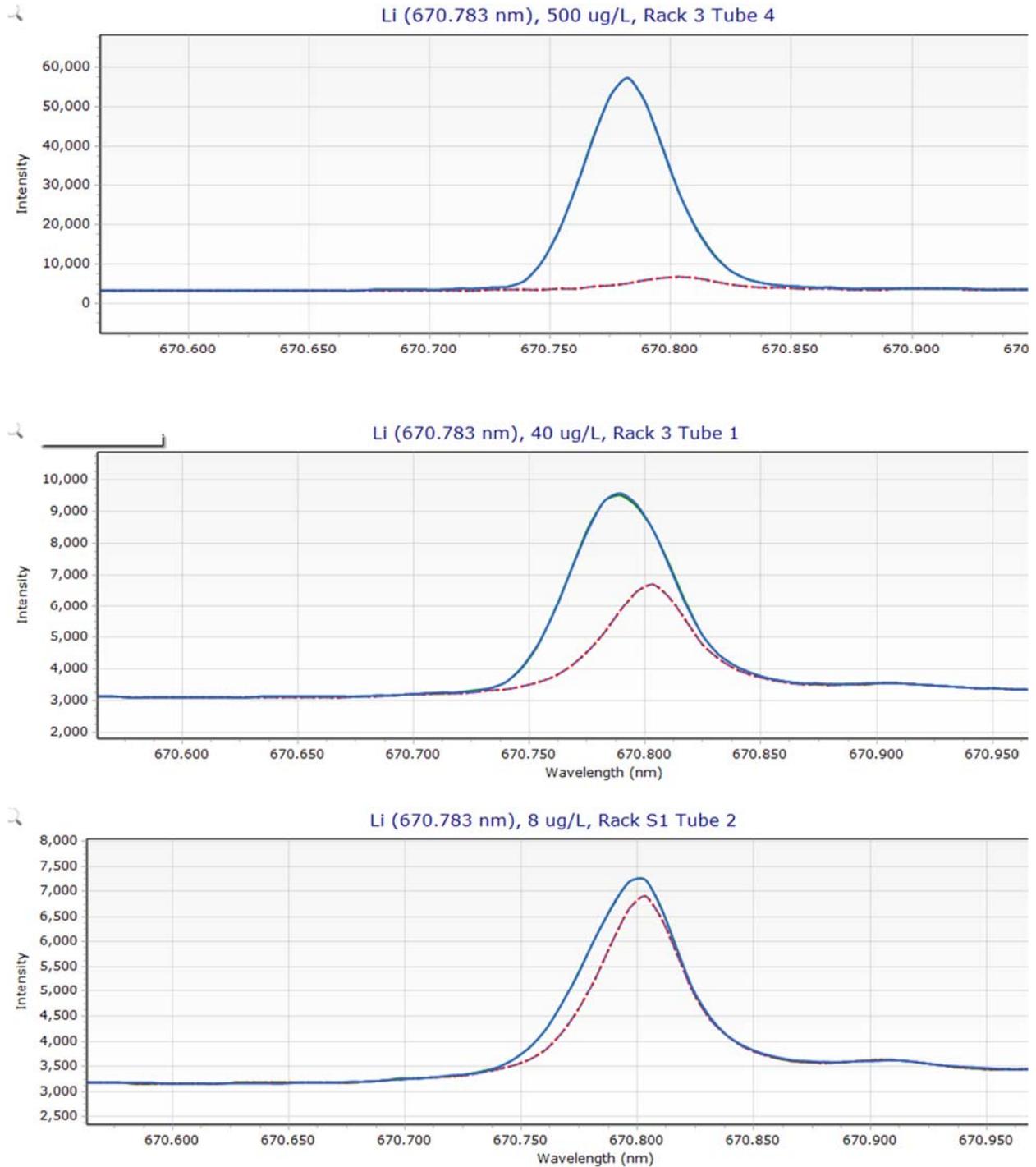
Table 1: Measurement Conditions

Viewing Mode	Radial
Viewing Height	14 mm
Power	1000 Watts
Nebulizer Flow	0.85 L/min
Read Time	14 seconds
Plasma Flow	12 L/min
Aux Flow	1 L/min

The key to success for this application is the use of FACT background correction. The reason for this is that there is a prominent argon line at 670.803 nm. Argon is the gas used to create the plasma; therefore, we have lots of signal from argon. FACT is a whole region background technique using spectral de-convolution to eliminate the structured background from the argon. This allows testing at much lower levels than when using traditional off-peak background correction or fitted background correction. While the argon is consistent, it does have an effect, especially at lower concentration levels. As shown in Table 2, spectra of differing levels (500 ug/L, 40 ug/L, and 8 ug/L respectively) of lithium demonstrates the varying influence of argon on the overall signal. The dotted line represents the argon background while the solid line is the overall signal. As seen in the spectra, at 8 ug/L argon represents a majority of the signal.



Table 2: Comparison of lithium spectra at 670.783 nm





Results

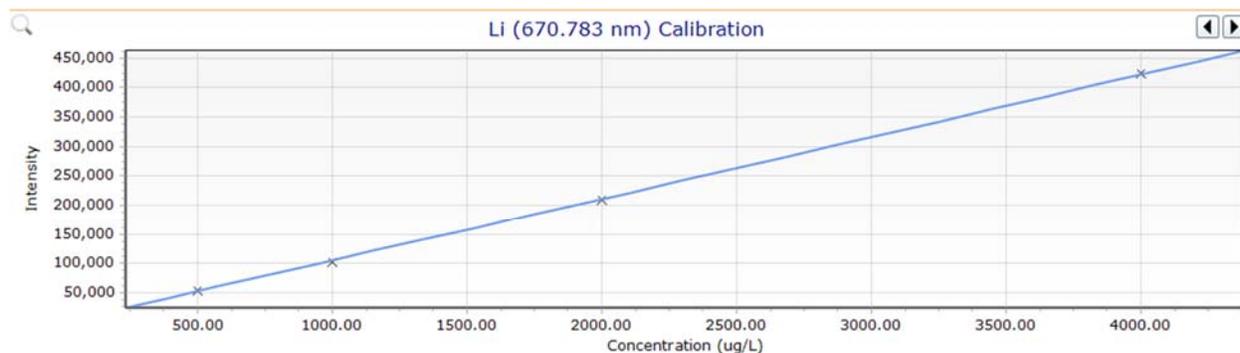
Table 3 shows the calibration graph from 8 ug/L to 4000 ug/L. The error was less than 3% across all levels. A linear curve fit was used to process the data. The correlation coefficient is 0.99995 and the %RSE is 1.7%.

Table 4 shows a series of seven spike replicates at 2 ug/L. The spikes are standards prepared on the same day. They are not digested. These are presented to demonstrate instrument precision and sensitivity. Actual MDLs will vary based on laboratory preparation procedures and reagents.

Table 3: Calibration Graph

Li (670.783 nm) Calibration

Standards	Intensity	Method Concentration	Calculated Concentration	% Error
Blank	3.788	0.000	0.083	N/A
8 ug/L	823.199	8.000	7.855	1.807
40 ug/L	4246.514	40.000	40.328	0.821
80 ug/L	8399.334	80.000	79.721	0.348
160 ug/L	17186.993	160.000	163.080	1.925
500 ug/L	52663.858	500.000	499.608	0.078
1000 ug/L	102288.213	1000.000	970.336	2.966
2000 ug/L	208812.970	2000.000	1980.813	0.959
4000 ug/L	423156.809	4000.000	4014.045	0.351



Intensity = 105.42028447 * Concentration - 4.92783332
 Correlation coefficient: 0.99995
 %RSE: 1.71334882

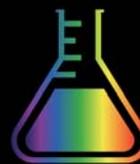


Table 4: Method Detection Limit

<input type="checkbox"/>	Rack:Tube	Solution Label	Li 670.783 nm ug/L	Y 488.368 nm Ratio
<input type="checkbox"/>	S1:4	CCV	2037.156	0.95
<input type="checkbox"/>	S1:5	CCB	0.223	0.95
<input checked="" type="checkbox"/>	S1:3	2 ug/L	2.110	0.94
<input type="checkbox"/>	S1:3	2 ug/L	2.248	0.96
<input type="checkbox"/>	S1:3	2 ug/L	2.264	0.95
<input type="checkbox"/>	S1:3	2 ug/L	2.170	0.94
<input type="checkbox"/>	S1:3	2 ug/L	2.003	0.94
<input type="checkbox"/>	S1:3	2 ug/L	2.265	0.94
<input type="checkbox"/>	S1:3	2 ug/L	2.317	0.94
<input type="checkbox"/>	S1:4	CCV	2022.418	0.95
<input type="checkbox"/>	S1:5	CCB	0.236	0.95

Solution Label	Li 670.783 nm ug/L
2 ug/L	2.110
2 ug/L	2.248
2 ug/L	2.264
2 ug/L	2.170
2 ug/L	2.003
2 ug/L	2.265
2 ug/L	2.317
Average	2.197
Standard Deviation	0.110
Method Detection Limit (MDL)	0.344



Discussion

The data clearly indicates the analysis method described above is more than adequate to meet the requirements of US EPA UCMR 5 and US EPA 200.7. The calibration curve encompasses the required reporting limit (RL) of 9 ug/L. The Method Detection Limit of 0.344 ug/L is an order of magnitude lower than what is required to support an RL of 9 ug/L. The data is linear over a wide range.

FACT is key to allowing this enhanced sensitivity. The Agilent 5110, as configured, exceeds expectations. It is expected that one would expect to get adequate results using any of the Agilent 5000 series instruments. In addition, it is expected that one should easily be able to get adequate results using alternative sample introduction systems. For example, one should be fine using the SeaSpray nebulizer.

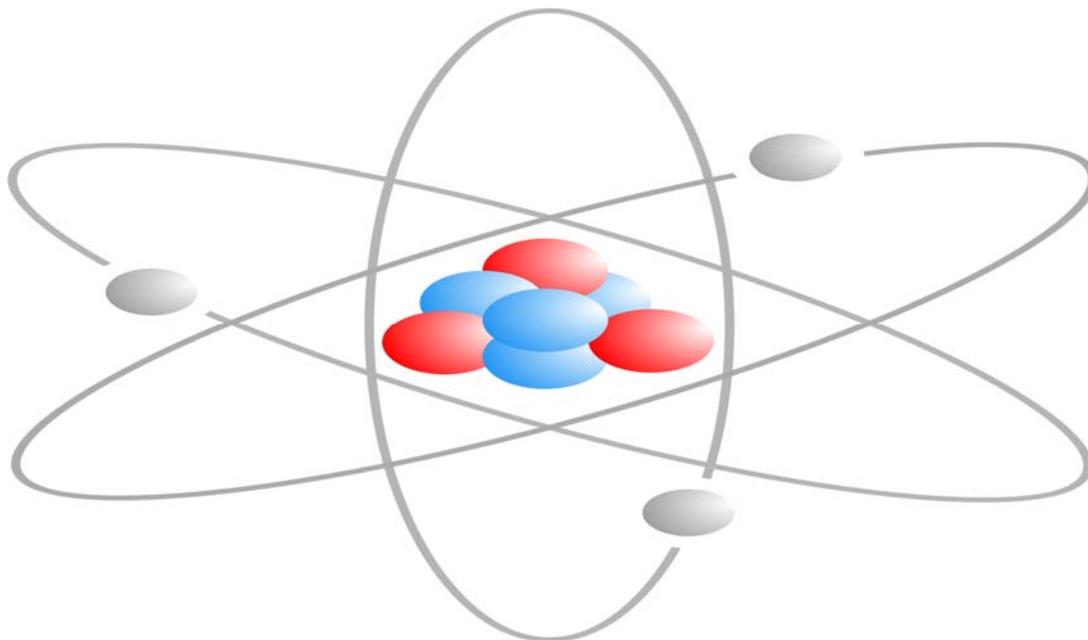
While this was not discussed in the scope of the data analysis, the system as fitted with the AVS-7, SPS-4, and configured with the method conditions above yielded an analysis time of approximately 1 minute and 36 seconds per sample (or 96 seconds per sample). Therefore, this method is appropriate for a high production laboratory setting.

References

US EPA FACT Sheet for the Fifth Unregulated Contaminant Monitoring Rule (UCMR 5)

This fact sheet may be found at the following web link

<https://www.epa.gov/dwucmr/fact-sheets-about-fifth-unregulated-contaminant-monitoring-rule-ucmr-5>



Atomic Structure of Lithium - 7