Application Note

Energy and Chemicals

ICP-OES Analysis of Electrolytes for All-Vanadium Redox Flow Batteries

Quantification of impurity elements in vanadium sulfate electrolytes using an Agilent 5800 VDV ICP-OES

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Introduction

The detrimental effects of burning fossil fuels on the climate, environment, and air quality are driving the shift towards cleaner and more sustainable sources of energy. However, challenges remain for the renewable energy sector, as both wind and solar power can be intermittent, leading to fluctuations in energy generation. To offset the uncontrollable nature of these weather-based technologies, there is increasing demand for large-scale energy storage solutions to balance the requirements of energy grids. Addressing these challenges is crucial for achieving sustainable, reliable, and secure systems that can meet both current and future energy needs.

Compared to traditional batteries, which store energy in the electrodes, flow batteries are electrochemical (redox) systems that store and release energy through chemical reactions within the electrolyte. This mechanism means that the capacity and power of flow batteries can be tailored separately, providing scalability and long lifespans. This flexibility makes them suitable for grid-scale energy storage and backup power systems.

There are various flow battery variants, but vanadium flow batteries (VRFBs) are currently the most common type.[1] The purity of the electrolyte, which consists of an electrocharged all-vanadium liquid, is vital to the cost-effectiveness of the battery's electricity production. So, accurate quantification of impurity elements in the electrolyte is needed to ensure the optimal functionality and reliability of VRFBs.[2]

Inductively coupled plasma optical emission spectroscopy (ICP-OES) is a fast, robust analytical technique that is widely used for the simultaneous measurement of multiple trace elements in complex samples. The high concentration of vanadium in the electrolyte of VRFBs creates a notable matrix effect that can be overcome using ICP-OES in radial view. However, traditional ICP radial observation modes of a horizontal plasma often suffer from limited instrument sensitivity, making them inadequate for meeting the increasingly stringent demands for impurity element control of electrolytes.

In response to this challenge, an Agilent 5800 Vertical Dual View (VDV) ICP-OES operating in radial view mode was used to determine low-concentration elemental impurities in the electrolytes of VRFBs. Agilent ICP-OES systems use a resilient, plug-and-play torch configuration to produce a vertical plasma that is especially good at handling the most challenging matrices, including battery-related samples.[3] Compared to a horizontally oriented torch, the vertical torch requires less cleaning, less-frequent torch replacement, and less downtime. The solid-state RF (SSRF) system of the Agilent ICP-OES instruments, operating at 27 MHz produces a reliable, robust, and maintenance-free plasma suitable for the analysis of high matrix samples, such as electrolytes.

The 5800 VDV ICP-OES method was used to determine 11 analytes in four vanadium sulfate electrolyte samples. The analytes included aluminum (Al), calcium (Ca), chromium (Cr), iron (Fe), potassium (K), magnesium (Mg), manganese (Mn), molybdenum (Mo), sodium (Na), nickel (Ni), and silicon (Si). The method was evaluated in terms of sensitivity, accuracy, and stability.

Experimental

Standard preparation

Agilent multi-element standards containing 100 mg/L Al, Ca, Cr, Fe, K, Mg, Mn, Mo, Na, Ni (part number 5191-3933) and 100 mg/L Si (p/n 5191-3937) were used to create calibration standards across a wide analytical range. The standards were diluted using high-purity de-ionized (DI) water prepared by a Millipore Milli-Q ultrapure water system. Details of the calibration standards used for each analyte are given in Table 1.

Table 1. Concentration level of standards used to generate the calibration curves for each element. Concentration units: mg/L.

	Calibration Standard					
Analyte	**Level 1**	**Level 2**	**Level 3**	**Level 4**	**Level 5**	**Level 6**
Al	0.10	0.20	0.50	1.00	2.00	5.00
Ca	0.10	0.20	0.50	1.00	2.00	5.00
Cr	0.10	0.20	0.50	1.00	2.00	5.00
Fe	0.10	0.20	0.50	1.00	2.00	5.00
K	1.00	2.00	5.00	-	-	-
Mg	0.02	0.05	0.10	0.20	0.50	1.00
Mn	0.02	0.05	0.10	0.20	0.50	
Mo	0.10	0.20	0.50	1.00	2.00	5.00
Na	0.10	0.20	0.50	1.00	2.00	5.00
Ni	0.02	0.05	0.10	0.20	0.50	
Si	0.10	0.20	0.50	1.00	2.00	5.00

Samples and sample preparation

Four vanadium sulfate electrolyte samples, including two commercial solutions (labeled A and B) and two research and development (R&D) solutions (labeled C and D), were supplied from a single manufacturer. All-vanadium flow battery electrolytes generally contain more than 1.50 mol/L of V and more than 2.30 mol/L of SO_4^{2-}, so each electrolyte was diluted 20-fold with DI water before analysis.

Instrumentation

Elemental analysis of the samples was carried out using the Agilent 5800 VDV ICP-OES. The instrument was fitted with a SeaSpray glass concentric nebulizer, double-pass cyclonic spray chamber, and an Easy-fit fully demountable torch with 1.8 mm quartz injector.

Agilent ICP Expert software was used to control the 5800 ICP-OES, optimize and run the method, and to process the data.

Instrument operating conditions are given in Table 2.

Table 2. Agilent 5800 VDV ICP-OES instrument and method parameters.

Parameter	Setting
Viewing Mode	Radial
Viewing Height (mm)	8
RF Power (kW)	1.3
Plasma Gas Flow (L/min)	15
Aux Flow (L/min)	1.0
Nebulizer Flow (L/min)	0.7
Pump Speed (rpm)	12
Replicates	3
Rinse Time (s)	15
Read Time (s)	10
Stabilization Time (s)	15
Sample Pump Tubing	Black/black, Solvaflex
Waste Pump Tubing	Gray/gray, Solvaflex
Background Correction	Fitted

Automatic background correction

The Fitted Background Correction (FBC) routine within the ICP Expert software was used for all elements in this study. FBC uses a sophisticated mathematical algorithm to automatically model and subtract simple and complex background structures produced by non-analyte signals.

Figure 1 shows the accurate correction of background emission lines by FBC for two representative elements. The software automatically applied correction, enabling the accurate detection of Fe 239.563 and Mg 279.553 nm. FBC eliminates the need to manually place off-peak background correction points, which can lead to incorrect results in the presence of unexpected peaks.

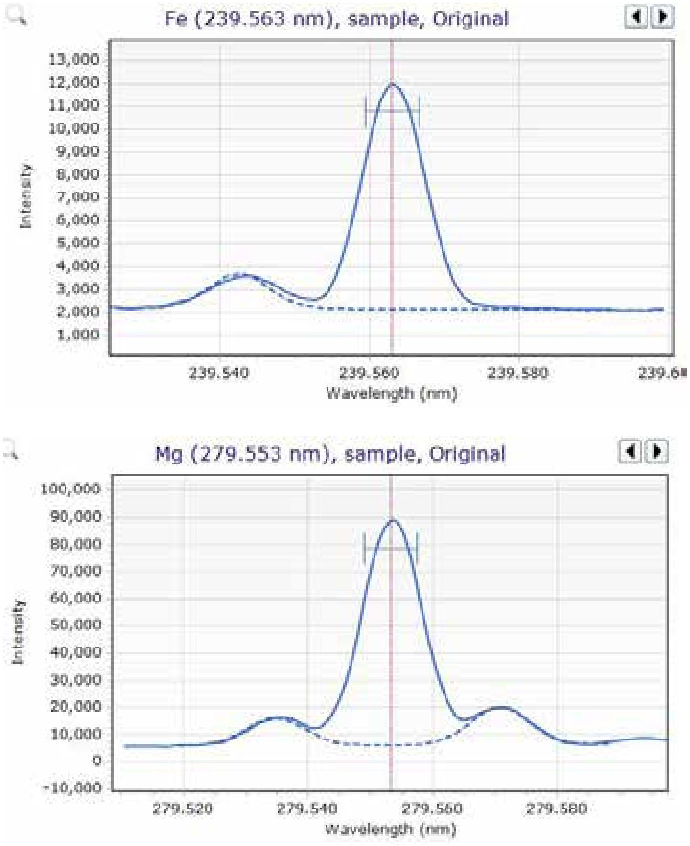
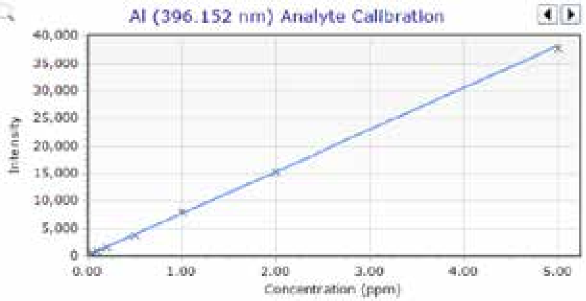


Figure 1. Examples of automatic background correction using FBC enabling the accurate measurement of (top) Fe 239.563 and (bottom) Mg 279.553.

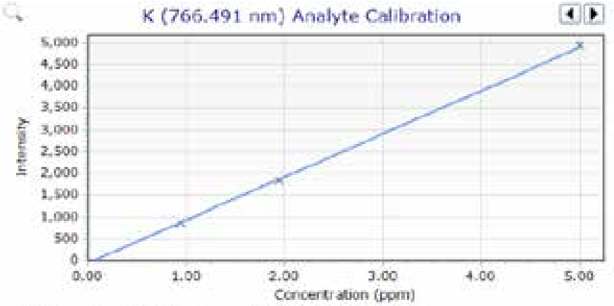
Results and discussion

Standard curve and background correction

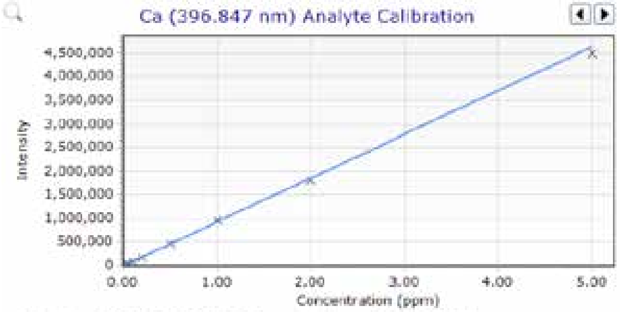
The external calibration standard method was used to quantify 11 impurity elements in the four electrolyte samples. The standard curves and linear regression results are shown in Figure 2. Excellent linearity (R>0.9999) was achieved for all elements across their respective analytical ranges.



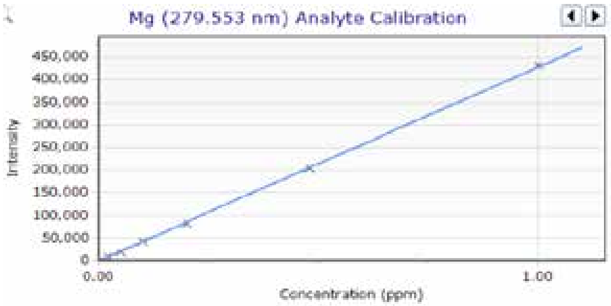
Intensity = 7652.46428747 * Concentration + 89.54283328
Correlation coefficient: 0.99992
%RSE:6.04395079



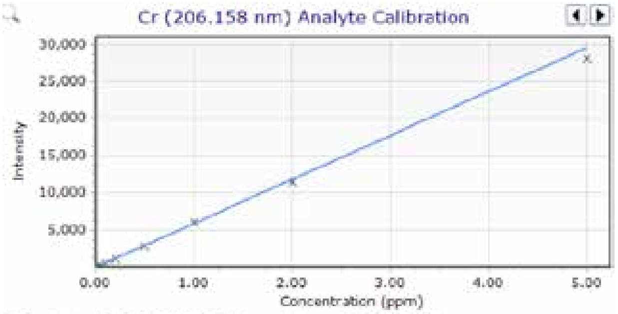
Intensity = 990.69369773 * Concentration - 54.67152871
Correlation coefficient: 0.99992
%RSE:2.45110012



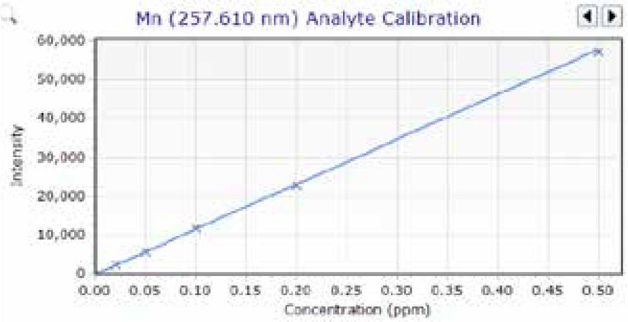
Intensity = 928151.22126612 * Concentration + 933.55723264
Correlation coefficient: 0.99990
%RSE:3.42809770



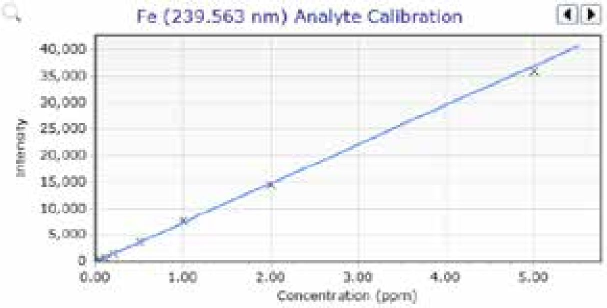
Intensity = 428690.34333425 * Concentration + 63.81508329
Correlation coefficient: 0.99995
%RSE:2.14396455



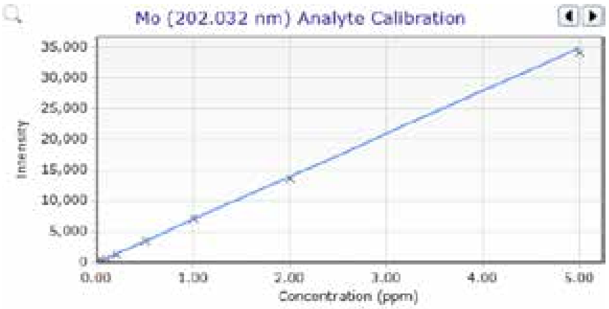
Intensity = 5923.34260039 * Concentration - 36.20605938
Correlation coefficient: 0.99990
%RSE:15.76468535



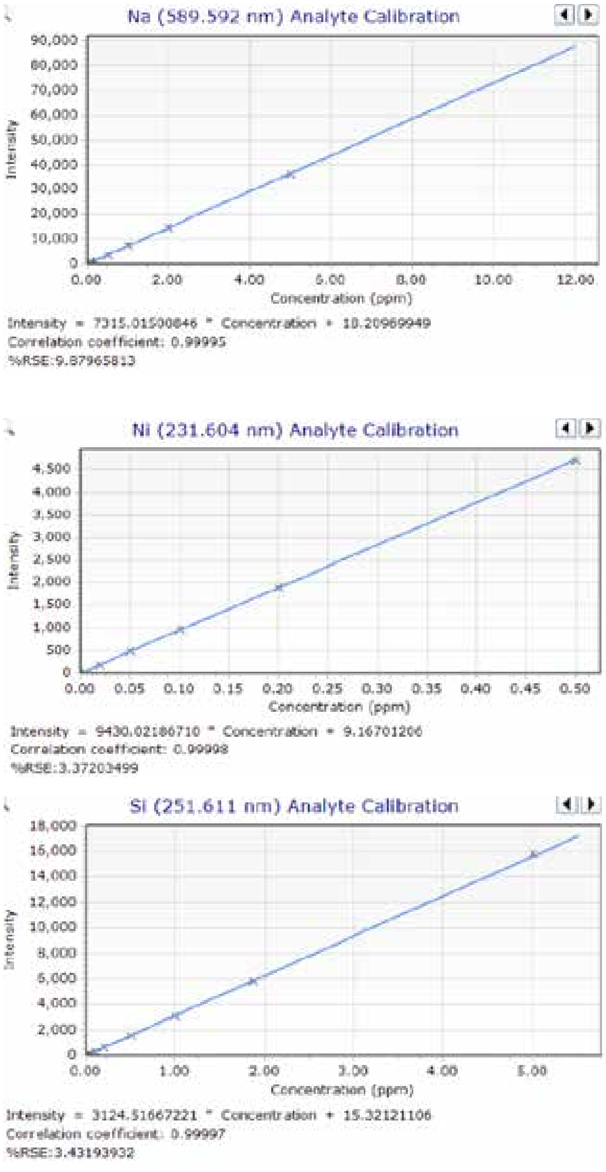
Intensity = 115805.23951459 * Concentration + 45.61270506
Correlation coefficient: 0.99998
%RSE:1.45853906



Intensity = 7398.53469583 * Concentration - 5.48755180
Correlation coefficient: 0.99990
%RSE:3.64539175



Intensity = 6975.90860092 * Concentration + 21.18038504
Correlation coefficient: 0.99993
%RSE:3.56174659



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Intensity = 7315.01500846 * Concentration + 10.20969949
Correlation coefficient: 0.99995
%RSE:9.87965813
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Intensity = 9430.02186710 * Concentration + 9.16701206
Correlation coefficient: 0.99998
%RSE:3.37203499
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Intensity = 3124.51667221 * Concentration + 15.32121106
Correlation coefficient: 0.99997
%RSE:3.43193932
```

Figure 2. Calibration curves for all 11 analytes.

Method detection limits

Method detection limits (MDLs) were determined by analyzing the method blank (DI water) 10 times. The MDLs were calculated as three sigma of the blank concentration of each element, multiplied by the dilution factor. The high sensitivity of the 5800 is demonstrated by the low MDLs for all analytes (Table 3), which were all detected in the blank.

Table 3. Analytical wavelengths and method detection limits for 11 impurity elements.

Analyte	Wavelength (nm)	MDL (mg/L)
Al	396.152	0.030
Ca	396.847	0.002
Cr	206.158	0.039
Fe	239.563	0.025
K	766.491	0.052
Mg	279.553	0.002
Mn	257.610	0.002
Mo	202.032	0.028
Na	589.592	0.022
Ni	231.604	0.025
Si	251.611	0.087

Quantitative data and spike recoveries

Quantitative data for the four electrolyte samples were acquired by the 5800 VDV ICP-OES following Chinese standard methods GB/T 23942-2009 (for ICP-OES) and GB/T37204-2018 (for testing electrolytes for all-vanadium flow batteries).[4, 5] As observed in Table 4, the elemental content varied significantly across the different electrolytes. According to the national standard concentration limit requirements, the two commercial electrolytes (samples A and B) met the criteria for all 11 analytes, while the two R&D samples C and D contained some elements that exceeded the maximum allowable limits. The results confirmed the grade-status of the samples A and B as high-quality electrolytes.

Electrolyte sample A was selected for the spike recovery test. According to GB/T37204-2018, the lowest concentration limit requirement for the target elements is below 5 mg/L. Therefore, for the spike recovery test, electrolyte sample A was spiked at 0.5 mg/L with each element.

As shown in Table 4, the spike recoveries ranged from 94 to 103% of the expected concentration. The excellent recoveries demonstrate the accuracy of the method for the analysis of the target analytes in vanadium sulfate battery electrolyte solutions.

Table 4. Quantitative results for four electrolytes (corrected for the dilution factor), spike recovery results for commercial electrolyte sample A, and concentration limit requirements specified in China National Standard method. Concentration units: mg/kg.

Analyte, Wavelength (nm)	Measured Concentration Electrolyte A	Spike Recovery (%)	Measured Concentration Electrolyte B	Measured Concentration Electrolyte C	Measured Concentration Electrolyte D	GB/T 37204-2018
Al 396.152	2.01	101	8.08	25.98	6.88	< 50
Ca 396.847	15.70	102	3.49	17.26	58.71	< 30
Cr 206.158	1.63	97	1.25	23.20	89.62	< 15
Fe 239.563	23.38	99	7.78	40.72	4.49	< 50
K 766.491	6.88	96	6.68	49.89	14.76	< 100
Mg 279.553	3.47	96	1.02	16.78	3.31	< 30
Mn 257.610	0.21	94	0.05	1.87	0.57	< 5
Mo 202.032	1.92	94	1.02	78.59	0.77	< 20
Na 589.592	9.59	103	6.62	227.78	47.49	< 80
Ni 231.604	0.59	100	0.21	0.75	<MDL	< 20
Si 251.611	16.16	96	3.68	1.52	8.14	< 10

Method stability

To investigate the robustness of the 5800 VDV ICP-OES method, electrolyte sample A was analyzed once every 20 minutes over four hours. As shown in Table 5, the precision of the measured concentrations of each analyte over a four-hour period was excellent, as indicated by the RSDs < 2.3%.

The excellent stability and repeatability of the measurements confirmed the suitability of the 5800 VDV ICP-OES method for the routine analysis of the vanadium sulfate electrolytes over four hours.

Table 5. Results of a four-hour stability test.

Analyte, Wavelength (nm)	Concentration (mg/L)	RSD (%)
Al 396.152	0.104	1.4
Ca 396.847	0.774	0.7
Cr 206.158	0.081	0.7
Fe 239.563	1.152	0.7
K 766.491	0.337	2.1
Mg 279.553	0.171	0.6
Mn 257.610	0.010	2.3
Mo 202.032	0.095	0.8
Na 589.592	0.466	1.7
Ni 231.604	0.029	1.9
Si 251.611	0.798	0.9

Conclusion

The Agilent 5800 VDV ICP-OES successfully determined 11 impurity elements in four all-vanadium flow battery electrolytes—an important quality control application within the battery production process. The main advantages of the analytical method include:

- Good calibration linearity (R>0.9999) and low method detection limits (<0.09 mg/L) for all target analytes.
- Confirmation of the method's accuracy demonstrated by 94 to 103% recoveries of 0.5 mg/L spikes added to one of the commercial vanadium sulfate electrolyte samples.
- Recovery of all elements within 100 ±10% indicating that the 5800 can tolerate the high concentration of vanadium in the electrolyte samples, due to its robust vertical plasma and SSRF generator.
- Excellent instrument stability, as shown by the precision of repeated measurements of a commercial electrolyte sample over four hours (RSDs < 2.3%).

The 5800 VDV ICP-OES method is suitable for the accurate quantification of some key impurity elements in electrolytes used in all-vanadium flow batteries, in accordance with China standard method GB/T 37204-2018.

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