Application Note

Energy and Chemicals

Determination of Trace Metal Impurities in High Purity Aluminum Nitrate using ICP-OES

Analysis of cathode raw materials for Li-ion batteries by Agilent 5900 ICP-OES

Author

Peter Riles

Agilent Technologies, Inc.

Introduction

The lithium-ion battery (LIB) industry requires the analysis of the elemental composition of materials at all stages of production (*1*). To prevent contamination of LIBs from impurities, suppliers of the chemicals used to produce cathode, anode, and electrolyte materials must quality assure (QA) their products using reliable, reproducible, and robust techniques. The accurate analysis of elemental impurities in the chemicals is especially important as these elements can affect the final performance of the battery.

ICP-OES is widely used to measure impurities in materials used to manufacture LIBs, as it is a specified technique in various standard methods used within the industry (*1*).

Many commercially available LIBs use nickel rich ternary cathode materials such as lithium-nickel-cobalt-aluminum oxide (NCA) or lithium-nickel-cobalt-manganese oxide (NCM) due to their high specific capacity and relatively low cost (*2*). The specific capacity of the cathode material affects the energy density of a LIB, so the choice and quality of material is important. NCA provides greater charge cycling stability and a higher energy density than NCM, while the cost of both raw materials is approximately the same (*2*).

Aluminum nitrate ($Al(NO_3)_3$) is a precursor for the production of NCA cathodes, but the analysis of $Al(NO_3)_3$ by ICP-OES is challenging due to the formation of matrix-based interferences in the plasma. The Agilent 5900 Synchronous Vertical Dual View (SVDV) ICP-OES uses various design features to overcome these interferences, ensuring the accurate determination of impurities in $Al(NO_3)_3$.

In this study, aluminum, barium, boron, calcium, chromium, cobalt, copper, gallium, iron, magnesium, manganese, nickel, phosphorus, potassium, sodium, sulfur, silicon, titanium, and zinc were quantified in three high purity $Al(NO_3)_3$ samples by the 5900 ICP-OES. Five liquid samples taken at various points during the production of $Al(NO_3)_3$ were also analyzed using the same method. The accuracy and robustness of the 5900 ICP-OES method was evaluated using a spike recovery test and a 7-hour stability test.

Experimental

Sample preparation

Three separate ultrahigh purity (>99.999%, 5N) samples of $Al(NO_3)_3$ were supplied as solid samples. Five solutions were also supplied for analysis. The solid samples were prepared as received (not dried or homogenized). Approximately 0.65 g of sample was dissolved in 5% Suprapur hydrochloric acid (HCl, Merck) and diluted to 50 mL in ultrapure water (UPW). The liquid samples were diluted 1:15 in 5% Suprapur HCl before analysis by the 5900 ICP-OES. All samples contained up to 3000 ppm Al in solution.

The instrument was calibrated using multi-element standards in 5% HCl, prepared from Agilent single element stock solutions. Percent level Al and ppb-level trace elements were measured in the samples in a single analysis using the 5900 ICP-OES.

Instrumentation

All measurements were performed using a 5900 SVDV ICP-OES fitted with a SeaSpray concentric nebulizer, double-pass cyclonic spray chamber, and an Agilent Easy-fit demountable VDV torch with a 1.8 mm injector. Samples were introduced to the instrument via the integrated Advanced Valve System (AVS 7) seven-port switching valve and an Agilent SPS 4 autosampler. The method can also be run on an Agilent 5800 VDV ICP-OES fitted with the optional AVS 7.

The AVS 7 uses a high-speed positive displacement pump to rapidly fill the sample loop, speeding up the analysis and reducing argon consumption (*3*). The valve also reduces maintenance and cleaning requirements of the torch, as less sample passes through the sample introduction system compared to conventional sample introduction.

The Vista Chip III detector of the 5900 provides high-speed continuous wavelength coverage from 167 to 785 nm, ensuring that a suitable, interference-free line can be found for most analytes. There is no time penalty when adding extra wavelengths for an element to the analysis. The wide linear dynamic range of the detector enables both major (e.g., Al) and trace elements (e.g., S and P) to be analyzed in the same sample, avoiding the need to perform multiple dilutions.

Typically, the 5900 combines and measures elevated levels of group I elements (e.g., Na and K) and trace levels of other elements, synchronously in SVDV mode. However, for the measurement of $Al(NO_3)_3$, only Al (group III) was required to be measured at high concentrations, and trace level analysis was required for K and Na, therefore VDV mode was selected. In some LIB material manufacturing processes, there may be a need to measure low levels of Al in intermediary samples, so an extra Al line run in axial view was also included in the method.

The high level of Al in the $Al(NO_3)_3$ sample and the need to analyze trace impurities in axial view generated some plasma-based interferences. Al tends to react in the plasma in a similar way to group I and II elements by producing an easily ionizable element (EIE) effect in the plasma. The EIE effect of the high concentration of Al results in energy being taken away from the plasma, causing it to cool. When the plasma cools, the signals for elements with low ionization energies or atomic wavelengths are enhanced, as these elements and wavelengths respond better to cooler plasma conditions. In contrast, elements with high ionization energies or ionic wavelengths are suppressed, as these elements and wavelengths respond better to the energy supplied by a hotter plasma. To compensate for the EIE effects of Al, a customized internal standard mix that was matched to the analytes was used, as detailed in Tables 1 and 4.

Table 1 outlines the custom internal standard that was used to correct the measurements due to the high Al concentration. Matching the element wavelength state (atomic or ionic) and ionization energy of the internal standard to the analyte ensures accurate correction.

Table 1. Concentration of internal standard elements used in the mix.

Internal Standard and Wavelength (nm)	Concentration (mg/L)	Atomic/Ionic State*	Ionization Energy (eV)	Analyte
Y 371.029	5	II	6.2	Ba, Ca, Co, Cr, Fe, Mg, Mn, Ni, Ti, Zn
Rb 780.026	25	I	4.2	K
Bi 223.061	10	I	7.3	Al, B, Cu, Ga, P, S, Si
Li 670.783	5	I	5.4	Na

** I = Atomic, II = Ionic*

Instrument conditions

The 5900 ICP-OES was set up with the standard configuration, however, due to the high concentration of Al in the samples, the RF power was increased to 1.5 kW to provide a hotter plasma. The Al wavelengths were read in both axial and radial viewing modes. Radial is suitable for the analysis of high levels of Al expected in many of the samples, while axial is suitable for the measurement of low levels of Al expected in some of the liquid samples. 5900 ICP-OES operating parameters are outlined in Table 2.

Table 2. Agilent 5900 ICP-OES instrument operating conditions.

Parameter	Axial	Radial
Read Time (s)	10	5
Replicates	3	
Sample Uptake Delay (s)	0	
Stabilization Time (s)	10	0
Rinse Time (s)	0	
Pump Speed (rpm)	12	
RF Power (kW)	1.5	
Aux Flow (L/min)	1	
Plasma Flow (L/min)	12	
Nebulizer Flow (L/min)	0.7	
Viewing Height (mm)	NA	8
Sample Pump Tubing	White-White	
Internal Standard Pump Tubing	Black-Black	
Waste Pump Tubing	Blue-Blue	
Background Correction	Fitted/FACT	

The AVS 7 switching valve, a standard feature of the 5900 ICP-OES, was used to provide faster analysis times and better stability. The AVS 7 also extends the lifetime of the torch and sample introduction system by reducing the sample load on the plasma. AVS 7 parameters are outlined in Table 3.

Table 3. AVS 7 switching valve system parameters.

Parameter	Setting
Sample Loop Size (mL)	1
Pump Rate - Uptake (mL/min)	36
Pump Rate - Inject (mL/min)	9
Valve Uptake Delay (s)	4.5
Bubble Inject Time (s)	1
Pre-emptive Rinse Time (s)	1

Wavelengths were selected based on their ability to provide the desired detection limits, accuracy, and precision. Initially three wavelengths were selected for most elements, which provided confidence and extra assurance that the method was providing accurate results. Internal standards were selected based on ionization energy and wavelength state (atomic/ionic) to best suit each analyte element and wavelength for this method (Table 1).

Table 4. Elements, wavelengths, viewing modes, internal standards, and background correction.

Element and Wavelength	View	Internal Std	Background Correction
Al 396.152	Axial	Bi 223.061	Fitted
Al 237.312	Radial	Bi 223.061	Fitted
B 249.772	Axial	Bi 223.061	Fitted
Ba 455.403	Axial	Y 371.029	Fitted
Ca 393.366	Radial	Y 371.029	Fitted
Co 230.786	Axial	Y 371.029	Fitted
Cr 267.716	Axial	Y 371.029	Fitted
Cu 324.754	Axial	Bi 223.061	Fitted
Fe 238.204	Axial	Y 371.029	Fitted
Ga 294.363	Axial	Bi 223.061	Fitted
K 766.491	Axial	Rb 780.026	Fitted
Mg 279.553	Axial	Y 371.029	Fitted
Mn 257.610	Axial	Y 371.029	Fitted
Na 589.592	Axial	Li 670.783	FACT
Ni 231.604	Axial	Y 371.029	Fitted
P 177.434	Axial	Bi 223.061	Fitted
S 180.669	Axial	Bi 223.061	Fitted
Si 251.611	Axial	Bi 223.061	Fitted
Ti 334.941	Axial	Y 371.029	Fitted
Zn 202.548	Axial	Y 371.029	Fitted

Background correction

The ICP Expert software includes easy-to-use background correction techniques including Fitted Background Correction (FBC) and Fast Automated Curve-fitting Technique (FACT). To reduce the impact of spectral interferences arising from the sample matrix and internal standards, different background correction methods were used. For elements where there were no direct overlaps, FBC was used (*4*). An example of FBC for P 177.434 nm is shown in Figure 1. The peak on the left of P is from the internal standard, Y 177.414 nm. FBC has accurately modeled this peak, providing excellent background correction for the off-peak interference.

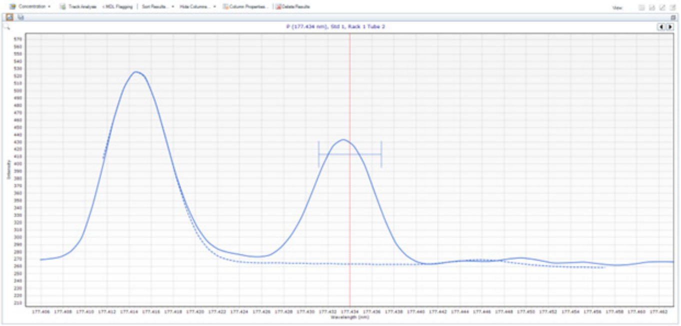

Figure 1. Fitted background correction of P 177.434 nm.

FACT is used when interferences are closer to or overlap the analyte of interest (*5*). As shown in Figure 2, FACT was used to effectively correct the overlap of Ba 589.610 nm on Na 589.592 nm. FACT provides an accurate model of the Ba interference on Na, and, once established, the correction is automatically applied to all Na measurements.

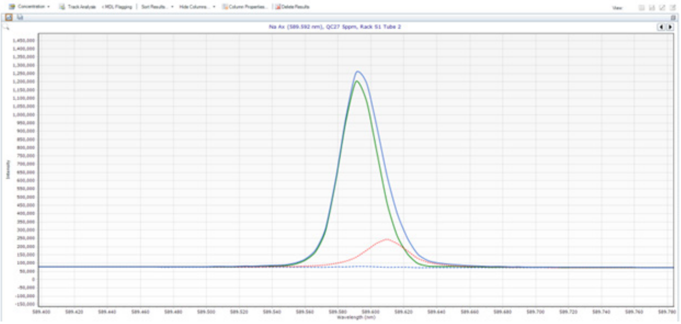

Figure 2. FACT model for correction of a Ba interference on Na (total signal shown by the solid blue line). The Ba 589.610 nm (red dashed) interference line is overlapping the Na 589.592 nm (solid green) analyte line. The signal from the blank is shown by the light blue dashed line.

Calibration

The instrument was calibrated to achieve accurate low-level detection for the trace elements, while maintaining a wide linear range for Al. An extra low calibration was added for Al to enable low-level measurement of the analyte in the liquid samples. Details are given in Table 5.

Table 5. Concentrations of calibration standards.

Element/ Wavelength	Std 1 (mg/L)	Std 2 (mg/L)	Std 3 (mg/L)	Std 4 (mg/L)	Std 5 (mg/L)	Std 6 (mg/L)	Std 7 (mg/L)	Std 8 (mg/L)	Std 9 (mg/L)
Al 396.152	0.1	1	10				100		
Al 237.312			10				100	2000	5000
B 249.772	0.1	1	10						
Ba 455.403	0.1	1	10						
Ca 393.366				0.1	1	10			
Co 230.786	0.1	1	10						
Cr 267.716	0.1	1	10						
Cu 324.754	0.1	1	10						
Fe 238.204				0.1	1	10			
Ga 294.363	0.1	1	10						
K 766.491					1	10			
Mg 279.553				0.1	1	10			
Mn 257.610	0.1	1	10						
Na 589.592				0.1	1	10	25		
Ni 231.604	0.1	1	10						
P 177.434	0.1	1	10						
S 180.669				0.1	1	10			
Si 251.611				0.1	1	10			
Ti 334.941				0.1	1	10			
Zn 202.548	0.1	1	10						

Method Detection Limits (MDLs)

MDLs were determined using two solutions. The MDL for Al was determined using a 5% HCl solution and the MDLs for the trace elements were determined using a 1000 mg/L Al solution. The 1000 mg/L Al matrix was used to evaluate the detection of low concentrations of trace elements in the presence of high Al. The MDLs for the solid and liquid samples are shown in Tables 6 and 7. The MDLs differ due to different dilution factors, weights, and volumes used during sample preparation. However, both sets of MDLs were calculated from the same set of data, as 3σ from three runs of 10 of each of the MDL solutions.

The quantitative results for the three solid $Al(NO_3)_3$ samples show a good level of consistency in terms of trace elemental content (Table 6). There is greater variation in the concentrations of elements measured in the liquid samples, as shown in Table 7.

Table 6. MDLs and quantitative results for the three solid samples of $Al(NO_3)_3$. The data has been corrected for dilution.

Element and Wavelength	MDL (Solids, mg/kg)	Sample 1 (mg/kg)	Sample 2 (mg/kg)	Sample 3 (mg/kg)
Al 396.152	0.1	>7500	>7500	>7500
Al 237.312	5	68773	69479	69899
B 249.772	0.1	0.2	0.1	0.1
Ba 455.403	0.005	0.045	0.057	0.044
Ca 393.366	0.05	3.68	0.41	2.17
Co 230.786	0.05	0.18	0.17	0.16
Cr 267.716	0.05	0.73	0.72	0.6
Cu 324.754	0.05	0.14	0.13	0.16
Fe 238.204	0.02	0.07	0.17	0.14
Ga 294.363	0.2	0.9	1.1	0.4
K 766.491	0.2	0.2	0.3	0.9
Mg 279.553	0.05	<0.05	<0.05	<0.05
Mn 257.610	0.01	<0.01	<0.01	<0.01
Na 589.592	0.1	<0.1	<0.1	1.3
Ni 231.604	0.1	0.1	0.1	<0.1
P 177.434	0.5	<0.5	0.8	<0.5
S 180.669	1	<1	<1	<1
Si 251.611	0.2	0.3	<0.2	0.2
Ti 334.941	0.01	0.02	0.02	0.02
Zn 202.548	0.02	0.07	0.11	0.11

Table 7. MDLs and quantitative results for the five liquid samples. The data has been corrected for dilution.

Element and Wavelength	MDL (Liquids, mg/L)	Liquid Sample 1 (mg/L)	Liquid Sample 2 (mg/L)	Liquid Sample 3 (mg/L)	Liquid Sample 4 (mg/L)	Liquid Sample 5 (mg/L)
Al 396.152	0.02	>1500	>1500	>1500	>1500	1.30
Al 237.312	1	3021	40265	5727	44183	1
B 249.772	0.02	0.06	0.06	0.04	0.06	<0.02
Ba 455.403	0.001	0.087	0.053	0.449	0.094	0.004
Ca 393.366	0.005	10.258	1.469	0.295	11.805	1.696
Co 230.786	0.01	0.05	0.05	0.04	0.06	<0.01
Cr 267.716	0.01	0.33	0.46	0.28	0.8	<0.01
Cu 324.754	0.01	0.04	0.08	0.03	0.06	<0.01
Fe 238.204	0.005	<0.005	0.005	3.275	0.104	0.883
Ga 294.363	0.05	<0.05	<0.05	0.13	<0.05	<0.05
K 766.491	0.05	0.2	0.06	<0.05	0.34	<0.05
Mg 279.553	0.001	0.473	0.241	0.702	0.54	0.172
Mn 257.610	0.002	0.091	0.051	<0.002	0.106	<0.002
Na 589.592	0.02	135.8	24.9	0.37	190.69	0.369
Ni 231.604	0.02	0.5	0.33	0.08	0.58	<0.02
P 177.434	0.1	7.8	18.2	13.9	9.7	9.4
S 180.669	0.2	0.5	0.4	0.3	0.7	<0.2
Si 251.611	0.05	6.78	2.06	0.94	8.26	0.80
Ti 334.941	0.002	0.011	0.003	1.273	0.238	0.906
Zn 202.548	0.002	0.526	1.901	0.124	0.684	0.028

Spike recoveries

In the absence of suitable certified reference materials (CRMs) for the application, spike recovery tests were used to check the accuracy of the method. Each of the three solid sample solutions was spiked with 100 ppb of the target impurity elements. The spike recoveries were within 100 ± 10% for all analytes (Table 8), providing confidence that the internal standards were correcting for the plasma interferences arising from the high concentration of Al. The excellent spike recovery data confirms the suitability of the 5900 VDV ICP-OES method for the accurate analysis of trace elemental impurities in $Al(NO_3)_3$.

Table 8. Recoveries of 100 ppb spikes in the three solid $Al(NO_3)_3$ samples.

Element and Wavelength (nm)	Sample 1 (%)	Sample 2 (%)	Sample 3 (%)
B 249.772	104	104	105
Ba 455.403	101	101	101
Ca 393.366	93	95	100
Co 230.786	101	101	100
Cr 267.716	100	101	100
Cu 324.754	101	101	101
Fe 238.204	100	101	100
Ga 294.363	99	102	100
K 766.491	100	100	102
Mg 279.553	101	100	101
Mn 257.610	101	101	100
Na 589.592	92	92	95
Ni 231.604	100	101	100
P 177.434	109	98	106
S 180.669	97	104	99
Si 251.611	104	105	105
Ti 334.941	101	101	100
Zn 202.548	101	102	101

Long-term stability

To determine the stability of the method, 384 solutions were analyzed over a 7-hour period, with a 5 ppm multi-element QC solution inserted every 10 solutions. Figure 3 shows the recovery of the QC solution with all results within ±10% of expected. The data shows that the 5900 ICP-OES remains stable over an entire working day, while generating accurate results over a long period without the need to recalibrate. All elements reported a relative standard deviation of less than 2.2% for the QC sample over the 7-hour run.

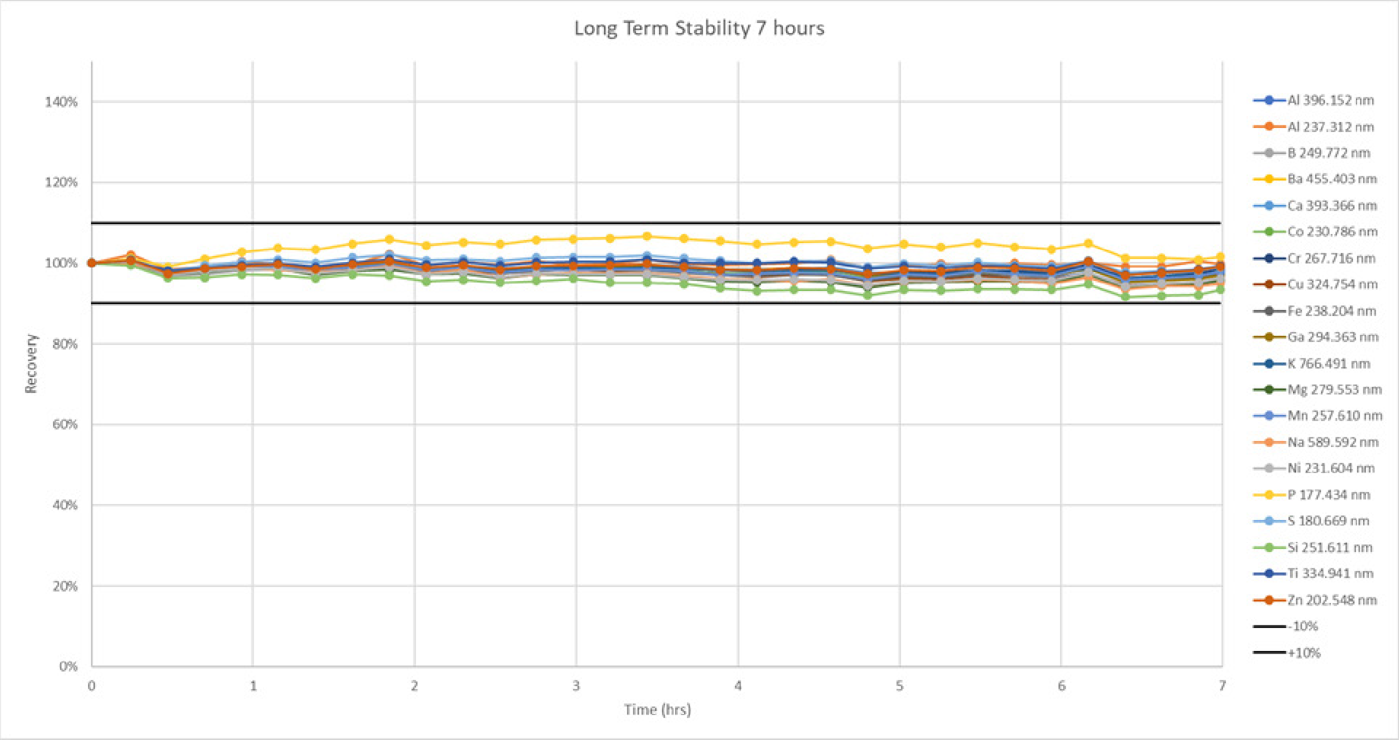

Figure 3. Long-term stability showing recoveries of the 5 mg/L QC solution measured over 7 hours.

Conclusion

The Agilent 5900 ICP-OES with integrated AVS 7 switching valve provided accurate and timely results for the analysis of high purity $Al(NO_3)_3$—a raw material used in the manufacture of NCA cathodes.

A customized internal standard mix was used to correct for the matrix (EIE) interferences arising from the high Al matrix that impede the accurate measurement of low ionization energy elements such as K and Na. The excellent recoveries of all analytes spiked at 100 ppb in three $Al(NO_3)_3$ samples demonstrated the effectiveness of the method for the determination of trace elements—including K and Na—in the presence of 6.9% Al.

The 5900 was able to measure high matrix samples and respond to the different plasma loading between samples and QC solutions due to the RF system. The RF system is free running and contains a feedback loop that identifies changes in plasma conditions. The long-term stability test run over seven hours showed the robustness of the plasma and stability of the optical system, further validating the 5900 ICP-OES for QA/QC applications within the LIB industry.

References

1. A Practical Guide To Elemental Analysis of Lithium Ion Battery Materials Using ICP-OES, Agilent publication 5994-5489EN
2. Wang, B., *et al*, Which of the nickel-rich NCM and NCA is structurally superior as a cathode material for lithium-ion batteries? *J. Mater. Chem. A*, **2021**, 9, 13540–13551, 23
3. Reduce Costs and Boost Productivity with the Advanced Valve System (AVS) 6 or 7 Port Switching Valve System, Agilent publication 5991-6863EN
4. Fitted Background Correction (FBC): Fast, accurate and fully automated background correction, Agilent publication 5991-4836EN
5. Real-time Spectral Correction of Complex Samples using FACT Spectral Deconvolution Software, Agilent publication 5991-4837EN

Agilent part numbers

G8010-60255	Seaspray Nebulizer (glass) U-series
G8010-60236	Demountable Easy-fit torch
3710044200	Peristaltic pump tubing, white/white, 12/pk
3710041900	Peristaltic pump tubing, black/black, 12/pk
3710044400	Peristaltic pump tubing, blue/blue, 12/pk
G8010-60256	Double-pass glass cyclonic spray chamber
190065200	Centrifuge tubes polyprop. 50 mL, 500/pk
6610026600	SPS3 sample rack 21 tubes x 30mm od 1/pk
5190-8243	Agilent 1000 ppm single element stock solution for Al
5190-8249	Agilent 1000 ppm single element stock solution for Ba
5190-8347	Agilent 1000 ppm single element stock solution for Co
5190-8349	Agilent 1000 ppm single element stock solution for Cu
5190-8472	Agilent 1000 ppm single element stock solution for Fe
5190-8504	Agilent 1000 ppm single element stock solution for K
5190-8482	Agilent 1000 ppm single element stock solution for Mg
5190-8484	Agilent 1000 ppm single element stock solution for Mn
5190-8492	Agilent 1000 ppm single element stock solution for Ni
5190-8546	Agilent 1000 ppm single element stock solution for Ti
5190-8365	Agilent 10,000 ppm single element stock solution for B
5190-8369	Agilent 10,000 ppm single element stock solution for Ca
5190-8375	Agilent 10,000 ppm single element stock solution for Cr
5190-8389	Agilent 10,000 ppm single element stock solution for Ga
5190-8206	Agilent 10,000 ppm single element stock solution for Na
5190-8210	Agilent 10,000 ppm single element stock solution for S
5190-8451	Agilent 10,000 ppm single element stock solution for Si
5190-8235	Agilent 10,000 ppm single element stock solution for Zn
5190-8362	Agilent 10,000 ppm single element stock solution for Bi
5190-8441	Agilent 10,000 ppm single element stock solution for Rb

www.agilent.com/chem/5900icp-oes

DE68324873

This information is subject to change without notice.

© Agilent Technologies, Inc. 2023
Printed in the USA, June 16, 2023
5994-6085EN