

Elemental Analysis of Lithium-Ion Battery Black Mass Recycling Material by ICP-OES

Enhancing instrument robustness for the analysis of high-TDS samples using an inert Agilent V-groove nebulizer



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Abstract

This study highlights the effectiveness of the Agilent 5900 SVDV ICP-OES, equipped with the Agilent inert V-groove nebulizer, for the multi-element analysis of acid-digests of black mass (BM) samples. This new nebulizer enables routine analysis of unfiltered samples with up to 30% total dissolved solids and suspended particles of up to 350 μm in size. The system demonstrated an outstanding long-term stability over 16 hours and excellent spike recoveries. Additionally, the V-groove nebulizer operated without blockages for over three weeks, reducing maintenance requirements while ensuring high accuracy and precision. This method offers BM producers a reliable solution for directly analyzing key analytes in unfiltered sample digests, supporting efforts to recover valuable metals from spent lithium-ion batteries.

Introduction

The increasing use of lithium-ion (Li-ion) batteries in electric vehicles, portable electronics, and renewable energy applications has made recycling spent cells vitally important for reducing waste and recovering valuable materials. BM, which is a metal concentrate in the form of a black powder, is obtained after crushing and separating waste battery components. High-value elements such as lithium, nickel, cobalt, and manganese are extracted through different refining processes. This material is then used in the development of new battery precursor materials. Recovering these valuable resources reduces the need for lithium extraction from mining or brines, processes that impact the environment and often disrupt communities. BM also contains toxic elements such as lead and cadmium that require monitoring as they pose a potential environmental hazard if not properly managed.

The value of BM is typically based on the prevailing spot price of virgin battery-grade minerals, after accounting for the processing costs, recyclers' margins, the type of BM, and demand. Accurate analysis of the critical battery elements is therefore important as it defines the value of the BM batch. This analysis is typically performed on the digestate obtained by acid-digesting the BM sample, using a multi-element technique such as inductively coupled plasma optical emission spectroscopy (ICP-OES). However, routine elemental analysis of these complex samples can be challenging. Since most of the sample is carbon (graphite), which is not acid soluble, the digestion process does not render a clear solution. These insoluble suspended particles create problems when introducing the sample into an ICP-OES instrument; they can block the narrow liquid lines of the sample introduction system (SIS), especially the nebulizer. Two common recommended practices to overcome this problem before analysis include filtering the digestate or allowing time for the suspended particles to settle at the bottom of the vial. Both processes are time-consuming, and in the case of filtration, also require additional consumables, such as disposable filters, which can be a source of contamination.

Quality control (QC) laboratories within battery recycling and refining companies are constantly searching for ways to enhance efficiency and improve sample throughput. Instrument downtime caused by blockages in the SIS may occur when analyzing BM digests and any unplanned downtime can significantly impact the efficiency of the laboratory. The use of a robust nebulizer for ICP-OES is an alternative strategy that can enable laboratories to run more samples that contain high levels of total dissolved solids (TDS) or suspended particles, with minimal blockages. This capability can improve the analytical workflow of the laboratory, reducing both instrument downtime and running costs.

The inert, high-TDS Agilent V-groove nebulizer (Figure 1) allows the introduction of challenging sample matrices containing up to 30% dissolved solids and suspended particles (with a maximum particle size of 350 μm) to the ICP-OES. The V-groove nebulizer ensures exceptional instrument performance, robustness, and durability during the analysis of the most challenging samples, enabling extended and reliable operation.

In this study, a BM sample obtained from Envirostream Australia, a battery recycling company, was analyzed using an Agilent 5900 SVDV ICP-OES equipped with the inert, high-TDS V-groove nebulizer.

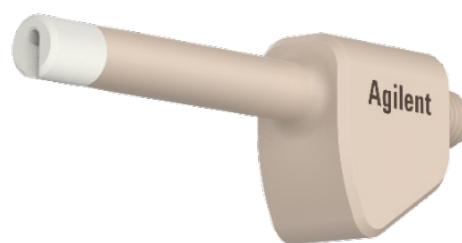


Figure 1. Agilent V-groove nebulizer optimized for the analysis of high-TDS samples.

Experimental

Instrumentation

All measurements were performed using a 5900 SVDV ICP-OES configured with the high capacity Agilent SPS 4 autosampler. The SIS consisted of the inert V-groove nebulizer, an Agilent inert cyclonic double pass spray chamber, and the fully demountable Agilent Easy-fit torch configured with a 2.4 mm id inert alumina injector. The inert SIS setup was chosen as some BM samples can generate hydrofluoric acid (HF) during the acid digestion process, although this was not the case with the sample analyzed in this study. Instrument and method settings are listed in Table 1. No argon humidifier was used during this study.

Table 1. Instrument operating and method parameters.

Parameter	Setting	
RF Power	1.40 kW	
Plasma Gas	15 L/min	
Auxiliary Gas	1.4 L/min	
Nebulizer	Agilent inert V-groove nebulizer	
Nebulizer Gas Flow	0.90 L/min	
Spray Chamber	Inert spray chamber for Agilent 5000 series ICP-OES and MP-AES	
Torch	Fully demountable 2.4 mm id inert alumina injector	
Replicates	3	
Read Time	5 s	
Pump Speed	15 rpm	
Stabilization Time	20 s	
Uptake Delay	16 s (Fast Pump)	
Rinse Time	60 s (Fast Pump)	
Viewing Mode	Axial and Radial	
Viewing Height	6 mm	
Peristaltic Pump Tubing	Sample/carrier	Gray/gray
	Waste	Blue/blue

Preparation of samples and standards

The BM sample was ground to a fine powder using a mortar and pestle. Approximately 0.4 g of the ground BM was weighed directly into 50 mL digestion tubes. Aqua regia (16 mL of a 3:1 mix of HCl and HNO₃) was added directly to each tube, including a blank, and covered with a polypropylene watch glass. After the initial reaction subsided (~15 minutes), the tubes were inserted into the digestion block (Figure 2), which was programmed at 105 °C (Environmental Express HotBlock 150). The samples were removed from the digestion block and allowed to cool. Once at room temperature, the samples and blank were diluted to 50 mL using de-ionized water. The digestion tubes were then capped, mixed well, and loaded in a 21-position autosampler rack, ready for analysis.



Figure 2. BM samples in the hot block digester.

The use of the inert V-groove nebulizer simplifies the sample preparation step by allowing the user to analyze the samples directly after dilution. This greatly improves the laboratory workflow by reducing sample handling and the need to wait for the solids to settle, as well as minimizing contamination risks and the use of consumables such as filters. The parallel path design of the inert V-groove nebulizer reduces the chance of blockage of the gas orifice, and the large 1 mm id sample channel ensures the flow of any suspended particles without inducing blockages.

Six calibration standards were prepared by serial dilution of Agilent single element standards (see the consumables table for details) in a 10% HNO₃ matrix. Table 2 lists the composition of the multi-element calibration standards and the Fast Automated Curve-Fitting Technique (FACT) interferent solution. The FACT solution was used for spectral modeling of the background signal on the sodium 589.592 nm wavelength used in the method.

Wavelength selection and background correction

Lithium-ion batteries are manufactured with different formulations, so the elemental composition of BM samples will vary greatly in concentration levels. A previous study that used the Agilent 5800 ICP-OES to analyze different BM samples was considered.¹ The author used a set of wavelengths that delivered the best results for the samples analyzed in that study. From the spectroscopic point of view, due to its complex elemental composition, instrumental methods must account for any inter-elemental interferences that arise. Also, the large disparities in concentration between different elements create additional challenges when seeking to quantify analytes at low concentrations. The elemental composition of the sample studied here is completely different to the samples described in the previous application note.¹

Table 2. Calibration standards and FACT solution. All concentrations in mg/L.

	Al	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	Li	Mg	Mn	Na	Ni	P	S	Si	Sn	Ti	Zn
Standard 1			0.15	0.25	0.10		0.10				0.13		1.50			0.50	0.50	0.50	0.15	0.50
Standard 2			0.90	1.50	0.60		0.60				0.75		9.00			3.00	3.00	3.00	0.90	3.00
Standard 3			2.10	3.50	1.40		1.40				1.75		21			7.00	7.00	7.00	2.10	7.00
Standard 4	14	0.20				150		10	4.0	40		60		100	4.0					
Standard 5	56	0.80				600		40	16	160		240		400	16					
Standard 6	112	1.60				1200		80	32	320		480		800	32					
FACT Solution			10										10							

Some of the wavelengths used in the previous application note could not be used for the analysis of this sample as the difference in elemental composition created additional interferences. Wavelengths were therefore selected to provide minimal spectral interferences and a wide dynamic range for this sample. Details of wavelength selection and background correction used for each analyte are listed in Table 3.

Table 3. Wavelength selection, background correction, and calibration correlation coefficients.

Wavelength (nm)	View mode	Background Correction	Calibration Fit	Correlation Coefficient
Al 396.152	Axial	Fitted	Linear	1.000
B 182.577	Axial	Fitted	Rational	1.000
Ba 233.527	Radial	Fitted	Linear	0.998
Ca 396.847	Radial	Fitted	Linear	0.998
Cd 228.802	Radial	Fitted	Linear	0.998
Co 238.345	Radial	Fitted	Rational	1.000
Cr 276.653	Radial	Fitted	Linear	0.997
Cu 327.395	Radial	Fitted	Linear	1.000
Fe 259.940	Radial	Fitted	Linear	1.000
Li 610.365	Radial	Fitted	Linear	1.000
Mg 279.553	Radial	Off-Peak right	Linear	0.997
Mn 293.305	Radial	Fitted	Linear	1.000
Na 589.592	Radial	FACT	Rational	1.000
Ni 227.021	Radial	Fitted	Linear	0.999
P 178.222	Radial	Fitted	Linear	1.000
S 181.972	Radial	Fitted	Linear	0.998
Si 212.41	Axial	Fitted	Linear	0.997
Sn 189.925	Axial	Fitted	Linear	0.997
Ti 334.941	Axial	Fitted	Linear	0.998
Zn 206.200	Axial	Fitted	Linear	0.997

FACT is one of the background correction methods available in the Agilent ICP Expert software.² This easy-to-use spectral modeling technique accurately models complex analytical spectra that are often observed when analyzing challenging matrices or interferences by ICP-OES. FACT was used as the background correction method for the Na 589.592 nm line (Figure 3). To ensure accurate quantification of sodium in the sample, a Ba 10 mg/kg FACT interferent solution was included in the sequence. The solution was used to successfully correct the background interference from barium, as demonstrated in the spike recovery test.

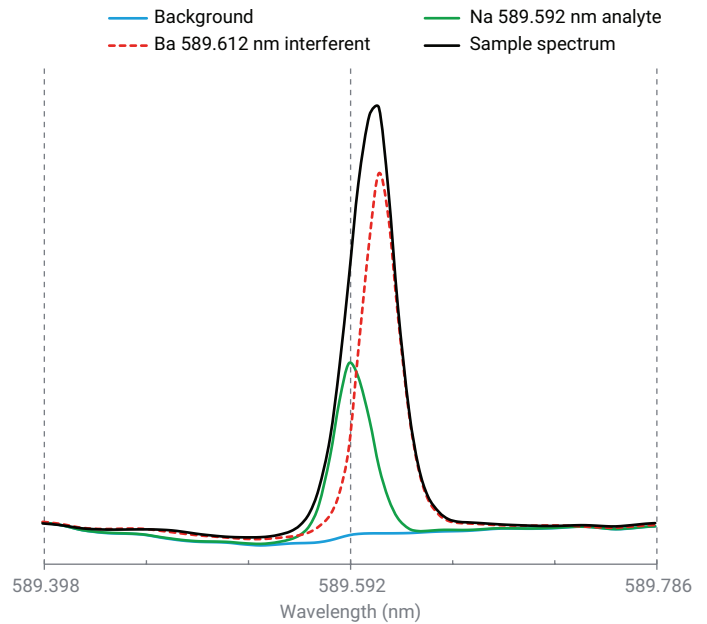


Figure 3. FACT model for Na 589.592 nm.

Results and discussion

Concentrations of the 20 target elements in the BM sample were quantified using the 5900 ICP-OES method. The quantitative results shown in Table 4 have been corrected for the dilution factor, and therefore are reported in mg/kg (or %) in the original solid BM sample. The values are the average results from three separate digestions of the sample. The low relative standard deviations (%RSDs) demonstrate the consistency and effectiveness of the digestion method. The results show the suitability of the 5900 ICP-OES fitted with the V-groove nebulizer for the analysis of both high and low concentration elements in the same run.

Evaluation of filtration

A test was performed to assess whether the analysis of the unfiltered samples affected the results. Three digestions of the BM sample were prepared and the sediment was left to settle for 48 hours. A 10 mL portion of the clear supernatant was collected from each digest. The samples were then stirred to re-suspend any insoluble solids and 10 mL of each digestate was filtered using a Captiva 0.45 µm syringe filter. The remainder of the sample was left in the vial for analysis.

These three sample portions, clear supernatant, filtered, and unfiltered, were analyzed. The differences in the concentration results were all within ± 5%. The results confirm that allowing the sample time to settle or filtering the sample during sample preparation is not necessary when using the V-groove nebulizer for the analysis.

Spike recovery study

To assess the robustness of the method, a digested sample was spiked with different elemental concentrations and analyzed. The difference between the concentration measured in the spiked samples and the unspiked samples was used to calculate the spike recoveries. For all the elements included in this study, the spike recoveries were well within ± 10% of the spiked concentration (Table 5).

Table 5. Spike recoveries for a black mass sample.

Element and Line (nm)	Concentration (mg/kg)				Spike Recovery (%)
	Solution	Spiked Solution	Difference	Spike	
Al 396.152	67.4	74.4	7.01	7.0	100
B 182.577	0.266	0.361	0.095	0.10	95
Ba 233.527	1.27	1.57	0.298	0.30	99
Ca 396.847	2.35	2.83	0.486	0.50	97
Cd 228.802	0.561	0.749	0.189	0.20	94
Co 238.345	855	935	80.4	75	107
Cr 276.653	0.113	0.323	0.210	0.20	105
Cu 327.395	58.1	62.8	4.73	5.0	95
Fe 259.940	22.2	24	1.97	2.0	99
Li 610.365	212	232	20.2	20	101
Mg 279.553	2.55	2.80	0.244	0.25	98
Mn 293.305	290	320	29.6	30	99
Na 589.592	1.88	4.81	2.93	3.0	98
Ni 227.021	633	682	49.0	50	98
P 178.222	21.3	23.2	1.96	2.0	98
S 181.972	4.84	5.91	1.06	1.0	106
Si 212.412	5.19	6.19	1.00	1.0	100
Sn 189.925	2.47	3.39	0.918	1.0	92
Ti 334.941	1.25	1.54	0.287	0.30	96
Zn 206.200	4.88	5.85	0.975	1.0	97

Table 4. Black mass sample analysis results in mg/kg, unless indicated as a percent (%).

Element	Al	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	Li
Mean Concentration (mg/kg)	0.79%	30	134	280	54	10.5%	12	0.65%	2,337	2.46%
RSD (%) n = 3	2.5	1.6	2.5	1.5	7.8	1.7	1.9	1.9	1.7	1.1
Element	Mg	Mn	Na	Ni	P	S	Si	Sn	Ti	Zn
Mean Concentration (mg/kg)	303	3.23%	232	7.09%	2,376	514	1,005	283	169	588
RSD (%) n = 3	1.0	1.3	6.2	1.4	2.0	1.8	7.5	2.5	1.6	4.5

Method detection limits

Method detection limits (MDLs) were determined by running the full calibration, followed by 10 repeat analyses of the digestion blank (Table 6). The MDL is defined as three times the mean standard deviation of the concentration readings for each element, multiplied by an average dilution factor of 125 (50 mL/0.4 g).

Table 6. Calculated method detection limits.

Element and Line (nm)	MDL (mg/kg)	Element and Line (nm)	MDL (mg/kg)
Al 396.152	0.65	Mg 279.553	0.02
B 182.577	0.20	Mn 293.305	0.75
Ba 233.527	0.25	Na 589.592	3.5
Ca 396.847	0.16	Ni 227.021	1.7
Cd 228.802	0.44	P 178.222	3.2
Co 238.345	0.91	S 181.972	3.1
Cr 276.653	1.0	Si 212.412	1.1
Cu 327.395	1.0	Sn 189.925	0.27
Fe 259.940	0.54	Ti 334.941	0.03
Li 610.365	2.5	Zn 206.200	0.14

Long term stability

To check the system and method stability, 8 g of the BM sample was acid-digested to produce 1 L of solution, which was then run for several hours. This sample was in constant recirculation and was gently stirred to keep the finer particles in suspension. A QC solution was prepared (Table 7) and measured after every 15 BM samples in this long-term measurement sequence. No argon humidifier was used.

The instrument ran continuously for 16 hours until the sample was depleted. No recalibration, internal standard correction, or re-slope was applied. Figure 4 shows the relative concentration of the QC solution, normalized against the first reading. Excellent long-term stability was achieved throughout the analysis period, which extended over 16 hours. All measurements were within $\pm 10\%$ of the expected value, with replicate precision better than 5% RSD in all cases.

Figure 4 demonstrates the stability of the 5900 ICP-OES and the suitability of the inert V-groove nebulizer for the routine QC analysis of BM samples or other challenging samples that contain suspended solids. Figure 5 shows the spray chamber and nebulizer at the end of the study. Neither the spray chamber nor the V-groove nebulizer was cleaned during the whole study. Despite the continued analysis of unfiltered BM samples, there were no blockages in the SIS due to the parallel path design of the nebulizer and optimized design of the sample channel.

Table 7. QC solution composition.

Element	Al	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	Li	Mg	Mn	Na	Ni	P	S	Si	Sn	Ti	Zn
Conc. (mg/L)	12	0.5	0.8	1.3	0.5	14	0.5	8.0	3.5	30	0.6	50	8	80	3	3	5	3	0.75	2.5

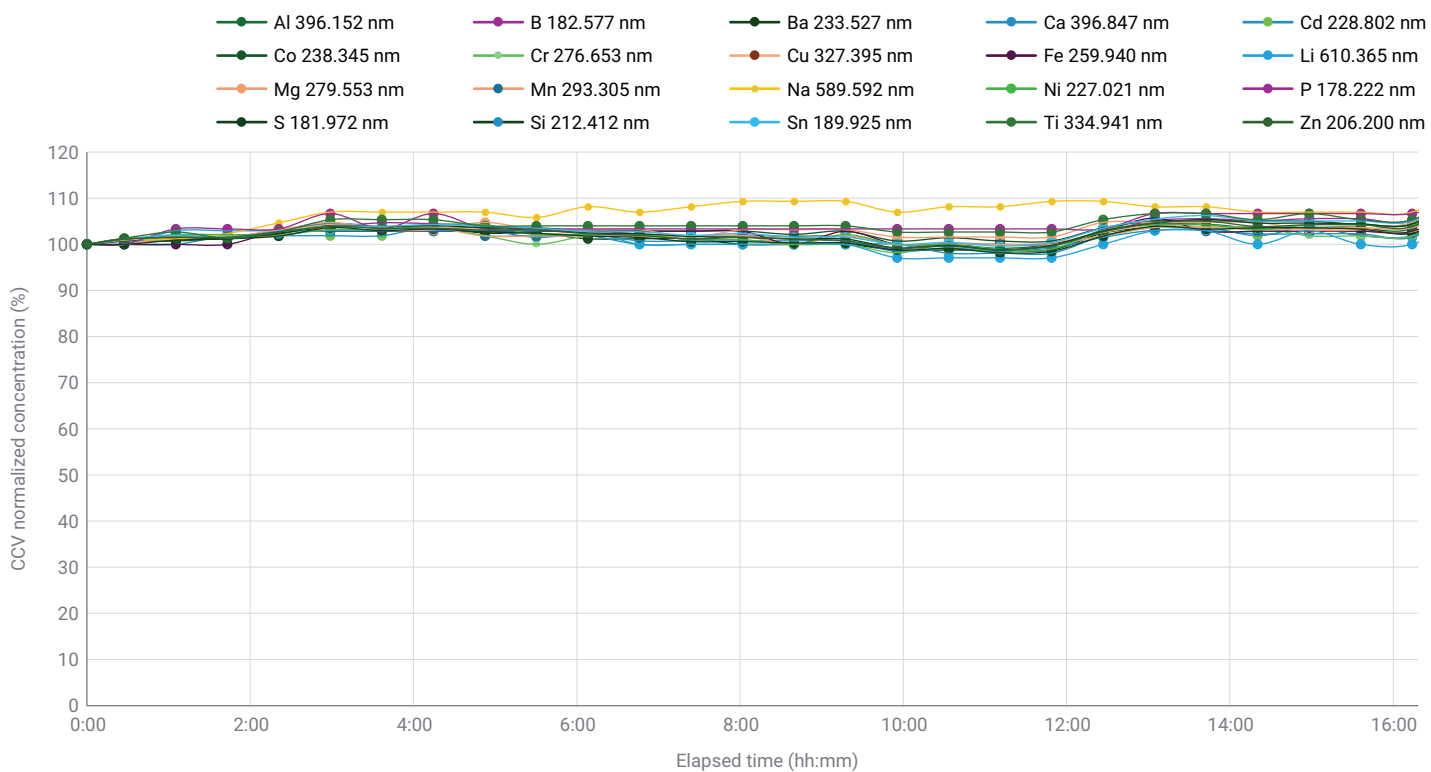


Figure 4. Long-term stability study over 16 hours showing normalized concentration (relative to the first reading) for a QC solution spiked with different elemental concentrations.



Figure 5. Spray chamber and inert Agilent V-groove nebulizer at the end of the study.

Conclusion

This study shows the suitability of the Agilent 5900 SVDV ICP-OES equipped with the Agilent inert V-groove nebulizer for the multi-element analysis of unfiltered acid-digests of black mass (BM) samples. The robust nebulizer is recommended for the routine analysis of samples with up to 30% total dissolved solids (TDS) and particle sizes less than 350 μm .

Excellent long-term stability was demonstrated when samples were analyzed over 16 hours. Measurements of the QC solution were within $\pm 10\%$ of the expected value, with precision better than 5% RSD. The spike recoveries were well within $\pm 10\%$ of the spiked concentration at both low and high concentration levels, confirming the accuracy of the method for the detection of a wide range of elemental concentrations in a single analysis. The V-groove nebulizer enabled the samples to be run for more than three weeks without any blockages, while maintaining a high level of accuracy and reducing the frequency of torch and nebulizer maintenance.

With an increased focus on recovering valuable metals from spent lithium-ion batteries, BM producers can confidently analyze key analytes in unfiltered sample digests directly using the V-groove nebulizer to enhance the robustness of the 5900 ICP-OES.

References

1. Li, S. Determination of Metals in Recycled Li-Ion Battery Samples by ICP-OES, *Agilent Technologies application note*, publication number **5994-5561EN, 2023**.
2. Real-time Spectral Correction of Complex Samples Using FACT Spectral Deconvolution Software, *Agilent Technologies technical overview*, publication number **5991-4837EN, 2021**.

Acknowledgments

Agilent Technologies would like to thank Mark Griffiths of Envirostream Australia for kindly supplying the black mass sample used throughout this study.

Agilent consumables

Description	Agilent Part Number
Inert V-groove, high-TDS nebulizer	G8020-69001
Inert spray chamber for Agilent 5000 series ICP-OES and MP-AES	G8014-68002
Easy-fit fully demountable DV torch with 2.4 mm id alumina (inert) injector	G8020-68022
PVC Solvaflex peristaltic pump tubing, gray/gray	3710035200
PVC Solvaflex peristaltic pump tubing, blue/blue	3710067900
Digestion tubes, 50 mL, with threaded cap, 500/pack	190047900
Watch glass, 41 mm diameter ribbed polypropylene	190037200
Captiva Econofilter, PES membrane, 25 mm dia. 0.45 µm pore size, 1,000/pack	5190-5276
Aluminum (Al) standard, 10,000 µg/mL, in 5% HNO ₃ , 100 mL	5190-8352
Boron (B) standard, 1,000 µg/mL, in H ₂ O, 100 mL	5190-8254
Barium (Ba) standard, 1,000 µg/mL, in 5% HNO ₃ , 100 mL	5190-8248
Calcium (Ca) standard, 1,000 µg/mL, in 5% HNO ₃ , 100 mL	5190-8329
Cadmium (Cd) standard, 1,000 µg/mL, in 5% HNO ₃ , 500 mL	5190-8328
Cobalt (Co) standard, 10,000 µg/mL, in 5% HNO ₃ , 100 mL	5190-8376
Chromium (Cr) standard, 1,000 µg/mL, in 5% HNO ₃ , 100 mL	5190-8344
Copper (Cu) standard, 10,000 µg/mL, in 5% HNO ₃ , 100 mL	5190-8378
Iron (Fe) standard, 1,000 µg/mL, in 5% HNO ₃ , 100 mL	5190-8471
Lithium (Li) standard, 10,000 µg/mL, in 5% HNO ₃ , 100 mL	5190-8408
Magnesium (Mg) standard, 1,000 µg/mL, in 5% HNO ₃ , 100 mL	5190-8481
Manganese (Mn) standard, 10,000 µg/mL in 5% HNO ₃ , 100 mL	5190-8414
Sodium (Na) standard, 1,000 µg/mL, in 5% HNO ₃ , 100 mL	5190-8525
Nickel (Ni) standard, 10,000 µg/mL, in 5% HNO ₃ , 100 mL	5190-8422
Phosphorus (P) standard, 1,000 µg/mL, in 5% HNO ₃ , 100 mL	5190-8499
Sulfur (S) standard, 1,000 µg/mL, in H ₂ O, 100 mL	5190-8529
Silicon (Si) standard, 1,000 µg/mL, in H ₂ O, 100 mL	5190-8521
Tin (Sn) standard, 1,000 µg/mL, in 20% HCl, 100 mL	5190-8543
Titanium (Ti) standard, 1,000 µg/mL, in H ₂ O, 100 mL	5190-8545
Zinc (Zn) standard, 1,000 µg/mL, in 5% HNO ₃ , 100 mL	5190-8557

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