Application Note

Chemicals & Electronics

Determination of Elemental Impurities in Copper Sulfate using ICP-OES

Accurate results using the Agilent 5800 VDV ICP-OES with smart tools

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Introduction

Due to its high electrical conductivity and low electric resistivity, copper (Cu) is one of the most crucial metals that is used in the manufacturing of electronic devices (*1*). Typically, the Cu present in many electrical components, such as printed circuit boards, is deposited via electroplating. Electroplating deposits positive Cu ions from a Cu electrolyte, such as copper sulfate ($CuSO_4$), onto the intended surface through the application of an electric current. Any other metal ions present in the electrolyte will also be electroplated onto the surface, which can adversely affect its conductivity. As lower conductivity properties of a component may reduce the quality of the final product, there is a clear need to control and measure impurity elements in electrolytes using a reliable technique.

A multi-elemental technique such as Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) facilitates fast, simultaneous measurements of $CuSO_4$, following minimal sample preparation. The technique is therefore suited for the quality control (QC) analysis of electrolytes, ensuring only the highest purity Cu is used for deposition applications.

The Agilent 5800 Vertical Dual View (VDV) ICP-OES is ideal for routine measurement of electrolytes, such as $CuSO_4$, and can be configured to process a large number of samples quickly and accurately. The 5800 and Agilent ICP Expert software with the optional Pro pack include several smart-tools that help with speed of analysis, method development, and data accuracy (*2–4*). Examples include:

- IntelliQuant Screening: a software feature that allows the user to perform a full semiquantitative spectrum scan of up to 70 elements in just a few seconds. The screening data provides sample insights that greatly simplify and speed up method development by removing the need for many conventional optimization steps.
- Intelligent Rinse: a software feature that adjusts rinse time depending on how long it takes to rinse out each element in a sample. The software applies the optimum rinse time by monitoring the intensities of nominated element wavelengths until they reach a user-specified threshold. Intelligent Rinse increases sample throughput while maintaining result accuracy.
- Early Maintenance Feedback (EMF): a smart instrument health tracker that alerts the user when maintenance is required based on sample load. EMF ensures that the instrument is delivering peak performance while reducing time wasted on carrying out unnecessary maintenance tasks.

In this study, the 5800 VDV ICP-OES with an Agilent SPS 4 autosampler was used to determine aluminum, arsenic, cadmium, calcium, chromium, cobalt, indium, iron, lead, magnesium, manganese, nickel, potassium, silver, sodium, thallium, tin, titanium, and zinc in electronic grade $CuSO_4$.

Experimental

Instrumentation

The 5800 VDV ICP-OES was fitted with a SeaSpray nebulizer, double-pass cyclonic spray chamber, and Agilent Easy-fit one-piece VDV torch with a 1.8 mm internal diameter (I.D.) injector. The SPS 4 autosampler was used for the automated delivery of samples to the instrument. The instrument was controlled using ICP Expert software with the optional Pro-pack that includes extra smart software functions like IntelliQuant Screening and Intelligent Rinse. Instrument operating parameters are listed in Table 1.

Table 1. Agilent 5800 VDV ICP-OES instrument and method parameters.

Parameter	Setting
Read Time (s)	25
Replicates	3
Sample Uptake Delay (s)	18
Stabilization Time (s)	12
Rinse Time (s)	Intelligent Rinse
Pump Speed (rpm)	12
Fast Pump	Enabled
RF Power (kW)	1.2
Auxiliary Flow (L/min)	1.00
Plasma Flow (L/min)	12.0
Nebulizer Flow (L/min)	0.7
Sample Pump Tubing	White-white
Waste Pump Tubing	Blue-blue
Background Correction	Fitted, FACT

Standard and sample preparation

Three different commercially available $CuSO_4$ samples were prepared for analysis. To prepare a 2% $CuSO_4$ solution ready for analysis by the 5800 ICP-OES, 1 g of each sample of electronic grade anhydrous $CuSO_4$ was dissolved in 50 mL of 18.2 MΩ de-ionized (DI) water (Merck Millipore). To evaluate the accuracy of the method, spike recoveries were performed on $CuSO_4$ sample 1 using 50 µg/L spikes for most elements and 200 µg/L spikes for elements present in the sample above 40 µg/L.

All calibration standards were prepared using Agilent single element calibration standard solutions at analyte concentrations between 5 and 1000 µg/L. Since all the required analytes were chemically stable in nitric acid (HNO_3), the mixed calibration standards were prepared from single element stocks in HNO_3. The solutions were matrix-matched using 99.99% purity $CuSO_4$ (Sigma-Aldrich) and diluted with 18.2 MΩ DI water (Merck Millipore) to form a final matrix of 2% $CuSO_4$. First, a multi-element stock solution was prepared and aliquoted at different concentrations into a standard tube and made up to 5 mL with DI water. The remainder of the 50 mL tube was then filled with 2.2% $CuSO_4$ in DI water to create a final matrix of 2% $CuSO_4$. The sample preparation procedure is outlined in Figure 1.

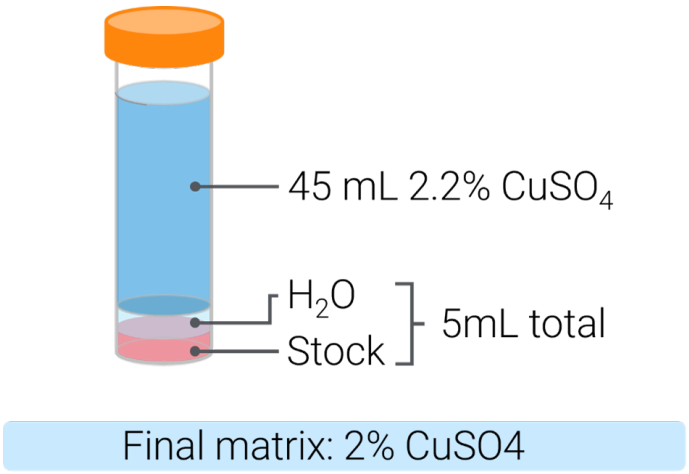

Figure 1. Standard matrix-matching preparation scheme for a 50 mL tube.

In the presence of a large quantity of sulfate ions (SO_4^{2-}) contributed by the $CuSO_4$, silver (Ag) and tin (Sn) are stable for a maximum of five hours. The standards should therefore be prepared on the same day as the analysis.

Method development

The IntelliQuant Screening software function was used to select wavelengths and estimate the concentration of elements in the samples. The analyst can use the periodic table 'heat map' view of the results (Figure 2) to identify an appropriate calibration range for each analyte, before starting the quantitative analysis. Reviewing the IntelliQuant Screening data is quick and easy, and the valuable sample-specific information provided by the software saves method development time.

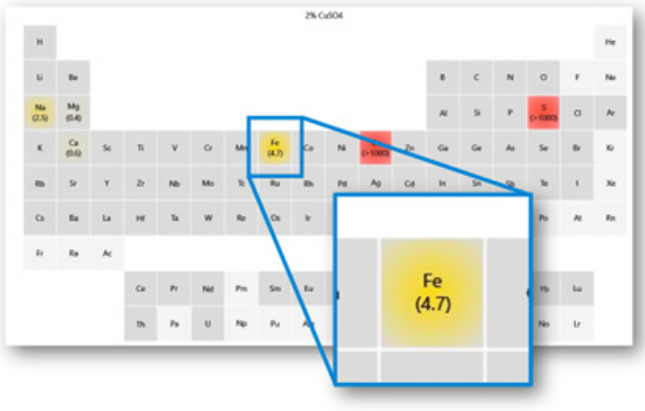

Figure 2. IntelliQuant Screening elemental 'heat map' of a $CuSO_4$ sample, with the semiquantitative concentration (in ppm) reported for any element present in the sample.

IntelliQuant Screening also provides a star-ranking system to indicate the best element wavelength to select for an analyte (Figure 3). The software also signals poor quality wavelengths that may be subject to spectral overlaps and other suspected interferences. The details provided by IntelliQuant help the analyst to set up the method for the quantitative analysis based on a specific sample or types of sample.

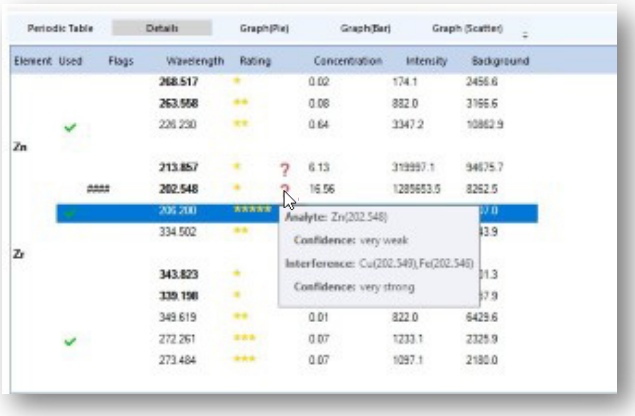

Figure 3. IntelliQuant star ranking system, indicating problematic wavelengths on some analyte lines. The information enables the analyst to select the best line for the quantitative method before starting the analysis.

Calibration

As shown in Table 2, all elements were calibrated between 5 and 1000 µg/L, and all calibration curves were linear over the range, as indicated by correlation coefficients between 0.99921 and 1.0000. A representative calibration curve for Co is shown in Figure 4.

Table 2. Background correction, internal standard, and calibration information.

Element and Wavelength (nm)	Background Correction	Calibration Range (µg/L)	Correlation Coefficient
Ag 328.068	Fitted	5 – 1000	1.00000
Al 237.312	Fitted	5 – 1000	1.00000
As 193.696	Fitted	5 – 1000	1.00000
Ca 396.847	Fitted	5 – 1000	1.00000
Cd 226.502	Fitted	5 – 1000	1.00000
Co 238.892	Fitted	5 – 1000	1.00000
Cr 267.716	Fitted	5 – 1000	1.00000
Fe 238.204	Fitted	5 – 1000	0.99993
In 410.176	Fitted	5 – 1000	0.99999
K 766.491	FACT	5 – 1000	0.99996
Mg 279.553	Fitted	5 – 1000	1.00000
Mn 257.610	Fitted	5 – 1000	1.00000
Na 589.592	Fitted	5 – 1000	0.99921
Ni 231.604	Fitted	5 – 1000	1.00000
Pb 220.353	Fitted	5 – 1000	0.99997
Sn 189.925	Fitted	5 – 1000	0.99998
Ti 337.280	Fitted	5 – 1000	1.00000
Tl 190.794	Fitted	5 – 1000	1.00000
Zn 206.200	Fitted	5 – 1000	1.00000

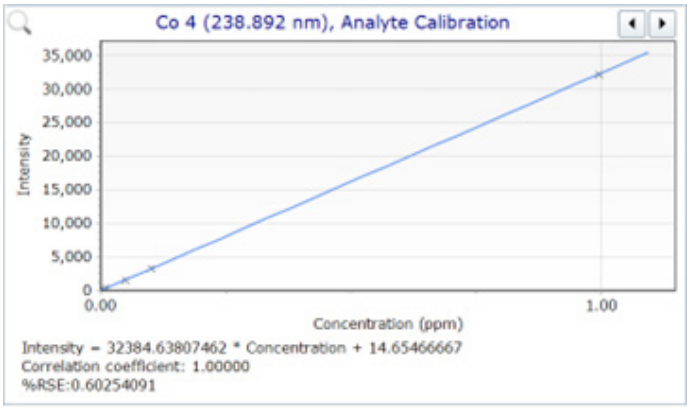

Figure 4. Calibration curve for Co 238.892 nm.

Automatic background correction

The ICP Expert software includes Fitted Background Correction (FBC) which corrects simple and complex background peaks automatically, requiring no input from the analyst. Figure 5 displays the accurate background correction of a Fe emission line at 238.863 nm by FBC. The software automatically applied correction enabled the low-level detection of Co 238.892 nm without manually placing off-peak correction markers, which can produce the wrong result in the presence of unexpected peaks.

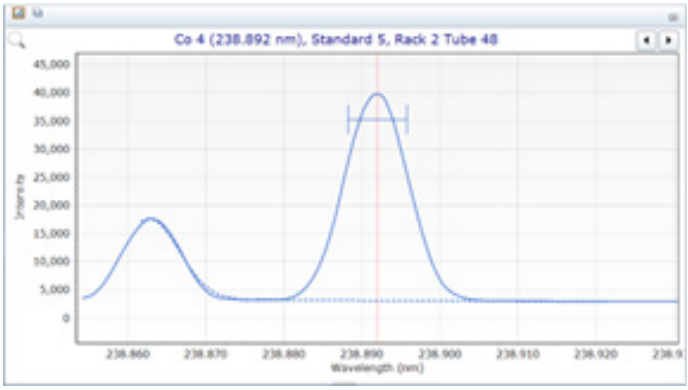

Figure 5. Automatic background correction using FBC for Co 238.892.

Automatic instrument health tracking

The 5800 instrument's EMF function uses a series of sensors and maintenance counters that alert the analyst when maintenance is required. Keeping the instrument in optimal condition reduces the need for QC remeasurements and improves instrument performance.

In this application, the high level of Cu in the samples resulted in Cu depositing on the outer tube of the torch after 10 hours of analysis time. The smart EMF software alerts the user to inspect the torch leading up to the user-defined time interval of 10 hours (Figure 6).

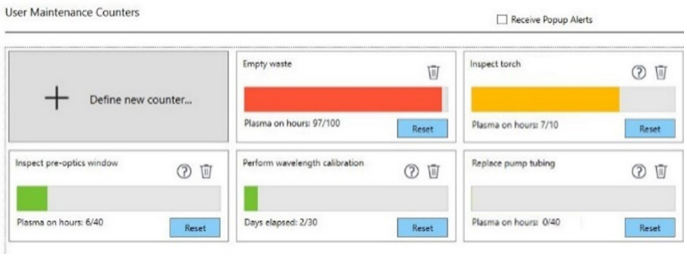

Figure 6. Early maintenance feedback counters.

Intelligent rinsing to increase throughput

The Intelligent Rinse software feature was used for this application. In cases where low-level analyte analysis is required, long rinse times are often used to minimize carry-over contamination. However, the same lengthy rinse is applied to all samples, regardless of whether it is required or not. In some cases, a five-second rinse time is sufficient to remove all carry-over, and the remaining rinse period is wasted time.

Intelligent Rinse adjusts the rinse time based on the actual time it takes to rinse out each element in a sample. The software monitors the intensities of analyte wavelengths against user-specified thresholds, minimizing time wasted on unnecessary rinsing. The optimized rinse function increases overall sample throughput while maintaining accurate results.

During a five-hour run, 130 samples were analyzed with Intelligent Rinse, compared with 103 samples when using the normal 60-second rinse function, as shown in Figure 7.

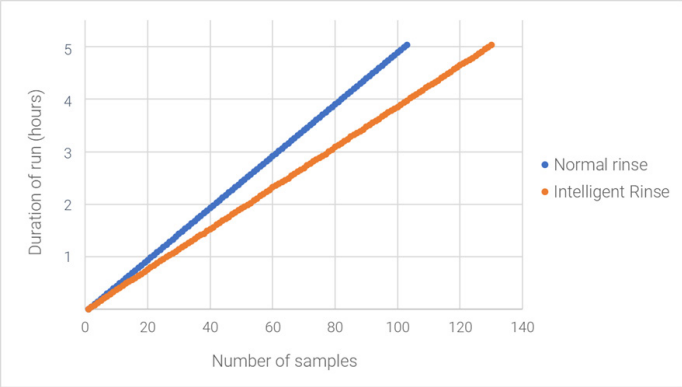

Figure 7. Number of samples analyzed in five hours using Intelligent Rinse (orange) compared to a normal 60 s rinse (blue).

Results and discussion

The method detection limits (MDLs) and spike results are displayed in Table 3. The MDLs were calculated by analyzing three sets of 10 method blank solutions over three non-consecutive days, and are based on 3 sigma of the 10 replicate measurements. $CuSO_4$ sample 1 was spiked at 50 µg/L (most elements) or 200 µg/L (higher concentration elements). All spike recoveries were within ±10% demonstrating the accuracy of the method for the analysis of $CuSO_4$ solutions.

Table 3. MDLs, measured spike concentration in $CuSO_4$ sample 1, and spike recoveries for all elements, before dilution factor applied.

Element and Wavelength (nm)	MDL (µg/L)	Measured Spike (µg/L)	Spike Recovery (%)
Ag 328.068	0.366	49.7	101
Al 396.152	0.787	52.2	99
As 193.696	2.86	48.9	99
Ca 396.847	8.43	48.1	95
Cd 226.502	0.0822	49.6	99
Co 238.892	0.279	50.4	101
Cr 267.716	0.357	50.8	101
Fe 238.204	1.54	213	107*
In 410.176	2.39	52.9	105
K 766.491	5.01	54.3	106
Mg 279.553	1.91	51.0	102
Mn 257.610	0.0813	50.7	101
Na 589.592	1.687	209	106*
Ni 231.604	0.693	50.5	101
Pb 220.353	1.00	206	103*
Sn 189.925	3.35	206	98*
Ti 337.280	0.675	49.5	100
Tl 190.794	2.77	49.0	97
Zn 206.200	1.04	199	100*

**Recovery of 200 µg/L spikes.*

The quantitative results of the three $CuSO_4$ samples, corrected for dilution, are shown in Table 4.

Table 4. Quantitative results of the three $CuSO_4$ samples (µg/kg), with 50x dilution factor applied.

Element and Wavelength (nm)	Sample 1	Sample 2	Sample 3
Ag 328.068	<MDL	<MDL	1696
Al 396.152	<MDL	3368	13800
As 193.696	<MDL	17148	30.8
Ca 396.847	<MDL	<MDL	<MDL
Cd 226.502	<MDL	88.3	<MDL
Co 238.892	91.2	17844	101.5
Cr 267.716	<MDL	1200	3587
Fe 238.204	2512	89823	<MDL
In 410.176	<MDL	200	<MDL
K 766.491	<MDL	<MDL	<MDL
Mg 279.553	1476	2612	<MDL
Mn 257.610	<MDL	715	<MDL
Na 589.592	2131	<MDL	52479
Ni 231.604	207	886237	4644
Pb 220.353	12459	23340	159
Sn 189.925	2754	<MDL	<MDL
Ti 337.280	<MDL	<MDL	<MDL
Tl 190.794	<MDL	<MDL	<MDL
Zn 206.200	25894	23756	18483

A QC block consisting of a Continuing Calibration Blank (CCB) and Continuing Calibration Verification (CCV) solution at 250 µg/L was measured immediately after calibration and then after every 10 samples. Table 5 shows the QC recoveries for all elements, which were within 100 ± 5%, and %RSDs of less than 1%, except for Sn, which was < 2.5%.

Table 5. Recoveries for all elements measured in QC solution during the analytical sequence by the Agilent 5800 VDV ICP-OES, n=3.

Element and Wavelength (nm)	Recovery (%)	%RSD
Ag 328.068	101	0.52
Al 396.152	104	0.20
As 193.696	102	0.49
Ca 396.847	102	0.29
Cd 226.502	102	0.10
Co 238.892	102	0.22
Cr 267.716	102	0.14
Fe 238.204	101	0.53
In 410.176	103	0.52
K 766.491	98	0.48
Mg 279.553	101	0.38
Mn 257.610	102	0.35
Na 589.592	93	0.41
Ni 231.604	102	0.18
Pb 220.353	100	0.38
Sn 189.925	95	2.24
Ti 337.280	102	0.27
Tl 190.794	101	0.80
Zn 206.200	101	0.06

Long-term stability

To assess the stability of the 5800 VDV ICP-OES, 138 solutions were measured over five hours without recalibration. The QC solution recoveries are plotted in Figure 8, showing the stability of all elements to be within ±10% throughout the run.

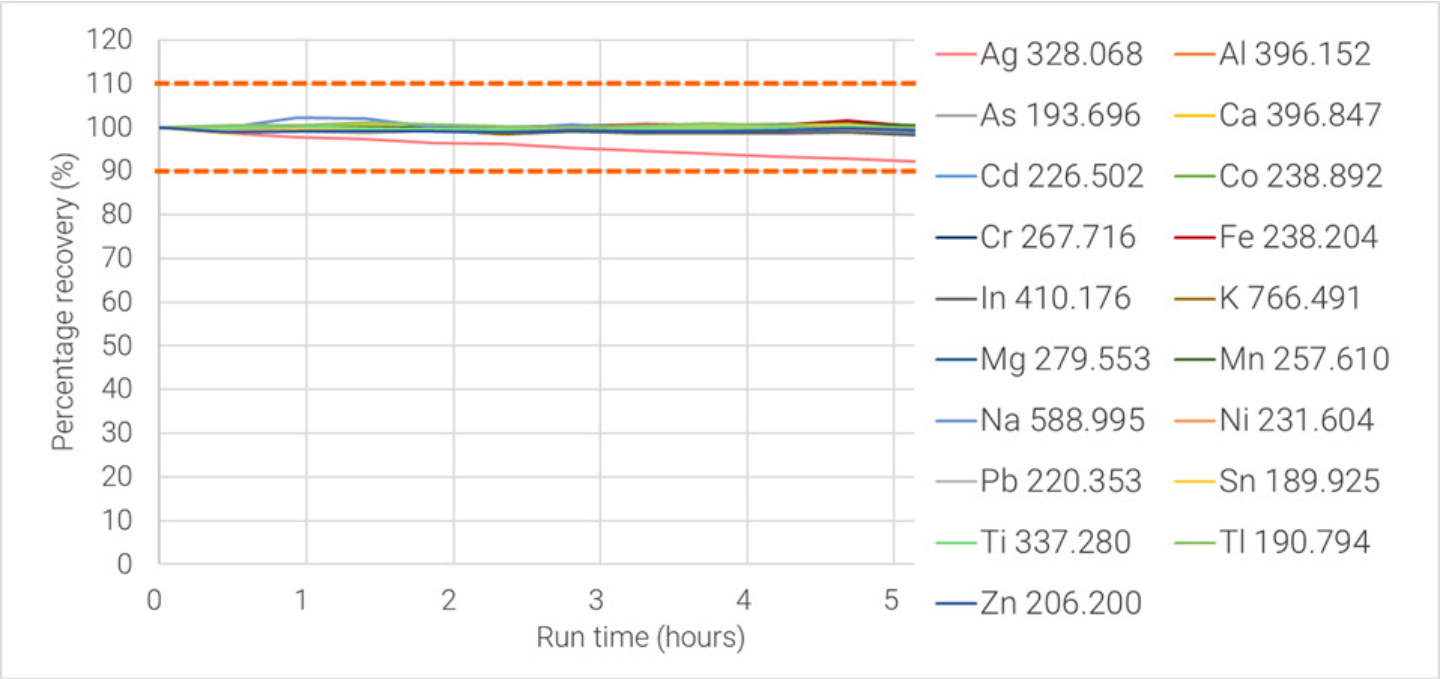

Figure 8. Recovery of QC solution for five hours, normalized.

Conclusion

The Agilent 5800 VDV ICP-OES was used for the accurate, precise, and stable analysis of multiple impurity elements in three $CuSO_4$ samples. Method development was greatly streamlined and simplified by use of the smart tools included in the ICP Expert Pro pack software.

- IntelliQuant Screening provided semiquantitative concentrations for all elements in each sample. It also signaled the presence on unexpected elements, aiding wavelength selection of analytes. By providing an estimation of the elemental content of the samples, a calibration range was quickly generated, reducing development time, argon consumption, and energy use.
- Intelligent Rinse allowed an additional 27 samples to be analyzed in the sequence through the monitoring of analyte intensities and rinsing each sample for an optimal time, improving sample analysis times while maintaining data accuracy.
- Early Maintenance Feedback alerted the analyst when maintenance was required based on actual use, maintaining instrument performance and reducing downtime.

The accuracy of the method was evaluated by conducting a sample spike recovery test of a $CuSO_4$ sample. Recoveries were within ±10% in all cases. Excellent precision was obtained as shown by the RSDs of less than 1% for most elements measured in the QC sample. The instrument also displayed excellent stability over a five-hour run without failing a single QC.

The study has shown that manufacturers, suppliers, and end users of electronic grade chemicals can rely on the 5800 VDV ICP-OES method for the measurement of elemental impurities in electronic grade chemicals.

References

1. Miura, S.; Honma, H. Advanced Copper Electroplating for Application of Electronics. *Surf. Coat. Technol.*, **2003**, 169–170, 91–95, https://doi.org/10.1016/s0257-8972(03)00165-8
2. Agilent ICP Expert Software: Powerful software with smart tools for ICP-OES, Agilent publication, 5994-1517EN
3. Agilent IntelliQuant Screening: Smarter and quicker semiquantitative ICP-OES analysis, Agilent publication, 5994-1518EN
4. Agilent Intelligent Rinse: Increase productivity and reduce errors, Agilent publication, 5991-8456EN

Note: The Agilent 5800 VDV ICP-OES requires ICP Expert Pro pack software to access IntelliQuant Screening and Intelligent Rinse. ICP Expert Pro pack software is standard with the Agilent 5900 SVDV system.

Agilent part numbers

Description	Part number
Easy-fit 1.8 mm semi-demountable torch for 5000 series VDV/SVDV ICP-OES	G8010-60228
Double-pass spray chamber, glass cyclonic design with ball joint socket and UniFit drain outlet, for Agilent 5000 series ICP-OES	G8010-60256
SeaSpray concentric glass nebulizer for 5000 series ICP-OES	G8010-60255
Peristaltic pump tubing, white/white, 12/pk	3710034400
Peristaltic pump tubing, blue/blue, 12/pk	3710034600
Agilent 1000 ppm single element stock solution for Ag, 500 mL	5190-8524
Agilent 1000 ppm single element stock solution for Al, 500 mL	5190-8243
Agilent 1000 ppm single element stock solution for As, 500 mL	5190-8247
Agilent 1000 ppm single element stock solution for Ca, 500 mL	5190-8330
Agilent 1000 ppm single element stock solution for Cd, 500 mL	5190-8328
Agilent 1000 ppm single element stock solution for Co, 500 mL	5190-8347
Agilent 1000 ppm single element stock solution for Cr, 500 mL	5190-8345
Agilent 1000 ppm single element stock solution for Fe, 500 mL	5190-8472
Agilent 1000 ppm single element stock solution for In, 500 mL	5190-8468
Agilent 1000 ppm single element stock solution for K, 500 mL	5190-8504
Agilent 1000 ppm single element stock solution for Mg, 500 mL	5190-8482
Agilent 1000 ppm single element stock solution for Mn, 500 mL	5190-8484
Agilent 1000 ppm single element stock solution for Na, 500 mL	5190-8526
Agilent 1000 ppm single element stock solution for Ni, 500 mL	5190-8492
Agilent 1000 ppm single element stock solution for Pb, 500 mL	5190-8476
Agilent 1000 ppm single element stock solution for Sn, 125 mL	ICP-050
Agilent 1000 ppm single element stock solution for Ti, 500 mL	5190-8546
Agilent 1000 ppm single element stock solution for Tl, 500 mL	5190-8538
Agilent 1000 ppm single element stock solution for Zn, 500 mL	5190-8558

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