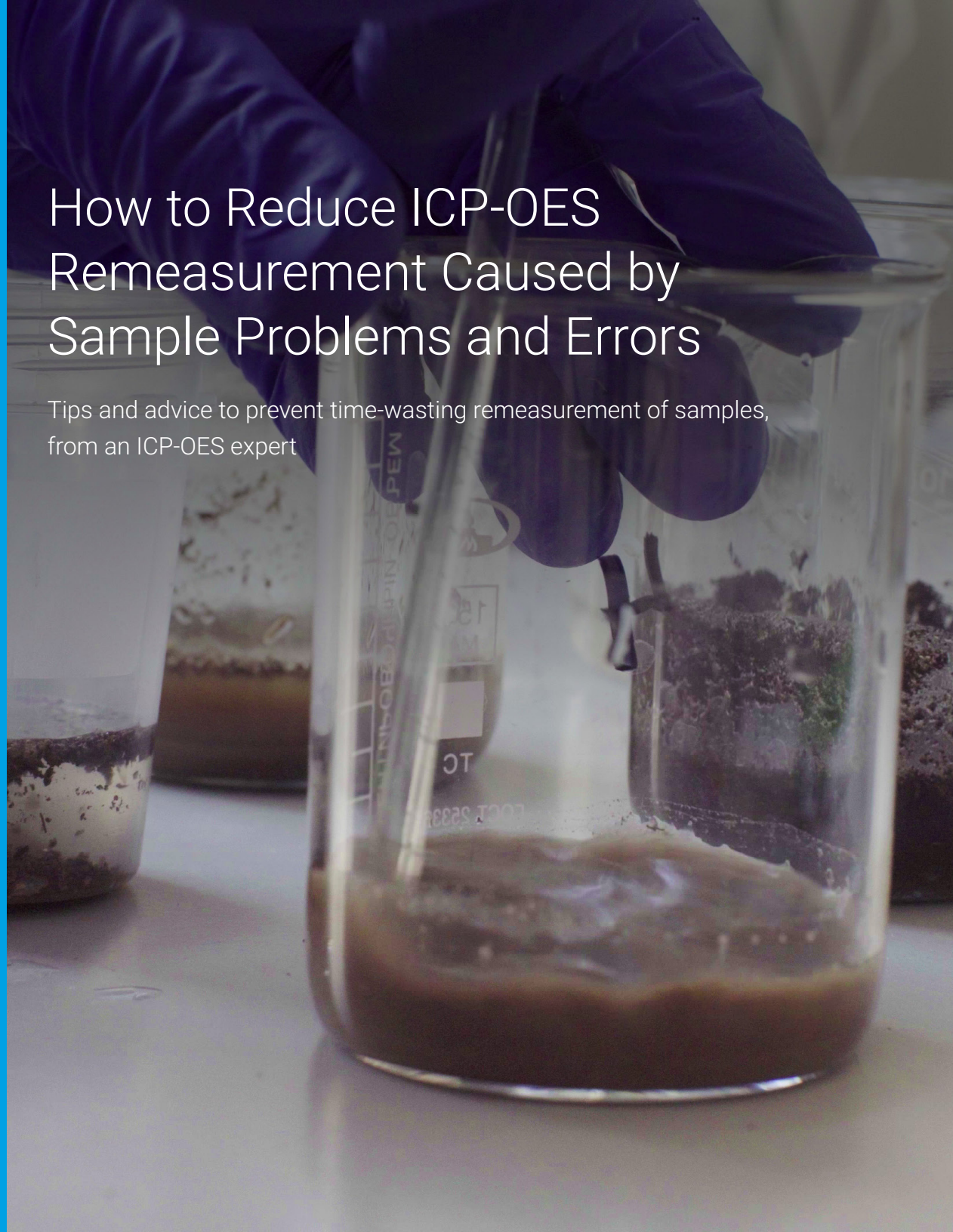


How to Reduce ICP-OES Remeasurement Caused by Sample Problems and Errors

Tips and advice to prevent time-wasting remeasurement of samples,
from an ICP-OES expert



Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) is a well-established technique for the measurement of elements in solution. ICP-OES is commonly used in the mining, food, agriculture, energy, chemical, environmental monitoring, and pharmaceutical industries. The technique delivers sensitive, accurate, and precise measurements of the concentration of elements in a wide range of sample types. From analyzing sludges and sediments, through to drinking water and wine, ICP-OES is fast and robust.

ICP-OES is just one of a suite of atomic spectroscopy techniques offered by Agilent. The origins of atomic spectroscopy lie in flame atomic absorption spectroscopy (FAAS), invented in the 1950s and still used in many labs today. At the other end of the family tree is Inductively Coupled Plasma Mass Spectrometry (ICP-MS). This technique is known for its high sensitivity, being able to measure elements at parts-per-trillion levels.

While the simple Beer–Lambert law is at the heart of all atomic spectroscopy techniques, most require a degree of knowledge and experience to achieve accurate and reproducible results. As instruments become more sophisticated, they can reduce the level of expertise required to do the analysis.

Modern cars have followed a similar development path. Features such as antilock braking, driver-assist technologies, and a multitude of monitoring systems have reduced the level of knowledge and skill required of the driver. Most people no longer carry the tool box that was needed for roadside repairs of cars in the 20th century. Similarly, current ICP-OES instruments offer a range of “smarts” that help the analyst identify and overcome problems. The analyst can then take action to avoid having to remeasure samples.

ICP-OES problems can be separated into three areas:

1. Problems caused by characteristics of the sample
2. Analytical mistakes made during sample preparation and measurement, and
3. Problems caused by something going wrong with the instrument.

In this e-book, Agilent Technologies ICP-OES Marketing Manager, Ross Ashdown, discusses ways laboratories can overcome sample-related ICP-OES problems. Using common quality control methods and advances in ICP-OES instrumentation, analysts can avoid having to remeasure samples and can be confident in getting the right answer the first time.

Q:

What are the common sample-related ICP-OES problems that you see in labs?

A:

Many of the problems are associated with all atomic spectroscopy techniques. They range from mistakes made when preparing calibration standards, sample mix-ups, and samples that have analyte concentrations that are higher than the calibration range. Then there are interferences. In all ICP-OES analysis, one particularly problematic source of interference is spectral interference.



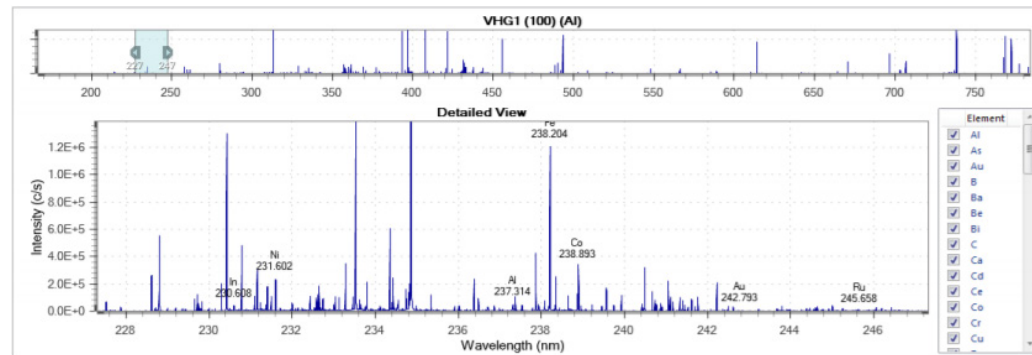
Q:

Can you explain more about spectral interferences?

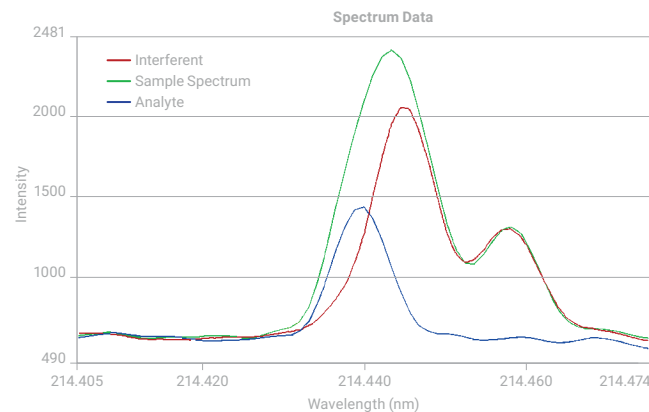
A:

Across the UV-Vis wavelength range, there are tens of thousands of elemental emission lines. These lines are created as an excited state atom or ion returns to ground state. Sometimes, emissions from different elements in the sample will occur at wavelengths that are close together.

An element that you either didn't know was there, or is present at a high concentration, might cause an erroneously high result for your analyte of interest. The diagram adjacent shows what happens.



Across the UV-Vis wavelength range (approximately 160 to 800 nm) there are tens of thousands of elemental emission lines. Shown here are the emission lines in just a 25 nm region from 225 nm to 250 nm.



This diagram illustrates how spectral interference occurs. The analyte of interest (shown in blue) has an emission line that is very close to another element (shown in red). The combined signal (shown in green) is measured as the emission for the analyte of interest. This causes an erroneously high result to be reported for that element.

Case Study

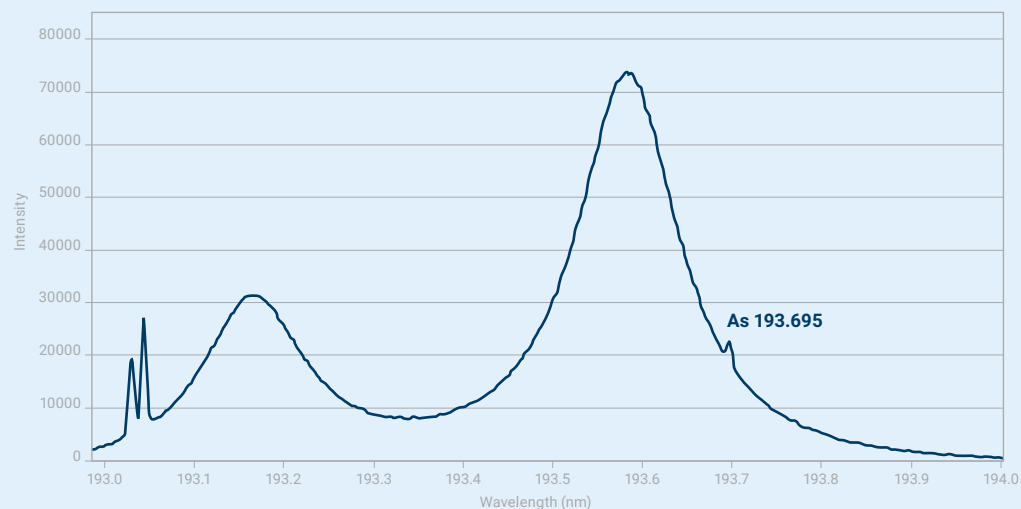
According to the US EPA Office of Technical Standards, labs measuring thallium in environmental samples are reporting falsely high results nearly 100% of the time. For arsenic, it's 25 to 50% of the time.

An EPA office of Technical Standards report¹ estimated that environmental data reported using ICP-OES may have a 25 to 50% false-positive rate for arsenic. This phenomenon still receives little attention and is not widely known in the environmental community.

Decision making based on data with a false-positive bias can result in costly, unnecessary response actions.

The potential for biased results on arsenic by ICP-OES is possible because relatively weak emission lines (wavelengths) for arsenic are located nearby or overlapped by one of several strong emission lines of aluminum. While US EPA method 6010 recommends the As193.696 nm emission line, the underlying background signal is

greatly affected by the presence of a broad and overlapping "auto-ionizing" (or dielectronic recombination) doublet of aluminum. This raised background signal ultimately reduces the detectability of arsenic in samples containing high concentrations of aluminum. The image below shows how the 193.696 nm emission line of a 2 mg/L arsenic sample is barely visible in a solution containing 5000 mg/L aluminum.



1. United States Environmental Protection Agency (US EPA). (2001a). OTS Alert #2, Use of the ICP analytical method (CLP SOW ILM04.1, SW-846 6010, MCAWW 200.7) for drinking water samples may result in false-positive detections of arsenic, lead, and/or thallium above their respective MCLs. Office of Technical Standards. Washington, DC.

Q:

How can you overcome spectral interferences to ensure that you get the right answers for a sample?

A:

If an analyst knows, or suspects, they are dealing with spectral interferences, then a simple first strategy is to measure multiple emission lines for each element.

Using an alternate emission line and avoiding the interference is one way to overcome spectral interference in complex matrix samples. It is very rare for multiple emission lines from the same element to be interfered with, so when there are multiple emission lines with the same result, discard outliers and choose the result from the remaining lines that give the best analytical performance.

But how can the analyst identify spectral overlap among a large and complex data set?

"The Agilent 5800 and 5900 ICP-OES use data analytics, programmed into ICP Expert, to do what an experienced analyst would do to identify spectral interferences."

The Agilent 5800 and 5900 ICP-OES feature a function called IntelliQuant that captures all emissions for a sample across the whole wavelength range. The function uses data analytics to do what an experienced analyst would do to identify spectral interferences.

When using multiple wavelengths for an element, the analyst can set a %RSD threshold. If the threshold is exceeded for a wavelength, the analyst will be alerted. The analyst can then use the IntelliQuant star rating to determine if there is interference at that wavelength.

IntelliQuant automatically performance ranks each emission line based on proximity and magnitude of interference signal to analyte signal, making it easier for the analyst to report the most accurate result.

For regulated or validated methods, if an analyst knows they have spectral interferences, then they may prepare solutions and develop Inter Element Correction (IEC) factors to compensate for them. Alternatively, spectral deconvolution models can be used to remove the contribution of the interfering element.



Element	Used	Flags	Wavelength	Rating	Concentration	Intensity	Background
As	✓		188.980	★★★★★	283.68	6054.4	11094.8
			193.696	★	150.49	2685.5	60215.4
			197.198	★	147.93	2780.4	15929.1
			228.812	★	197.55	1659.7	2916.2
			234.984	★	144.97	3122.3	5965.1
			200.334	★	271.94	1674.9	24115.1
			198.971	★	235.05	1170.7	18294.9
			278.022	★	75.87	684.1	12687.4
			175.800	★	276.80	112.1	1368.3
			180.554	★	147.58	112.8	1899.6

IntelliQuant gives a star rating to the result from each wavelength. You can then easily select the best wavelength to use for reporting or for adjusting a method. In this case, the As line at 193.696 nm suffers from interference from Al, so IntelliQuant has rated the 188.980 nm line as the best to use.

What about calibration problems? What do you typically see going wrong in labs?

A:

Calibration problems are a common cause of analytical errors. We often see analysts struggling to work out what's wrong with their results, only to realize that it was caused by something as simple as an error during standard preparation. It could be a pipette that is out of calibration, or accidental selection of the wrong stock solution.

Eliminating human error is key to reducing calibration errors. Automate what you can—autodilutors can prepare calibration standards. Multi-element standards can be bought, rather than made. Review your processes, aiming to make them mistake-proof. The Japanese *Poka-yoke*³ approach is useful for this purpose. Document the final process and train your analysts on it.

Regulatory bodies like the US EPA are driving good analytical practice; their methods have built-in quality control (QC) that helps with finding calibration errors.

For example, US EPA methods include both an Initial Calibration Verification (ICV) test and a Continuing Calibration Verification (CCV) test. These are used to ensure the validity of the calibration. Modern instruments will help set up methods that build in these tests. Use these quality control measures for nonregulated methods to ensure calibration quality.

A simple measure of the quality of the calibration is the correlation coefficient, the R value. R is a measure of the linearity of the calibration. It is typically calculated by the instrument software and presented on the calibration curve. A better indication of calibration quality is % Relative Standard Error (%RSE). Large contract labs typically set limits for this value to guide their analysts about whether a calibration is suitable or not. Alert thresholds can be set within the software of the new Agilent 5800 and 5900 ICP-OES instruments.

Laboratory publications that cover spectroscopy are useful sources of information too. They help you keep up-to-date with instrumentation and techniques that can help eliminate calibration errors. The AOAC Official Methods of Analysis and the ASTM methods are also useful sources of information.

A good tip for ICP-OES analysis is to use a less sensitive wavelength for an element to extend the linear range of your calibration curve. You can also choose to use the radial (side-on) view of a dual-view ICP-OES to achieve the same thing. Agilent instruments will automatically recommend the best wavelength, based on what's in the sample (determined using the IntelliQuant function). This approach helps prevent time-wasting sample remeasurements due to over-range results.



Multi-element standards reduce the risk of mistakes during standard solution preparation. Agilent offers a wide range of multi-element standards at: www.agilent.com/en/product/chemical-standards

Q:

Is contamination still an issue in labs these days?

A:

Yes, contamination still causes problems with elemental analysis. Obviously, it's more of a problem with highly sensitive techniques like ICP-MS, but contamination also impacts ICP-OES. It can come from a range of sources.

Poor lab practices can cause contamination problems, particularly if you are looking for trace levels of analytes in your sample. For example, you may be doing an acid digestion in a microwave vessel. If you didn't clean the microwave vessel well after a previous sample, you are going to get carryover that will contaminate the next sample.

You can detect contamination caused by inadequate cleaning by including a preparation blank in your samples. A preparation blank is a blank solution that has been taken through the same sample preparation process as your samples. By setting a QC threshold for the preparation blank, any contamination will be flagged when it is analyzed during the run.

"A surprise high-matrix sample in the sample batch can lead to contamination of the next sample due to carryover of highly adsorptive or "sticky" elements such as boron, molybdenum, or tungsten."

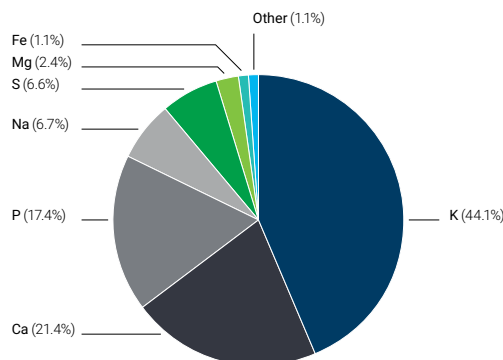
Contamination can also be introduced by the previously analyzed sample. A surprise high-matrix sample in the sample batch can lead to contamination of the next sample particularly with the carryover of highly adsorptive or "sticky" elements such as boron, molybdenum, or tungsten. These elements stick to the components of the sample introduction system. These situations cause erroneous results in subsequent samples.

ICP-OES instruments offer ways to overcome sample-to-sample contamination. Some offer automated rinse functions that monitor the signal during the rinse cycle. Agilent 5800 and 5900 ICP-OES instruments include an Intelligent Rinse feature that automatically pumps rinse solution until the signal drops below a set threshold.

Using dual rinse stations will also help with contamination from sticky elements. One rinse solution will be a strong acid or complexing agent that removes the sticky elements from the sample introduction system. The second rinse solution should have the same matrix as the samples you are analyzing. Switching valves can also help by minimizing exposure of the sample introduction system to a sample matrix.

If you have a completely unknown sample, it is worthwhile performing a quick scan to ascertain what elements are in the sample, and what their concentrations are.

Agilent 5800 and 5900 instruments have an IntelliQuant Screening function that can quickly determine how much of over 70 elements are in a solution. It takes as little as 15 seconds per sample and you may discover incompatible elements in the sample. With this knowledge, you can change your method to accommodate the incompatibility. It will save hours of wasted time preparing and remeasuring samples.



The IntelliQuant Screen function of Agilent ICP-OES instruments can determine the relative concentration of elements in a sample in just 5 seconds.

Q:

You mentioned sample preparation mistakes being sources of error. What can be done about these?

A:

Purchased Certified Reference Materials (CRM) are great for highlighting sample preparation problems (and even mix-ups). There are many suppliers, and they come in a wide range of matrix types. You can usually find one that is close to the matrix of your samples. For example, a tomato leaf reference material can be used for a range of plants, as this is a similar matrix.

Reference material should go through exactly the same sample preparation process as your samples. If you get results that match the certified results for each element, then you know that your sample preparation process is good and your results will be accurate.



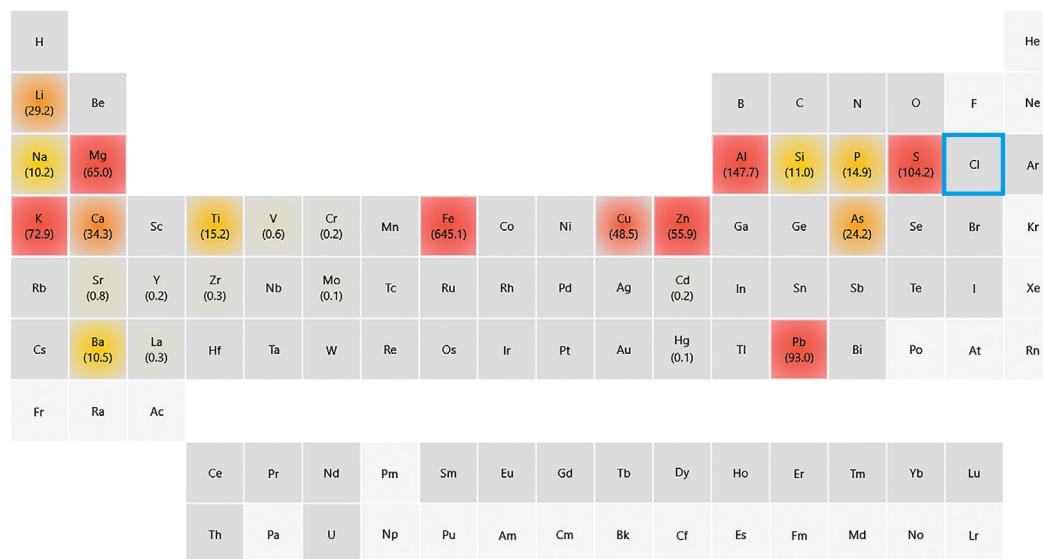
A secondary benefit of using a certified reference is to check how good your calibration is. If you get the right results for the CRM, then you can trust your calibration.

One of the biggest reasons for having to remeasure samples is due to mistakes made during acid digestion. In this situation, someone forgets to put in one of the acids or puts in the wrong acid. This is a common mistake made by busy technicians.

"A common reason for having to remeasure samples is mistakes made during sample digestion. A busy analyst can easily forget to add an acid or put in the wrong acid. There's an easy way to detect such a mistake—before you have many samples to remeasure."

A great tip to find such mistakes is to monitor elements that should be there if the sample preparation procedure has been done correctly. For example, if hydrochloric acid should have been added, then monitor the chlorine content of your samples. For phosphoric acid it's phosphorus, and for nitric acid it's nitrogen. If those elements don't appear in the results, or their levels aren't high enough, then you know someone forgot to put the acid in during the digest process.

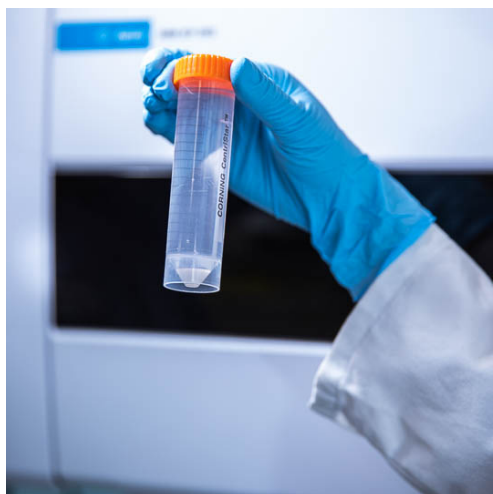
Again, the IntelliQuant function is very useful for detecting sample preparation mistakes. It can measure the concentration of around 70 elements in a sample. You can quickly run your eye over the color-coded periodic table it produces for each sample and see if the elements that should have been contributed by the acids during digest are there. If you routinely do this for a preparation blank solution at the start of your run, it's an early warning system. If there's no chlorine or sulfur or whatever element should be in there from the digestion acid, then you can stop the run before you've wasted all that time analyzing samples that have been incorrectly prepared.



Oops! Someone forgot to put HCl acid in the sample for digestion. The IntelliQuant function determines up to 70 elements in a sample, displaying relative concentrations of elements as a heat map. Elements shaded red are in high concentration, elements in orange are in mid-range concentration and those in yellow are in low concentrations. Unshaded elements are not at detectable levels in the sample. In this case, Cl is missing, indicating that HCl was not used during sample preparation.

The IntelliQuant function can also be used to troubleshoot sample chemistry problems. For example, lead and barium can both precipitate out of solution when there are high levels of sulfur in a sample. The sulfur is commonly introduced as sulfuric acid to digest the sample. The precipitate appears at the bottom of the container and is not aspirated into the plasma. This situation results in low results for those two elements. If you are getting low recoveries for lead and barium for your certified reference material samples, then you can use the IntelliQuant function to troubleshoot. If it shows high levels of sulfur and low levels of lead and barium — there's your problem.

Standard reference material suppliers have a lot of information about chemical incompatibilities. You can use this information during method development or if you are troubleshooting problems with results.



Periodic Table																						
Details																						
Graph(Pie)																						
Graph(Bar)																						
Ba and Pb 1 ppm H2SO4 1%																						
H																	He					
Li	Be																B	C	N	O	F	Ne
Na	Mg																Al	Si	P	S (>1000)	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr					
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe					
Cs	Ba (0.8)	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb (0.7)	Bi	Po	At	Rn					
Fr	Ra	Ac																				
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu						
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr						

High levels of sulfur cause the precipitation of barium sulfate and lead sulfate, resulting in erroneously low results for Ba and Pb.

Q:

What about sample mix-ups?
How can you prevent those?

A:

In terms of sample mix-ups, the common cause is mixing up samples when placing them in an autosampler rack. Mixing up the racks when loading them onto the autosampler can also be a problem.

Using a sample barcoding system can help minimize mix-ups. By bar coding a sample test tube at the very start of a sample preparation, then using that same test tube throughout sample preparation, through to analysis, you can minimize sample mix ups. The Agilent ICP Expert software is compatible with bar code readers. This assists in reducing sample mix ups that then lead to sample remeasurement. Using QC solutions and sample duplicates in your run can also help.

Some labs have started doing sample digestion in the same tube as they then use in the autosampler. They use a microwave digester or a hot block sample digestion system, transferring the tube that the sample has been digested in straight into autosampler racks. This eliminates a sample transfer step, reducing the chances of a mix-up. If the digest tube has a bar code on it, then you can transfer it straight to the autosampler rack and have the sample added to the batch automatically.



Q:

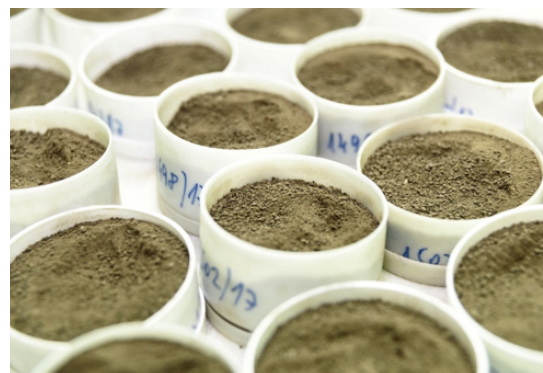
High-matrix samples have been difficult to analyze via most atomic techniques for a long time. What innovations have you seen to make it easier?

A:

Analysts will often have to digest a large quantity of a sample to get good recoveries on trace levels of elements in that sample. Trace mercury in food samples or trace gold in mineral samples are a good example of this situation. This approach might result in the sample having total dissolved solids content greater than 20%. These solids can play havoc with the sample introduction system and the torch of an ICP-OES as they build up and cause blockages.

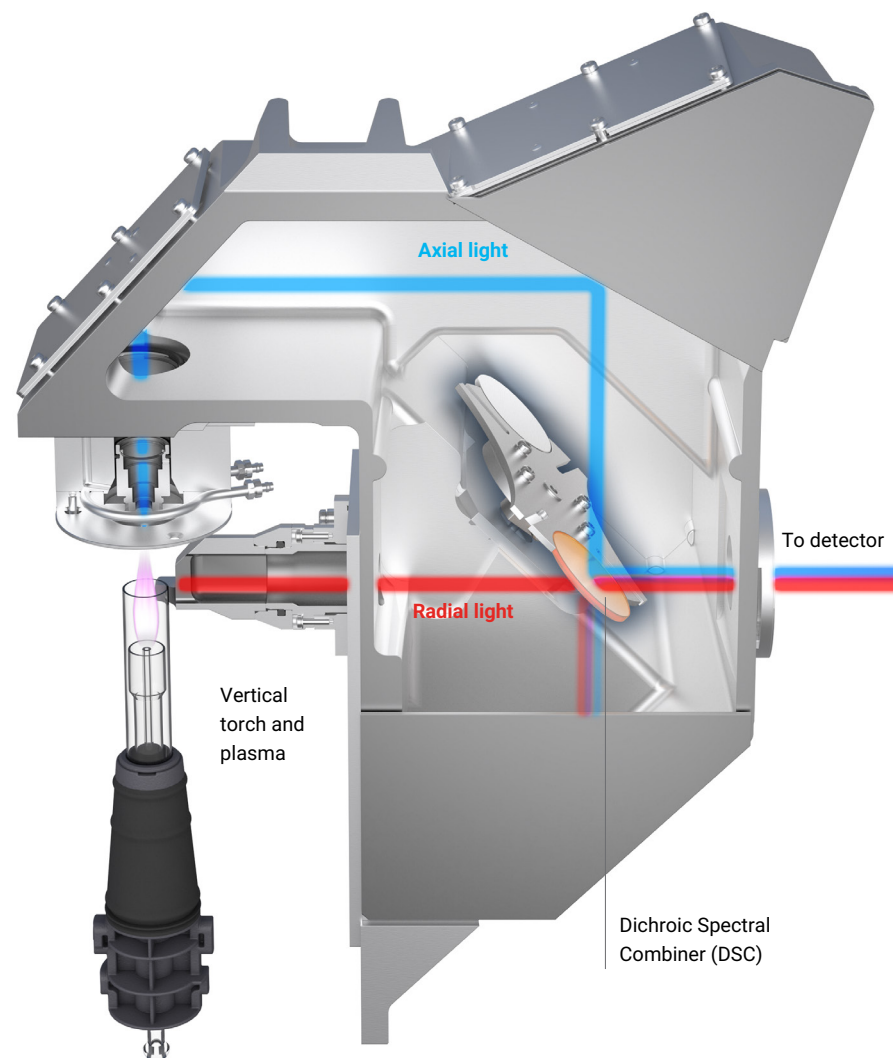
The biggest change in ICP-OES instrumentation that helps with the analysis of these high-matrix samples is the vertical torch. A horizontal torch will quickly suffer from the accumulation of salts when aspirating high-matrix samples. Vertical torches are a lot more resistant to this problem.

Most ICP-OES instruments are now dual view. You can elect to use either an axial view of the torch or a radial view, depending on the element you are looking for. An axial view will capture light by looking down the length of the plasma. A radial view will capture light side-on from the plasma. A radial view is best for elements that emit a lot of light or that are likely to be in high concentration. Conversely, an axial view will capture the most light from poorly emitting elements or those elements at trace levels. The problem is that switching views during a run can add wasted time to the analysis. We've fixed that with a clever optical design, first introduced in our 5100 instrument and now in our 5900 instrument.



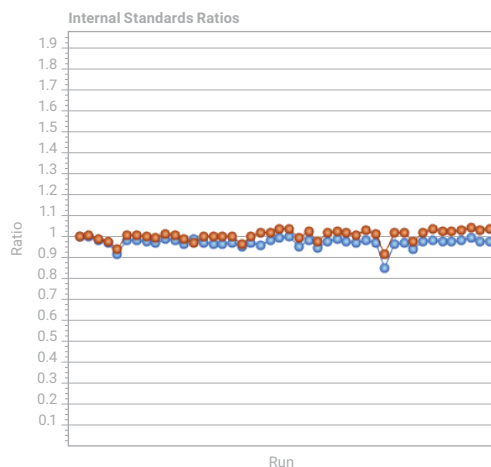
"The biggest change in ICP-OES instrumentation that helps with the analysis of these high matrix samples is the vertical torch, with the option of a radial or axial view. A horizontal torch will quickly suffer from the accumulation of salts when aspirating high matrix samples. Vertical torches are a lot more resistant to this problem."

We invented a special optical component called the dichroic spectral combiner. This was included in our 5110 instrument and is standard in our 5900 instrument. This component can capture light from both the axial view and the radial view of the torch at the same time (see the figure, adjacent). When you are setting up the run, the instrument automatically selects the view of the plasma to use for each element you select. Say, for example, you are analyzing abundant elements such as potassium and sodium, as well as trace levels of magnesium and boron. This situation is common for agricultural samples. The 5900 instrument will automatically select a radial view for the measurement of potassium and sodium, and an axial view for the trace elements. The Agilent IntelliQuant Screening function is also useful in this situation. You can use it to quickly screen samples to see which elements are in the sample, and in what proportions. You can then adjust your method, or dilute the sample, to get around problems like samples that are more concentrated than your calibration range.



The Agilent 5900 Agilent ICP-OES instrument includes a special optical component, the Dichroic Spectral Combiner (DSC), shown in orange in this diagram. It allows emissions from both the axial and radial plasma views to be measured at the same time. This approach represents a huge time saving compared to measuring each view separately.

"If you forget to fill up the internal standard bottle, the internal standard monitor will highlight this problem."



Monitor all your internal standards live through a graphical display to rapidly understand what is happening in your sample. In this example we see the monitoring of 2 internal standards (red line = Sc, blue line = Y) during a run – the dip of the trend line below a ratio of 1 indicates possible signal suppression alerting the operator that internal standard correction will be needed for that sample.

Internal standards are commonly used with high-matrix samples. This is particularly the case if your calibration standards aren't matrix-matched to your samples. By monitoring the results of the internal standards, the software will automatically correct your sample results for any signal suppression caused by the high-matrix samples.

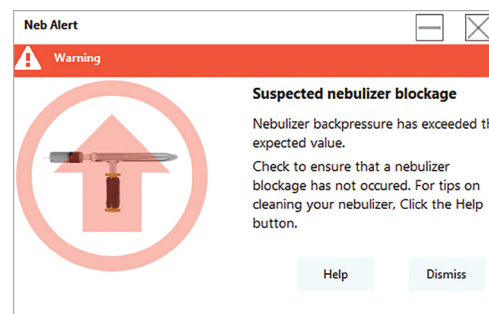
Agilent 5800 and 5900 instruments have a function that monitors and displays the trend in internal standard emission over the course of a run. If you can see that the emission of

the internal standard is going down, then you know that the signal is being suppressed by the high-matrix samples. You can choose to rely on the automated internal standard correction, or you can dilute the sample to reduce the suppression.

The internal standard monitor is also great for the busy analyst juggling multiple functions at once. Being in a busy, stressful environment makes it easy to forget to do the smallest of tasks. It is conceivable that you may forget to fill up the internal standard bottle. If the internal standard runs out, the internal standard monitor will show a dip.

We've also introduced another function called Outlier Conditional Formatting (OCF). Using this function, you can set a threshold value for the internal standard results, with any results outside of this threshold being immediately flagged.

High-matrix samples can cause the deposition of crystalline particles onto components of the sample introduction system. These crystals will gradually lead to blockages and reduced analytical signal. Blocked nebulizers can cause ICP-OES failure and the subsequent need for sample remeasurement. The "Neb Alert" feature in the Agilent 5800 and 5900 instruments utilizes smart sensors that monitor the nebulizer argon pressure. If there is a nebulizer blockage, the analyst is alerted. Leakage from a nebulizer gas line also triggers an alert.



We've also built smarts into the Agilent 5800 and 5900 instruments that facilitate a new feature called Early Maintenance Feedback (EMF). This feature allows alerts to be set for instrument use based metrics.

This feature allows alerts to be set to remind the analyst when to:

- clean the torch, spray chamber, nebulizer
- replace pump tubing
- clean/change the pre-optics window
- clean the switching valve
- perform a wavelength calibration

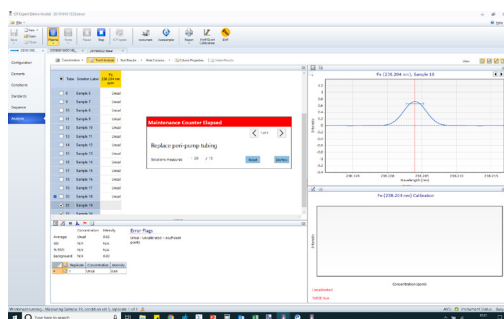
These alerts are based on usage, rather than at set time intervals, allowing you to optimize your maintenance schedule.

Q:

What other built-in monitoring do modern instruments offer to save time in the lab?

A:

Most labs do instrument cleaning and maintenance on a time-based schedule to reduce incidence of QC failures. However, for labs with a variable sample load, this could mean cleaning after just 100 samples in a week. For a high-volume lab, it could mean cleaning after measuring 5000 samples in a week. It's much better to schedule maintenance based on usage, just like car servicing.



The 5800 and 5900 ICP-OES instruments have smart instrument health tracking functionality. You'll be prompted to perform maintenance activities, based on the number of samples you set as the threshold.



Q:

Samples that are beyond the range of a calibration are another problem that has been around for a long time. Is there anything new out there that can help?

A:

Typically, an analyst faced with an over-range sample will have to dilute the sample and rerun it. If you are running many unknown or atypical samples, this could mean much wasted time diluting and rerunning samples.

Modern ICP-OES instruments will usually allow you to select multiple emission lines for the elements you are measuring and, as I mentioned earlier, this is a good practice for all methods. If the emission line of interest is saturated, you can switch to a less sensitive line for that analyte. You then avoid the need to dilute the sample. You will have to run a higher standard, to check for linearity, but you save time by not having to dilute then run the sample again.

Again, our IntelliQuant function really pays off in this situation. Using IntelliQuant Screening to preview samples, you can quickly determine if there are any high concentrations of particular elements. You can then either opt to dilute a sample before the sample run, or you can switch to a less sensitive line for that element. IntelliQuant will recommend the wavelength to use based on what it finds in the sample.

There are autodilutors like the ESI prepFAST that will automatically dilute a sample if it's over range. If the instrument flags a sample as being over range, the prepFAST will automatically include that sample at the end of the run, diluted by a suitable amount to bring it into the calibration range. If you've used IntelliQuant to determine the estimated element concentration in a sample, you can set up a predetermined dilution level. If you are having to dilute and remeasure samples a lot, these systems can quickly pay for themselves.



"If the emission line of interest is saturated, you can switch to a less sensitive line for that analyte and avoid the need to dilute."

Which ICP-OES best meets your needs?



Agilent 5800 ICP-OES

The 5800 has an ecosystem of embedded sensors and powerful processors, with smart algorithms and diagnostics, that identify problems that could impact results, preempt maintenance, and automate troubleshooting. Always working behind the scenes, the 5800 thinks like an expert, and can make recommendations and solve problems before they happen. This smart functionality reduces the number of samples you have to remeasure and gives you more confidence in your results.

Learn more: www.agilent.com/chem/5800icpoes

Agilent 5900 ICP-OES

The 5900 includes the smart features of the 5800, but offers the fastest sample measurement time of any ICP-OES, allowing you to increase revenue. The fast sample measurement time results in the lowest argon use, delivering more profits for your lab, and results you can confidently share with your customers.

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