Are you measuring ICP-OES samples more than once?

How to stop time-wasting remeasurements

The Story of Luke

Luke (not his real name), was an analyst at Always Right Labs. His job included analyzing samples on an ICP-OES, as well as running a GC and performing other lab tasks. Luke had a couple of years of experience, but he didn't consider himself an expert on either technique. He usually asked one of the more experienced analysts for help if he had trouble with one of the instruments.

The lab analyzed samples for a range of clients – from food companies needing QC on their products, through to water samples from the local government agency. The company prided itself on providing accurate, timely results to their clients. Those clients used the results to ensure that their products were meeting specifications and whether to release them for consumption. Reporting the wrong results could have big implications for Always Right Labs' reputation.

Luke followed all the standard quality control practices. He prepared samples and standards carefully to avoid contamination and the introduction of errors. Yet, despite his best efforts, he often had to remeasure samples. This problem was due to either the QC checks failing, something going wrong during the analysis, or the results of some samples not looking right. On some days, Luke would have to remeasure as many as 20% of samples. Sometimes he even crosschecked results by running the samples using another technique, like ICP-MS. It was both stressful and time consuming and often required him to work overtime. It also introduced delays in getting results to clients, which they were not happy about.

Luke would really like to reduce the number of times he has to remeasure samples. Then he'd be able to spend time on other things that added more value to his work.

Luckily, there are ways that Luke can improve the reliability of his analytical process. This e-book contains the most common causes of having to remeasure samples and how to avoid them.
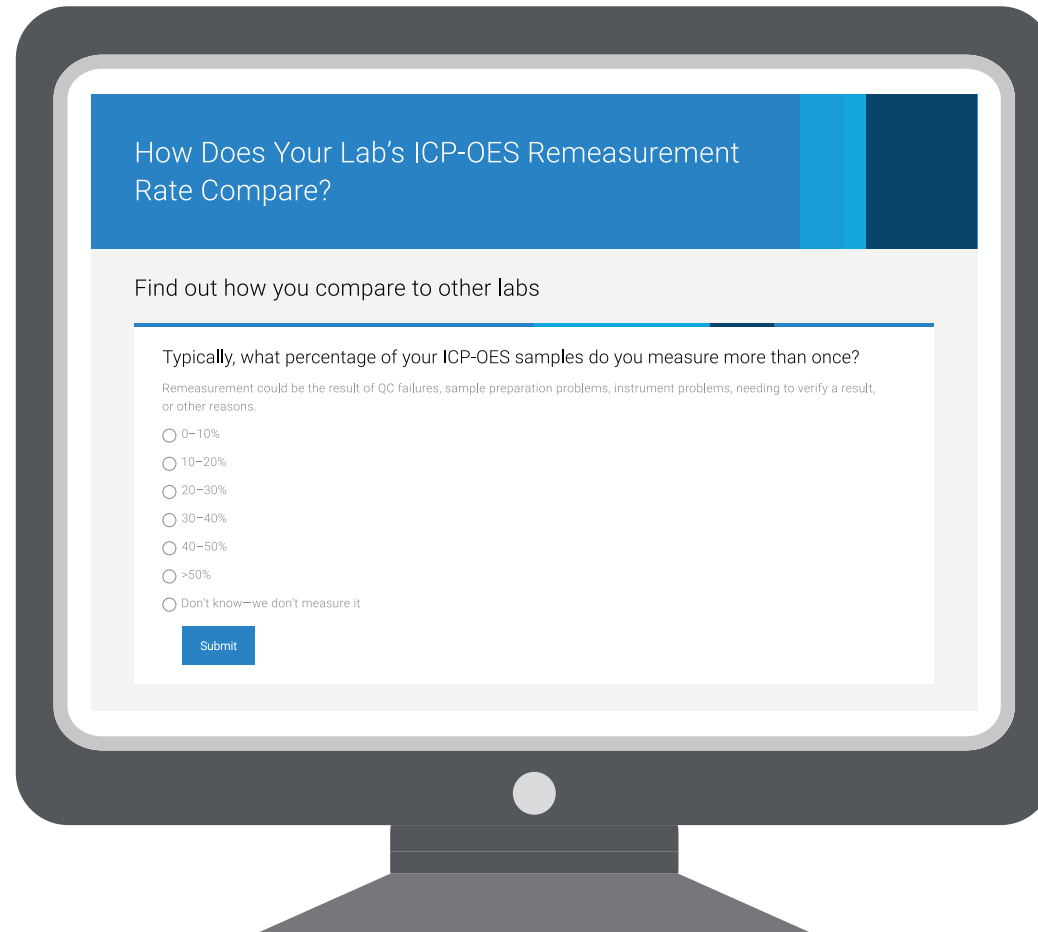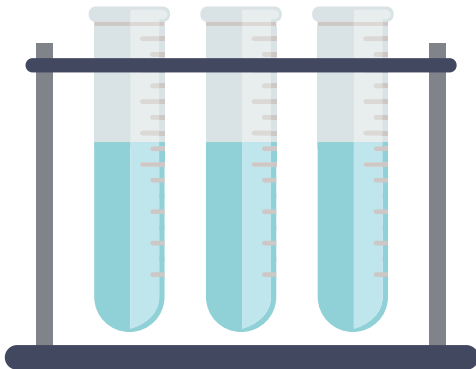
Luke often found himself wasting time, remeasuring samples due to failed QC checks, or something else going wrong.

How many samples are being remeasured in labs?

In an online poll, conducted in 2019, over 200 respondents indicated the percentage of ICP-OES samples they were measuring more than once.

Respondents indicated, on average, they were remeasuring 15% of their samples. Interestingly, over 15% don't measure their level of sample remeasurement, so have no idea of the time they are wasting or how much it is costing them.

How Does Your Lab's ICP-OES Remeasurement Rate Compare?

Find out how you compare to other labs

Typically, what percentage of your ICP-OES samples do you measure more than once?

Remeasurement could be the result of QC failures, sample preparation problems, instrument problems, needing to verify a result, or other reasons.

- ○ 0–10%
- ○ 10–20%
- ○ 20–30%
- ○ 30–40%
- ○ 40–50%
- ○ >50%
- ○ Don't know—we don't measure it

Submit

How much is remeasuring ICP-OES samples costing?

Most labs understand the cost of instrument downtime – when breakdowns or scheduled maintenance means that samples can not be run. But what about the cost of having to measure samples more than once?

A QC failure while using a regulated or lab-created method may result in having to rerun the calibration, an Instrument Performance Check (IPC), a blank, and then repeat the last 10+ samples. For more difficult samples, rerunning samples will likely include redigestion of the sample, as well as the ICP-OES analysis.

"Most labs understand the cost of downtime. But what about having to remeasure samples?"

This rework costs in severals ways:

Obvious costs:

Lab consumables and supplies, including argon, electricity, reagents

Staff wages

Not so obvious costs:

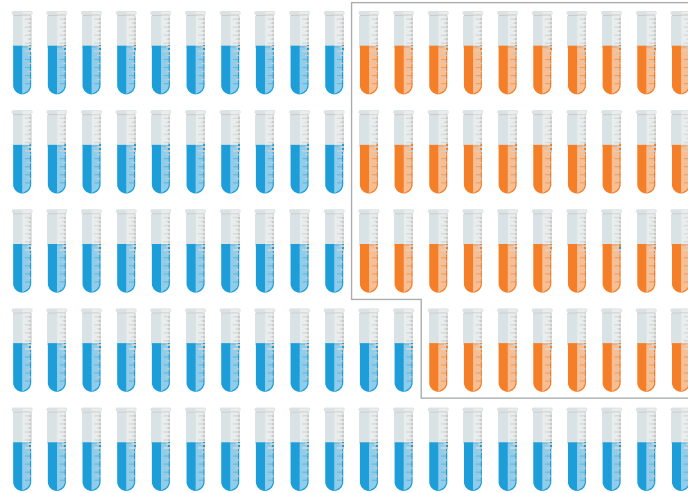Lost opportunities to run other revenue-generating samples

Increased staff turnover due to job dissatisfaction and being required to work overtime

Loss of reputation or even losing customers, due to result delays or errors

Calculating the impact of remeasuring samples

250
Samples per week

15%
need to be remeasured for some reason or another – that's 38 samples per week.

▼

⏱ **2.5** Minutes
to measure a sample using ICP-OES is fairly typical when using a fast instrument.

▼

38 samples x 2.5 minutes is

⏱ **95** Minutes

▼

📅

Over a year, that adds up to 82 hours or two working weeks!

As you can see from the example, the cost of remeasuring samples can really add up.

The common causes of having to remeasure samples and how to prevent them

There are many reasons why you might have to measure a sample a second time. A sample mix-up may have occurred, or something went wrong during the measurement. You might find out there's a problem only when a QC solution fails, or you check the results and notice something amiss. No matter the reason, remeasuring samples is time consuming, stressful, and costly.

The causes of having to remeasure samples typically fall into two categories: **Instrument-related problems** and **sample-related problems**. Sample-related problems include everything from sample digestion and preparation through to sample matrix problems and mix-ups.

Here's how to prevent the most common causes of having to remeasure a sample – and save wasting time.

QC solutions

Not familiar with QC solutions? Don't know your Internal Standard from your Instrument Performance Check Solution? The definitions of these terms can be found on page 5 of the US EPA Method 200.7 available here, and in the US EPA Method 6010c available here

Instrument-related problems

1. Nebulizer blockages

Problem and causes

Fine particles may be invisible in an aqueous solution, yet they can block a nebulizer. Blockages can also be caused by the deposition of salt particles at the tip of the nebulizer. Either sources of particles can cause a partially or fully blocked capillary tube at the tip of a glass concentric nebulizer. These blockages lead to many performance problems which, inevitably, lead to having to remeasure samples.

A typical symptom of a partial nebulizer blockage is a drifting result for a Continuing Calibration Verification (CCV) solution. The CCV solution is usually monitored periodically throughout an analysis.

A complete nebulizer blockage results in no signal at all, so is easy to diagnose as no results will be produced.

You can avoid having to remeasure samples due to a nebulizer blockage by watching both the CCV results and sample results over the course of an analytical run.

What to do?

If you are frequently suffering from nebulizer blockages, consider taking the following actions:

– Filter or centrifuge the samples

– Set the autosampler probe depth to just be a small distance into the solution. This setting will minimize the chance of particles on the bottom of the test tube being sucked up the probe.

– Change the type of nebulizer you are using to one with a larger internal diameter on the sample line.

– Use an argon humidifier to keep tip of the nebulizer moist. The moist tip means solids won't be deposited on the end of the nebulizer. Blockages from solutions with high % total dissolved solids (TDS) will be reduced.

Nebulizer blockages
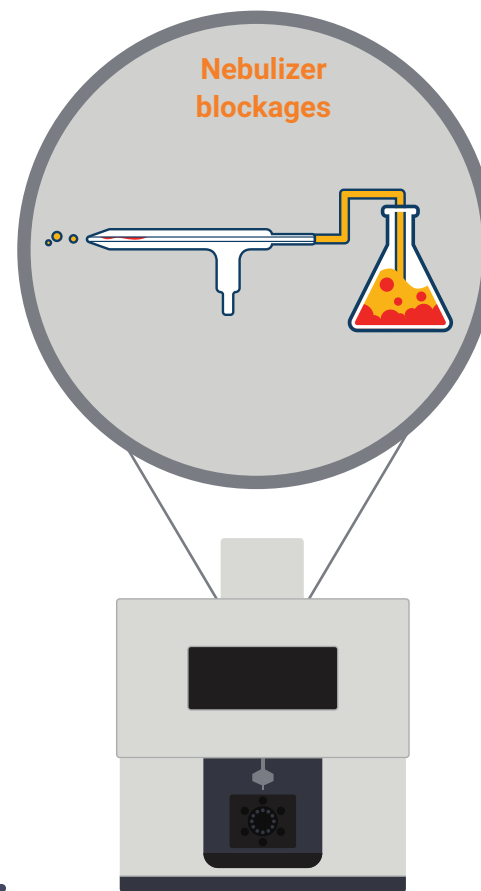
2. Torch issues

Problem and causes

Sample remeasurement may be caused by issues arising from poor maintenance of the instrument torch. Aspiration of strong matrix samples, such as 100 g/L solutions, can lead to crystalline deposition in the injector of the torch. These deposits can lead to a partially blocked torch injector and a reduced signal. If various QC solutions are being monitored, downwards drift in the signal is a sign that torch blockage maybe happening.

Different QCs can pick up this drifting signal as follows:

– Frequent monitoring of a certified reference material (CRM), included in a Laboratory Control Sample QC solution, will show declining recoveries. Signal drift can also be observed as a decline in the internal standard ratio.

– Poor (low) recovery for quality control check solutions, such as continuing calibration verification solutions (CCV) is also an indication of signal drift.

What to do?

If the instrument no longer produces the same readings for the calibration solutions, then drift has occurred, and a blockage is likely. Horizontal torches experience this at the highest frequency. Vertical torches are more immune. Using a torch with a wider diameter injector can prevent blockages.

Running automated instrument performance tests at the start of each day that indicate a pass or fail based on values set by the manufacturer will highlight any sensitivity problems. A pass on the sensitivity test using the correct solution will indicate that the torch is clean and has been correctly assembled and installed.

3. Carry over between samples

Problem and causes

A surprise high matrix sample in the sample batch can lead to contamination of the next sample due to carry over of highly absorptive or "sticky" elements. E.g., B, Mo, W. This contamination can cause an erroneously high result.

What to do?

Periodic monitoring of a Continuing Calibration Blank throughout the analysis will help identify unexpected carryover contamination. However, this approach has a low probability of capturing all issues caused by carry over unless it is included into the sequence at high frequency. Use of an automatically determined rinse duration will provide protection from carry over contamination for every sample.

Torch Issues

Carry over between samples

Rinse
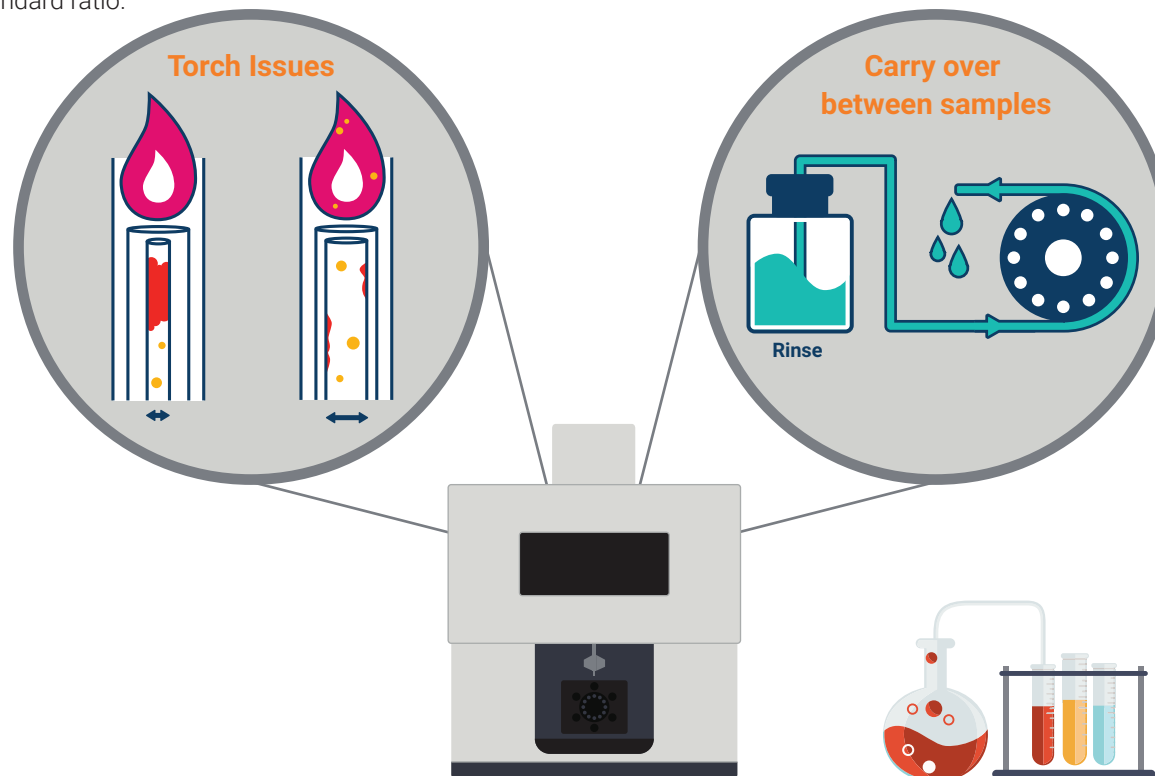
4. Instrument is out of specification

Problem and causes

If an instrument or utility (e.g. argon or chilled water) malfunction has occurred, analytical performance will be compromised. This situation can impact result sensitivity, precision, linear dynamic range as well as other aspects of performance.

These problems can be difficult to troubleshoot. You may be forced to remeasure many samples before you uncover the cause of the problem.

What to do?

To prevent having to remeasure samples because of instrument problems, always run an automated instrument performance test before starting analysis each day.

5. Incorrect method settings

Problem and causes

Instrument method settings such as gas flows, RF power, pump speed, delay time can dramatically impact your results. For example, inadequate RF power and argon gas flows into the plasma will cause inadequate plasma temperature. Not all the atoms and ions in your sample will be excited, with the result being reduced emission and reduced sensitivity. This will impact precision for analytes at trace levels. The precision will sometimes fall outside the lab threshold and when this occurs, it will mean that the samples will need to be remeasured, wasting time.

What to do?

To prevent such situations, analyse a certified reference material (CRM) introduced into your sequence as an Laboratory Control Sample (LCS). You should always try to include a CRM with a similar matrix to that of your samples as part of your method development process. You should aim to get good recoveries at the trace levels when you measure the CRM (assuming the trace levels are within manufacturer's specification for your instrument). If you are unable to get good recoveries at trace levels, further optimization of the method will be required.

The sample pump speed or delay time settings in your method can be assessed by monitoring the precision of a QC solution. Test both of these settings before starting an analysis. To test if the pump speed and uptake delay time are correct, manually start the high pump speed and time how long it takes for the solution to travel from the autosampler test tube to the spray chamber. The measured time is the uptake delay. The high pump speed should also be manually inserted into the method.

Instrument is out of specification

Incorrect method settings
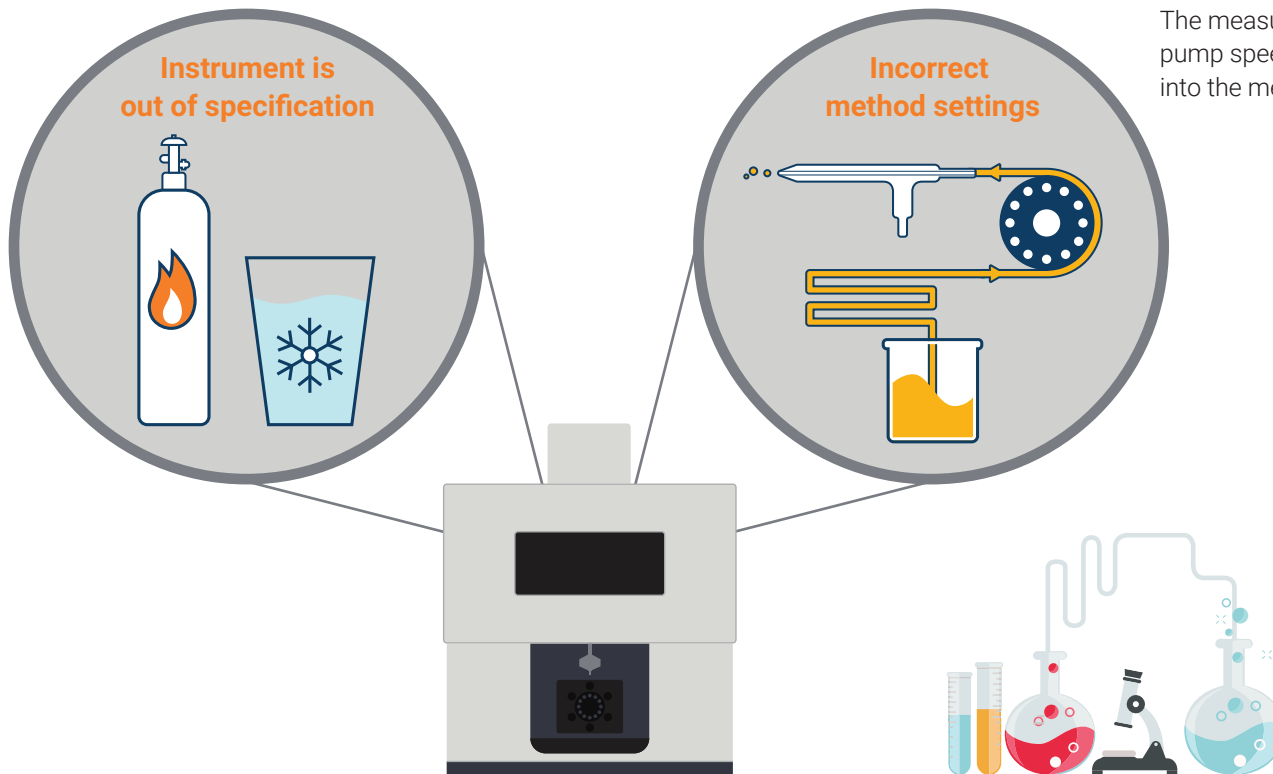
6. Dirty preoptic windows

Problem and causes

Preoptic windows are the glass windows between the torch chamber and the chamber holding the optical components of the instrument. As contamination builds up on the windows, it reduces the amount of emitted light that passes into the optics and onto the detector. Dirty preoptic windows will cause reduced sensitivity.

Reduced sensitivity leads to poor precision, which may result in samples having to be remeasured, particularly those samples with trace level analytes. Monitoring the precision of QC sample results will identify this problem. However, there are many analytical performance issues that result in poor result precision. This makes it hard to pin point one cause.

What to do?

You should include the cleaning of preoptic windows in the regular maintenance schedule for the instrument. Running the automated instrument performance tests each day will also uncover any loss in instrument sensitivity.

## 7. Sample tubing problems – leaking connections, bubbles, or incorrect tension

Problem and causes

Worn, leaking, or maladjusted peristaltic pump tubes will cause poor result precision. Precision can be monitored through QC solutions, but they are often spaced 30 to 40 minutes apart. Waiting until a failed QC solution to address an issue wastes time as you'll only discover the failure after 30-40 minutes.

What to do?

Regular routine maintenance prevents the occurrence of peristaltic pump tube problems. Checking the tube's elasticity, roundness, connection and tension at the start of each day, or when your standard operating procedure mandates it, is important. Remembering to unclamp the peristaltic pump tubing at the end of each day will also preserve its life. These checks can reduce the risk of having to remeasure samples due to pump tubing problems. You'll also avoid wasting time, waiting for new pump tubing to wear in.

Again, running automated instrument performance tests at the start of each day's analysis will determine if result precision is passing manufacturer's specifications.

Dirty preoptic windows

Sample tubing problems
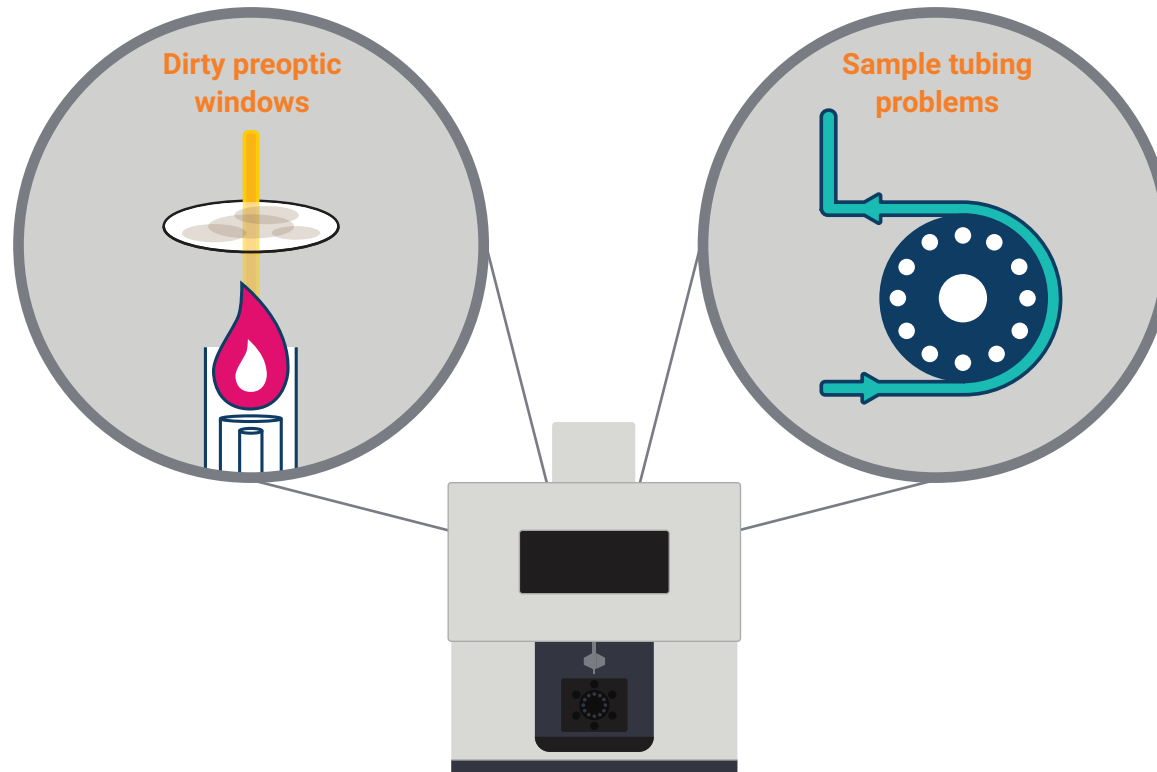
8. Dirty or contaminated spray chamber

Problem and causes

A dirty or contaminated spray chamber leads to poor drainage and uneven aspiration of the aerosol through to the plasma. To uncover this issue, watch how the solution runs down the inside the spray chamber. The liquid should be running down the spray chamber as a uniform film. If there are droplets running down instead of a film, then the spray chamber is dirty.

Poor drainage from a dirty spray chamber leads to poor precision. Precision can be monitored by using a QC solution or an internal standard.The problem is that QC solutions are often spaced 30 minutes apart. If a QC solution failure identifies the issue, you'll have wasted 30 minutes of time.

What to do?

Include spray chamber cleaning as part of your routine maintenance. You should also run the automated instrument performance tests at the start of each day. This action will determine if result precision is passing manufacturer's specification

Dirty or contaminated spray chamber
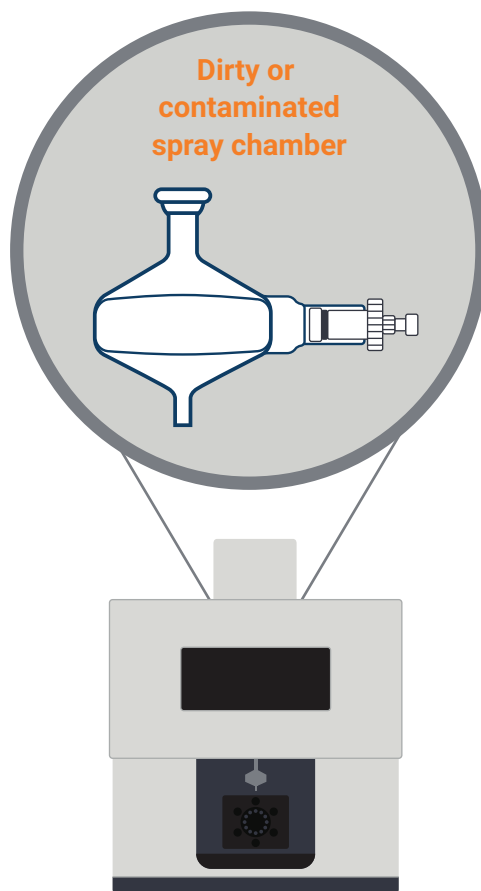
How to clean a spray chamber

This video provides information about choosing and cleaning ICP-OES spray chambers

www.agilent.com/en/video/spraychamber

Sample-related problems

1. Spectral interferences

Problem and causes

Across the wavelength range of an ICP-OES, there are tens of thousands of elemental atomic and ionic emission lines. Emissions from elements other than the ones you are analyzing for can sometimes cause erroneously high results. This situation often happens when you have a completely unknown sample. Such a sample may contain a whole range of 'hidden' elements that can overlap with the emission lines of the elements you are measuring. There might also be unexpectedly high concentrations of elements you are measuring, which causes an interference. The interference will impact your results.

What to do?

Use the following approaches to prevent spectral interferences creating problems with your results.

- If you don't know what's in a sample, choose multiple emission lines for each element you want to measure. This simple tactic is a great way to build in quality control to identify and avoid interferences. When you get the concentration results for multiple wavelengths for the same element, check that each emission line for the element is giving the same result. Unknown spectral interference can cause an erroneous high result. Any result outliers should be rejected. Of the wavelengths that have the same result, take the value from the wavelength that had best analytical performance. Analytical performance is indicated by the precision (i.e. low %RSD), sensitivity (i.e. maximized SRBR), and no obvious spectral interference causing shoulders (i.e. smooth gaussian spectrum peak shape.)

- If you suspect spectral interference problems, and you know the elements that will cause the interference, prepare solutions and develop Inter Element Correction (IEC) factors to compensate for the interference.

- A simple alternative to developing IEC factors is to develop spectral deconvolution models. See the online help for your ICP-OES software for guidance on how to do this.
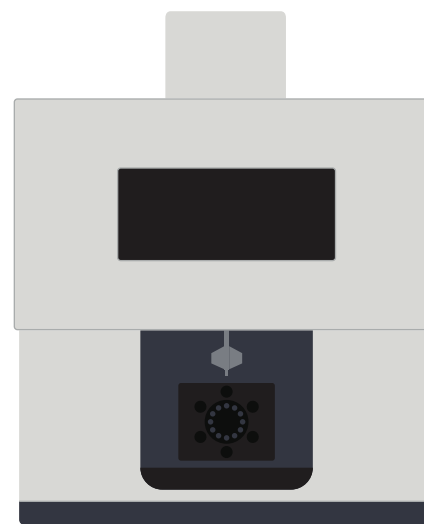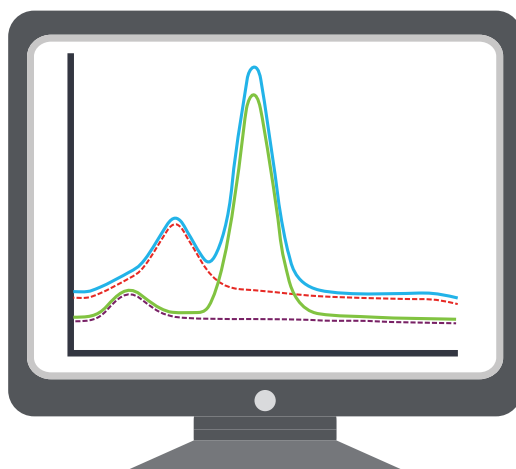
2. Calibration problems
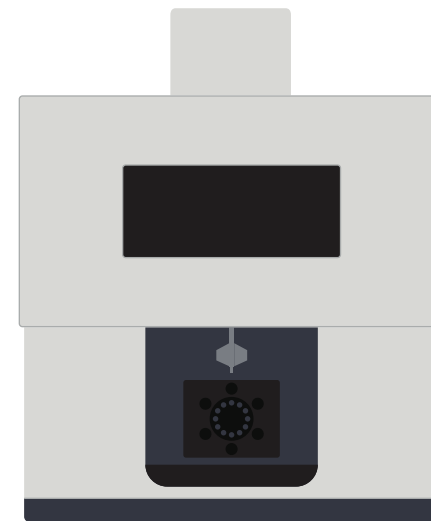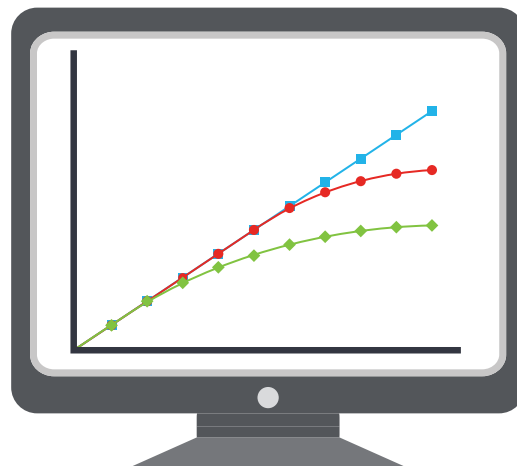
Problem and causes

The manual preparation of calibration standards can introduce errors. These errors will lead to incorrect linear regressions being developed and the calculated concentration of unknown samples will then be erroneous. Some of the causes of calibration errors come from the following problems:

– Pipettes that are out of calibration

– Contaminated glassware from inadequate cleaning/soaking

– Cross-contamination of stock solutions by pipetting directly from the container. Always decant into a separate tube and dispose of unused stock solution

– Accidental selection of the wrong stock solution when preparing a multi element standard from single-element stock solutions

– Missing or doubling up on a required element in a multi element standard

– Stock solutions that are past their expiry date

– Degradation of stock solutions or standards due to incorrect storage

– Poor reagent quality

– Incorrect acid used to stabilize

What to do?

To ensure the accuracy of your calibrations, try the following:

– Always check the accuracy of calibration standards by measuring an Initial Calibration Verification made from a stock from a different supplier.

– When creating multi-element standards from single element stock solutions, always check contamination levels on the Certificate of Analysis (CoA) to make sure that they are at negligible levels.

– ICP quality standards are recommended. Avoid atomic absorption spectroscopy quality standards as they often contain higher levels of contamination and can be prepared from salts that are incompatible with other elements.

– Calibration standards containing the elements Mo, Ti, Sb & Sn should be prepared more often when prepared in a dilute nitric acid matrix. This practice is recommended due to their lower stability.

– Use a weighted calibration fit to improve accuracy at low analyte concentrations, especially when measuring over a large concentration range.

Documenting good laboratory procedures through a Standard Operating Procedure (SOP) can help prevent many of the issues around incorrect calibration solution preparation. The solution to calibration problems could include:

– Adding a reference number to all pipettes, with an electronic record of recalibration dates. A recalibration date sticker should be stuck onto each pipette.

– The lab follows a strict, proven, protocol around cleaning labware after use.

– Multi element stock standards are used for the preparation of calibration solutions.

– Stock solutions have expiry date electronically recorded so the lab quality system can trigger disposal as expiry date is passed.

3. Contamination – of blank, standards, and samples

Problem and causes

An indicator of chemical contamination of the blank, standards, and samples is the incorrect QC readback of the identically prepared Laboratory Reagent blank. Other indicators include poor results for a Laboratory Control Sample (LCS), or a poor comparison with a Matrix Spike Duplicate (MSD).

Contamination might be due to a range of reasons:

– Poor sampling procedures

– Contaminated reagents

– Inadequately cleaned digestion and storage vessels

– Defective lab grade water purifier.

It is also common to have carry over in the instrument's sample introduction system from one sample to another. Carry over often occurs when there is a high concentration of an absorptive element in a sample. If this is the case, you will observe erroneously high results, inaccuracy, and poor precision. You will see high emission counts for the first replicate, with decreasing counts for the second replicate, before the signal stabilizes.

What to do?

To help with identifying a contamination issue, run periodic, fully prepared digest duplicates of samples to identify contamination. You can also check the intensity of the blank solution and compare this value with a blank solution that was run in a previous analysis. If the readings are excessively high, replace the blank solution as it's likely been contaminated.

If a sample is being contaminated by carry-over from a previous sample, then increase the rinse time between samples.

To prevent contamination, make sure there's instructions in lab SOPs about how the take samples and prepare them and how to clean labware. Then you just have to make sure the SOPs are followed!

4. Sample preparation problems and mix-ups

Problem and causes

Incorrect preparation of a sample will cause erroneous results. You may have forgotten to include one of the acids before digestion. For example, HCl acid is needed, as well as HNO_3 acid, when trying to digest platinum group metals. You may also have used a chemically incompatible acid for the elements you wish to analyse. For example, adding H_2SO_4 to a sample when looking for Ba or Pb will cause those elements to precipitate out of solution.

What to do?

To identify sample preparation problems, always include a Laboratory Control Sample (LCS) with a similar matrix to the samples of interest into every analysis. Make sure the certified reference material is prepared in the same way as samples. Then you have a sample with a known concentration that you can use to detect problems in your sample preparation.

Tip:
If your sample digestion procedure uses HCl acid, include chlorine into the ICP method. This inclusion will help you troubleshoot problems – no Cl? Someone forgot to put the HCl acid in during sample preparation.

5. High matrix samples

Problem and causes

If there are numerous elements in the sample, all of differing concentration, some complicated interactions can occur. This situation can lead to enhanced or suppressed results. For example, elevated concentrations of easily ionizable elements (EIE's) like the alkali metals of Na and K, and even alkali earth elements Ca and Mg, can enhance or suppress results for other analytes.

Quick identification of the presence and approximate concentration of the alkali metals or alkali earth elements in unknown samples is important before analysis. This step allows you to put strategies in place to accommodate for differing concentrations.

Poor Matrix Spike Duplicate (MSD) recoveries are a good way to identify if an EIE interference is occurring. For most analytes, the outcome of the EIE interference will be a supressed result. In the case of alkali metals and alkali earth elements results will be higher than they should be.
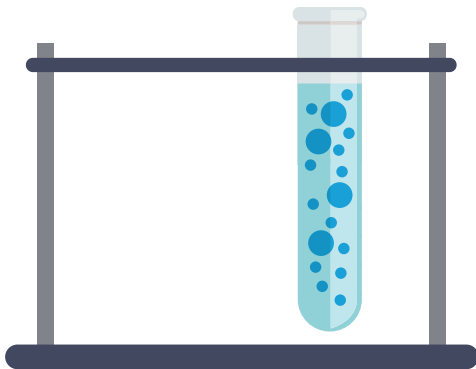
What to do?

Some strategies to avoid the effects of EIEs include:

– Inclusion of an internal standard element and activating internal standard correction

– Diluting the sample maybe all that is needed to get good recoveries again. This advice assumes that the elements of interest are not diluted beyond the instrument's method detection limit (MDL)

– Matrix matching the calibration standards with the matrix in the samples. This method is not always easy if the samples are complete unknowns

– Measure the sample using a radial view of the plasma

5 ppm K Readback

[K] ppm vs [Na] ppm

Axial

Radial
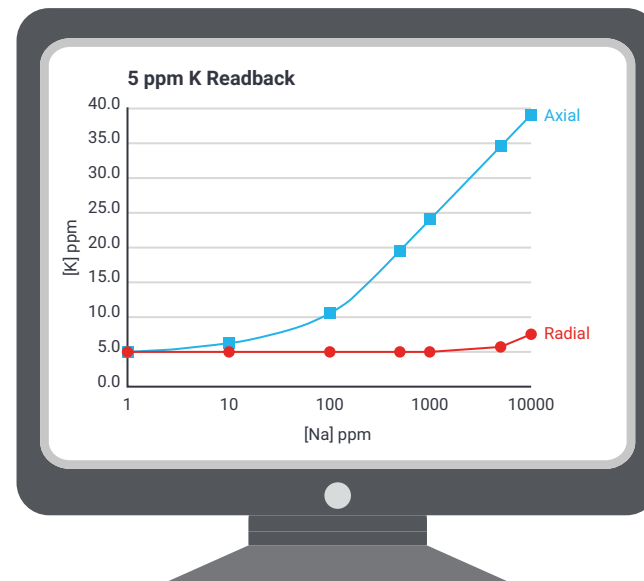
As the concentration of Na increases in a sample, the recovery of K can get worse. The impact is pronounced when viewing the plasma in axial viewing mode.

## 6. Overrange samples

Problem and causes

An unexpected high concentration of analytes can mean that a measured sample concentration is outside the calibration range. This situation is a common reason for remeasuring a sample. It is easily identified within the results, as an error flag will appear, indicating the result is outside the calibration range. You should not report a result that is outside the calibrated range without checking calibration linearity to the overrange concentration.

To recover from the error, a simple dilution or adding an extra standard as a sample and check for linearity can be used. Care should be taken not to introduce contamination when performing the dilution.

What to do?

There are easy ways to immediately avoid overrange problems.

– Modern ICP-OES instruments give you access to a huge range of wavelengths you can monitor. You can select multiple emission lines for the elements you are measuring. Some will be highly sensitive and others less so. If you get an overrange alert on some wavelengths, simply switch to a less sensitive line for that analyte and avoid the need to dilute.

– If you don't want to use an alternate, less sensitive, wavelength, then use an auto diluter integrated with your ICP-OES software. Any overrange sample will then be automatically diluted.

– Measure highly concentrated samples using a radial view of the plasma.
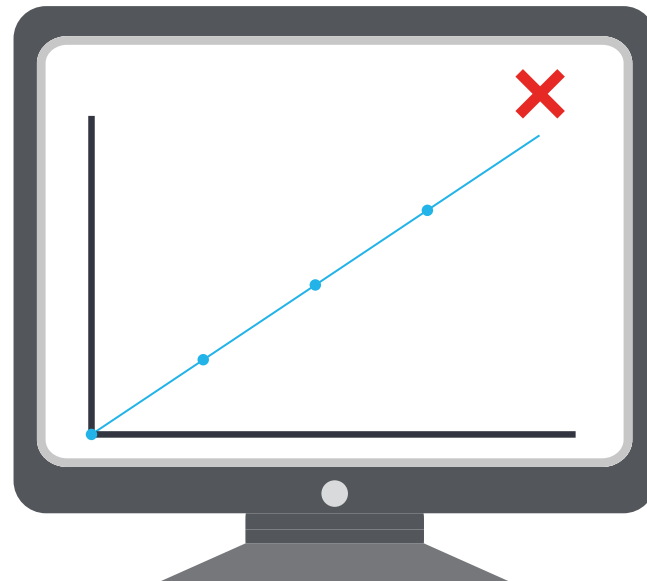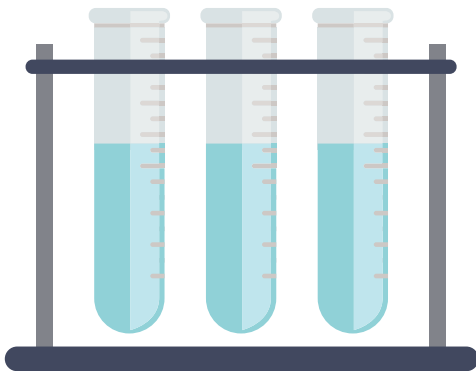
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