

Controlling Cell-Formed Reaction Product Ions in ICP-QQQ

Agilent ICP-MS technology brief

Helium (He) collision cell gas in ICP-MS.

He is inert, so it acts as a collision gas in the ICP-MS collision/reaction cell (CRC). He mode provides effective reduction of most common polyatomic ions, improving accuracy and detection limits. He mode works because polyatomic ions are larger than the analyte ions at the same mass. The polyatomic ions collide more frequently with the cell gas and lose more energy, so they can be rejected using KED at the cell exit.

KED (Kinetic energy discrimination).

KED uses a positive bias voltage (where the quadrupole voltage is more positive than the octopole) to repel positive ions. Ions with lower kinetic energy (KE) are rejected, while ions with higher KE pass through, so KED discriminates between (low KE) polyatomic ions and (high KE) analyte ions.

The role of He mode in ICP-QQQ.

ICP-QQQ operates in MS/MS, where Q1 (before the CRC) provides control of the reaction chemistry in reaction mode. It is sometimes assumed that this means He KED is redundant on ICP-QQQ. But these two modes are complementary, not competing.

ICP-QQQ offers both a powerful, universal He mode, and controlled reaction chemistry, which is highly effective but more specific.

Extending the scope of He mode

On single quadrupole ICP-MS, He mode with KED has become the de facto standard approach to resolve common polyatomic overlaps and improve data quality for interfered analytes. Matrix- and plasma-based polyatomic ions cause most of the spectral overlaps in ICP-MS, so effective He collision mode is essential to enable the ICP-MS to address challenging applications.

Triple quadrupole ICP-MS (ICP-QQQ) provides control of reaction chemistry, extending the range of analytes and interferences that can be addressed. But He cell gas can still be useful for ICP-QQQ methods. A well-designed cell with optimized He mode can often match reaction mode performance for the attenuation of intense polyatomic ion signals. The plot in Figure 1 shows how He mode on the Agilent 8900 ICP-QQQ can reduce the ArC+ background signal to sub-ppt level in a 100% xylene solution. This background reduction allows Cr to be measured accurately at ppt levels in high purity solvents.

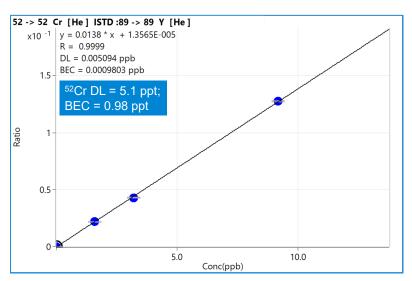


Figure 1. Calibration for 52 Cr in 100% xylene, showing effective removal of ArC+ polyatomic using He cell gas. Chromium BEC of 0.98 ppt; DL of 5.1 ppt.



Use of He cell gas in reaction gas modes

Reactive cell gases such as H_2 , O_2 , NH_3 , and N_2O are very efficient. The reaction between the ion and the cell gas molecule typically occurs within the first few collisions. This reactivity provides efficient reduction of interferences, but can lead to the creation of cell-formed product ions. In some cases, these product ions can go on to form new overlaps at the analyte mass.

An example is the use of NH_3 cell gas for the analysis of V at m/z 51 in a sample that contains a high concentration of Cl. In ICP-QQQ, Q1 only allows ions at m/z 51 to enter the CRC. But $^{35}\text{Cl}^{16}\text{O}^+$ will pass through Q1 together with the $^{51}\text{V}^+$, since both ions occur at mass 51. Once in the CRC, the ClO+reacts with the NH_3 cell gas and is neutralized by charge transfer:

$$CIO^{+} + NH_{3} \rightarrow CIO + NH_{3}^{+}$$

This is how the CIO^+ overlap is resolved. However, the NH_3^+ ion formed from this reaction can react further with the NH_2 cell gas:

$$NH_{3}^{+} + NH_{3} \rightarrow (NH_{3})_{2}^{+}$$

 $(NH_{3})_{2}^{+} + NH_{3} \rightarrow (NH_{3})_{3}^{+}$

The $(NH_3)_3^+$ product ion formed by these reactions appears at mass 51, where it would overlap $^{51}V^+$. He cell gas, added to the cell as a buffer gas alongside the NH_3 reaction gas, provides the solution, as shown in Figure 2.

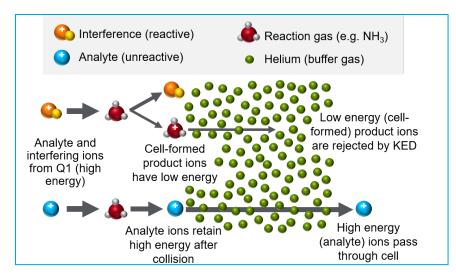


Figure 2. He KED rejects (low energy) cell formed NH₃⁺ product ions, preventing the formation of higher mass product ions such as $(NH_2)_2$ ⁺ which would overlap V⁺ at m/z 51.

Product ions formed from the cell gas invariably have low energy, because the cell gas is essentially stagnant in the pressurized cell. This means that gas molecule ions only have the energy they gain from the reactive collision.

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© Agilent Technologies, Inc. 2021 Published in the USA, May 17, 2021 5994-3548EN This low energy is not sufficient to overcome the retarding effect of multiple collisions with the He buffer gas. As a result, the cell formed product ions can be rejected in the same way as the low energy polyatomic ions in conventional He mode KED.

With an optimized cell design and operating conditions, this process can be extremely effective, as shown in Figure 3 for the analysis of V in HCl using NH₃ cell gas.

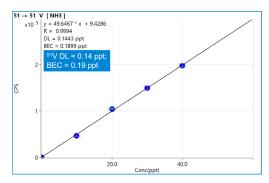


Figure 3. Calibration for ⁵¹V in 20% HCl, showing effective removal of ClO⁺ overlap using NH₃/He cell gas. Vanadium BEC of 0.19 ppt; DL of 0.14 ppt.

The calibration plot in Figure 3 confirms a background equivalent concentration (BEC) of 0.19 ppt and a detection limit (DL) of 0.14 ppt for V in high purity HCl (20%). The sub-ppt BEC and DL confirm that the Agilent 8900 operating in $\mathrm{NH_3}$ reaction mode with He buffer gas prevents overlaps due to cellformed reaction product ions.

Conclusion

He cell gas is the default mode for control of polyatomic interferences in single quadrupole ICP-MS. But the optimized design and operating conditions of the Agilent 8900 ORS cell mean He mode also provides exceptional control of polyatomic ion overlaps in triple quadrupole ICP-MS methods. The 8900 can also use He as a buffer gas to provide effective control of reaction product ions in reactive cell gas methods.

