

Resolving REE²⁺ Overlaps on Arsenic and Selenium With Hydrogen Cell Gas

Accurate analysis of As and Se in a REE matrix using Agilent single quadrupole ICP-MS

Introduction

ICP-MS is the technique of choice for rapid multi-element analysis of a wide range of trace and higher-level elements in sample-types ranging from environmental, food, and biological to geological, nuclear, and semiconductor. Reasons for the wide adoption of ICP-MS include the very low detection limits it offers for critical elements such as As, Cd, Hg, and Pb. These elements are widely regulated and monitored in routine analytical laboratories, along with other essential and nutrient elements, such as Fe, Mn, Cu, Zn, and Se. ICP-MS can measure all these elements at low levels in typical sample types with helium collision cell mode ensuring results are generally free from significant error due to spectral overlaps (1–3).

In recent years, analytical requirements have changed, with regulated limits being reduced, and more elements being added to typical analysis suites. Among the novel contaminants being monitored are a series of 'technology critical elements' (TCEs) that are increasingly mined for use in industrial processes and manufactured goods. An important sub-group of the TCEs is the Rare Earth Elements (REEs), which are used in products including industrial materials, catalysts, consumer electronics, and pharmaceuticals. REE-based products include magnets, abrasives, touch screens, optical fibers, some rechargeable batteries, exhaust gas catalysts, and MRI contrast agents. As REEs become more widely extracted and distributed, their levels need to be monitored in waste streams, the environment, and foods. Single quadrupole ICP-MS offers ppt level detection for the REEs, so these elements can usually be added to the existing suite of elements being measured.

However, some sample types may contain levels of REEs that are high enough to cause interferences on other analytes. Most notable among these interferences are the overlaps caused by doubly charged REE ions (REE^{2+}). Doubly charged (M^{2+}) ions form when an atom loses two electrons in the ICP ion source, rather than the usual one (M^+). Most elements form insignificant amounts of M^{2+} ions in an argon plasma, but some elements—including the REEs—do form a small percentage of REE^{2+} ions. Since a quadrupole separates ions based on their mass-to-charge ratio (m/z), doubly charged ions appear at half their true mass, where they can overlap other analytes. For example, $^{150}\text{Nd}^{2+}$ and $^{150}\text{Sm}^{2+}$ overlap singly charged arsenic (As^+) at m/z 75, and $^{156}\text{Gd}^{2+}$ and $^{156}\text{Dy}^{2+}$ overlap singly charged selenium (Se^+) at m/z 78.

The standard approach to controlling common spectral interferences in ICP-MS is the use of a collision/reaction cell (CRC) with helium (He) cell gas and kinetic energy discrimination (KED). He KED provides effective control of polyatomic ion interferences, allowing accurate analysis of all target analytes in typical sample types. But He mode alone is not effective for M^{2+} overlaps, so analysts have developed alternative approaches to address REE^{2+} overlaps, such as the half-mass correction function available on Agilent ICP-MS systems (4). For most sample types, He mode and half-mass correction provide sufficient reduction of polyatomic ion and REE^{2+} interferences, allowing accurate analysis of trace As and Se at the required levels. However, in some sample types, for example when the REE concentrations are raised due to industrial processes, resolving the REE^{2+} overlaps on As and Se requires an alternative approach. In these cases, H_2 cell gas can provide more effective reduction of the REE^{2+} contribution, allowing lower levels of As and Se to be determined accurately.

This technical overview describes a method using the Agilent 7900 ICP-MS with H_2 cell gas and REE^{2+} correction for accurate, low-level As and Se determination in ppm level REE matrices.

Resolving spectral interferences on As and Se

Several different approaches can be applied to resolving the spectral interferences that can affect As and Se in ICP-MS analysis, depending on the instrument type available. The most suitable approach will depend on the level of As and Se being measured, and the possible sources of spectral overlaps i.e., the composition of the sample matrix.

1. He KED mode

Analysis of As (m/z 75) by single quadrupole ICP-MS can be affected by polyatomic ion overlaps formed from typical matrix elements. Common interferences include ArCl , CaCl , and, less commonly, ArSH and Cl_2H . Selenium is usually measured at its second most abundant isotope at mass 78, where the main spectral overlap is from Ar_2 . The standard mode of operation on Agilent ICP-MS systems is He KED mode, which uses an optimized ORS⁴ cell combined with good control of ion energy using the Agilent ShieldTorch system. With this configuration, He mode works well to resolve all the typical polyatomic overlaps, giving reliable results for trace As and Se in most sample types. But He KED mode alone does not successfully resolve REE^{2+} overlaps.

2. He KED mode with REE^{2+} correction

In relatively unusual cases, sample types such as soil and plant material may contain REEs at high enough levels to cause significant doubly charged ion overlaps on As and Se. REEs have low second ionization potentials, so form relatively high levels (up to a few %) of doubly charged ions in the plasma. These M^{2+} ions appear at half their true mass when measured using a quadrupole mass filter, so can overlap the singly charged ions of As and Se. If the level of As and Se in a sample is much lower than the interfering REEs, the REE^{2+} ions can contribute enough signal to affect the accuracy of the As and Se measurement.

He mode alone does not resolve the REE^{2+} ions, but, for these less common sample types, Agilent single quadrupole ICP-MS users can use an automated half-mass (narrow peak) mode with REE^{2+} correction to correct the REE^{2+} contribution. This mode provides accurate As and Se results in typical samples with raised levels of REEs (4).

3. Hydrogen (H_2) cell gas – described in this overview

In some sample types, the level of REEs is several orders of magnitude higher than the level of the interfered analytes. At these levels, the REE^{2+} overlap on As and Se is beyond the capability of He mode and half mass correction to resolve. Users of single quadrupole ICP-MS can use an optional cell gas, H_2 , to provide an alternative approach for the analysis. H_2 cell gas offers different collision characteristics compared to He, providing more effective resolution of the REE^{2+} overlaps (5).

4. Triple quadrupole ICP-MS (ICP-QQQ) with oxygen (O₂) cell gas and mass shift

Laboratories equipped with ICP-QQQ can use other reaction gas methods with tandem mass spectrometry (MS/MS) to provide an advanced solution for resolving doubly charged ion overlaps in the most demanding applications. Analyses where ICP-QQQ is appropriate include trace As and Se analysis in REE oxide materials, where the matrix level is extremely high and the analyte levels are very low (6). Other measurements where the best available accuracy and certainty is required include reference methods in metrology labs, and reference material certification.

Interaction of M²⁺ ions with He and H₂ cell gas

In an optimized cell configuration, He collision mode with KED provides a consistent, easy to use, and effective solution to control common polyatomic ion interferences. KED works because of the different collision rates of polyatomic and analyte ions, due to their different ionic cross sections. Ions passing through the ICP-MS all have approximately the same velocity (due to thermal expansion in the plasma), so their kinetic energy (KE) is proportional to their mass ($KE = mv^2$). When the ORS⁴ cell is pressurized with He cell gas, all ions passing through the cell will collide multiple times with the He atoms, losing KE with each collision. Polyatomic ions have the same mass as the analyte ions they overlap, and therefore enter the cell with the same initial KE. But polyatomic (molecular) ions have a larger ionic cross section, so they collide with the cell gas atoms more frequently than the analyte ions do, and so lose more energy. At the cell exit, a positive KED bias voltage prevents the low KE (polyatomic) ions from entering the quadrupole mass filter, while the higher KE (analyte) ions pass through.

Helium is a nonreactive, monatomic gas, and the likelihood of a collisional event between an ion and a He atom depends primarily on the ionic radius (collision cross section) of the ion. However, M²⁺ ions are not polyatomic ions and their true mass is twice the apparent mass (m/z) that they appear at in the quadrupole mass spectrum. Taking the example of a REE²⁺ ion overlap, ¹⁵⁰Nd²⁺ appears at m/z 75, the same as singly charged ⁷⁵As⁺. But ¹⁵⁰Nd²⁺ has an actual mass twice that of ⁷⁵As⁺, so Nd²⁺ has much higher initial KE and loses less kinetic energy per collision than As⁺. Therefore, the total energy loss for Nd²⁺ as it passes through the He-filled cell, is less than for As⁺. As a result, Nd²⁺ cannot be removed effectively using KED.

The relative energy losses for As⁺, ArCl⁺, and Nd²⁺ in a He-filled cell are shown in Figure 1a. The figure shows that Nd²⁺ does not lose enough energy to be rejected by the KED bias voltage, shown as the horizontal dashed line. Figure 1a also includes the plot of energy loss for the ArCl⁺ polyatomic ion, confirming that the KED bias voltage cutoff can discriminate effectively between As and ArCl.

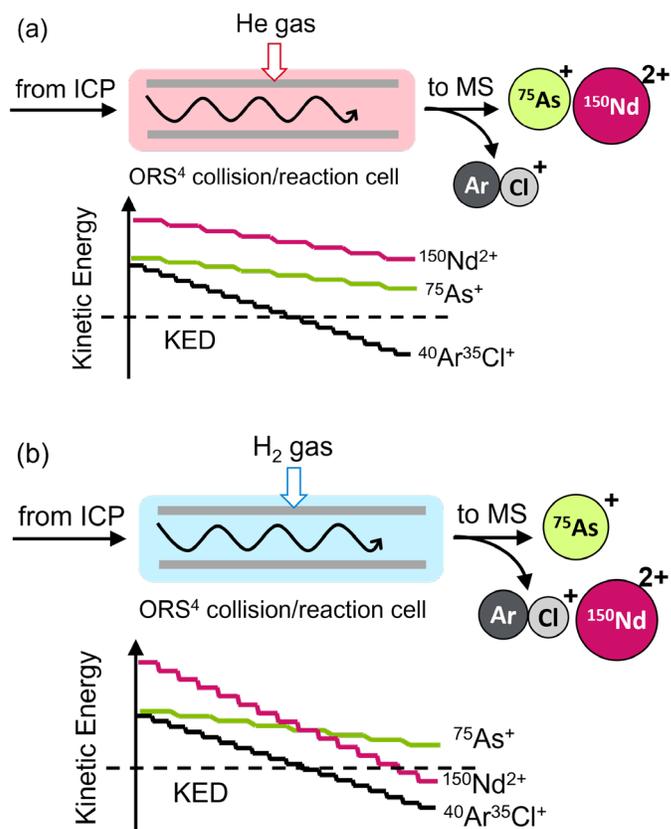


Figure 1. Energy loss through collision of As⁺, ArCl⁺, and Nd²⁺ with (a) He and (b) H₂ cell gas.

In contrast to He, H₂ is a reactive molecular gas. Therefore, an ion's collision cross section with H₂ depends not only on the ion's ionic radius, but also its electrical interaction with H₂. When an ion approaches a H₂ cell gas molecule, a dipole (charge redistribution) is induced in the H₂ molecule. This dipole generates an attraction force between the ion and the H₂ molecule, including a long-distance attraction between them, as shown in Figure 2. Nd²⁺ has a double charge and so induces a stronger dipole with H₂ than does a singly charged ion such as As⁺. The stronger dipole increases the effective collision cross section of Nd²⁺ with H₂, so Nd²⁺ ions passing through the cell suffer a higher collision rate and therefore greater energy loss. The greater loss of KE enables the Nd²⁺ ions—as well as the ArCl⁺ polyatomic ions—to be discriminated from the (higher KE) As⁺ ions at the cell exit (Figure 1b). Other REE²⁺ ions such as Sm²⁺, Gd²⁺, and Dy²⁺ also suffer greater KE loss with H₂ cell gas, so multiple REE²⁺ interferences on As⁺ and Se⁺ can be resolved using the same H₂ KED conditions.

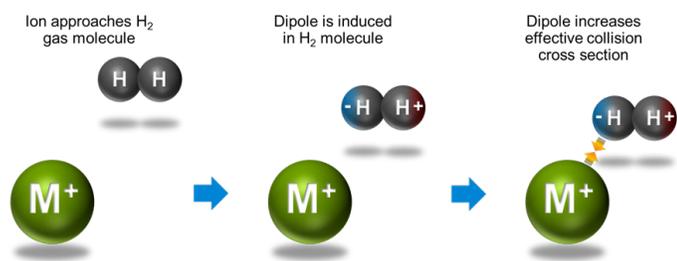


Figure 2. Illustration of increased effective collision cross section due to induced dipole in H₂ cell gas molecule.

Experimental

H₂ KED mode for trace As and Se determination in ppm-level REE matrix

To assess the capability of H₂ KED mode to resolve REE²⁺ interferences, As and Se were measured in a mixed REE standard (1 ppm each of Nd, Sm, Gd, and Dy) using the 7900 ICP-MS. For comparison, the same measurements were made using no gas mode and He mode (with half mass correction). Operating conditions for the three modes are shown in Table 1. The level of REE²⁺ interference on ⁷⁵As and ⁷⁸Se was determined for H₂ mode and compared to the levels in no gas mode and He KED mode.

Table 1. Agilent 7900 ICP-MS tuning conditions.

	No Gas	He KED*	H ₂ KED*
ICP-MS Configuration	x-lens, optional H ₂ cell gas line		
Plasma Conditions	General purpose		
Cell Gas Flow Rate (mL/min)	0	4.3	3
Octopole Bias (V)	-8	-18	-6
Quadrupole Bias (V)	-3	-13	-1
KED (V)	5	5	5

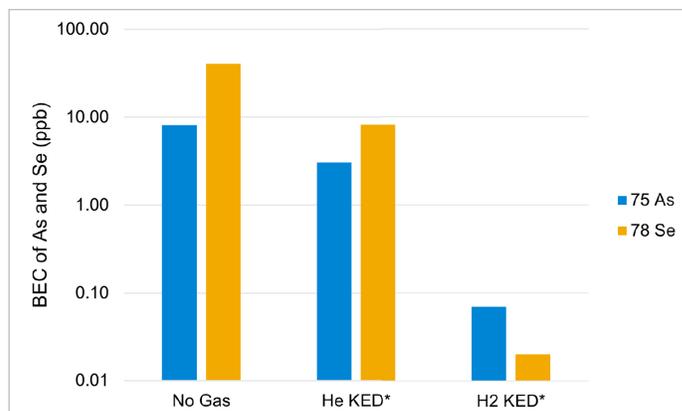
*Half mass correction was applied.

Results and discussion

Background equivalent concentrations

Previous work showed that He mode and half-mass correction reduced the REE²⁺ contribution sufficiently to allow As and Se to be determined accurately in the presence of ppb-levels of REEs (4). However, Figure 3 shows that He mode with half mass correction cannot completely eliminate the doubly charged ion contribution from ppm levels of REE matrix. Figure 3 also shows that the new, optimized H₂ KED mode gives much lower background equivalent concentrations (BECs) than He KED in ppm levels of REE matrix. As described previously, the mechanism of ion molecule interaction with H₂ cell gas causes preferential loss of KE for REE²⁺ ions, resulting in their effective elimination by KED.

The BEC for ⁷⁸Se is decreased even more significantly in H₂ KED mode. The major interference on ⁷⁸Se, ³⁸Ar⁴⁰Ar⁺, reacts with H₂ cell gas by proton transfer, leaving the ⁷⁸Se mass essentially free from interference. This efficient reaction process enables H₂ mode to deliver a Se BEC two orders of magnitude lower than can be achieved with He mode.



*Half mass correction was applied.

Figure 3. Background equivalent concentrations (BEC) of As and Se in the presence of 1 ppm Nd, Sm, Gd, and Dy. Log scale is used for vertical axis.

Spike recoveries

The recovery of a 1 ppb As and Se spike in the 1 ppm REE mix was investigated. The spike recovery results obtained using H₂ KED with half mass correction shown in Table 2, indicate 100 ± 2% recoveries of 1 ppb As and Se in the 1 ppm REE matrix. Table 2 also illustrates how the optimized H₂ cell gas mode with KED, using the conditions shown in Table 1, provides around a factor of 100 lower As and Se BEC than was obtained in optimized He cell gas mode.

The performance improvement in H₂ mode is partly due to the use of less negative octopole and quadrupole bias voltages. Less negative bias voltages cause the ions to slow down as they pass through the cell. Slower moving ions interact with more H₂ cell gas molecules, increasing the number of collisions and improving the discrimination between M²⁺ and M⁺ ions. Using H₂ KED mode with half mass correction, the REE²⁺ ion overlaps were reduced so effectively that the As BEC in the 1 ppm REE matrix was decreased to 0.07 ppb. For Se, the combination of H₂ reactions to remove the Ar dimer overlap and H₂ KED with half mass correction to resolve the REE²⁺ overlaps meant the BEC was reduced to 0.02 ppb.

The low BECs and excellent recoveries for As and Se confirmed the effectiveness of the new method to control REE²⁺ interferences using the 7900 ICP-MS with H₂ cell gas.

Table 2. REEs spike test comparing no gas, optimized He, and optimized H₂ collision modes.

Sample	No Gas		He KED*		H ₂ KED*	
	As (ppb)	Se (ppb)	As (ppb)	Se (ppb)	As (ppb)	Se (ppb)
0 ppb As & Se + 1000 ppb REEs	8.08	40.3	3.05	8.22	0.07	0.02
1 ppb As & Se	1.11	<DL*	1.09	1.03	1.02	0.99
1 ppb As & Se + 1000 ppb REEs	9.38	43.1	4.05	10.4	1.02	0.98

*Se background and DL in no gas mode is high due to Ar dimer interference.

*Half mass correction was applied.

Conclusion

Single quadrupole ICP-MS instruments utilizing He cell gas and KED are used successfully for most typical ICP-MS applications. But some combinations of sample matrix elements and analytes can lead to spectral overlaps that are not easy to resolve using He KED methods. Triple quadrupole ICP-MS instruments such as the Agilent 8900 ICP-QQQ offer a solution, but these instruments are not available in every laboratory. So, there is a need for single quadrupole ICP-MS methods that provide improved performance for demanding and unusual applications

This study investigated an alternative analytical approach for the analysis of As and Se in samples that contain significant levels of the REEs, Nd, Sm, Gd, and Dy. These matrix elements can cause doubly charged ion interferences on As and Se. Standard He mode and half mass correction can provide accurate analysis of As and Se in samples that contain typical concentrations (up to a few ppb) of the REEs. However, H₂ cell gas with KED and half mass correction provides even better removal of REE²⁺ interference, allowing As and Se to be measured in REE concentrations up to ppm level.

The data demonstrated how the Agilent 7900 ICP-MS provides high performance and flexibility for more demanding and unusual applications. H₂ gas with KED and half mass correction was used to successfully resolve doubly charged ion interferences from a 1 ppm REE mix. The H₂ KED method enabled BECs of less than 0.1 ppb to be achieved and accurate analysis at single ppb levels for As and Se in the REE matrix. The method can also be used to resolve Sr²⁺ interference on Ca and Ba²⁺ overlaps on Zn.

More information

Doubly charged ion correction approach used in this study requires the following:

- Agilent 7850 ICP-MS or Agilent 7900 ICP-MS with optional H₂ cell gas line
- Agilent ICP-MS MassHunter for 7850 or 7900, version 5.1 or later.

References

1. Jenny Nelson, Elaine Hasty, Leanne Anderson, Macy Harris, Determination of Critical Elements in Foods in Accordance with US FDA EAM 4.7 ICP-MS Method, Agilent publication, [5994-2839EN](#)
2. Tetsuo Kubota, Routine Analysis of Soils using ICP-MS and Discrete Sampling, Agilent publication, [5994-2933EN](#)
3. E. McCurdy and G. Woods, *J. Anal. At. Spectrom.*, **2004**, 19, 607-615, <https://doi.org/10.1039/B312250F>
4. Tetsuo Kubota, Simplifying Correction of Doubly Charged Ion Interferences with Agilent ICP-MS MassHunter, Fast, automated M²⁺ correction routine improves data accuracy for Zn, As, and Se, Agilent publication, [5994-1435EN](#)
5. Naoki Sugiyama, Attenuation of doubly charged ion interferences on arsenic and selenium by ICP-MS under low kinetic energy collision cell conditions with hydrogen cell gas, *J. Anal. At. Spectrom.*, **2021**, 36, 294–302, <https://doi.org/10.1039/D0JA00301H>
6. Naoki Sugiyama, Solving Doubly Charged Ion Interferences using an Agilent 8900 ICP-QQQ, Agilent publication, [5994-1155EN](#)

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