

Comparison of Collision and Reaction Cell Regimes for the Removal of Spectral Interferences

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Overview

Modern quadrupole-based ICP-MS instrumentation comprises an enclosed n-pole (n = 4, 6, 8) that is pressurized with a gas. Depending on the chemical reactivity of the gas used, these cells are either reaction or collision cells.

Reactive chemistry can be applied to polyatomic species that react with the gas and are consequently either eliminated or modified. In addition to this strategy by means of reactive chemistry, analyte ions can be modified ("derivatized") and analyzed at masses different from their natural isotope mass.

Molecular ions that do not chemically react with the gases introduced to the cell cannot be eliminated by means of the processes described above. Collision cell mechanisms, however, allow the separation of analyte ions from overlapping polyatomic molecular ions if they differ in kinetic energy. This process is called "kinetic energy discrimination" or KED.

The aim of this work is to investigate the potential of both mechanisms and compare their efficiencies. Efficiency will be understood as limits of detection (LOD), achievable background equivalent concentrations (BEC) and ability to remove overlapping molecular ions.

Introduction

The aim of every chemical analysis is to achieve accurate results. In ICP-MS, however, a large number of molecular species overlap with analyte masses.

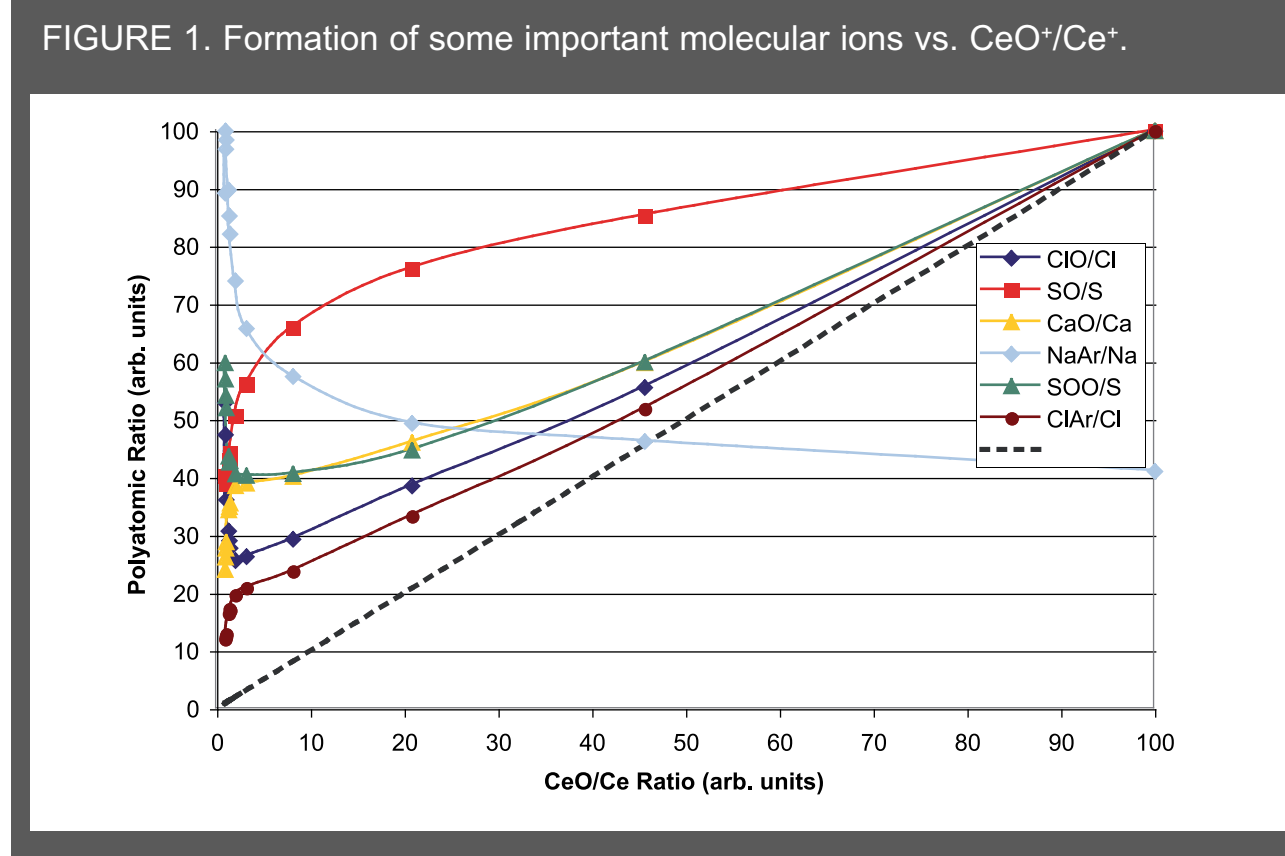
Those are either remains of incomplete destruction of molecules introduced into the ICP, or recombination products of ions generated by the plasma.

Several techniques have been developed to overcome the spectral interferences caused by such molecular ions, like optimized sample introduction systems, high resolution mass spectrometers, and collision/reaction cells.

THE BEST INTERFERENCE IS THE ONE THAT DOES NOT EXIST!

Based upon this analytical wisdom a careful instrument tuning is a good starting point. A widely accepted indicator for potential spectral interferences is the CeO^+/Ce^+ ratio. Many molecule formation rates follow the CeO^+/Ce^+ ratio. However, some do not. Figure 1 shows formation rates of some important matrix-dependant molecular ions against the CeO^+/Ce^+ ratio. Especially $NaAr^+$ does not follow the general trend. Therefore special attention has to be paid to operating the collision/reaction cell in its most appropriate way.

In addition to the matrix-derived poly-atomic species a large number of gas-based molecular ions exist, e.g. ArC , ArO , and $ArAr$. They may co-exist with matrix-specific ions.

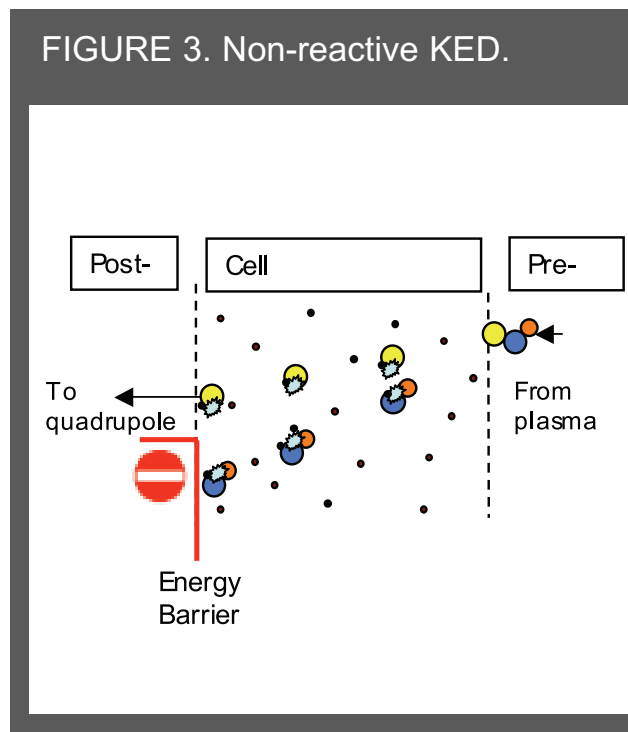
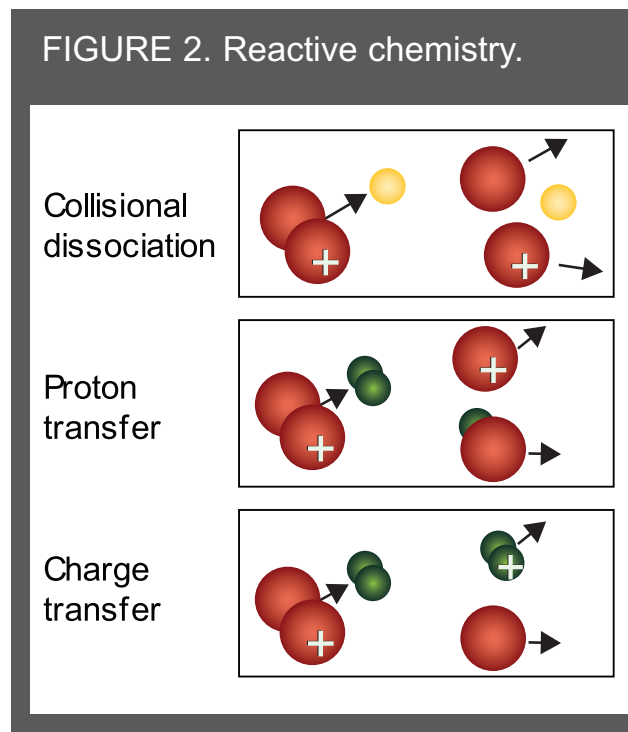


Reaction cell or Collision cell?

Basically, both types of cell share the same technology. In what they differ is the regime established inside. Applying reactive gases like H_2 or NH_3 the cell becomes a reaction cell. Pressurizing with a non-reactive gas such as He it turns into a collision cell.

There are several chemical reactions that take place simultaneously inside a reaction cell. The most prominent reactions are charge transfer and proton transfer reactions. Figure 2 shows a selection of mechanisms for a reaction cell. However, only such reactions can be performed that are in agreement with thermodynamic laws. Hence, especially Ar-linked molecular ions can be destroyed by reactive chemistry while metal oxides and some non-metal oxides cannot.

Without the need of chemical reactivity all kinds of molecular ions can be separated from mono-atomic analyte ions. This process is based on collisions with inert gases like He and is called Kinetic Energy Discrimination (KED). Figure 3 illustrates this mode of operation. The disadvantage with KED is a significant loss in sensitivity.



Methods

For all the work described here the following equipment was used:

- XSERIES 2 ICP-MS (Thermo Fisher Scientific) with CCT and Peltier-cooled spray chamber (1 °C)
- CH_4 addition to the ICP (75 mL/min 2% CH_4 in Ar)
- Combined reaction/collision cell operated with
 - + 8% H_2 in He (8 mL/min)
 - + 2% NH_3 in He (6 mL/min)
 - + high-purity He (8 mL/min)
 - + 8% H_2 in He or high-purity He for KED (5.5 mL/min)
- "TraceMetal" grade acids (Thermo Fisher Scientific)
- Single element standards "Peak Performance" (CPI International, Amsterdam, The Netherlands)
- Multi element standard "M21" (Merck KGaA, Darmstadt, Germany)

The matrices investigated play an important role in many application areas like environmental and food analysis and include:

HNO_3	(1%)
Cl	(1 g/L, as HCl)
S	(1 g/L as H_2SO_4)
Na	(500 mg/L, as $NaNO_3$)
Ca	(500 mg/L, as $Ca(NO_3)_2$)
NaCl	(1.5 g/L)

Each matrix was analyzed separately under the following conditions:

- Standard mode, CCT inactive
- Reactive chemistry: H_2/He and NH_3/He
- Collision cell without KED: He
- KED (1 V, 2 V and 3 V) with either H_2/He or high-purity He only

Under these conditions, the ability of the CCT to reduce spectral interferences was compared.

Results

Figures 4 - 6 show the BEC and LOD levels for a selection of prominent spectral interferences resulting from the investigated matrices. Each chart displays the results for increasing KED voltages, standard mode, H_2 , He, and NH_3 modes (left to right). BECs are shown as bars and LODs as lines.

Both reactive chemistry and collision cell modes with KED were able to reduce spectral interferences. There was no "best choice": in some cases reactive chemistry gave lowest BECs and LODs, in others KED modes were clearly better.

FIGURE 4. Spectral interferences observed in HNO_3 .

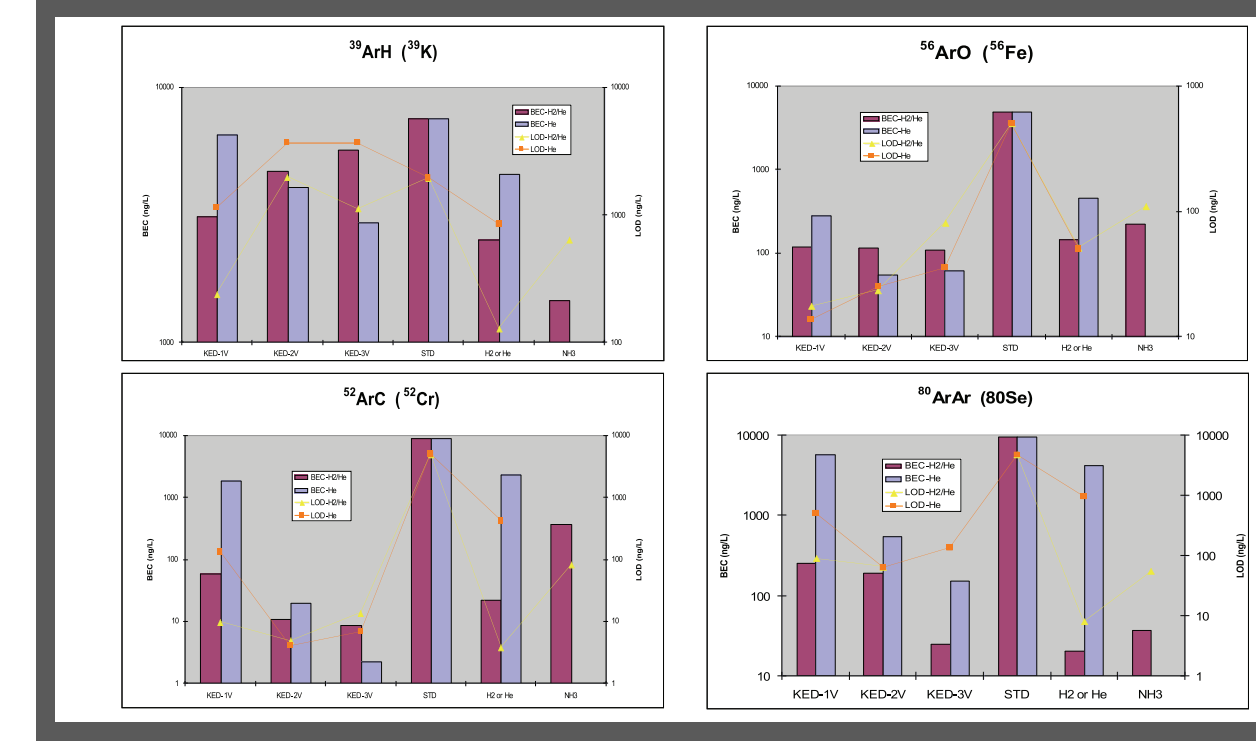


FIGURE 5. Spectral interferences observed in HCl and H_2SO_4 .

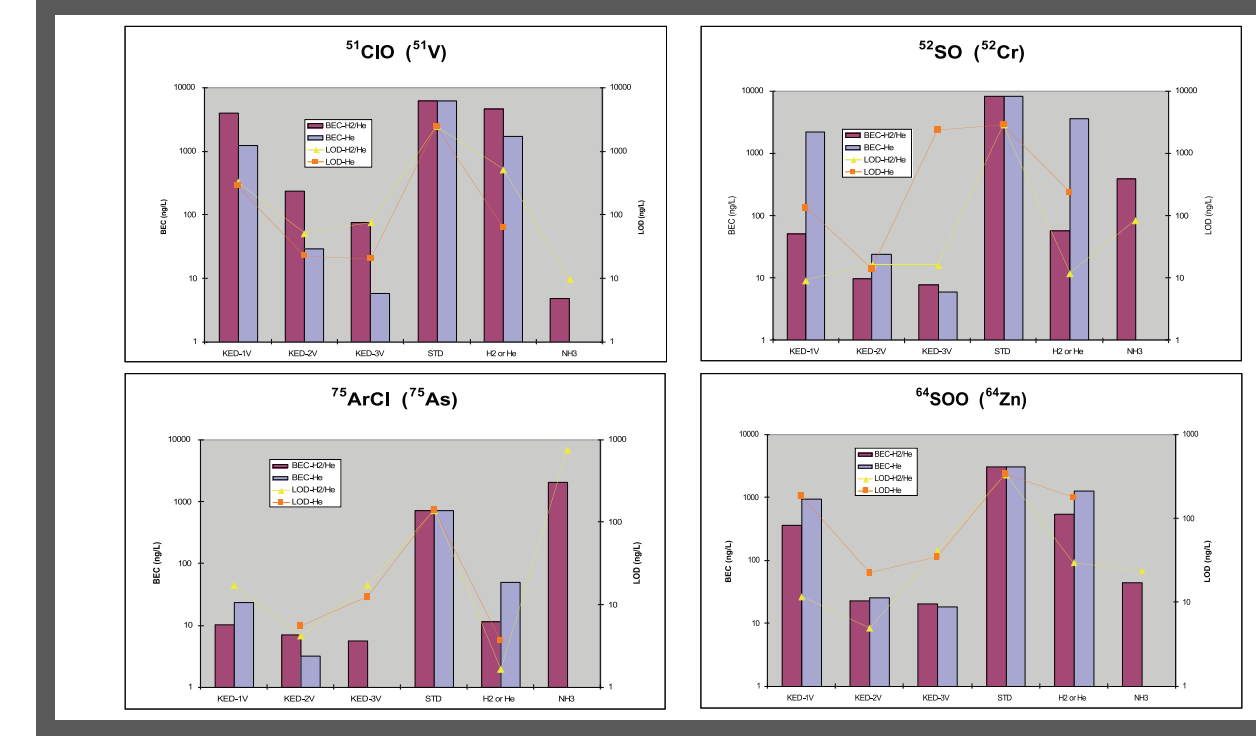
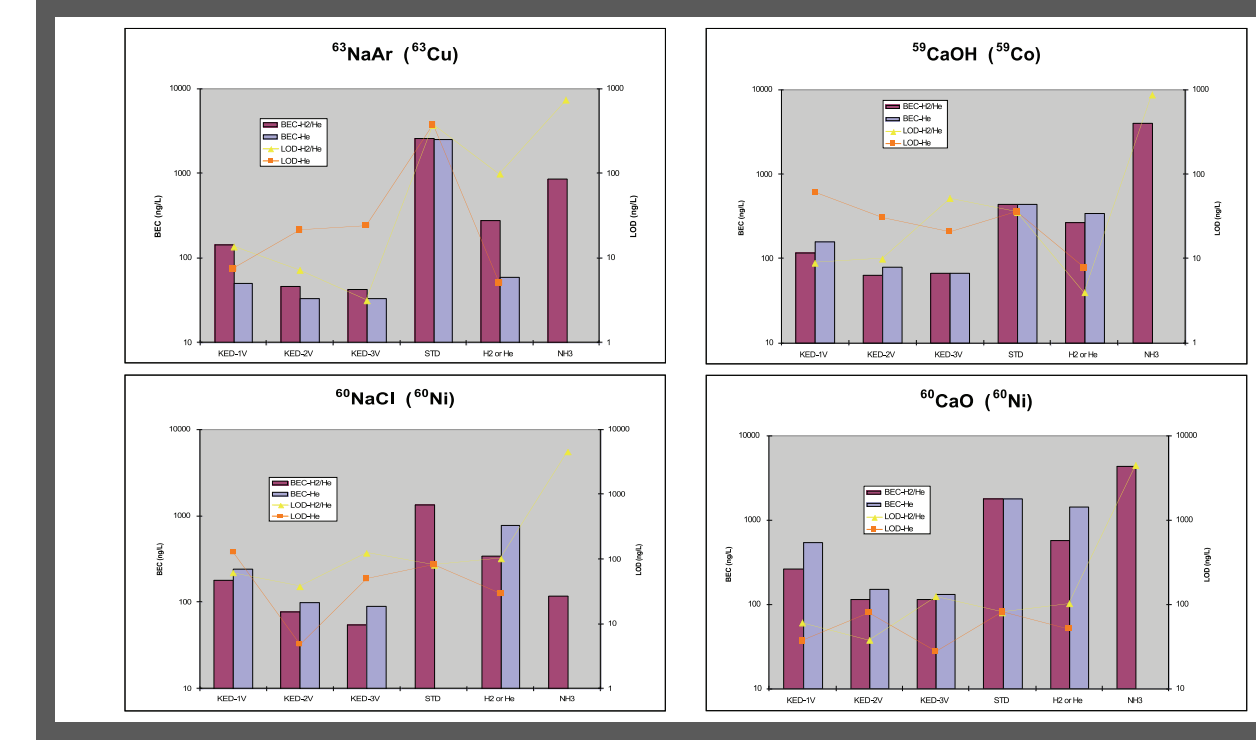


FIGURE 6. Spectral interferences observed in dissolved salts.



Reactive molecular ions, e.g. Ar-linked ions, could be efficiently removed by reactive chemistry. For the ArH ion causing a spectral interference on K, the NH_3/He mixture gave lowest BECs. In terms of LODs, however, the H_2/He mixture proved to be the best regime. For the analysis of V in the presence of chlorides again the NH_3/He gas mixture gave best results.

Collision cell modes with either He or H_2/He mixture could be identified as versatile regimes for removing most molecular ions that may cause spectral interferences. They worked well with both reactive molecules like ArC and non-reactive compounds, e.g. CaO . KED modes cause significant loss in sensitivity. Nonetheless, in many cases investigated both BECs and LODs were best with KED modes.

The question which gas works best with KED modes cannot be answered clearly. There is a tendency that the H_2/He gas mixture gives better LODs. In a few cases, however, He as a collision gas showed lower BECs or LODs.

All LODs shown in figures 4 - 6 can be interpreted qualitatively, only. Although all reagents used for matrix preparations were of highest purity available, remaining contaminations increased BECs and LODs. Example: the Ca matrix was prepared from a 10 g/L solution with 99.997% purity with a certified Ni contamination of 3 µg/L. As the prepared solution was diluted to 500 mg/L, it contained a Ni level of ca. 0.15 µg/L. Consequently, under no regime investigated BECs could be better than that level.

Conclusions

Modern ICP-MS instruments equipped with state-of-the-art collision/reaction cells can efficiently reduce spectral interferences to negligible levels so that accurate analysis at low concentration levels can be performed even in difficult matrices. The question which regime – reactive chemistry or collision cell with KED – cannot be answered in one way or the other. There are a number of spectral interferences that can be reduced ideally with reactive chemistry while others are better treated under KED conditions.

High-purity He only works well in many KED cases. The mixture of H_2 with He, however, gives even better results. It is assumed that this gas mixture employs KED and reactive chemistry regimes simultaneously. Consequently, it shows superior performance when there is more than one type of molecular ions overlapping with analyte ions.

For highest flexibility and best detection power in sample analysis experiments should switch between several cell regimes.