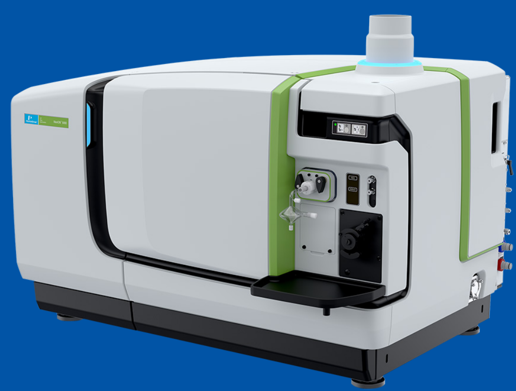
TECHNICAL NOTE

ICP - Mass Spectrometry



Novel Interference Removal Opportunities with the NexION 5000 ICP-MS

Introduction

Multi-quadrupole technology, in combination with controlled reactions in the Universal Cell (UCT) of the NexION® 5000 ICP-MS, has opened new possibilities for spectral interference removal.[1] As was described in the technical note "Interferences in ICP-MS: Do we still have to worry about them?"[2], the MS/MS and Mass Shift modes, in conjunction with three cell analytical modes (Std, KED and DRC), can solve many challenging problems, not previously possible using a single quadrupole system. This work is a continuation of a discussion on spectral interference removal and presents dynamic reactions with three gases (O_2, NH_3 and CH_4) that, in tandem with multi-quadrupole technology, are a powerful tool in interference management on the NexION 5000 ICP-MS.

Quadrupoles in the NexION 5000 ICP-MS

Each quadrupole in the NexION 5000 system plays a significant role in transmitting elements of interest to the detector. The Quadrupole Ion Deflector (QID – Q0) rejects photons and neutral species and, at the same time, transfers a selected mass range into the spectrometer, enhancing sensitivity and, in some cases, rejecting some sample matrices. The second quadrupole (Q1), placed before the Universal Cell (Q2), can work as a mass-filtering device with a nominal resolution of 0.7 amu. The mass-filtering ability of Q1 allows only ions of a specific mass to be passed into the Universal Cell, while all other ions from the matrix, solvents and plasma not residing at the mass of interest are rejected. This capability has a significant impact on the reduction of spectral interferences which may arise from reactions of lower mass matrix ions with gases in the cell. Q1 works together with the quadrupole Universal Cell where up to four reactive or non-reactive gases can be used to create desirable reactions or collisions. Q3, the fourth quadrupole in the NexION 5000 ICP-MS, works predominantly as a resolving transmission analyzer. In MS/MS mode, Q1 and Q3 are set to the same analyte mass, while in Mass Shift mode, Q1 is set to a mass of interest and Q3 is set to a higher mass where the polyatomic ion, product of a reaction of an analyte with a reaction gas, resides. In Mass Shift mode, analyte products are measured on masses free from interferences, as discussed in the following sections.

PerkinElmer®
For the Better

Universal Cell (UCT) in the NexION 5000 ICP-MS

When analyte and interfering ions enter the Universal Cell, which is filled with a reactive gas, they interact with the gas and reactions occur. The outcome of these reactions is that the analyte or interfering ions either form ions at new masses or are changed into neutral particles.[3,4]

For the reaction gas to be considered suitable for interference correction, three criteria need to be met.[5] First, the reaction of the gas should preferentially be allowed to proceed thermodynamically with either the interferant species or the analyte of interest through an exothermic reaction. The UCT has the unique capability of adjusting the available energy for reactions to proceed. Second, the reaction kinetics in the gas phase suggest that the reaction between the reaction gas and the target polyatomic or analyte ion should be relatively fast. Finally, the use of a selected reaction gas should not lead to reaction by-product species that would be considered new interferences on the target mass or other analyte. Utilizing the quadrupole in the Universal Cell has a major advantage over systems with multipoles in the reaction/collision cells because it has a well-defined stability diagram with controlling parameters RPq and RPa, as previously described in the first technical note on interferences.[2] These parameters create a dynamic bandpass that makes gas-phase reactions more specific and permits only desirable reaction products to enter Q3.

Combination of Multi-Quad Technology and UCT in the NexION 5000 ICP-MS

Since the introduction of cell technology, spectral interference removal has dramatically improved.

In the NexION 5000 ICP-MS, due to the presence of multi-quadrupole technology in combination with the UCT, spectral interference elimination can be achieved in MS/MS mode by changing the interferences into different ions or neutrals which do not interfere with the mass of the analyte. If the analyte reacts quickly and efficiently with a gas, instead of removing interferences on an analyte mass, Mass Shift mode moves the analyte ion as a product of the gas-phase reaction to a higher mass where no interferences are present, and the background is clean.

This note describes the reaction results of 67 elements with O_2, NH_3 and CH_4 using product ion scans, which allow both the mass and intensities of product ions to be determined. Even though the results are not quantitative and reaction rates were estimated based on a sensitivity ratio of the highest cluster to an analyte, the following periodic tables with color-coded elements provide a strong indication of their reactivities. Elements were divided into four categories based on the reactivity rates: strong, medium, weak and no or minimal reaction. The estimated reactivity rates are generally in good agreement with values found in the literature.[6,7] In some cases, our indicated reaction rates are higher than those in the literature since more energy can be imparted on the ions through optimized UCT parameters such as AFT (Axial Field Technology) voltage and RPq.

Reactions with Oxygen (O_2)

The periodic table of reactions with O_2 shown in Figure 1 indicates that several elements shaded in dark blue react very strongly with O_2. The mechanism of these reactions could be explained by O-atom transfer or O_2 clustering, creating oxide ions at masses 16 or 32 amu higher than the analyte. For example, $^{48}Ti^+$, as shown in Figure 2, creates a strong cluster at mass 64 and a weak one at mass 80. However, in the case of $^{238}U^+$,

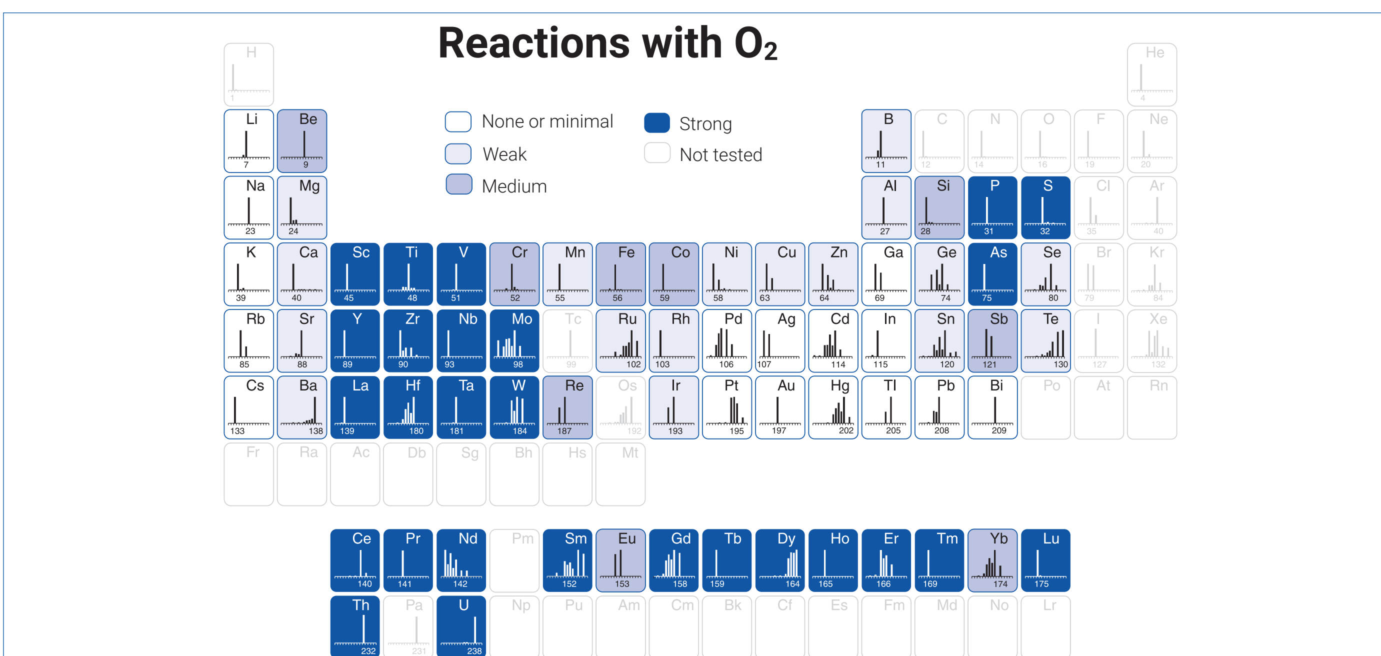


Figure 1: Elements' reactivity with O_2.

it is the opposite (Figure 3): a weak cluster at mass 254 and a strong one at mass 270. Of course, when an analyte creates multiple product ions, their sensitivity depends on the reaction gas density in the UCT. In general, the optimization of the gas flow can change the sensitivity ratio of the analyte's product ions – higher flows promote higher mass clusters.

In this next example (Figure 4), $^{98}MoO^+$ creates an interference on the Cd isotope at mass 114. However, if the UCT is pressurized with O_2 and gas density increases, MoO_2^+ at mass 130 becomes a dominant species and Cd can be determined in MS/MS mode at mass 114 free from interference.

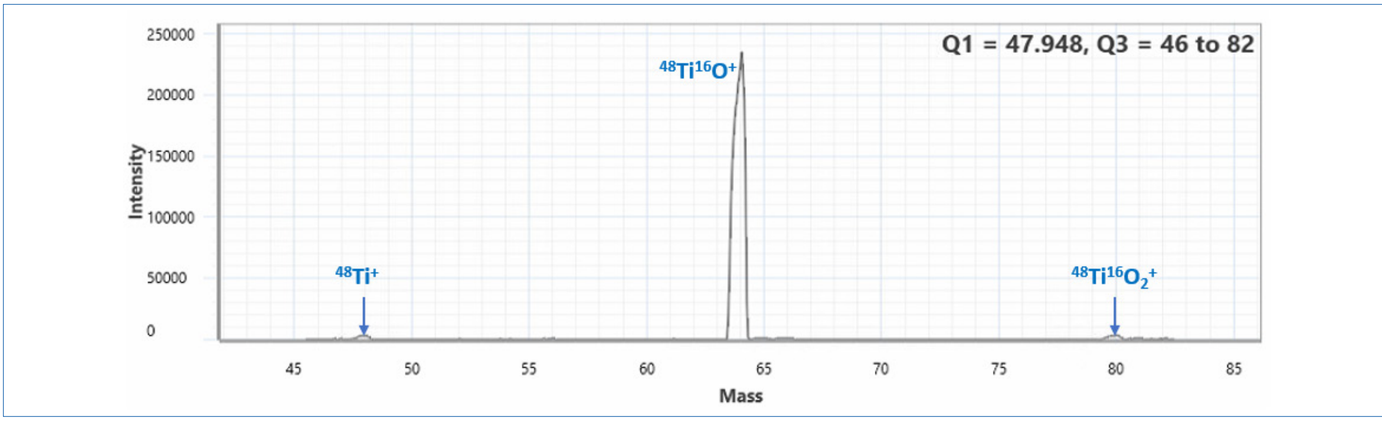


Figure 2: Ti product ion scan with O_2.

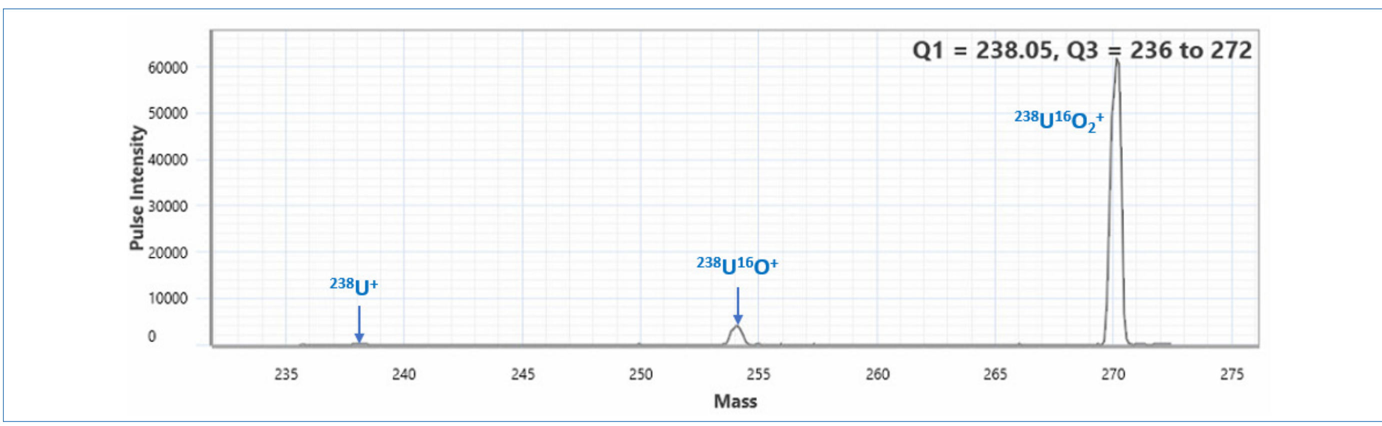


Figure 3: U product ion scan with O_2.

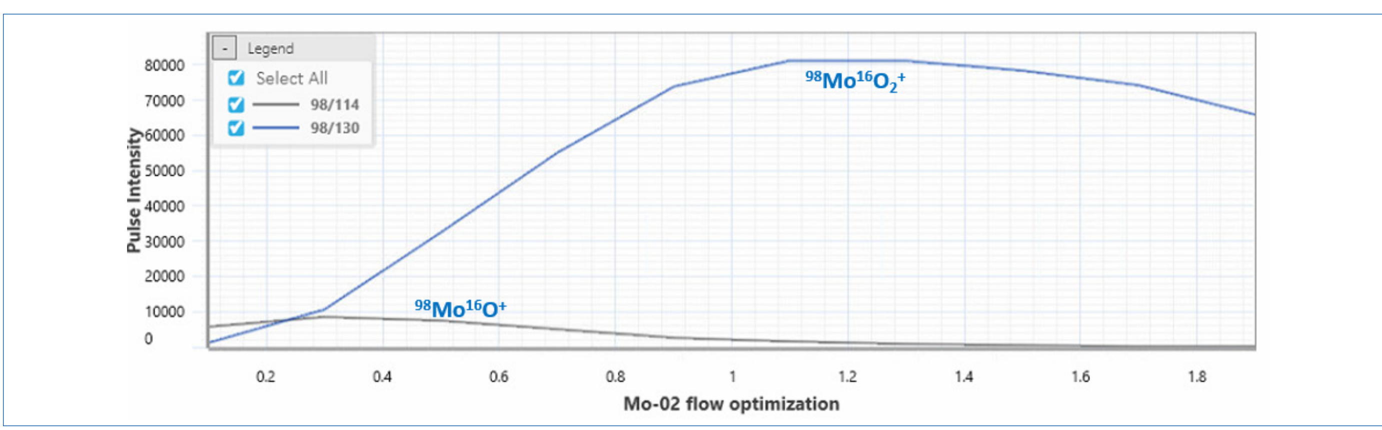


Figure 4: Optimization of O_2 flow for MoO^+ at mass 114 and MoO_2^+ at mass 130.

The dynamic bandpass, especially the RPq parameter, could promote some clustering reactions by increasing the reaction efficiency for some analytes (e.g. Cr, Mn, Fe, Co, Ni, Cu, Zn and Se) that do not react or that react weakly with O_2 under standard conditions with RPq values of 0.4-0.6.

In Figure 5, an optimization of the RPq parameter indicates that sensitivity of the CrO^+ cluster at mass 68 is the highest at RPq=0.8. The Mass Shift approach can be an option when spectral interferences on Cr at mass 52 cannot be completely removed by MS/MS in DRC or KED modes.

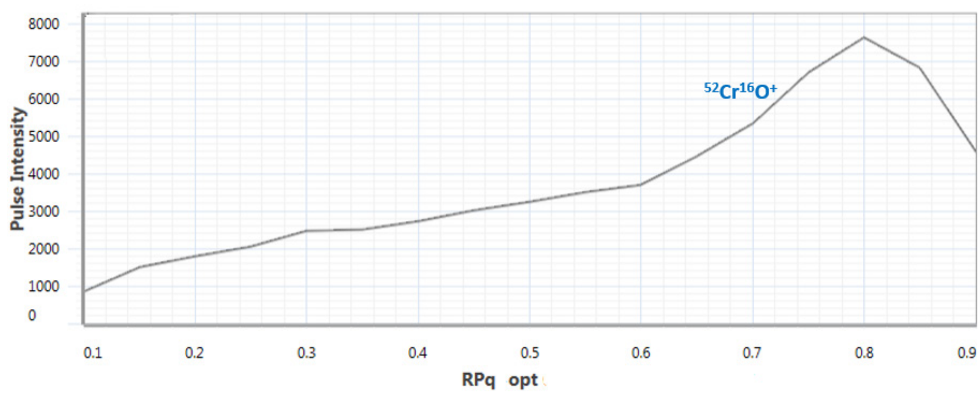


Figure 5: Optimization of Rpq parameter for CrO^+.

Reactions with Ammonia (NH_3)

Ammonia is another reaction gas that can be very useful in moving some reactive elements to higher masses and measuring them in Mass Shift mode as clusters or products escaping spectral interferences residing on their original masses. Figure 6 shows a periodic table with elements where different shades of green indicate their reactivity with NH_3.

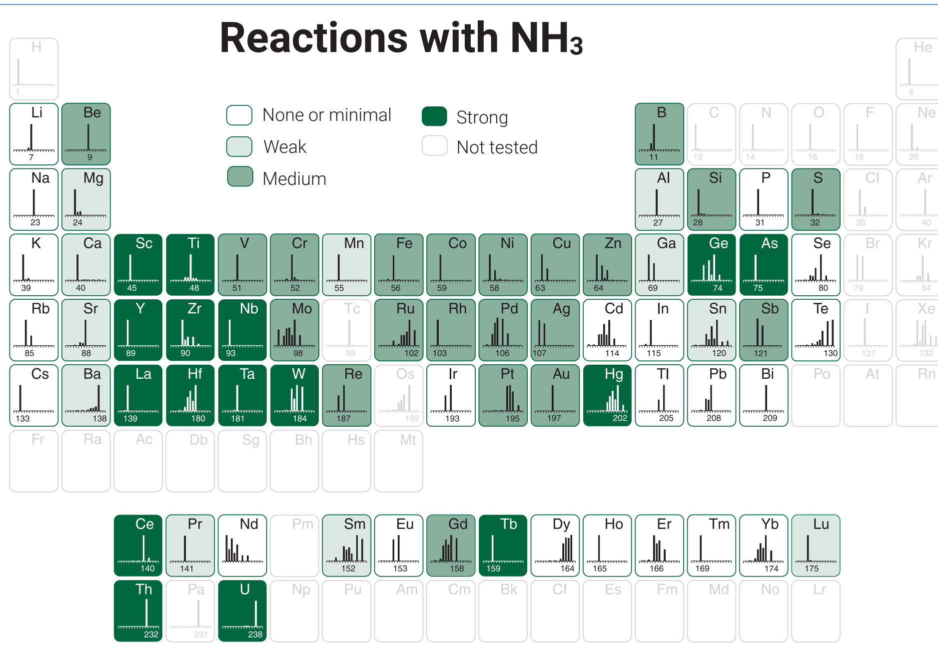


Figure 6: Elements' reactivity with NH_3.

A few elements that react strongly with NH_3 create multiple clusters with NH_3, and the optimization of the NH_3 flow can change sensitivity of individual clusters quite dramatically. Germanium (Ge) is a good example; it creates clusters with ammonia at masses 90, 107, 124 and 141. The product ion scan run with 0.8 mL/min of NH_3 shows the highest sensitivity cluster at mass 107 (Figure 7). However, when the NH_3 flow was increased to 1.2 mL/min, the cluster at mass 124 became the most prominent (Figure 8). Such flexibility in the selection clusters can be very useful when analyzing trace elements in complex matrices.

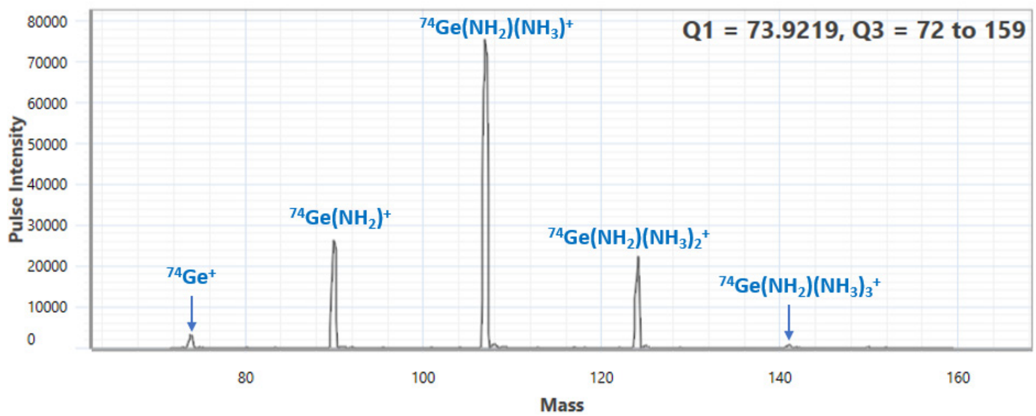


Figure 7: Ge product ion scan with 0.8 mL/min NH_3 flow.

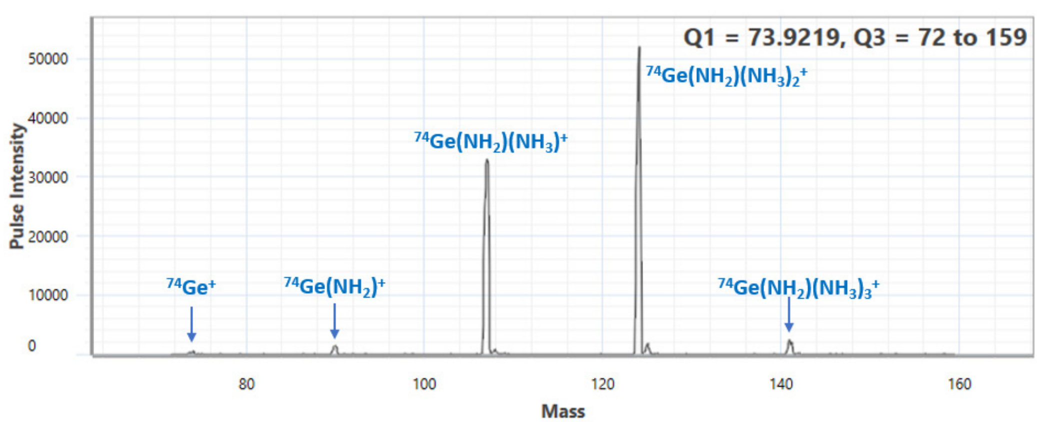


Figure 8: Ge product ion scan with 1.2 mL/min NH_3 flow.

Reactions with Methane (CH_4)

Methane is less powerful for clustering individual elements than O_2 or NH_3, however, in certain situations, it can be useful as well. One of the CH_4 characteristics is strong reactions with some ions that create spectral interferences such as Ar^+, $ArAr^+$ or ArO^+. In such cases, instead of Mass Shift, MS/MS would be a preferable mode of analysis.

Figure 9 shows a periodic table with elements where different shades of orange indicate their reactivity with CH_4.

A few elements, such as As, Zr, Ta, W, Ir and Pt, react relatively strongly with CH_4 and their Mass Shift results could be a confirmation of results obtained in Mass Shift mode with a different gas. For example, As is historically measured as AsO^+ at mass 91 (Figure 10), but due to a strong reaction with CH_4, it can also be measured as $AsCH_2^+$ at mass 89 (Figure 11).

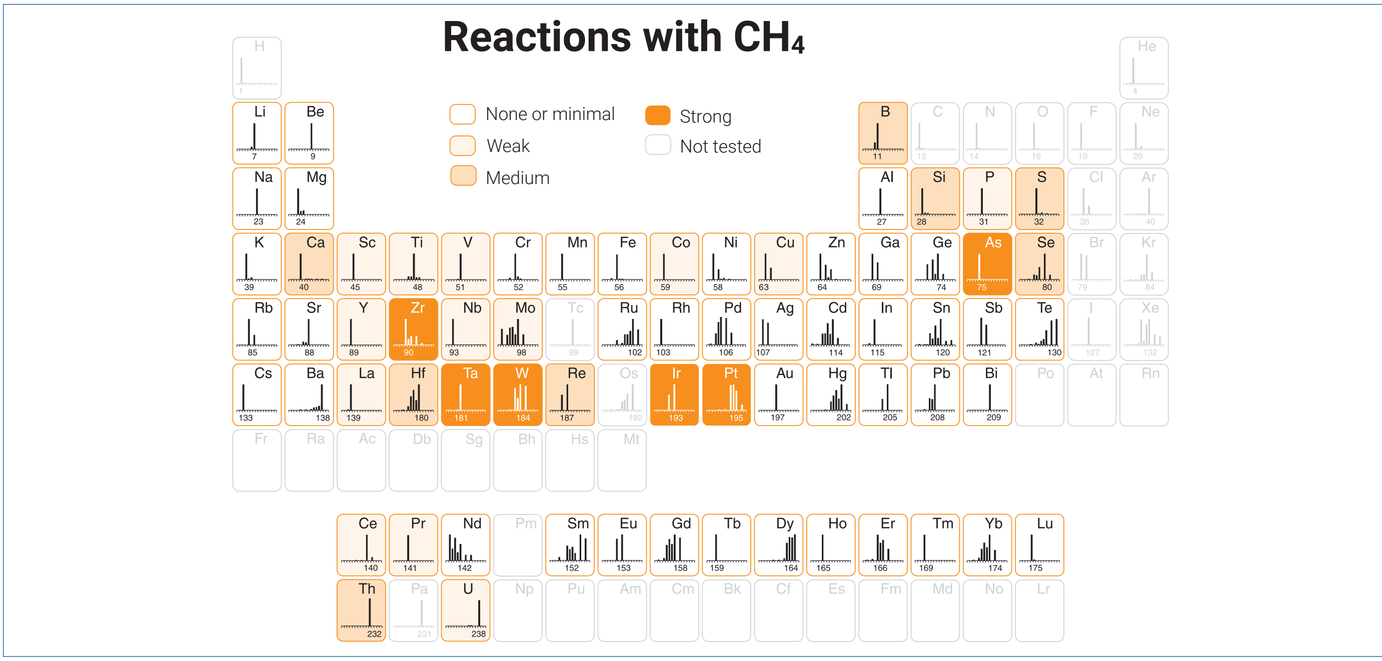


Figure 9: Elements' reactivity with CH_4.

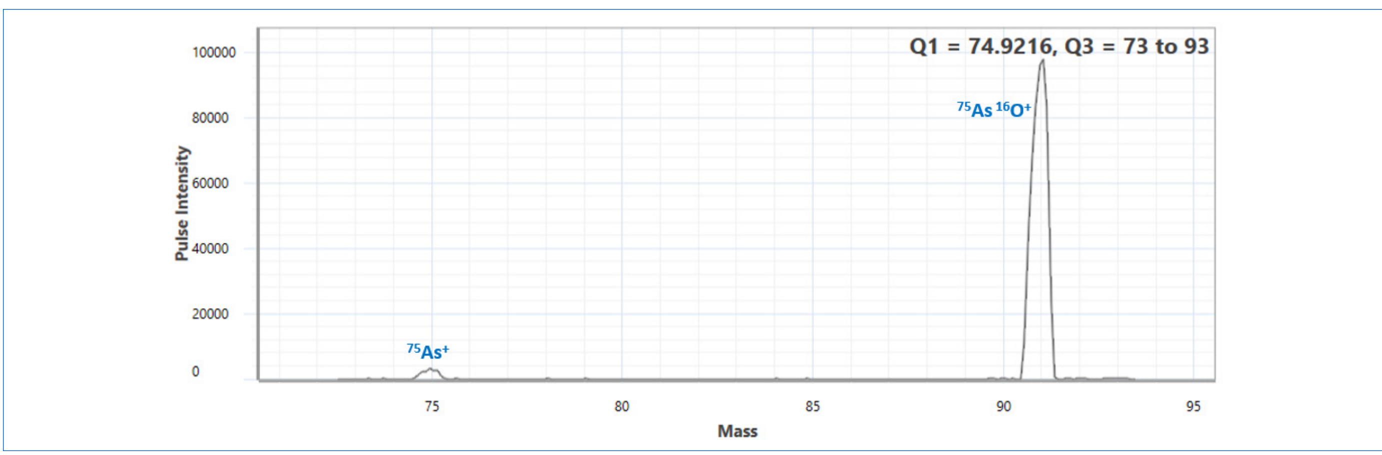


Figure 10: As product ion scan with O_2.

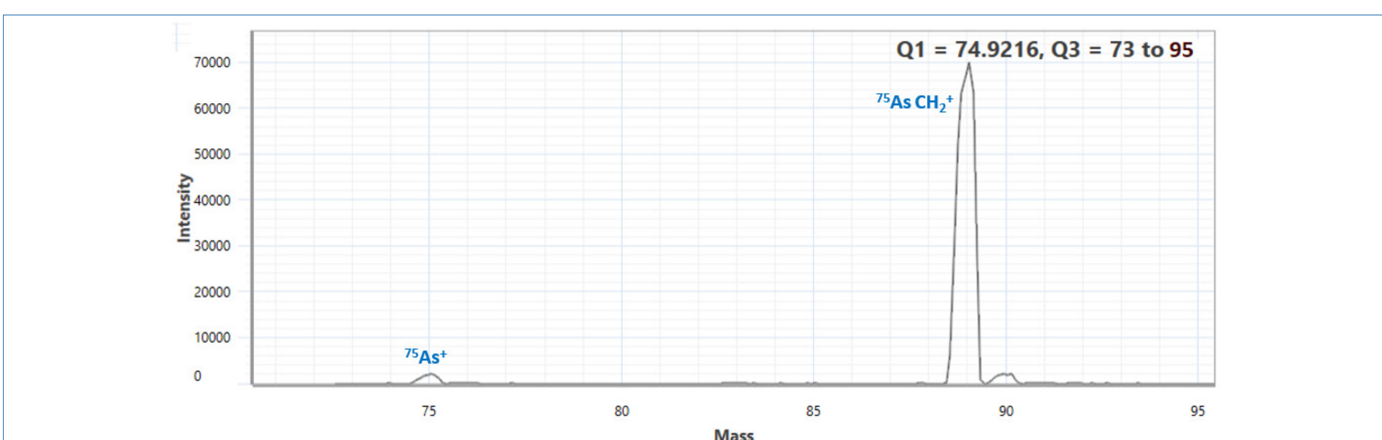


Figure 11: As product ion scan with CH_4.

Conclusion

The NexION 5000 ICP-MS with multi-quadrupole technology and Universal Cell is able to take full advantage of element reactivity with 100% pure gases by analyzing them as cluster ions at higher masses where no interferences reside, and the background is clean. The UCT, thanks to its quadrupole design in combination with dynamic bandpass tuning, provides the unique ability of controlling desirable reactions, promoting some weak reactions, rejecting interferences, and preventing side reactions from taking place.[5] Periodic tables with color-coded elements indicating their reactivity with a specific gas are a useful tool for method development in complicated matrices, effectively predicting spectral interferences and providing a way to prevent them.

Author

Ewa Pruszkowski
PerkinElmer, Inc.
Shelton, CT USA

Reference

1. "NexION 5000 Multi-Quadrupole ICP-MS", PerkinElmer Product Note, 2020.
2. Pruszkowski E., "Interferences in ICP-MS: Do we still have to worry about them?", PerkinElmer Technical note, 2021.
3. Tanner S.D. et al., "Theory, Design, and Operation of a Dynamic Reaction Cell for ICP-MS", Atomic Spectroscopy, 20, (2), 45-52, 1999.
4. Bandura D.R. et al., "Reaction chemistry and collisional processes in multipole devices for resolving isobaric interferences in ICP-MS", Fresenius J Anal Chem, 2001.
5. Badiei H. et al., "Multimode Cells and Methods of Using Them", United States Patent 8,426,804 B2, Apr.23, 2013.
6. Anicich V.G., "An Index of the Literature for Bimolecular Gas Phase Cation-Molecule Reaction Kinetics", JPL Publication 03-19.
7. "Interactive Tables of Reaction Rates", Ion Chemistry Laboratory, York University, Toronto, Canada, http://www.yorku.ca/dkbohme/research/selection_table.html.

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

405790 PKI