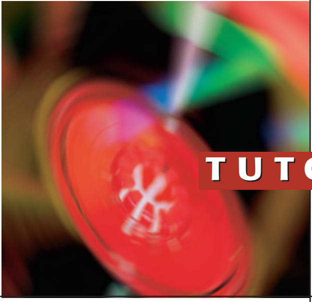

TUTORIAL

A Beginner's Guide to ICP-MS

Part IX — Mass Analyzers: Collision/Reaction Cell Technology

Robert Thomas

The detection capability of traditional quadrupole mass analyzers for some critical elements is severely compromised by the formation of polyatomic spectral interferences generated by either argon, solvent, or sample-based ionic species. Although there are ways to minimize these interferences — including correction equations, cool plasma technology, and matrix separation — they cannot be completely eliminated. However, a new approach called collision/reaction cell technology has recently been developed that virtually stops the formation of many of these harmful species before they enter the mass analyzer. Part IX of this series takes a detailed look at this innovative new technique and the exciting potential it has to offer.

A small number of elements are recognized as having poor detection limits by inductively coupled plasma mass spectrometry (ICP-MS). These elements are predominantly ones that suffer from major spectral interferences generated by ions derived from the plasma gas, matrix components, or the solvent–acid used to get the sample into solution. Examples of these interferences include:

- $^{40}Ar^{16}O$ on the determination of ^{56}Fe
- ^{38}ArH on the determination of ^{39}K
- ^{40}Ar on the determination of ^{40}Ca
- $^{40}Ar^{40}Ar$ on the determination of ^{80}Se
- $^{40}Ar^{35}Cl$ on the determination of ^{75}As
- $^{40}Ar^{12}C$ on the determination of ^{52}Cr
- $^{35}Cl^{16}O$ on the determination of ^{51}V.

The cold/cool plasma approach, which uses a lower temperature to reduce the formation of the argon-based interferences, is a very effective way to get around some of these problems (1); however, it is sometimes difficult to optimize, it is only suitable for a few of the interferences, it is susceptible to more severe matrix effects, and it can be time consuming to change back and forth between normal- and cool-plasma conditions. These limitations and the desire to improve performance led to the development of collision/reaction cells in the late 1990s. Designed originally for organic MS to generate daughter species to confirm identification of the structure of the parent molecule (2), they were used in ICP-MS to stop the appearance of many argon-based spectral interferences.

Basic Principles of Collision/Reaction Cells

With this approach, ions enter the interface in the normal manner, where they are extracted under vacuum into a collision/reaction cell that is positioned before the analyzer quadrupole. A collision/reaction gas such as hydrogen or helium is then bled into the cell, which consists of a multipole (a quadrupole, hexapole, or octapole), usually operated in the radio frequency (rf)-only mode. The rf-only field does not separate the masses like a traditional quadrupole, but instead has the effect of focusing the ions, which then collide and react with molecules of the collision/reaction gas. By a number of different ion-molecule collision and reaction mechanisms, polyatomic interfering ions like ^{40}Ar, $^{40}Ar^{16}O$, and ^{38}ArH, will either be converted to harmless noninterfering species, or the analyte will be converted to another ion which is not interfered with. This is exemplified by the reaction [1], which shows the use of hydrogen gas to reduce the ^{38}ArH polyatomic interference in the determination of ^{39}K. Hydrogen gas converts ^{38}ArH to the harmless H_3^+ ion and atomic argon, but does not react with the potassium. The ^{39}K analyte ions, free of the interference, then emerge from the collision/reaction cell, where they are directed toward the quadrupole analyzer for normal mass separation.

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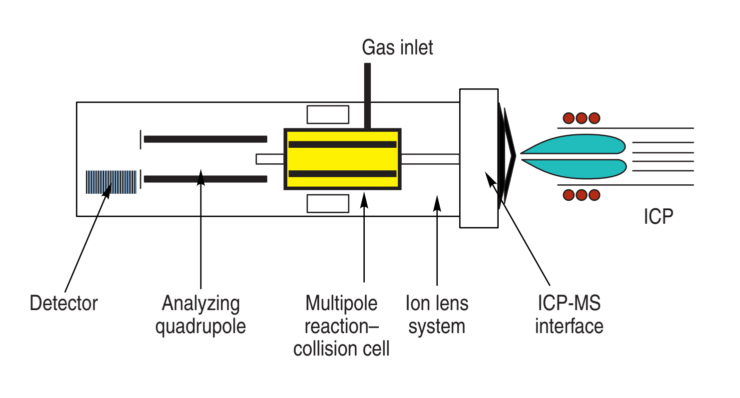

Figure 1. Layout of a typical collision/reaction cell instrument.

$^{38}ArH^+ + H_2 = H_3^+ + Ar$
$^{39}K^+ + H_2 = {}^{39}K^+ + H_2$ (no reaction) [1]

The layout of a typical collision/reaction cell instrument is shown in Figure 1.

Different Collision/Reaction Approaches

The previous example is a very simplistic explanation of how a collision/reaction cell works. In practice, complex secondary reactions and collisions take place, which generate many undesirable interfering species. If these species were not eliminated or rejected, they could potentially lead to additional spectral interferences. Basically two approaches are used to reject the products of these unwanted interactions:

- Discrimination by kinetic energy
- Discrimination by mass.

The major differences between the two approaches are in the types of multipoles used and their basic mechanism for rejection of the interferences. Let's take a closer look at how they differ.

Discrimination by Kinetic Energy

The first commercial collision cells for ICP-MS were based on hexapole technology (3), which was originally designed for the study of organic molecules using tandem MS. The more collision-induced daughter species that were generated, the better the chance of identifying the structure of the parent molecule; however, this very desirable characteristic for liquid chromatography or electrospray MS studies was a disadvantage in inorganic MS, where secondary reaction–product ions are something to be avoided. There were ways to minimize this problem, but they were still limited by the type of collision gas that could be used. Unfortunately, highly reactive gases — such as ammonia and methane, which are more efficient at interference reduction — could not be used because of the limitations of a non-scanning hexapole (in rf-only mode) to adequately control the secondary reactions. The fundamental reason is that hexapoles do not provide adequate mass discrimination capabilities to suppress the unwanted secondary reactions, which necessitates the need for kinetic energy discrimination to distinguish the collision product ions from the analyte ions. This is typically achieved by setting the collision cell bias slightly less positive than the mass filter bias. This means that the collision-product ions, which have the same energy as the cell bias, are discriminated against and rejected, while the analyte ions, which have a higher energy than the cell bias, are transmitted.

The inability to adequately control the secondary reactions meant that low reactivity gases like He, H_2, and Xe were the only option. The result was that ion-molecule collisional fragmentation (and not reactions) was thought to be the dominant mechanism of interference reduction. So even though the ion transmission characteristics of a hexapole were considered very good (with respect to the range of energies and masses transmitted), background levels were still relatively high because the interference rejection process was not very efficient. For this reason, its detection capability — particularly for some of the more difficult elements, like Fe, K, and Ca — offered little improvement over the cool plasma approach. Table I shows some typical detection limits in ppb achievable with a hexapole-based collision cell ICP-MS system (4).

Recent modifications to the hexapole design have significantly improved its

Table I. Typical detection limits (in ppb) achievable with a hexapole-based collision cell ICP-MS system (4).

Element	Isotope	Elemental Sensitivity (cps/[μg/mL])	Detection Limit (ppb)
Be	9	6.9×10^7	0.0077
Mg	24	1.3×10^8	0.028
Ca	40	2.8×10^8	0.07
V	51	1.7×10^8	0.0009
Cr	52	2.4×10^8	0.0007
Mn	55	3.4×10^8	0.0017
Fe	56	3.0×10^8	0.017
Co	59	2.7×10^8	0.0007
Ni	60	2.1×10^8	0.016
Cu	63	1.9×10^8	0.003
Zn	68	1.1×10^8	0.008
Sr	88	4.9×10^8	0.0003
Ag	107	3.5×10^8	0.0003
Cd	114	2.4×10^8	0.0004
Te	128	1.3×10^8	0.009
Ba	138	5.9×10^8	0.0002
Tl	205	4.0×10^8	0.0002
Pb	208	3.7×10^8	0.0007
Bi	209	3.4×10^8	0.0005
U	238	2.3×10^8	0.0001

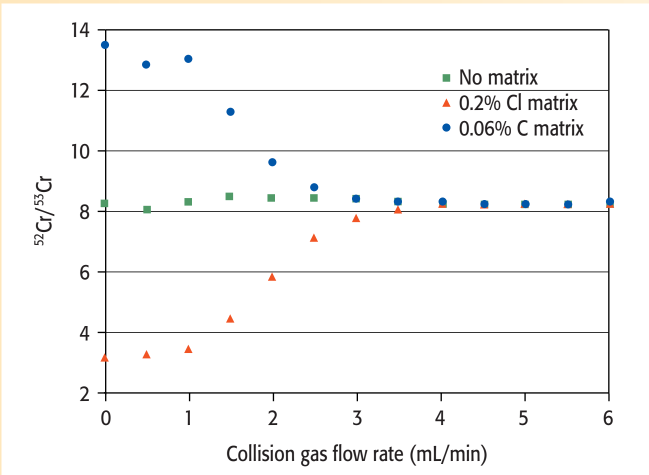

Figure 2. The use of a helium/ammonia mixture with a hexapole-based collision cell for the successful determination of $^{52}Cr/^{53}Cr$ isotopic ratios (courtesy of Thermo Elemental, Franklin, MA).

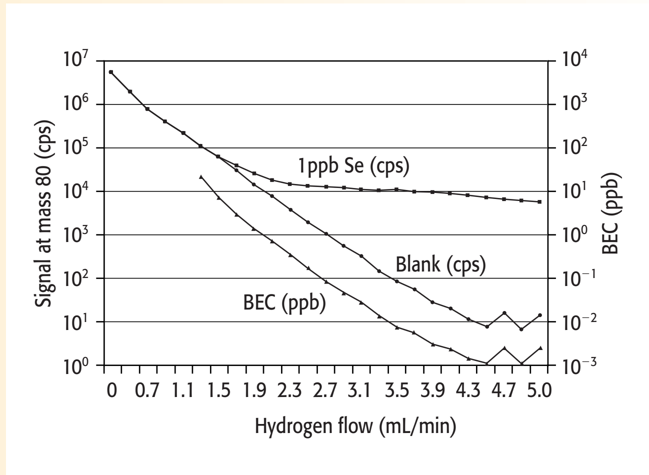

Figure 3. Background reduction of the argon dimer ($^{40}Ar_2^+$) with hydrogen gas using an octapole reaction cell (Courtesy of Agilent Technologies, Wilmington, DE).

collision/reaction characteristics. In addition to offering good transmission characteristics and kinetic energy discrimination, they now appear to offer basic mass-dependent discrimination capabilities. This means that the kinetic energy discrimination barrier can be adjusted with analytical mass, which offers the capability of using small amounts of highly reactive gases. Figure 2 shows an example of the reduction of both $^{40}Ar^{12}C$ and $^{37}Cl^{16}O$ using helium with a small amount of ammonia, in the isotopic ratio determination of $^{52}Cr/^{53}Cr$ (^{52}Cr is 83.789% and ^{53}Cr is 9.401% abundant). It can be seen that the $^{52}Cr/^{53}Cr$ ratio is virtually the same in the chloride and carbon matrices as it is with no matrix present when the optimum flow of collision/reaction gas is used (5).

Another way to discriminate by kinetic energy is to use an octapole in the collision/reaction cell instead of a hexapole. The benefit of using a higher order design is that its transmission characteristics, particularly at the low mass end, are slightly higher than lower order multipoles. Similar in design to the hexapole, collisional fragmentation and energy discrimination are the predominant mechanisms for interference reduction, which means that lower reactivity gases like hydrogen and helium are preferred. By careful design of the interface and the entrance to the cell, the collision/reaction capabilities can be improved, by reducing the number of sample/solvent/plasma-based ions entering the cell. This enables the collision gas to be more effective at reducing the interferences. An example of this is the use of H_2 as the cell gas to reduce the argon dimer ($^{40}Ar_2^+$) interference in the determination of the major isotope of selenium at mass 80 (^{80}Se). Figure 3 shows an example of a dramatic reduction in the $^{40}Ar_2^+$ background at mass 80 using an ICP-MS fitted with an octapole reaction cell. By using the optimum flow of H_2, the spectral background is reduced by about six orders of magnitude, from 10,000,000 cps to 10 cps, producing a background equivalent concentration of approximately 1 ppt for ^{80}Se (6).

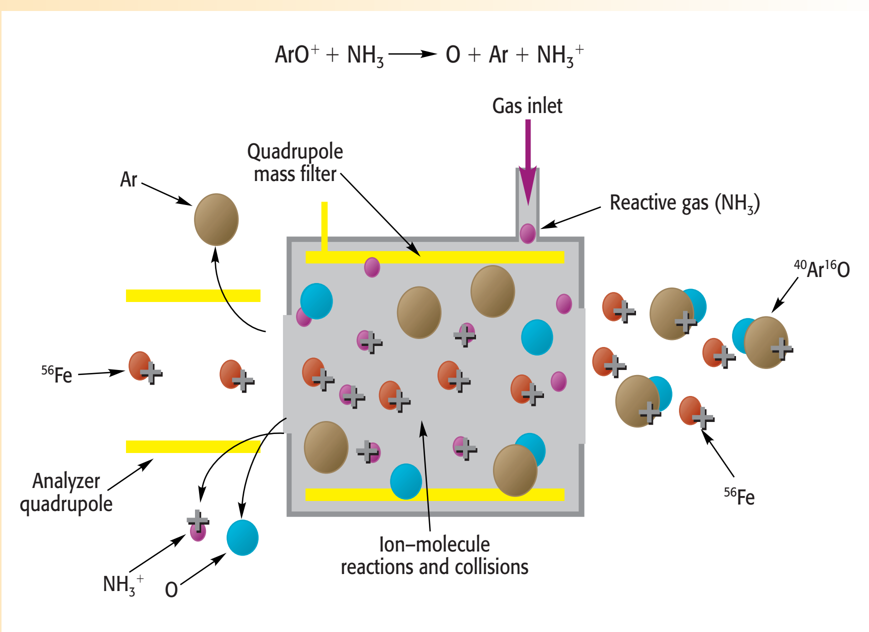

Figure 4. Elimination of the ArO interference with a dynamic reaction cell.

Discrimination by Mass

The other way to reject the products of the secondary reactions/collisions is to discriminate them by mass. Unfortunately, higher order multipoles cannot be used for efficient mass discrimination because the stability boundaries are diffuse, and sequential secondary

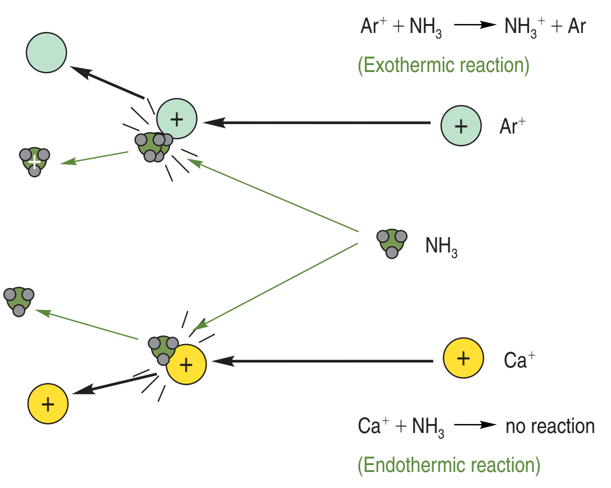

Figure 5. The reaction between NH_3 and Ar^+ is exothermic and fast, while there is no reaction between NH_3 and Ca^+ in the dynamic reaction cell.

reactions cannot be easily intercepted. The way around this problem is to use a quadrupole (instead of a hexapole or octapole) inside the reaction/collision cell, and use it as a selective bandpass filter. The benefit of this approach is that highly reactive gases can be used, which tend to be more efficient at interference reduction. One such development that uses this approach is called dynamic reaction cell technology (7, 8). Similar in appearance to the hexapole and octapole collision/reaction cells, the dynamic reaction cell is a pressurized multipole positioned before the analyzer quadrupole. However, the similarity ends there. In dynamic reaction cell technology, a quadrupole is used instead of a hexapole or octapole. A highly reactive gas, such as ammonia or methane, is bled into the cell, which is a catalyst for ion molecule chemistry to take place. By a number of different reaction mechanisms, the gaseous molecules react with the interfering ions to convert them either into an innocuous species different from the analyte mass or a harmless neutral species. The analyte mass then emerges from the dynamic reaction cell free of its interference and steered into the analyzer quadrupole for conventional mass separation. The advantages of using a quadrupole in the reaction cell is that the stability regions are much better defined than a hexapole or an octapole, so it is relatively straightforward to operate the quadrupole inside the reaction cell as a mass or bandpass filter, and not just an ion-focusing guide. Therefore, by careful optimization of the quadrupole electrical fields, unwanted reactions between the gas and the sample matrix or solvent (which could potentially lead to new interferences) are prevented. Therefore, every time an analyte and interfering ions enter the dynamic reaction cell, the bandpass of the quadrupole can be optimized for that specific problem and then changed on-the-fly for the next one. Figure 4 shows a schematic of an analyte ion ^{56}Fe and an isobaric interference $^{40}Ar^{16}O$ entering the dynamic reaction cell. The reaction gas NH_3 reacts with the ArO^+ to form atomic oxygen and argon together with a positive NH_3 ion. The quadrupole's electrical field is then set to allow the transmission of the analyte ion ^{56}Fe to the analyzer quadrupole, free of the problematic isobaric interference, $^{40}Ar^{16}O$. In addition, the NH_3^+ is prevented from reacting further to produce a new interfering ion. The advantage of this approach is that highly reactive gases can be used, which increases the number of ion–molecule reactions taking place and therefore more efficient removal of the interfering species. Of course, this also potentially generates more side reactions between the gas and the sample matrix and solvent; however, by dynamically scanning the bandpass of the quadrupole in the reaction cell, these reaction by-products are rejected before they can react to form new interfering ions.

Collision/reaction cells have given a new lease on life to quadrupole mass analyzers used in ICP-MS.

Table II. Typical detection limits in ppt of an ICP-MS system fitted with a dynamic reaction cell (9).

Analyte	Detection Limit (ppt)	Analyte	Detection Limit (ppt)
Li	0.08	Co	0.07
Be	0.6	^{60}Ni	0.4
B	1.1	Zn	1
Na	0.3	As	1.2
Mg	0.6	Se*	5
Al	0.07	Sr	0.02
K*	1	Rh	0.01
^{40}Ca*	1	In	0.01
V*	0.3	Sb	0.06
Cr*	0.25	Cs	0.03
Mn*	0.09	Pb	0.03
^{56}Fe*	0.15	U	0.01

* Indicates elements determined in dynamic reaction cell mode.

The benefit of the dynamic reaction cell is that by careful selection of the reaction gas, the user takes advantage of the different rates of reaction of the analyte and the interfering species. This process is exemplified by the elimination of $^{40}Ar^+$ by NH_3 gas in the determination of ^{40}Ca. The reaction between

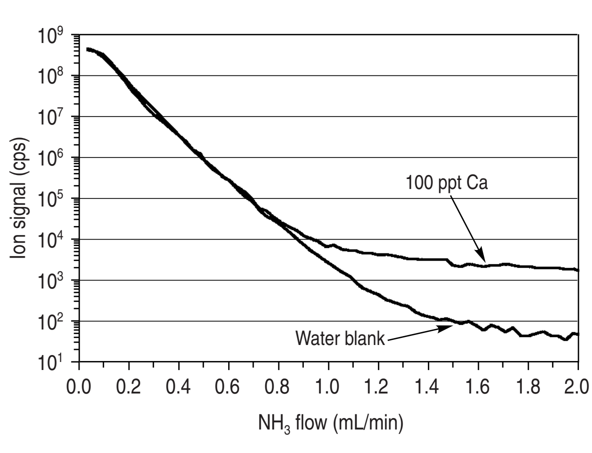

Figure 6. A reduction of eight orders of magnitude in the ^{40}Ar background signal is achievable with the dynamic reaction cell — resulting in <1 ppt detection limit for ^{40}Ca.

NH_3 gas and the $^{40}Ar^+$ interference, which is predominantly a charge exchange, occurs because the ionization potential of NH_3 (10.2 eV) is low compared with that of Ar (15.8 eV). Therefore, the reaction is exothermic and fast; however, the ionization potential of Ca (6.1 eV) is significantly less than that of NH_3, so the reaction, which is endothermic, is not allowed to proceed (8). Figure 5 shows this process in greater detail.

This highly efficient reaction mechanism translates into a dramatic reduction of the spectral background at mass 40, which is shown graphically in Figure 6. At the optimum NH_3 flow, a reduction in the ^{40}Ar background signal of about eight orders of magnitude is achieved, resulting in a detection limit of 0.5–1.0 ppt for ^{40}Ca.

Table II shows some typical detection limits in parts per trillion (ppt) of an ICP-MS system fitted with a dynamic reaction cell. The elements with an asterisk were determined using ammonia or methane as the reaction gas, while the other elements were determined in the standard mode (no reaction gas).

Collision/reaction cells have given a new lease on life to quadrupole mass analyzers used in ICP-MS. They have enhanced its performance and flexibility, and most definitely opened up the technique to more-demanding applications that were previously beyond its capabilities. However, it must be emphasized that even though differences exist between commercially available instruments, they all perform very well. The intent of this tutorial is to present the benefits of the technology to beginners and give an overview of the different approaches available. If it has created an interest, I strongly suggest that a performance evaluation is made based on your own sample matrices.

References

1. K. Sakata and K. Kawabata, *Spectrochimica Acta* **49B,** 1027 (1994).
2. B.A. Thomson, D.J. Douglas, J.J. Corr, J.W. Hager, and C.A. Joliffe, *Anal. Chem.* **67,** 1696–1704 (1995).
3. P. Turner, T. Merren, J. Speakman, and C. Haines, in *Plasma Source Mass Spectrometry: Developments and Applications*, eds. G. Holland and S. Tanner (Royal Society of Chemistry, Cambridge, UK, 1996).
4. I. Feldmann, N. Jakubowski, C. Thomas, and D. Stuewer, *Fresenius' J. Anal. Chem.* **365,** 422–428 (1999).
5. "Collision Cell Technology with Energy Discrimination," *Thermo Elemental Application Note* (Thermo Elemental, Franklin, MA, September 2001).
6. E. McCurdy and D. Potter, *Agilent Technologies ICP-MS Journal* **10,** October 2001.
7. Covered by U.S. Patent No. 6140638.
8. S.D. Tanner and V.I. Baranov, *At. Spectr.* **20**(2), 45–52, (1999).
9. U. Voellkopf, K. Klemm, and M. Pfluger, *At. Spectr.* **20**(2), 53–59, (1999). ■