The Principles and Performance of the integrated Collision Reaction Cell (iCRC)

Introduction

The new and improved integrated Collision Reaction Cell design of the PlasmaQuant MS achieves an even greater level of performance in the removal of problematic spectroscopic interferences typically observed with quadrupole ICP-MS. The fully integrated design provides faster switching between collision and reaction gases, greater sensitivity and lower limits of detection than traditional collision cell systems.

The patented iCRC design works by injecting collisional-helium and reactive-hydrogen gases into the plasma expansion at the skimmer cone tip, removing common plasma and matrix based interferences that deteriorate the detection limits of important elements like As, Se, Cr, V, Ca and Fe. The iCRC allows much lower detection limits to be achieved, especially for samples with complex matrices.

Your Benefits

- Effective elimination of spectroscopic interferences

- Use of simple, non-corrosive gases – H_2 and He

- High productivity thanks to fast switching between gases

- Excellent long term stability with tough samples

- No additional maintenance as interferences are removed before they enter the mass analyzer

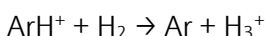Compared to other cell-based interference management systems, the iCRC does not use a pressurized multipole prior to the mass analyzer. While the collision and reaction mechanisms are similar, this innovative approach removes interferences before they are extracted into the ion optics. More efficient vacuum pumping within the cone interface region means switching between gas and no-gas modes is very rapid, allowing multiple and optimized instrument conditions to be set.

New improvements to iCRC on the PlasmaQuant MS include:

- Updated gasbox design with reduced gas volume and faster purging

- Higher capacity vacuum pump system for even faster switching between gases

- Stainless-steel gas lines eliminating outgassing and contamination.

- Optimized cone interface delivering higher analyte sensitivity and lower interferences

Application

Basic Principles of integrated Collision Reaction Cell (iCRC)

As shown in figure 1, the iCRC works simply by injecting the reactive/collision gases into the plasma through the tip of the skimmer cone to induce collisions and/or ion-molecule reactions with interfering ions. Plasma conditions at the interface cone aperture are ideal for collisions and reactions to occur. The high plasma density and temperature leads to a high collision/reaction frequency between the interfering ions and the injected gases. As a result, most argon-based polyatomic interferences are destroyed or removed before they are extracted into the ion optics. Hydrogen and helium are used as iCRC gases, as these gases provide efficient interference attenuation and avoid the need to use expensive or corrosive gases such as methane or ammonia that can produce complex by-products. When a collision/reaction gas is added to the plasma, a number of processes occur including charge transfer, proton transfer, electron-ion reactions and ion-molecule interactions.

For example, when hydrogen gas is injected, a polyatomic interfering ion such as $^{40}Ar^{40}Ar^+$ and $^{40}Ar^{38}Ar^+$ (that interferes with ^{80}Se and ^{78}Se determinations, respectively) reacts with a hydrogen molecule. A proton is transferred from the H_2 molecule to the Ar_2^+ ion, forming ArH^+, a neutral H atom and a neutral Ar atom. The ArH^+ ion then reacts with another H_2 molecule and a proton is transferred from the ion to the molecule, forming a neutral Ar atom and an H_3^+ ion. The H_3^+ ion (m/z = 3 amu) does not interfere with any isotopes of interest in ICP-MS.

Figure 1: principle of iCRC

$$Ar_2^+ + H_2 \rightarrow ArH^+ + Ar + H$$

$$ArH^+ + H_2 \rightarrow Ar + H_3^+$$

The reactivity of hydrogen and exponential reduction of interferences resulting from collisions and reactions within the iCRC means that this simple gas is more than sufficient at removing interferences, particularly argon based interferences.
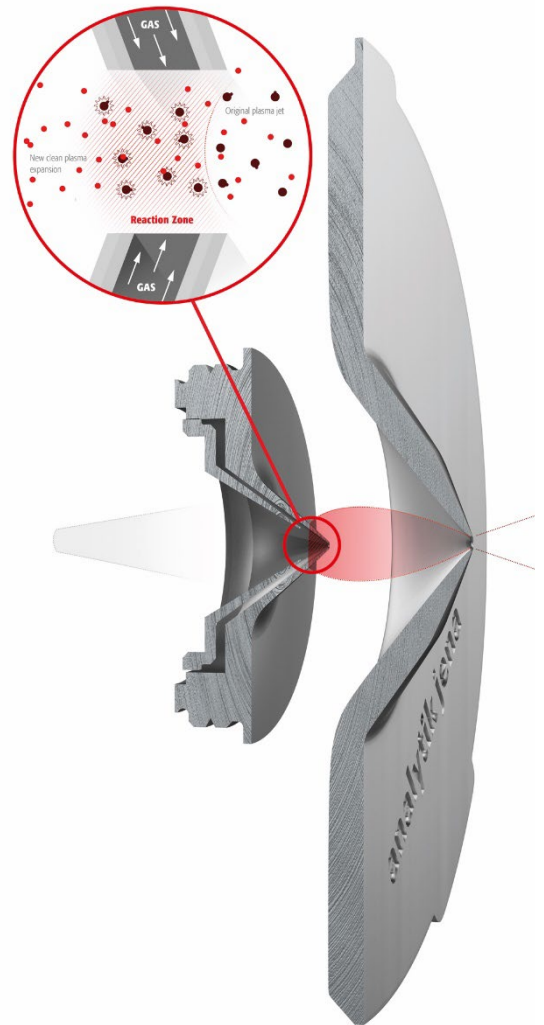
Analytik Jena GmbH
Konrad-Zuse-Strasse 1
07745 Jena · Germany

Phone   +49 3641 77 70
Fax   +49 3641 77 9279
info@analytik-jena.com
www.analytik-jena.com

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As helium gas is not reactive, when it is injected into the iCRC, the interaction between the electron clouds of the helium atoms and those of interfering polyatomic ions can make a large polyatomic interfering ion such as $^{35}Cl^{16}O^+$ (which interferes with $^{51}V^+$) rotationally and vibrationally excited. In subsequent collisions, an excited $^{35}Cl^{16}O^+$ ion can receive sufficient energy to bring about its dissociation, removing the $^{35}Cl^{16}O^+$ interference from the ^{51}V determination.

While collisions with interferences may not always bring about complete dissociation, the larger cross-section of a typical interference (eg. $^{40}Ar^{35}Cl^+$ and $^{40}Ca^{35}Cl^+$ on $^{75}As^+$) will result in many more kinetic-energy reducing collisions. The kinetic energy of the interference is reduced to a point whereby it is simply eliminated by the ReflexION ion optics.

Meanwhile, analyte ions are unreactive and not removed by the iCRC technique. They may lose some energy as they collide with the iCRC gases but far less often than the physically larger interferences. Many analyte ions will retain sufficient kinetic energy to be focused by the ReflexION ion optics and directed towards the mass analyzer.

Which iCRC gas is best

The effectiveness of collisional helium and reactive hydrogen gases for interference removal is typically related to the nature of the interference. As explained earlier, the removal of the argon dimer interference on selenium is best removed by reacting with hydrogen gas for achieving lowest detection limits.

Whereas interferences, such as $^{16}O^{35}Cl^+$ on $^{51}V^+$, formed from matrix elements are more effectively removed via collisions using helium. Interferences that occur from the combination of argon and matrix elements (eg. $^{40}Ar^{35}Cl^+$ on $^{75}As^+$) can often be effectively removed with either gas.

Gas requirements of the iCRC

The iCRC promotes more collisions and reactions in a much smaller cell volume and requires approximately 80-150 mL/min of helium or hydrogen gas for effective interference removal. While these flows may be higher than traditional collision-reaction systems, they are still essentially very small with a gas cylinder typically lasting several years.

The gas purity required for the iCRC is >99.996% and as it is not susceptible to contamination, requires no additional gas filtering system. The benefit being lower operating cost as there is no need to replace the gas filters on a regular basis or a contaminated cell.

The robust design of the **iCRC** makes it suitable for **use with hydrogen generation units**, providing a safer laboratory environment and the preferred choice of both helium collision gas and hydrogen reaction gas for best analytical performance. Although laboratories are often reluctant or prohibited from using high-pressure hydrogen cylinders due to safety concerns, the iCRC is fully compatible with many commercially available hydrogen generators that offer comprehensive safety systems, generating only a small volume of hydrogen gas on demand.

iCRC performance and optimization

The iCRC provides simple, yet powerful performance in the removal of troublesome interferences. An example of this is shown in figure 2 with the removal of the argon dimer Ar_2^+ interference on selenium. The time scan graph shows the signal measured for a solution containing 1 µg/L indium and that of the argon dimer ion produced from the plasma gas. Also shown in Figure 2 is the signal ratio of ^{115}In analyte ion and the argon dimer interference.

Hydrogen gas was incrementally added to the iCRC as is demonstrated in the stepwise change in the signals. The H_2 flow rate was increased in steps of 0, 20, 50, 80, 100, to 120 mL/min with about 50 seconds measurement time between each step. The efficiency of interference removal using iCRC is clearly demonstrated with the signal for the interfering species progressively decreasing with increasing H_2 gas flow rate, while the ratio of analyte to interference improves. At a H_2 flow rate around 120 mL/min, the interference from Ar_2^+ is completely removed and good sensitivity for the analyte $^{115}In^+$ is still maintained, allowing low parts per trillion (ng/L) detection of selenium.
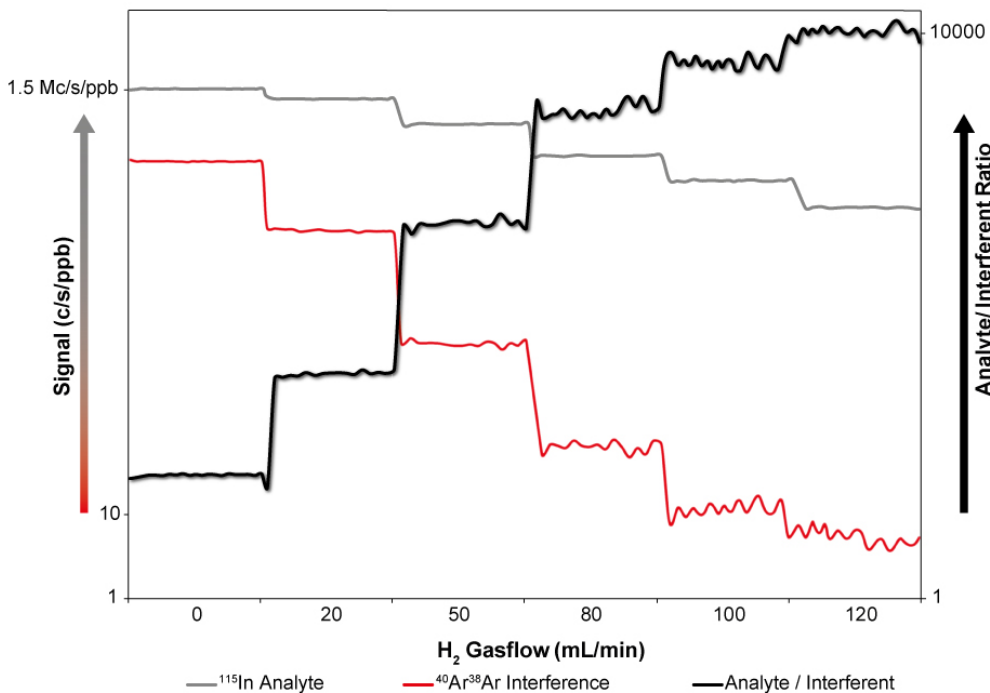

Figure 2: Increasing ratio of analyte signal ($^{115}In^+$) to argon dimer interference (Ar_2^+) with iCRC

Simplicity and Speed

The beauty of iCRC is in its simplicity. Simple to optimize, simple to operate and simple to maintain. There are no cell voltages to be set or element specific gas flows to be defined. Just select the best gas for the expected interference and ASpect MS software will find the optimum gas flow.

Another major advantage of the iCRC is its ability to quickly switch between the different gas and non-gas modes, as figure 3 demonstrates. A timescan measurement of a 1µg/L Indium solution in 1% HCl shows the presence of $^{40}Ar^{35}Cl$ and $^{40}Ar^{38}Ar$ polyatomic interferences at masses 75 and 78, respectively, when the iCRC gas flow is switched off. When hydrogen gas is injected into the iCRC gas at the optimum flow, immediate removal of both interferences is observed while a strong signal is retained for $^{115}In^+$. When switched off again, the gas is quickly removed within a few seconds by the vacuum system in preparation for the next measurement.
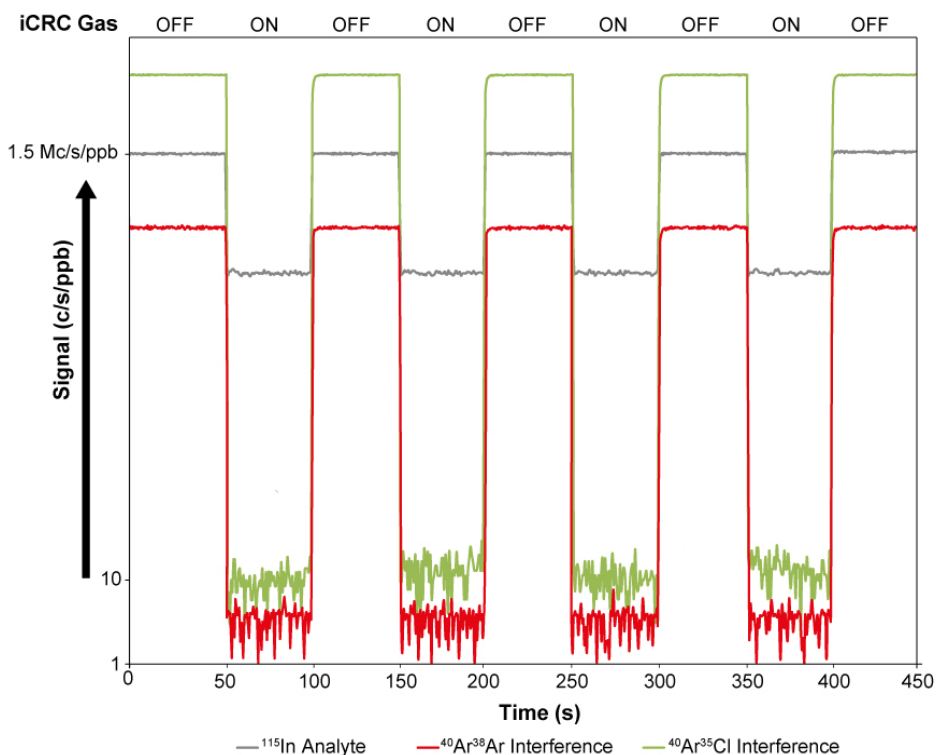

Figure 3: The advantage of fast switching between gas modes.

Results

Typical detection limits in iCRC mode

The principal benefit of interference removal techniques is to eliminate common interferences on key elements and thereby greatly improve instrument detection limits (IDL). Table 1 list's the typical detection limits for elements that often experience spectroscopic interference from plasma and major sample-matrix components. All DLs were determined as the concentration corresponding to 3 times the standard deviation of 10 replicates of a blank (i.e., 1% HNO_3). The measurements were made under routine analytical laboratory and not under 'clean-room', conditions. Hence, the IDL values listed in table 1 can be routinely achieved outside a 'clean-room' environment, under typical laboratory conditions

Table 1: Typical IDL's for elements benefitting from iCRC

Isotope	IDL with iCRC (ng/L)	IDL without iCRC (ng/L)	Major Interference	Recommended iCRC Gas
^{39}K	<43	500	$^{38}Ar^1H^+$	H_2
^{40}Ca	<3	-	$^{40}Ar^+$	H_2
^{44}Ca	<7	81	$^{12}C^{16}O^{2+}$	H_2
^{51}V	<0.2	3	$^{35}Cl^{16}O^+$	He
^{52}Cr	<0.6	8	$^{40}Ar^{12}C^+$, $^{40}Ca^{12}C^+$ $^{35}Cl^{16}O^1H^+$	H_2 or He
^{56}Fe	<2	4000	$^{40}Ar^{16}O^+$, $^{40}Ca^{16}O^+$	H_2
^{75}As	<0.6	20	$^{40}Ar^{35}Cl^+$, $^{40}Ca^{35}Cl^+$	H_2 or He
^{78}Se	<2	400	$^{40}Ar^{38}Ar^+$ $^{38}Ar^{40}Ca^+$	H_2
^{80}Se	<9	-	$^{40}Ar^{40}Ar^+$ $^{40}Ar^{40}Ca^+$	H_2

Matrix tolerance and iCRC

Studies on real samples have demonstrated that the iCRC is superior when it comes to matrix tolerance. Not only in its ability to handle samples containing high levels of total dissolved solids, but also in how it handles varying matrices within an analysis.

Figure 4 shows the long term signal stability of a high total dissolved solids matrix in iCRC mode. The stability was tested over a period of 5 hours using a solution containing 0.1% w/v (1000 mg/L) NaCl spiked with 1 µg/L of various analytes. The results in figure 4 demonstrates that the PlasmaQuant MS, running in the iCRC mode, is extremely stable when analyzing complex matrices. The relative standard deviations (RSD) of the measured signals for most analytes did not exceed 5% over the 5 hours.

Table 2 lists the results of various clinical samples with different matrices determined from a single, universal calibration. Low and high level whole blood, plasma, urine and serum reference materials were analyzed within the same analysis for As, Se, V and Cr. These important clinical elements are interfered with in ICP-MS by argon and matrix-based polyatomic interferences resulting from the high organic, alkali/alkaline metal and chloride ion content of the samples. The effectiveness of the iCRC is demonstrated in its tolerance to the changing matrices with the measured concentrations of all four critical elements falling within the reporting range for each sample matrix.
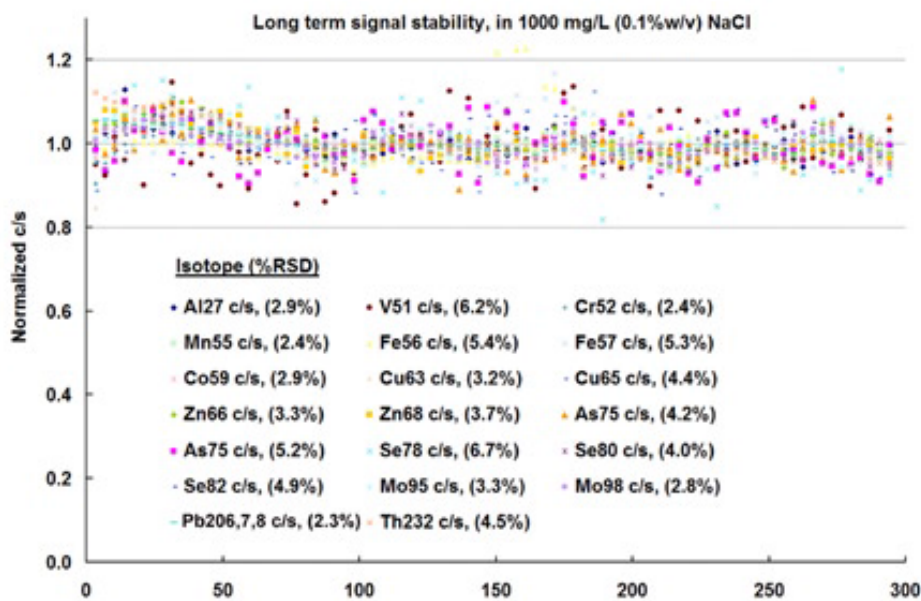

Figure 4: Long-term signal stability in 1000 mg/L NaCl with 100mL/min H_2 iCRC gas

Table 2: Results of various clinical samples determined from a single, universal calibration

Sample	As	Certified Range (µg/L)	Se	Certified Range (µg/L)
Urine	39.6	35.7 – 53.5	24.3	23.4 – 35.2
Plasma Control	48.0	38.2 – 57.4	85.0	64.0 – 96.0
Serum	11.0	9.04 – 13.6	61.3	50.6 – 76.0
Whole Blood	5.51	4.42 – 6.62	79.1	59.5 – 89.2

Sample	V	Certified Range (µg/L)	Cr	Certified Range (µg/L)
Urine	19.9	15.7 – 23.5	16.3	16.2 – 24.4
Plasma Control	11.5	8.00 – 12.0	12.7	8.88 – 13.3
Serum	24.5	19.6 – 29.4	7.9	5.24 – 8.74
Whole Blood	-	NA	12.4	9.52 – 14.3

Analytik Jena GmbH
Konrad-Zuse-Strasse 1
07745 Jena · Germany

Phone +49 3641 77 70
Fax   +49 3641 77 9279
info@analytik-jena.com
www.analytik-jena.com

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Summary

The advantage of iCRC is in its ability to offer fast, simple and flexible interference removal for all matrices without compromise, providing accurate and precise results at the lowest possible detection limits.

Further information

For further updates, applications and other literature, please visit the Analytik Jena website at www.analytik-jena.com.