Theory, Design, and Operation of a Dynamic Reaction Cell for ICP-MS

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THEORY

Because an ion is charged, it can interact with the dipole moment of a polar molecule or induce a dipole in a non-polar molecule. Ion-dipole interactions are effective at long inter-atomic distances, and so the collision rate between ions and neutral molecules is high. The ion-dipole interaction is usually sufficiently strong to exceed the activation energy potential barrier to exothermic reactions, and so thermodynamically allowed ion-molecule reactions are usually fast. Because the activation energy barrier to reaction is usually insignificant, the probability of simple ion-molecule small particle (electron, hydrogen atom, and proton) transfer reactions is binary (it happens or does not) and depends on the reaction exothermicity (e.g., the difference in the ionization potential of the product and reactant neutrals for electron transfer reactions). Therefore, thermodynamically allowed ion-molecule reactions are usually fast and highly specific. For example, the reaction:

\[ \text{Ar}^+ + \text{NH}_3 \rightarrow \text{NH}_3^+ + \text{Ar} \]  \hspace{1cm} (1)

is fast, having a rate constant of 1.7 \( \times 10^{-9} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) (1). Reaction (1) is an example of electron transfer (or charge exchange), and occurs because the ionization potential of NH\(_3\) (10.2 eV) is less than that of Ar (15.7775 eV). The reaction is exothermic. On the other hand, the ionization potential of Ca (6.111 eV) is less than that of NH\(_3\), and so the corresponding endothermic reaction:

\[ \text{Ca}^+ + \text{NH}_3 \rightarrow \text{NH}_3^+ + \text{Ca} \]  \hspace{1cm} (2)

is not observed to proceed (the rate constant is less than \( 10^{-13} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\)). As will be seen later, the difference in the rate constants for the reactions of the isobars Ar\(^+\) and Ca\(^+\) with NH\(_3\) allows the ion signal for Ar\(^+\) at m/z=40 to be suppressed by nine of orders of magnitude while simultaneously the ion signal for Ca\(^+\) is virtually unaffected. This specificity of reaction allows a dramatic improvement in detection limits when the inductively coupled plasma mass spectrometry (ICP-MS) instrument is configured to take advantage of it.

The rf-only multipole has found great use in the study of ion-molecule reactions (2,3). A multipole is usually characterized by its order, which is the number of pairs of poles (a quadrupole is second order, a hexapole is third order, an octapole is fourth order, etc.). The order describes the shape of the effective potential well within the rod array. Hence, a higher order multipole has a wider potential well near the axis and a stronger field gradient closer to the rods. It is well-known that a higher order multipole is preferred when it is used to study ion-molecule reactions, particularly when it is desired to monitor the product ions of the reaction over a wide range of masses. It will be shown that this latter characteristic, the efficient confinement of ions over a wide range of masses, is the major detriment for the use of a multipole for analytical purposes in ICP-MS. In fact, the preferred configuration is a quadrupole, which defies the conventional wisdom (3).

An ion is said to be stable in a multipole if it can be confined and transmitted through the device. Stability is affected by the amplitude and frequency of the applied rf, the mass of the ion, the size of the multipole array, and the dc voltage applied between pole pairs (if any). It is convenient to describe the regions of stability and instability in terms of the Mathieu parameters, a and q:

\[
a_n = 2n(n-1) \frac{e V_{dc}}{m \omega^2 r_0^2} \] \hspace{1cm} (1)

\[
q_n = n(n-1) \frac{e \omega \omega_{rf}}{m \omega^2 r_0^2} \] \hspace{1cm} (2)

where \( n \) is the order of the multipole, e is the electronic charge, \( V_{dc} \) and \( V_{rf} \) are, respectively, the dc and the zero-to-peak rf amplitude applied between pole pairs [note that this definition follows that of Dawson (4)], m is the ion mass, \( \omega \) is the rf angular frequency, and \( r_0 \) is the field radius of the multipole array. Because of its symmetry, a quadrupole is characterized by well-defined stability boundaries, as shown in Figure 1, and these are independent of the initial position of the ion. By contrast, the higher order multipole has more diffuse stability boundaries (there are wide regions of partial stability), and these are dependent on the initial position of the ion within the field. This is why the quadrupole has found unique application as a mass filter and, as will be seen, is necessary for optimal performance as an ion-molecule reactor for analytical ICP-MS.

Referring to Figure 1, the quadrupole may be operated as an rf-only device along the a=0 axis. Ions having a value of \( q<0.908 \) have stable trajectories. Lower mass ions, having \( q>0.908 \), are unstable and are rapidly lost from the quadrupole. Therefore, the rf-only quadrupole is a high pass filter characterized by a well-defined low mass cut-off. The addition of a dc voltage between the pole pairs moves the
operating point away from the 
$a=0$ axis, and introduces both a low 
mass (at high $q$) and high mass (at 
low $q$) stability cut-off. Operation 
at the apex of the stability region 
(near $q=0.706$, $a=0.24$) provides 
a narrow bandpass, and is the usual 
operating point for a quadrupole 
mass filter.

The quadrupole can be operated 
as an ion-molecule reactor by 
enclosing it so that it can be pres- 
surized with a reactive gas. Efficient 
elimination of plasma-based inter-
ference ions may be obtained at pressures in the vicinity of 10–20 
mTorr. Under these conditions, 
the input ion beam is thermalized 
through collisions, resulting in a near-thermal distribution of ion 
energies and the ions are focused 
towards the axis of the quadrupole 
(5,6). We have discussed the 
processes which lead to this state, 
and the implications that these 
have for analytical use in ICP-MS 
(7). We have shown that the contribu-
tion of the rf-field energy to the 
ion kinetic energy (and hence the 
reaction energy) increases with an 
increase in the amplitude of the rf, 
a decrease in the rf frequency, 
a decrease in the number of colli-
sions per rf cycle, and particularly 
near the high-$q$ stability boundary.

For the ICP-MS application, it is desirable to resolve isobaric inter-
ferences on the basis of their ion-
molecule reactivity. Operation of 
the reaction cell under non-thermal 
conditions (i.e., with a significant 
contribution of the rf-field energy 
to the reaction energy) can 
promote otherwise endothermic 
reaction processes. Hence, in order 
to retain the specificity of the 
chemistry it is desirable to minimize 
the contribution of the rf-field 
energy to the reaction energy. This 
can be assured, in large measure, by 
operation at low rf amplitude. Con-
ventional operation of the quadrupole employs a fixed rf frequency, 
while the rf amplitude is increased with the ion mass. It is clear, from 
equations (1) and (2), that the 
device may also be frequency-
scanned at fixed rf amplitude, 
which has the advantage that the 
rf amplitude can be maintained 
at a sufficiently low level to mini-
mize the promotion of endothermic 
processes while retaining the 
efficient confinement of the ions 
of interest.

For analytical purposes, for which 
it is desired to eliminate an isobaric interference in order to allow deter-
mination of an analyte at ultra-trace 
levels, it is evident that the 
efficiency of the reaction cell must 
be enormous. To enable the deter-
mination of Ca+ at $m/z=40$ at sub-
ppt levels, the ion signal for $^{40}$Ar+ 
must be suppressed by about 9 
orders of magnitude (from $10^{10}$ cps 
to 10 cps). Because of the distri-
bution of the number of collisions that 
any ion may suffer, 9 orders of mag-
nitude of reactive decay requires 
that, on average, each ion suffers 
approximately 20 reactive collisions 
(which may require many more col-
lisions, depending on the reaction 
efficiency). This means that succes-
sive, sequential reaction chemistry 
is promoted. Through a series of 
reactions, new isobaric interfer-
ces may be produced at many 
masses. Consider, for example, the 
use of methane as the reactive gas. 
The dominant plasma ion, Ar+, is 
known to react according to:

$$\text{Ar}^+ + \text{CH}_4 \rightarrow \text{CH}_2^+ + \text{Ar} + \text{H}$$
$$\rightarrow \text{CH}_3^+ + \text{Ar} + \text{H}_2$$
$$\rightarrow \text{CH}_4^+ + \text{Ar}$$

Subsequently, these intermediate 
products react according to:

$$\text{CH}_3^+ + \text{CH}_4 \rightarrow \text{C}_2\text{H}_5^+ + 2\text{H}_2$$
$$\rightarrow \text{C}_2\text{H}_5^+ + \text{H}_2$$

and other similar reactions. Now, 
$\text{C}_2\text{H}_5^+$ and $\text{C}_2\text{H}_5^+$ are good proton 
donors. If, for example, there is a 
trace of acetone in the reaction cell, 
it may be protonated according to:

$$\text{C}_2\text{H}_2^+ + \text{C}_2\text{H}_5\text{O} \rightarrow \text{C}_2\text{H}_7\text{O}^+ + \text{C}_2\text{H}_2$$
$$\text{C}_2\text{H}_2^+ + \text{C}_2\text{H}_5\text{O} \rightarrow \text{C}_3\text{H}_7\text{O}^+ + \text{C}_2\text{H}_4$$

which produces an isobaric inter-
ference for Co+ at $m/z=59$. More 
generally, if a hydrocarbon neutral 
is in the reaction cell, complex 
chemistry is promoted.
which are examples of proton transfer and dissociative proton transfer reactions. Of course, all of the reactions shown here are simply representative of the types of reactions that may take place within the reaction cell when a relatively complex reaction gas is used. The reactions take place nearly simultaneously and continuously as long as the intermediate ions and the neutrals are within the cell.

Because of the efficiency (99.9999999%) of the reaction cell, even a very trace amount of hydrocarbon will enable the production of a wide range of interferences. It is simply not possible to maintain the contamination level of the reaction cell low enough to completely suppress this chemistry.

The special ion stability characteristics of a quadrupole reaction cell may be used to efficiently intercept this sequential chemistry and eliminate the interferences produced within the reaction cell. The representative chemistry discussed above is presented in Figure 2a in roughly chronological order. Alternatively, this may be reorganized in order of the mass of the intermediate product ions, as shown in Figure 2b. As long as the neutral species are present in the cell and all of the intermediate product ions are retained as well (i.e., by operation of the cell in the rf-only mode at low q), this chemistry proceeds nearly simultaneously and continuously. The efficiency of the reaction cell cannot be realized because of the production of new interferences at many masses. However, the quadrupole reaction cell is characterized by well-defined stability boundaries. Selection of the parameters a and q allow the definition of a mass bandpass; ions having m/z outside of the stability boundary are efficiently and rapidly ejected from the cell. Therefore, the sequential chemistry which leads to new interferences can be efficiently interrupted. Further, the bandpass can be swept in concert with the mass of the ion being determined by the downstream mass analyzer. Therefore, a dynamic bandpass can be defined for the reaction cell which allows efficient transfer of the analyte ion being measured downstream; this also allows for efficient reaction of the plasma-based isotopic interference ion and simultaneously suppresses the formation of new interferences at the analytical mass within the reaction cell. This is shown schematically in Figures 2c through 2f. In this case, a bandpass with both a high and low mass cut-off is shown, and is progressively shifted with the analytical mass (in the sequence of Figures 2c through 2f). The neutral reactant species are, of course, always present (they are unaffected by the operating point of the reaction cell). However, only those reactions for which the reactant ion is simultaneously confined within the cell may proceed. These reactions are shown by solid arrows; the dashed arrows indicate reactions that are suppressed because the reactant (intermediate product) ion is unstable under the operating conditions. It is therefore evident that the reactions which remove an interference ion from the bandpass are allowed to proceed (with high efficiency), but those reactions that would otherwise produce an interference ion within the bandpass are suppressed. We therefore have the interesting situation where the bandpass is operated in order to suppress the formation of new interferences within the bandpass by destabilizing the intermediate product ions outside of the bandpass. At the same time, operation in this bandpass mode does not affect the efficiency of removal of plasma-based ions, and the unreacted analyte ion is transmitted efficiently without interference.

The low mass boundary of the bandpass is determined by the selection of the parameter q at the analytical mass. Recall that this parameter specifies the frequency of the rf at the operating rf amplitude, and that therefore lower mass ions are simultaneously confined within the cell according to the value of q at their masses. The lower mass edge of the bandpass is defined by the mass below which the value of q is greater than the stability boundary limit (i.e., q > 0.908 for a perfect quadrupole without collisions). In some instances it may also be desired to invoke a high mass cut-off for the bandpass, and this is achieved by specifying a non-zero value for a. Because the bandpass width is adjusted by changing the frequency of a low amplitude rf and a low dc voltage, these may be adjusted rapidly and on a per-element basis.

Thus, the Dynamic Reaction Cell (DRC) is a low constant rf amplitude quadrupole which is characterized by a dynamic mass bandpass, which is dynamically moved in concert with the analyte mass and whose bandpass width may be adjusted dynamically. It is these dynamic characteristics that distinguish the Dynamic Reaction Cell from generic rf-only multipole reaction cells. Since the DRC efficiently suppresses interferences that would otherwise be produced through a complex sequence of reactions, the analyst has a wider selection of reaction gases at his disposal. Further, the cell may be operated at near thermal equilibrium conditions, for which the efficiency is maximized, since kinetic energy discrimination (the alternative for product ion discrimination with higher order multipoles) is not required.
The Dynamic Reaction Cell (DRC) is an enclosed quadrupole which acts as the interface between the single lens ion optics chamber and the mass analyzer high vacuum chamber. Reaction gas is introduced through a clean gas manifold and controlled by one or both of two low flow (3 sccm) mass flow controllers. The ion beam is introduced to the DRC through an entrance aperture inlet. Ions exit the cell through an aperture which communicates with the AC-only prefilter, and hence are transferred to the quadrupole mass filter. Reaction gas exits the cell through both the entrance and exit apertures. For experiments without reaction gas, the gas flow is stopped and the DRC enclosure is remotely opened for venting into the high vacuum chamber. A schematic of the instrument is given in Figure 3.

**Fig. 2. Sequential, secondary ion chemistry that has the potential to produce chemical interference within a reaction cell.**

(a) Chronology of a representative sequential chemistry. (b) The chemistry reorganized as a function of the mass of the intermediate products of reaction. As long as the reactant neutral is within the cell and the intermediate ions are stable (as in a conventional reaction cell), this chemistry will proceed nearly simultaneously and continuously. (c) through (f) A bandpass is introduced, defined by the stability boundaries of a quadrupole, which intercepts the chemistry. Only those reactions for which the reactant ion is within the stability bandpass may proceed; other reactions are suppressed. The bandpass is swept (in c through f) in concert with the analyzed mass, and the bandpass width may be adjusted on the fly as required for chemical resolution.

**Fig. 3. Schematic of the DRC-ICP-MS.** The DRC is a rf/dc quadrupole which may be enclosed and pressurized with a reactive gas. The DRC may be vented into the high vacuum chamber in order to emulate conventional ICP-MS.
A separate power supply provides the rf and dc voltages to the DRC. The rf drive frequency is determined by the mass of the ion currently being transmitted through the downstream mass analyzer and the value of \( q \) specified in the method for the DRC for this mass. This frequency is digitally synthesized and amplified to the specified rf amplitude. The dc voltage between pole pairs specified by the value of \( a \) is offset by the reaction cell rod offset and applied on top of the rf. Therefore, the DRC is frequency-scanned with the analyzer mass, and the frequency is chosen to provide the operating parameter, \( q \), defined on a per-mass basis. For given values of \( a \) and \( q \), the dc voltage is independent of ion mass. Accordingly, the mass bandpass window of the DRC is dynamically adjusted with the reference \( a \) and \( q \) defined for the mass being transmitted through the mass filter. The bandpass is adjusted on a per-element basis; that is, the value of \( q \) and of \( a \) is defined for each element in the peak hopping mode and the bandpass is adjusted prior to measurement of each signal. For spectral scanning, a constant value of \( q \) and of \( a \) is applied through a scan segment. In addition, the selection of reaction gas (with the two-channel option) and reaction cell pressure may be adjusted for a given spectral scan segment or on a per-element basis through specification of a reaction gas flow in the method.

For the determination of elements that are not normally interfered, it may be desirable to emulate “conventional” ICP-MS operation with the DRC-ICP-MS. If reaction gas is not added to the DRC, plasma gas from the ion optics chamber is entrained into the reaction cell. If the reaction cell remains enclosed, the plasma gas pressurizes the cell and facilitates ion-molecule reactions which increase the spectral background. Suppression of this chemistry can be achieved by increasing the mean-free path within the reaction cell. This is most readily achieved by increasing its conductance into the high vacuum (mass analyzer) chamber. The DRC is equipped with an externally activated venting mechanism which opens the reaction cell. With the vent open and reaction gas flow stopped, the instrument is said to be operating in “standard mode.” Mode switching is performed automatically.

**OPERATION**

The DRC parameters are optimized independently of the remainder of the ICP-MS system. Typically, optimization of the plasma conditions and ion optic (AutoLens™) are performed as for a standard ELAN® instrument. Since the DRC in the “enhanced mode” (with reaction gas) eliminates plasma-based interferences, the plasma is operated in the “normal” mode (high power and optimum nebulizer flow for “robust” analytical conditions. We have yet to find an analytical challenge that requires the use of “cold plasma,” although operation in this mode is also available.

Insight into an appropriate reaction gas for use in the enhanced mode can be obtained by checking the database of ion-molecule reaction rate constants (1). A preferred reaction gas is one for which the rate constant for reaction of the analyte ion is considerably smaller than that for the isobaric interference ion. In this instance, the analyte ion is to be measured at its atomic m/z. Alternatively, a suitable gas is one for which the analyte ion produces a product ion having a different m/z than the isobaric interference produces (and it is additionally desirable that the mass ratio of the product ion/analyte ion is small, preferably less than two, and that the product ion does not interfere with another analyte ion of interest and is not interfered by another ion). It is further preferred that the reaction gas have a molecular weight that is less than the atomic mass of the analyte ion (to suppress scattering losses). Other considerations in the selection of the gas, such as its toxicity or reactivity with the gas manifold or vacuum system components, will be evident.

Once a candidate reaction gas is selected, the appropriate bandpass for the DRC should be determined. Most often, this will be determined empirically by scanning the ion signal as a function of the parameter \( q \) for a blank solution and for a solution containing the analyte. An example of this type of optimization is given in Figure 4 for Fe⁺ with NH₃ as the reaction gas. The analyte ion signal has a broad maximum in the vicinity of \( q = 0.45 \). The blank signal shows a maximum near \( q = 0.15 \). The signal in the blank is a m/z=56 ion (not Fe⁺) which is formed in a series of reactions that include at least one intermediate product ion of lower mass. Operation at \( q > 0.3 \) clearly suppresses the chemistry which creates this interference. Therefore, in this instance, it is convenient to optimize \( q \) for the maximum analyte ion signal (\( q = 0.45 \)). In some instances, it may be necessary to add a high mass cut-off in order to suppress chemistry involving higher mass intermediate product ions.

It might be noted that a lower than otherwise optimum value of \( q \) is required if a reaction chemistry is chosen which converts the analyte to a higher m/z polyatomic ion which is to be measured as indicative of the analyte. This is because the product ion will only be observed if both the analyte ion and its product ion are simultaneously stable. Since the product ion will be higher mass than the analyte ion (presumably it is a polyatomic of the analyte), the operating point \( q \) for the product ion must be sufficiently small to provide a \( q \)-value
standard deviation of the signal is well-approximated by counting statistics. Therefore, the detection limit can be estimated according to:

$$EDL = 3 \sqrt{B}$$

where $EDL$ is the estimated detection limit in ppt, $B$ is the background signal (in cps, from Figure 5) and $S$ is the net sensitivity in cps per ppt (from Figure 6). This estimated detection limit (3 $\sigma$ for 1 second measurement period) can thus be determined as a function of the reaction gas flow, as shown in Figure 7 for Fe⁺. The estimated detection limit typically passes through a minimum (at ca. 1.2 mL/min for Fe⁺). Measurements of the detection limit at this flow (3 $\sigma$, 1 second dwell, 10 replicates) are found to agree well with the estimated detection limit.

Having chosen the reaction gas and the operating point for the DRC, it remains to optimize the pressure of the reaction cell. Generally, a higher pressure is required for slow reactions or for intense isobaric interferences (more collisions are required in either event). It is convenient to monitor the ion signal for the analyte as a function of the reaction gas for the same two solutions (blank and standard) as above. Typical results for an optimization of this type are given in Figure 5, again for Fe⁺ with NH₃ as the reaction gas. The difference between the signal levels for these solutions provides the net sensitivity to the analyte as a function of flow (pressure) of the reaction gas. Figure 6 shows this result for data taken from Figure 5. The net Fe⁺ signal initially increases due to collisional focusing, attains a maximum, and then decreases. The loss of ion signal at high flow may be due either to reaction of the analyte ion with the reaction gas or scattering by the gas. It is important to recognize, however, that the optimum reaction gas flow does not necessarily correspond to the flow which gives the maximum net sensitivity. This is because the detection limit is determined both by the sensitivity and by the noise on the background signal. It can be shown that, for ion signals below ca. 10⁴ cps with the DRC pressurized, the

![Fig. 5. Optimization of the reaction gas (NH₃) flow for Fe⁺ as the analyte. The solid line is the ion signal for a blank (Distilled Deionized Water) as a function of NH₃ flow; the dashed line is for a standard containing 100 ppt Fe.](image)

![Fig. 6. Net sensitivity for Fe as a function of reaction gas (NH₃) flow. The data are derived from the difference of the curves given in Figure 5.](image)

for the lower mass analyte (reactant) ion which remains within the stability bandpass. It might be further noted that the converse of this is also true: operation at a sufficiently high $q$ that the product of a reaction of the analyte ion is not stable, allows suppression of, for example, cluster ions which could interfere with the determination of other analyte ions at higher m/z.

Having chosen the reaction gas and the operating point for the DRC, it remains to optimize the pressure of the reaction cell. Generally, a higher pressure is required for slow reactions or for intense isobaric interferences (more collisions are required in either event). It is convenient to monitor the ion signal for the analyte as a function of the reaction gas for the same two solutions (blank and standard) as above. Typical results for an optimization of this type are given in Figure 5, again for Fe⁺ with NH₃ as the reaction gas. The difference between the signal levels for these solutions provides the net sensitivity to the analyte as a function of flow (pressure) of the reaction gas. Figure 6 shows this result for data taken from Figure 5. The net Fe⁺ signal initially increases due to collisional focusing, attains a maximum, and then decreases. The loss of ion signal at high flow may be due either to reaction of the analyte ion with the reaction gas or scattering by the gas. It is important to recognize, however, that the optimum reaction gas flow does not necessarily correspond to the flow which gives the maximum net sensitivity. This is because the detection limit is determined both by the sensitivity and by the noise on the background signal. It can be shown that, for ion signals below ca. 10⁴ cps with the DRC pressurized, the

![Fig. 4. Ion signals at m/z=56 for a blank (dashed line) and a standard containing 100 ppt Fe (solid line) as a function of the parameter q. The ion signal for the blank has been multiplied by a factor of 10 relative to the signal for the standard. The rf amplitude was fixed at 200 V peak-to-peak, and the frequency was scanned to adjust q. The peak near q=0.15 for the blank solution corresponds to an ion of m/z=56 which is formed through a series of reactions involving at least one significantly lower mass intermediate product ion. This interference ion is suppressed at q>0.3.](image)
An example of the specificity and efficiency of the DRC is given in the reaction profiles for Ar⁺/Ca⁺ in Figure 8. The ion signal corresponding to ⁴⁰Ar⁺ in the blank solution in the standard mode is ca. 10¹⁰ cps. At the lowest flow of NH₃ shown in Figure 8, the ⁴⁰Ar⁺ signal is already attenuated by an order of magnitude, and thereafter decreases semilogarithmic linearly to less than 100 cps (for the blank solution) at a flow of 1.4 mL/min. The curvature above this flow rate is due to the contribution of contaminant Ca⁺ in the blank solution (corresponding to ca. 3 ppt). The corresponding reaction profile for 100 ppt Ca shows a plateau which decreases only slowly, indicating that Ca⁺ is unreactive with NH₃ (the slow decay is due to scattering at high cell pressure). Allowing for the signal contributed by the contaminant Ca in the blank solution, these data show some 9 orders of magnitude suppression for Ar⁺ and only marginal scattering loss for Ca⁺. Clearly, the ion-molecule chemistry is highly specific (ca. 9 orders of magnitude discrimination) and efficient (again, 9 orders of magnitude, or 99.9999999%).

Data emulating conventional ICP-MS are shown in Figure 9, where the spectra for a blank (DDIW) and 100 ppt mixed element standard are overlaid. These spectra were obtained in the “standard mode,” for which the reaction cell is evacuated to the mass analyzer chamber. Performance in this mode is at least equivalent to current generation ICP-MS systems. Simply because of the geometry of the device and the design of the optics, the continuum background signal is reduced to below 1 cps. As a result, elements that are not interfered by plasma ions may be determined at very low levels (sub 0.1 ppt). As an example, Figure 10 shows the mass spectra for 1 ppt U and the corresponding DDIW blank. The signal/noise for 1 ppt is of the order of 80, and the detection limit is below 0.03 ppt (for a 3-second measurement time in peak hopping mode).

For elements which are interfered by polyatomic and argide ions, the Dynamic Reaction Cell offers an enormous improvement in detection limits. Figure 11 shows the spectra for the same solutions as Figure 9, but with the reaction cell optimized for Ca determination (i.e., high NH₃ reaction gas flow, which is greater than optimum for most elements). The chemical background signals are reduced to contamination levels. Many of the elements are unreactive (e.g., K⁺, Ca⁺, Cr⁺, and Mn⁺) or slowly reactive (e.g., Fe⁺ and Al⁺) with NH₃, and these may be determined at exceedingly low levels because of...
the reduced interferences and the low continuum background signal. Of course, not all elements are readily determined using NH3 as the reaction gas. A case in point is As+, which suffers interference from ArCl+ (in solutions containing chloride). While ArCl+ is highly reactive with NH3, it is found that As+ is as well [see Baranov and Tanner (7)]. In this instance, an alternate reaction gas, such as CH4 or H2, is prescribed, or As may be determined as the product of a condensation reaction [see Bollinger and Schleisman (8)]. Nonetheless, the impressive capability of the reaction cell is shown in the spectra of Figure 12 for which the signal for 1 ppt Fe is readily observed above the blank for DDIW. The continuum background signal remains below 1 cps, and permits the determination of the isotope ratios for 54Fe+/56Fe+/57Fe+ even at the level of 1 ppt.

REFERENCES