Nanoparticle Characterization, Fundamental Studies and Computer Simulations of Dynamic Reaction Cell Inductively Coupled Plasma Mass Spectrometry

Dissertation

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Abstract

An Inductively Coupled Plasma Mass Spectrometer (ICP-MS) equipped with a Dynamic Reaction Cell (DRC) was used to study the effects of locating a pressurized reaction cell between the ICP ion source and quadrupole mass filter. Improvements in the precision of isotope ratio measurements and reductions of overlap signals by collision induced dissociation and ion-molecule reactions were shown as compared to ICP-MS without a DRC. The rate of signal decay from ion-molecule reactions was related to kinetic rate constants, and a simulation was written to visualize ion trajectories in the DRC. A new method of determining ion-molecule kinetic rate constants and efficiencies was established. Finally, ICP-MS was used to characterize nanoparticle sizes, particle mass distributions and elemental compositions of both single size standards and mixtures. Particular focus in this work was paid to relate fundamental concepts, models and simulations to experimental data in order to further understanding of ICP-DRC-MS.

High precision measurements might be achieved from a noisy sample source by passing the ion beam through the pressurized reaction cell and dampening signal fluctuations. Laser ablation was coupled to the ICP-DRC-MS to provide a noisy sample source and large signal fluctuations. Isotope ratio precision from a homogeneous solid sample was compared among ICP-DRC-MS, ICP-q-MS, ICP-SF-MS and ICP-OES. Counting statistics limited precision was achieved when the reaction cell was pressurized
with NH$_3$. Improved precision of trace metal concentration gradients mapped in both homogeneous and heterogeneous solid samples was found using a pressurized DRC.

Inert collision gases were tested to determine which polyatomic overlaps could be attenuated via collision induced dissociation (CID) without sacrificing analyte sensitivity. Ar offered the best compromise between efficient CID and minimal scattering losses. A simple calculation was shown to reliably predict under what conditions CID will occur, and polyatomic overlap reduction was related to bond energy and collision gas mass. CID was compared to ion-molecule reactions using a common spectral overlap, ArN$^+$. Ion-molecule reactions were found to reduce the ArN$^+$ signal more rapidly, but CID with Ar also offered blank contamination limited detection limits.

14 reaction gases were studied to determine the best gas for chemical resolution of all Se$^+$ isotopes from argide, chloride and bromide matrices and rare earth overlaps in the +2 ionization state (REE$^{2+}$). N$_2$ and CO were found to provide contamination limited detection limits and produce no unwanted reaction chemistry, but could not resolve Se$^+$ from REE$^{2+}$ overlaps. Detection limits as low as 3 ng L$^{-1}$ were measured for $^{80}$Se$^+$. NH$_3$ was found to improve the signal to background (S/B) ratio in matrices with high concentrations of REE’s.

The chemical resolution of Sr$^+$ from Rb$^+$ was studied using SF$_6$ reaction gas and a F atom addition reaction, which produced numerous unwanted byproducts. The byproducts were successfully rejected by operating the DRC as a low resolution mass filter.
A simple calculation based on gas effusion from the DRC was related ICP-DRC-MS signal decay rates to kinetic rate constants. A calibration procedure was derived and rate constants for the reaction between CH$_3$F and both Ar$^+$ and Ar$_2^+$ were established for the first time. The method was also used to quantify the contributions of both CID and reactions to the rate of Ar$_2^+$ signal decay for 13 different gases.

SIMION 8.0, an ion trajectory simulation, was used to simulate ion-gas collisions in the DRC. The simulation used a hard sphere collision model to calculate the average number of ion-gas collisions and ion time of flight. The simulated collision rate was used to calculate reaction efficiencies that agreed well with values found in the literature when kinetic rate law assumptions were obeyed. The simulation was also used to visualize collisional focusing and scattering of the ion beam.

ICP-MS had not previously been used to characterize single nanoparticles with no pretreatment or separation. In this work, nanoparticles were delivered to the ICP-MS one at a time in dilute suspensions for mass and elemental characterization. The nanoparticle delivery system and influence of data recording and ICP parameters were discussed. Sensitivity, linear range and detection limits of single SiO$_2$ and Au nanoparticles were assessed. Additionally, nanoparticle mass and size distributions were compared and found slightly larger than those measured by SEM. Finally, 2 unknown mixtures were analyzed and correctly identified by ICP-MS, showing that ICP-MS is capable of analyzing both size and elemental mixtures of nanoparticles.
Dedicated to my wife.
Acknowledgments

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1 Introduction

1.1 Inductively Coupled Plasma Mass Spectrometry

Inductively coupled plasma mass spectrometry (ICP-MS) is adept at measuring trace and ultratrace elemental composition of samples.\textsuperscript{1-4} Samples are vaporized, atomized and ionized in the high temperature ICP and then analyzed based on their mass to charge (m/z) ratio. ICP-MS is utilized in geology,\textsuperscript{5} toxicology,\textsuperscript{6} proteomics,\textsuperscript{7} nuclear,\textsuperscript{8} and environmental research.\textsuperscript{9,10} Quality assurance using ICP-MS is performed in the food and drug\textsuperscript{11,12} as well as electronics and semiconductor industries.\textsuperscript{13}

ICP-MS provides species independent sensitivity, analysis of a large portion (metals) of the periodic table, sub-part per trillion (ng L\textsuperscript{-1}) detection limits and a linear range of up to nine orders of magnitude.\textsuperscript{8} It offers lower background levels and better detection limits than similar elemental analytical techniques such as ICP-optical emission spectroscopy (ICP-OES) and flame/graphite furnace atomic absorption (AA) spectroscopy.\textsuperscript{14} ICP-MS also enables isotope specific detection and isotope ratio measurements for applications spanning from geochronology\textsuperscript{15,16} to metabolic tracer studies.\textsuperscript{17}
1.2  The Inductively Coupled Plasma ion source

The ICP is a hot, partially ionized gas composed of neutral Ar atoms, Ar ions, and electrons.\textsuperscript{18} The plasma is generated inside of the plasma torch which consists of a set of three concentric quartz tubes.\textsuperscript{19} The torch is surrounded by a copper or sometimes gold coil near the downstream end of the torch. The outer annulus of the plasma inductively receives energy through the radio frequency (RF) coil operating at 800-1500 watts and at a frequency of 27.1 MHz. Temperature in the ICP has been estimated to range between 5,000 and 9,000 K.\textsuperscript{20} Samples can be introduced to the ICP as either liquid droplets or small particles. The sample is carried from an injector tip into the center of the hot plasma where it undergoes vaporization, atomization, ionization and excitation.\textsuperscript{21}

1.2.1  The ICP-Mass Spectrometer

The ICP is a good source of singly charged elemental ions and so was first coupled to a mass spectrometer in 1980.\textsuperscript{22} Ions produced in the atmospheric ICP are entrained into the mass spectrometer through a two stage vacuum interface composed of sampling and skimmer cones 10-12 mm downstream of the load coil.\textsuperscript{23} After passing into the mass spectrometer’s vacuum, ions are focused into the mass analyzer, separated by their mass to charge ratio (m/z) and counted by an electron multiplier.

The mass analyzers in most (> 95%) commercially available mass spectrometers are quadrupole mass filters. A quadrupole mass filter is composed of 4 parallel rods with both RF and DC voltages applied in combinations that allow ions of a narrow range (typically $\Delta m \approx 1$) of m/z to pass.\textsuperscript{24} The quadrupole filters the ion beam by allowing
stable trajectories for only a narrow range of m/z ratios for 10-1,000 ms and then quickly (< 1 ms) changes to allow another m/z to pass. The ions are counted using a dual stage electron multiplier located at the end of the quadrupole. Figure 1.1 shows an example ICP-MS schematic.

![Figure 1.1: The inductively coupled plasma mass spectrometer (ICP-MS) with a quadrupole mass filter.](image)

The stability of an ion through the quadrupole is determined by the quadrupole’s geometry, the amplitude and frequency of the applied RF and DC voltages and the ion m/z. The regions of stability for a quadrupole can be described using the Mathieu parameters $a$ and $q$.\(^{26}\)

$$a = 4 \frac{eV_{DC}}{m \omega^2 r_0^2} \quad (1.1)$$

$$q = 2 \frac{eV_{RF}}{m \omega^2 r_0^2} \quad (1.2)$$

where $e$ is the electronic charge; $V_{DC}$ and $V_{RF}$ are the direct current and zero to peak radio frequency voltages applied between pole pairs; $m$ is the ion mass; $\omega$ is the angular
frequency; and $r_0$ is the field radius of the quadrupole array. The values of $a$ and $q$ that produce a stable trajectory are described graphically by the stability diagram in figure 1.2.

![Stability diagram for a linear quadrupole mass filter. Solid lines separate stable and unstable regions, diagonal dashed line represents scan line and vertical dashed lines represent resolution.](image)

**Figure 1.2:** Stability diagram for a linear quadrupole mass filter. Solid lines separate stable and unstable regions, diagonal dashed line represents scan line and vertical dashed lines represent resolution.

Quadrupoles are “scanned” across the mass range by shifting the entire stability diagram along the “scan line” because each m/z has a stability diagram of its own. Resolution is represented by the horizontal distance the scan line passes through the stability diagram. Quadrupoles are almost always operated by allowing a single m/z ± 0.5 amu to pass, providing unit resolution, with $a$ and $q$ near the apex of the stability
The potentials applied to the quadrupole rods are shown in figure 1.3 where $V_{\text{DC}}$ is the DC potential, $V_{\text{RF}}$ is the peak to peak RF amplitude, $\omega$ is the RF frequency in radians/s, and $t$ is the flight time in seconds. The rods are coupled so that there is a $\pi$ radian phase difference between the x and y pairs. At a fixed frequency, the RF and DC potentials act as low and high mass cutoff parameters, respectively. Ions outside the stability region of the quadrupole have unstable trajectories in the x-direction (m/z too small) or y-direction (m/z too large).

**1.3 Mass spectral overlaps in ICP-MS**

Isobaric overlaps less than 1 amu from the elemental ion m/z degrade detection limits by decreasing the signal to background (S/B) ratio. For example, it is difficult to...
measure small variations of the $^{80}$Se$^+$ signal (e.g. $10^3$ cps) on top of a large background $^{40}$Ar$_2^+$ signal (~2 x $10^6$ cps). In this example, small (~1%) fluctuations in the background signal are greater than the elemental ion signal which makes precise measurements of Se$^+$ difficult for samples with ppb or lower concentrations. Measuring concentrations at or below the part per billion ($\mu$g L$^{-1}$) concentration range requires high sensitivity and low background signals. However, many elements with m/z less than 80 suffer from mass spectral overlaps. Table 1.1 lists some of the most common overlaps in ICP-MS that cannot be resolved using a quadrupole mass filter.

Table 1.1: Some common mass spectral overlaps in ICP-MS.

<table>
<thead>
<tr>
<th>m/z</th>
<th>Element</th>
<th>Overlaps</th>
<th>m/z</th>
<th>Element</th>
<th>Overlaps</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>B</td>
<td>12C$^+$ wing</td>
<td>52</td>
<td>Cr</td>
<td>$^{40}$Ar, $^{12}$C$^+$, $^{36}$Ar, $^{16}$O$^+$</td>
</tr>
<tr>
<td>23</td>
<td>Na</td>
<td>$^{40}$Ca$^+$, $^{40}$Ti$^{2+}$</td>
<td>53</td>
<td>Cr</td>
<td>$^{36}$Cl$^-$, $^{36}$Ar, $^{16}$O$^+$</td>
</tr>
<tr>
<td>24</td>
<td>Mg</td>
<td>C$_2^+$</td>
<td>55</td>
<td>Mn</td>
<td>$^{40}$Ar, $^{18}$H$^+$, $^{38}$Ar, $^{16}$O$^+$, $^{23}$Na$^{2+}$</td>
</tr>
<tr>
<td>27</td>
<td>Al</td>
<td>$^{11}$B$^{16}$O$^+$</td>
<td>56</td>
<td>Fe</td>
<td>$^{40}$Ar, $^{18}$O$^+$, $^{40}$Ca$^{16}$O$^+$, $^{112}$Cd$^{2+}$</td>
</tr>
<tr>
<td>28</td>
<td>Si</td>
<td>$^{14}$N$_2^+$, $^{12}$C$^{16}$O$^+$</td>
<td>57</td>
<td>Fe</td>
<td>$^{40}$Ar$^{18}$O$^+$, $^{38}$Ar$^{16}$O$^+$, $^{40}$Ca$^{16}$O$^+$</td>
</tr>
<tr>
<td>31</td>
<td>P</td>
<td>$^{16}$OH$^+$</td>
<td>58</td>
<td>Ni</td>
<td>$^{58}$Fe$^+$, $^{40}$Ar, $^{18}$O$^+$, $^{23}$Na, $^{35}$Cl$^+$</td>
</tr>
<tr>
<td>32</td>
<td>S</td>
<td>$^{16}$O$_2^+$</td>
<td>60</td>
<td>Ni</td>
<td>$^{44}$Ca$^{16}$O$^+$, $^{23}$Na$^+$Cl$^-$</td>
</tr>
<tr>
<td>39</td>
<td>K</td>
<td>$^{38}$Ar$^{1+}$H$^+$</td>
<td>63</td>
<td>Cu</td>
<td>$^{16}$Ar$^{17}$Cl$^+$, $^{31}$P$^{16}$O$^+$</td>
</tr>
<tr>
<td>40</td>
<td>Ca</td>
<td>$^{40}$Ar$^+$</td>
<td>64</td>
<td>Zn</td>
<td>$^{60}$Ni$^{1+}$, $^{32}$S$^2$, $^{40}$Ar, $^{12}$C$^{16}$N$^+$, $^{48}$Ti$^{16}$O$^+$</td>
</tr>
<tr>
<td>41</td>
<td>K</td>
<td>$^{40}$Ar$^+$H$^+$</td>
<td>69</td>
<td>Ga</td>
<td>$^{136}$Ba$^{2+}$</td>
</tr>
<tr>
<td>42</td>
<td>Ca</td>
<td>$^{40}$Ar$^+$H$^+$</td>
<td>70</td>
<td>Ge</td>
<td>$^{35}$Cl$^2$, $^{140}$Ce$^{2+}$</td>
</tr>
<tr>
<td>44</td>
<td>Ca</td>
<td>$^{12}$C$^{16}$O$_2^+$, $^{14}$N$_2^+$ $^{16}$O$^+$, $^{12}$C$^{32}$S$^+$</td>
<td>72</td>
<td>Ge</td>
<td>$^{36}$Ar$^+$, $^{37}$Cl$^{32}$Cl$^-$, $^{56}$Fe$^{16}$O$^+$</td>
</tr>
<tr>
<td>45</td>
<td>Sc</td>
<td>$^{12}$C$^{16}$O$_2^+$, $^{14}$N$_2^+$ $^{16}$O$^+$, $^{12}$C$^{32}$S$^+$</td>
<td>75</td>
<td>As</td>
<td>$^{46}$Ar$^{35}$Cl$^+$, $^{46}$Ca$^{35}$Cl$^+$, $^{150}$Sm$^{2+}$, $^{150}$Nd$^{2+}$</td>
</tr>
<tr>
<td>48</td>
<td>Ti</td>
<td>$^{48}$Ca$^+$, $^{54}$S$^{16}$O$^+$, $^{36}$Ar$^{12}$C$^+$, $^{28}$Mg$^2+$, $^{31}$P$^{16}$O$^+$</td>
<td>78</td>
<td>Se</td>
<td>$^{40}$Ar$^{38}$Ar$^+$, $^{23}$Kr$^{38}$Gd$^{2+}$, $^{62}$Ni$^{16}$O$^+$</td>
</tr>
<tr>
<td>51</td>
<td>V</td>
<td>$^{35}$Cl$^{16}$O$^+$</td>
<td>80</td>
<td>Se</td>
<td>$^{40}$Ar$^2$, $^{40}$Ar$^2$, $^{48}$Ti$^{16}$O$^+$</td>
</tr>
</tbody>
</table>
Despite the high temperature of the ICP, some polyatomic ions survive and are often the source of elevated background signal. The presence and identity of polyatomic ions were noted in the very first ICP-MS publication and have been studied and characterized by numerous researchers. Polyatomic ions may form from combinations of plasma gas atoms or ions, atmospheric gases, the acid or sample matrix and many have been characterized using “high resolution” sector field mass spectrometers.

The Elan 6100PLUS ICP-DRC-MS used in this work produced background signals greater than 100 c s\(^{-1}\) from a deionized water solution at 59 different m/z less than 80 amu, and at 41 different m/z having intensities greater than 1000 c s\(^{-1}\) in agreement with previous experiments. A 2% v/v HNO\(_3\) solution produced a signal at 62 m/z with intensity greater than 100 c s\(^{-1}\) and 42 m/z with intensity greater than 1,000 c s\(^{-1}\). The increase in the number of elevated intensities from a HNO\(_3\) solution is due to NO\(_3^-\) and its constituents that form polyatomic overlaps in the ICP. Other common acidic matrices produce similar increases in the number m/z ratios with elevated blank signals.

1.4 First approaches to overcoming spectral overlaps

The simplest way to overcome a spectral overlap on a particular m/z is to measure a different isotope of that element. For example, \(^{40}\)Ar\(^{16}\)O\(^+\) overlaps the most abundant Fe isotope at m/z 56. However, ppb detection limits can be reached by measuring the second most abundant isotope, \(^{54}\)Fe\(^+\) (if ArN\(^+\) is not present at m/z 54). Although \(^{38}\)Ar\(^{16}\)O\(^+\) will also be present at m/z 54, the isotopic abundance of \(^{38}\)Ar is 0.063% whereas
the abundance of $^{40}$Ar is 99.6%. Due to the differences in isotopic abundance of $^{36}$Ar and $^{40}$Ar, the $^{38}$ArO$^+$ signal is $10^3$ times smaller than the $^{40}$ArO$^+$ signal.

The second most common approach is to use mathematical correction procedures and known (natural) isotopic ratios to calculate signals at m/z where more than 1 ion is measured. For example, $^{115}$In$^+$ and $^{115}$Sn$^+$ are isobaric elemental overlaps ($\Delta m = 0.000536$). If $^{118}$Sn$^+$ can be measured with a high degree of certainty, the known $^{115}$Sn/$^{118}$Sn isotopic ratio can be used to calculate the $^{115}$Sn$^+$ signal. Mathematical corrections can be used for accurate measurements only if at least one isotope can be measured with sufficiently high signal to background (S/B) ratio, which is not always possible.\(^{45}\)

The magnitude of overlap signals that arise from the plasma gas or solvent matrix can be reduced by solvent removal\(^{46}\) or by operating under “cool” plasma conditions.\(^{34,47,48}\) Other overlaps can be overcome by coupling a separation technique such as ion chromatography\(^{49,50}\) or capillary electrophoresis,\(^{51}\) or by volatility differences such and electrothermal vaporization.\(^{52}\) These techniques cannot be universally applied if the samples to be analyzed are in complex or changing matrices, or if the desired analysis is multi-elemental.

Overlaps have also been overcome by increasing the instrument resolution by using a reverse Nier-Johnson geometry double focusing sector field mass spectrometer.\(^{34,53,54}\) The commercially available instrument can provide resolution of $\Delta m = 10,000$ (10% valley definition) which is sufficient to resolve elemental ions from many polyatomic overlaps. However, isobaric elemental overlaps (e.g. $^{115}$In/$^{115}$Sn) are often
too close in m/z to resolve by using the sector field instruments, and ion-molecule reactions are needed to chemically resolve the analyte from overlap.

1.5 Overcoming spectral overlaps by use of ion-molecule reactions

Ion-molecule reactions have been used to provide chemical resolution in ICP-MS for more than a decade.\(^{55}\) In this approach, both analyte and overlap ions are produced in the ICP, sampled into the mass spectrometer, and allowed to interact with a neutral reaction gas. Chemical resolution is achieved when the overlap ion is reacted away or the analyte ion reacts to form a molecular ion at a new, higher, overlap free m/z.

Rowan and Houk first used Xe and CH\(_4\) to attenuate polyatomic signals\(^{56}\) around the same time that Douglas introduced atom addition reactions to overcome overlaps.\(^{57}\) The idea of selective removal of overlaps was revived in 1996 by Koppenaal’s report of selective removal of matrix by reactions with H\(_2\) in an ion trap.\(^{58,59}\) Since that time, numerous ICP-MS configurations equipped with reaction and collision cells to facilitate ion-molecule reactions have been described.\(^{26}\) Chemical resolution is able to circumvent spectral overlaps in a cost-effective and simple way, including difficult overlaps where suitable resolution is unattainable by double focusing sector field instruments. Tanner and coworkers have reviewed the use of ion-molecule reactions in a dynamic reaction cell (DRC) to chemically resolve overlaps in ICP-MS.\(^{26,60,61}\) Olesik and Jones\(^{62}\) have published method development strategies to overcome spectral overlaps using ion-molecule reaction chemistry while Armentrout has described the fundamentals of ion-
molecule chemistry from a theoretical point of view. A schematic of the Elan 6100PLUS ICP-DRC-MS is shown in figure 1.4.

Figure 1.4: Perkin Elmer Sciex Elan 6100PLUS ICP-DRC-MS schematic.

The choice of an appropriate reaction gas will depend on whether or not it reacts efficiently enough with the overlap ion, avoids the formation of undesired product ions, and does not cause extensive loss of analyte ion signal due to reaction or scattering. The dynamically scanning quadrupole inside the reaction cell acts as an ion guide and can be used to reject precursor ions to unwanted secondary reactions. The Mathieu parameters $a$ and $q$ are selected by the user by adjusting the related parameters $RPq$ and $RPa$.

$$a = 1.9 * RPa$$

$$q = 0.95 * RPq$$

The quadrupole inside the DRC is synchronized with the mass filter quadrupole to provide optimum analyte transmission and controlled ion-molecule reaction chemistry. It
is normally operated as an RF only quadrupole ($a = RPa = 0$) and acts as a high pass filter characterized by a well defined low mass cutoff.

The change in Gibbs free energy of the reaction will determine if the reaction is spontaneous. For many bimolecular ion-molecule reactions, the change in entropy is small and may be negated.

$$\Delta G = \Delta H - T \Delta S \quad (1.5)$$

$$\Delta G \cong \Delta H \quad (1.6)$$

The change in enthalpy can be calculated by the difference in the sums of the heats of formation of the products and the sums of the heats of formation of the reactants.

$65, 66$

$$\Delta H_{\text{rxn}} = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants}) \quad (1.7)$$

Endothermic reactions are unlikely to occur if ions in the reaction cell are completely thermalized. However, ions enter the reaction cell with kinetic energy normally $\lesssim 12$ eV.$26, 67, 68$ Ions can also gain up to 0.4 eV of radial energy from the RF field applied to the quadrupole inside the reaction cell.$55, 61$ Thermodynamics provide reaction specificity if gases provide spontaneous (exothermic) reactions with interfering ions and non-spontaneous (endothermic) reactions with analyte ions.$58$

The kinetic rates of ion-molecule reactions are not as easily predicted as reaction spontaneity. Although a reaction may be highly exothermic, the efficiency of the reaction may be low and thus not a good candidate to provide chemical resolution. Experimentally measured ion-molecule kinetic rate constants, including many that are
applicable to ICP-MS, have been compiled by Anicich.\textsuperscript{69, 70} ICP-SIFT-MS rate constants are also available from Bohme’s group at York University.\textsuperscript{71}

Charge transfer reactions can be used to selectively and efficiently reduce or eliminate overlap ion signals with little effect on the analyte ion signal in ICP-DRC-MS. Charge transfer reactions that are exothermic are typically high efficiency reactions that produce up to 9 orders of magnitude improvements in analyte elemental ion to overlap ion signal ratios.\textsuperscript{26, 60, 61, 72} One of the first ion-molecule reactions in ICP-DRC-MS reported was the chemical resolution of \( ^{40}\text{Ca}^+ \) from \( ^{40}\text{Ar}^+ \) by using NH\(_3\) as a neutral reactant.\textsuperscript{60}

\[
\text{Ar}^+ + \text{NH}_3 \rightarrow \text{Ar} + \text{NH}_3^+ \quad \Delta H_f = -5.69 \text{ eV}
\]

\[
\text{Ca}^+ + \text{NH}_3 \rightarrow \text{Ca} + \text{NH}_3^+ \quad \Delta H_f = +3.96 \text{ eV}
\]

The charge transfer reaction between \( \text{Ar}^+ \) and NH\(_3\) is exothermic and should be spontaneous. The charge transfer reaction between \( \text{Ca}^+ \) and NH\(_3\) is endothermic and unlikely to occur. Figure 1.5 shows the signals measured at m/z 40 as a function of NH\(_3\) flow into the reaction cell.
Figure 1.5: Measured signals from a blank (○, left y-axis) and 10 ppb Ca (●, left y-axis) standard as a function of NH₃ flow into the reaction cell with RPq = 0.5. Ar signal extrapolated to 1 c s⁻¹ (—). Estimated detection limits based on Poisson counting statistics (□, right y-axis) also shown. Minimum LOD (■) is at 0.75 Ar equiv. mL min⁻¹.

The ⁴⁰Ar⁺ signal is reduced by 7 orders of magnitude according to pseudo-first order reaction kinetics as NH₃ flow rate increases. At reaction gas flow rates greater than 0.7 Ar equivalent mL min⁻¹, the contribution of ⁴⁰Ar⁺ to the measured signal is less than 1 c s⁻¹. At reaction gas flow rates of 0.6 Ar equivalent mL min⁻¹ the signal from the blank solution is likely due to Ca contamination. The noise at low count rates is dominated by Poisson counting statistics⁷³ which can be used to estimate detection limits. Counting
statistics state that the standard deviation is equal to the square of the total counts and can be used to estimate the limit of detection (LOD).

\[ s = \sqrt{N_{\text{total}}} \]  \hspace{1cm} (1.8)

A convenient method to choose the optimum reaction gas flow rate is based on estimated limits of detection. Estimated LODs assume that the standard deviation of the matrix-matched blank is due to Poisson counting statistics (shot noise):

\[ \text{Est LOD (ppb)} = 3 \times \frac{\text{Blank st dev}}{\text{sensitivity}} = 3 \times \frac{\sqrt{\text{Blank (c s}^{-1}) \times \text{time(s)}}}{\text{sensitivity (c s}^{-1} \text{ng}^{-1} \text{L} \times \text{time(s)}}} \]  \hspace{1cm} (1.9)

By adding NH\textsubscript{3} to the reaction cell, estimated detection limits were as low as 4 ng L\textsuperscript{-1} (marked ■ in figure 1.5). Lower detection limits could be obtained if there was less Ca contamination in the blank. The best reaction gas flow rate is usually chosen by optimizing flow rate for the best estimated LOD.

NH\textsubscript{3} is commonly used as a charge transfer reaction gas because its first ionization energy is higher than that of many elemental ions, but lower than many common polyatomic ion overlaps. This allows an exothermic reaction channel with many undesired polyatomic overlaps and an endothermic reaction channel with elemental analyte ions. Changes in signal magnitude across the mass spectrum can be seen in figure 1.6 by the addition of 1.0 Ar equivalent mL min\textsuperscript{-1} NH\textsubscript{3}. 

14
The addition of NH$_3$ to the reaction cell reduces many of the overlaps observed when no gas is used. These measurements agree with previous work done to determine the behavior of background ions and NH$_3$.\textsuperscript{44}

1.6 **Dissertation Contents and Organization**

This dissertation includes research aimed at enhancing understanding of ICP-MS. In particular, focus was on the emerging reaction cell techniques that can provide
resolution from many problematic overlaps. The dissertation is organized in four main sections: Chapters 2-5 cover experimental findings using DRC technology, chapter 6 relates experimental results to fundamental concepts, chapter 7 compares results to computer simulations, and chapter 8 explores the possibility of nanoparticle characterization by ICP-MS.

The dynamic reaction cell has been shown to improve the precision of element or isotope ratios by using the DRC to homogenize the ion beam. In chapter 2, the ICP-DRC-MS was compared to an ICP-quadrupole-MS without a reaction cell, an ICP double focusing sector field MS, and an ICP-optical emission spectrometer.

Collision induced dissociation (chapter 3) and ion molecule reactions (chapters 4 and 5) were investigated for improvements in detection limits of “difficult” mass spectral overlaps. These overlaps include Fe/ArN (chapter 3), Se/Ar\(_2\) (chapter 4), and Sr/Rb (chapter 5). Suitable reaction gases, instrument parameters and solution matrices were independently examined to assess the impact of each. In addition, the effectiveness of collision induced dissociation (CID, chapter 3) to improve S/B ratios was studied and compared to ion-molecule reactions.

To understand the fundamental ion-molecule collision and reaction events in the ICP-DRC-MS, a correlation was established between kinetic rate constants of the bimolecular reactions and the signals measured on the ICP-DRC-MS (chapter 6). A simple spreadsheet simulation was created to estimate the gas density inside the reaction cell and relate signal decays to fundamental kinetic rate constants.
A computer simulation model, using the ion trajectory program SIMION 8.0, calculated ion flights including collisions. The modeled results were compared to experimental measurements and used to estimate the efficiency of various reaction gases to provide chemical resolution (chapter 7). A custom written hard sphere collision model was used to model the ion’s interactions with gas atoms and molecules in the reaction cell.

The final portion of the dissertation involves investigations on the ability of ICP-MS to characterize nanoparticles (chapter 8). ICP-MS is uniquely positioned in that it has the capability to simultaneously offer mass (size) and elemental composition analysis of nanoparticles in dilute suspensions. A nanoparticle delivery system was developed to allow measurement of individual nanoparticles and validated by scanning electron microscopy (SEM). Nanoparticle signals were measured using both triggered, oscilloscope traces with microsecond resolution and discrete, integrated signal recording using the ICP-MS software. The pros and cons of each technique were examined with regards to nanoparticle size and mass distributions. Calibration curves and mass distributions of nanoparticles were compared to those by SEM. ICP-MS was, for the first time, used to characterize individual nanoparticles.


41. Matheson M. Fraser and Diane Beauchemin, Effect of concomitant elements on the distribution of ions in inductively coupled plasma mass spectrometry — part 2:


44. Deanna M. Rago Jones, A study of ion-molecule reactions in a dynamic reaction cell to improve elemental analysis with inductively coupled plasma-mass spectrometry. 2007, PhD, The Ohio State University.


2 Improvements in ICP-MS precision via temporal homogenization

2.1 Abstract

The ability of a pressurized, dynamic reaction cell to dampen signal fluctuations from inductively coupled plasma flicker noise to improve elemental ratios or isotopic ratios was assessed. He, Ne, Ar and NH$_3$ were studied as possible collision gases, and optimized experimental conditions for minimizing signal fluctuations were determined. Comparisons were made of ICP-Q-MS, ICP-SF-MS and ICP-OES precision from noisy laser ablation sampling. Only ICP-DRC-MS and ICP-OES were able to offer counting statistics limited precision. The method was applied to attempt to improve precision from laser ablation mapping of an extremely heterogeneous coral skeleton.

2.2 Introduction

Variations of isotope and elemental ratios can be used to analyze differences in sample origin, age and identity.$^{1, 2}$ Many of these ratios vary less than 1%, and so high precision measurements are necessary. The most significant factor affecting the precision of isotope or elemental ratios is density fluctuations in the ion beam extracted from the ICP due to flicker noise.$^{3, 4}$ Precision may be improved if the ion beam density fluctuations can be dampened using the dynamic reaction cell (DRC).$^3$
The mass analyzers in most (> 99%) commercially available ICP-MS’s use either quadrupole mass filters or double focusing sector fields mass analyzers that measure a single m/z charge at one time, but can hop from one m/z to another quickly.\textsuperscript{5, 6} In a low resolution setting, ICP-SF-MS provides flat topped peaks that results in a intensity that is independent of the exact position at which the peak is measured and have attained isotope ratio precision of \( \leq 0.05\% \).\textsuperscript{7}

Quadrupole mass filters provide round topped peaks and are susceptible to small fluctuations in the measured mass location. Quadrupole mass spectrometers have been shown to offer precision as low as 0.025\% if extensive bracketing methodologies are used, but this level of precision is not routine.\textsuperscript{8}

ICP optical emission spectrometers (OES) offer simultaneous detection of light from excited analyte atoms and ion in the ICP. By simultaneously measuring multiple wavelengths, high precision (~0.1\% relative expanded uncertainties)\textsuperscript{9, 10} elemental ratio measurements have been made using OES systems.\textsuperscript{11} However, OES has higher detection limits than MS, and therefore has limited applicability to ultra-trace metals analysis.

The ICP produces an ion beam of uneven density which can fluctuate due to oscillations of the plasma,\textsuperscript{12, 13} variations in the total mass of sample delivered,\textsuperscript{14, 15} and incompletely vaporized droplets or incompletely vaporized particles.\textsuperscript{16, 17} Ion signal fluctuations from the ICP in the kHz range which degrades precision from the theoretical counting statistics limit.\textsuperscript{4} As a general rule, if the instrumental dwell time is longer than the signal fluctuations, then the isotope ratio precision will be degraded.\textsuperscript{18}
The two dominant sources of uncertainty in isotope ratio measurements stem from flicker noise which originates in the ICP, and white (shot) noise associated with the ion counting process. The contributions of flicker noise will first be shown using a simulated isotope ratio measurement process shown in figure 2.1.

![Figure 2.1](image)

**Figure 2.1:** Example of vented mode signals from two isotopes A (blue) and B (red). Real time signals shown in a., quadrupole action with 2 ms dwell time and 200 µs settling time shown in b., and detected signal of both isotope A and B shown in c.

The top plot in figure 2.1a shows two series from one real signal when the reaction cell was not pressurized with any gas. “Isotope A” (red) is the signal of “Isotope B” (blue) multiplied by 1.5. If signals were measured simultaneously and in the absence
of shot noise, A/B would be exactly 1.5 with a precision of 0% relative standard deviation (RSD). However, the quadrupole ICP-MS measures one m/z at a time, (figure 2.1b). The dwell time in this example is 2 ms with a settling time of 200 μs. For the four complete sweeps shown in figure 2.1, the measured RSD was 9%. Typically, the precision observed for isotope ratio measurements by ICP-MS are two to three times as large as the counting statistics limited precision. This example shows how single channel detection results in poor precision from a noisy sampling source.

Ion beam fluctuations due to flicker noise may be dampened by passing the ion beam through a pressurized reaction cell. Figure 2.2 shows an example of dampened signal fluctuations using a pressurized reaction cell.
**Figure 2.2:** Example of signals from two isotopes A (blue) and B (red) when the reaction cell is pressurized with NH$_3$. Real time signals are shown in a) quadrupole action with 2 ms dwell time and 200 $\mu$s settling time shown in b) and detected signal of both isotope A and B shown in c).

Figure 2.2 may be directly compared to figure 2.1, except the reaction cell has now been pressurized with 6.5 mTorr NH$_3$ (1.0 Ar equivalent mL min$^{-1}$). Signal fluctuations were noticeably dampened by collisions with NH$_3$ in the DRC. Precision was improved (reported as %RSD) from 9% (figure 2.1) to 2%. Figures 2.1 and 2.2 show how dampening of ion beam density fluctuations may improve isotope ratio precision in single channel ICP-MS.
2.2.1 Poisson counting statistics

The ion counting process may contribute to measurement uncertainty in addition to flicker noise. Any electronic counting process may be represented by the Poisson distribution, which is often termed counting statistics distribution:

\[ y = \frac{\mu^x}{x!} e^{-\mu} \]  \hspace{1cm} (2.1)

where \( y \) is the frequency of occurrence of a given count \( x_i \) and \( \mu \) is the mean. The standard deviation, \( \sigma_M \), of the counting measurement is dependent only upon the total number of counts (\( M \)).

\[ \sigma_M = \sqrt{M} \]  \hspace{1cm} (2.2)

\[ \frac{\sigma_M}{M} = \frac{\sqrt{M}}{M} = \frac{1}{\sqrt{M}} \]  \hspace{1cm} (2.3)

The theoretical precision limit can be calculated by assuming a Poisson distribution and no other significant noise sources.

\[ \%RSD = \sqrt{\left(\frac{N_A}{N_B}\right)^{-1} + \left(\frac{N_B}{N_A}\right)^{-1}} \]  \hspace{1cm} (2.4)

where the total counts of isotopes A and B (\( N_A \) and \( N_B \)) can be calculated by multiplying the count rate (\( c \) s\(^{-1}\)) by the total integration time (s). Counting statistics may be improved by increasing integration time (total counts), but long integration times are susceptible to flicker noise. Measurement time should be selected so that it is short enough to allow a scan cycle to be completed in a faster time than the period of noise fluctuation. If signal fluctuations can be successfully dampened, then longer measurement times can be used and precision can be improved.
2.2.2 Collisional dampening of noise fluctuations

Ion signal fluctuations are dampened after collisions with gas atoms or molecules inside the reaction cell.\(^3\) As the ions collide with the gas, they take a random path through the reaction cell and the signal fluctuations are dampened.\(^3\)

Bandura, Baranov and Tanner were the first to show improved precision for Pb, Ag and Fe isotope ratios.\(^3\) Other research groups have shown improvements in precision for multielement,\(^22\) Se,\(^23\) Ca,\(^24,25\) and Sr/Rb ratios,\(^26,27\) and in reviews of stable isotope tracers.\(^28,29\)

It would be beneficial to know how the dwell times, collision gas, and gas flow rates affect precision. This chapter compares the properties of various collision gases and instrument settings in order to determine the best possible parameters for high precision measurements. Laser ablation sampling was used to determine if high precision elemental ratios could be obtained from a noisy sample source by using a pressurized DRC while peak hopping between two different elemental ions or isotopes. Precision from quadrupole (both with a pressurized cell and without) and sector field ICP-MS instruments (both using peak hopping) was measured and compared to optical emission ICP-OES measurements where emission from two different element was measured simultaneously.

2.3 Experimental details

A PerkinElmer Sciex Elan 6100 DRC\(^\text{plus}\) ICP-DRC-MS,\(^30\) Thermo Finnigan Element 2 sector field ICP-MS and a PerkinElmer Optima 3000 were used as noted. A
peristaltic pump (Gilson Minipuls 3) delivered solution into a quartz, concentric nebulizer (TQ-30-A3, Meinhard Glass Products, Golden CO, USA) at a solution uptake rate of 1 mL min\(^{-1}\). A quartz, baffled cyclonic spray chamber (Quartz Cyclonic Spray Chamber for ELAN DRC (WE025221), PerkinElmer Sciex) at ambient temperature was used with a 2.0 mm id quartz injector (WE023948, PerkinElmer Sciex) for solutions introduction to the Elan ICP-DRC-MS. Solutions were made by serial dilution from 1,000 µg mL\(^{-1}\) standard solutions (CPI International, Santa Rosa CA, USA) in deionized water (18.2 MΩ cm, Millipore Milli-RO-10 and Milli-Q). Solid samples were measured using a New Wave Research UP-193HE laser ablation system including a TuliStar Ar-F 193 nm excimer laser. The laser ablation aerosol was introduced to the Optima ICP-OES, the Elan ICP-DRC-MS and the Element 2 ICP-SF-MS via tygon tubing connected to the injector using a polished glass ball joint.

For most measurements the static voltage on the ion optics lens was provided by an external DC power supply (Hewlett Packard model E3612A). For some experiments used to measure the effective time-constant of DRC, the ion optics lens was connected to a square wave pulse generator (Systron Donner 101, Concord CA) in order to start and stop the flow of ions into the reaction cell. The cell exit lens potential was disconnected from the instrument control electronics and controlled by external power supplies (Heath Zenith model 2717-A). Ion currents were measured from the analog output of the detector via a current amplifier (Keithley 428, Cleveland OH) and monitored on a digital oscilloscope (Nicolet 310, Middleton WI and LeCroy 9450A, Chestnut Ridge NY). Data were retrieved from the Nicolet oscilloscope using a program\(^{31}\) written in LabView.
(National Instruments, Austin TX over an RS-232 interface) and retrieved from the LeCroy oscilloscope using ScopeExplorer version 2.21.0 (LeCroy, Chestnut Ridge NY over an IEEE interface).

Collision/reaction gases included nitrogen (99.998%, Praxair), argon (99.998%, Praxair), neon (99.999%, Praxair), helium (99.999%, Praxair), and ammonia (99.999%, Scott Specialty Gases). Flows were maintained by mass flow controllers (MKS Instruments, USA) calibrated for Ar flow with calibration factors listed in Table 2.2.

Table 2.1: ICP-DRC-MS and oscilloscope experimental parameters.

<table>
<thead>
<tr>
<th>ICP-DRC-MS instrumental parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>RF power/W</td>
<td>1200</td>
</tr>
<tr>
<td>Lens Voltage</td>
<td>Optimized for each analyte</td>
</tr>
<tr>
<td>AutoLens</td>
<td>Off</td>
</tr>
<tr>
<td>Auxiliary gas flow</td>
<td>1.2 L min⁻¹</td>
</tr>
<tr>
<td>Plasma gas flow</td>
<td>15 L min⁻¹</td>
</tr>
<tr>
<td>Nebulizer gas flow (optimized daily)</td>
<td>~0.8 L min⁻¹</td>
</tr>
<tr>
<td>Settling time (μs)</td>
<td>200</td>
</tr>
<tr>
<td>Dynamic Reaction Cell parameters</td>
<td></td>
</tr>
<tr>
<td>Entrance lens voltage</td>
<td>Varied</td>
</tr>
<tr>
<td>Exit lens voltage</td>
<td>Varied</td>
</tr>
<tr>
<td>Quadrupole rod offset/v</td>
<td>-1</td>
</tr>
<tr>
<td>Cell rod offset/V</td>
<td>-10</td>
</tr>
<tr>
<td>RPa</td>
<td>0.00</td>
</tr>
<tr>
<td>RPq</td>
<td>Varied</td>
</tr>
<tr>
<td>Oscilloscope settings</td>
<td></td>
</tr>
<tr>
<td>Amplification</td>
<td>10³-10⁷</td>
</tr>
<tr>
<td>Time constant (μs)</td>
<td>10 or 30, as noted</td>
</tr>
</tbody>
</table>
Table 2.2: Actual flow (mL min\(^{-1}\)) reaction gas per Ar equivalent mL min\(^{-1}\) gas flow. Actual gas flow rate calculated by multiplying conversion factor by reported gas flow rate.\(^{32}\)

<table>
<thead>
<tr>
<th>Reaction Gas</th>
<th>Gas calibration factors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>1.00</td>
</tr>
<tr>
<td>He</td>
<td>1.01</td>
</tr>
<tr>
<td>N(_2)</td>
<td>0.72</td>
</tr>
<tr>
<td>Ne</td>
<td>1.05</td>
</tr>
<tr>
<td>NH(_3)</td>
<td>0.53</td>
</tr>
</tbody>
</table>

2.4 Optimized conditions for temporal homogenization

The choice of collision gas, instrument electrode voltages and dwell times were systematically studied. The collision gases He, Ne and Ar were studied as was the most commonly used ICP-DRC-MS reaction gas, NH\(_3\). Voltages applied to the axial field electrodes surrounding the DRC were varied, and the influence of dwell time on precision was studied. Once the optimized conditions were determined, then the method was applied with noisy laser ablation as the sampling source.

2.4.1 Collision gas choice

Collision gases were systematically studied to determine which gas might offer the best route for high precision measurements. Gases were studied on the basis of mass, dipole moment and polarizability using a pulsed ion optics set up which is capable of instantaneously stopping the flow of ions into the reaction cell. Ion packet broadening (the amount of time that passed until the signal falls to 50% of the original signal) was then measured for each gas.
Table 2.3: Mass, permanent dipole moments and dipolar polarizabilities of He, Ne, Ar and NH₃:

<table>
<thead>
<tr>
<th>Gas</th>
<th>Mass (amu)</th>
<th>Dipole Moment (d)</th>
<th>Dipolar Polarizability (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>4</td>
<td>0</td>
<td>0.205</td>
</tr>
<tr>
<td>Ne</td>
<td>21</td>
<td>0</td>
<td>0.396</td>
</tr>
<tr>
<td>Ar</td>
<td>40</td>
<td>0</td>
<td>1.64</td>
</tr>
<tr>
<td>NH₃</td>
<td>17</td>
<td>1.5</td>
<td>2.81</td>
</tr>
</tbody>
</table>

A square wave pulse generator instantaneously started (5 ns voltage rise time) and stopped (7 ns voltage fall time) ion flow into the reaction cell. A 20 ms square wave pulse was applied to the lens immediately in front of the dynamic reaction cell (6.5 V “on”, 0 V “off”). When the lens was off, the flow of ions into the reaction cell was almost instantaneously stopped. A 5 ppm solution of Ag was freely aspirated into the plasma via a combined cyclonic-double pass spray chamber and ¹⁰⁷Ag⁺ was monitored. The entrance lens of the reaction cell was held at -50 V to create a potential energy well at the front of the reaction cell.³ The exit lens was held at -15 V to extract ions from the cell that had lost significant radial kinetic energy. Figure 2.3 shows the effect of turning the focusing lens off (time = 0) when the cell was vented (no gas).
Figure 2.3: Normalized signal resulting from 5 ppm Ag solution measured on digital oscilloscope with 6.5 V applied to optics lens at $t < 0$ ms and 0 V applied at $t > 0$ ms.

When the optics lens is turned off, the signal decreases to background levels in approximately 60 µs, which is close to the rise time of the current amplifier (30 µs).

Figures 2.4 a – d show the effect of collision gas mass on ion packet broadening. Gas flow rates were chosen to provide 14 mTorr pressure inside the reaction cell.
Figure 2.4: Normalized signal resulting from 5 ppm Ag solution measured on digital oscilloscope with 6.5 V applied to optics lens at t < 0 ms and 0 V applied at t > 0 ms. The cell was pressurized with approximately a) 14 mTorr He, b) 14 mTorr Ne, c) 13 mTorr Ar and d) 7 mTorr NH₃. 10⁶ V/A amplification, \( \tau = 30 \mu s \).

Figures 2.4 a – c show the extent of ion packet broadening due to inert collision gases. He (280 \( \mu \)s), Ne (340 \( \mu \)s) and Ar (600 \( \mu \)s) broadened the signal decay less than the shortest practical dwell time (1 ms). These gases did not have permanent dipole
moments. Higher pressures might be able to further homogenize the ion beam, but will only be useful if sensitivity is not lost to ion scattering.

If the number of ion-molecule collisions increases, then ions will lose increasing amounts of kinetic energy and signal fluctuations dampened further. NH$_3$ has a permanent dipole moment and undergoes more collisions due to ion-dipole attraction. When the cell was pressurized with NH$_3$, the signal took 2.2 ms to decay by 50% and 4.9 ms to decay to 30%. This should be sufficient for precision improvement if a 1 ms dwell time was used.$^{3,31}$ Of the four gases examined, NH$_3$ is the most suitable candidate to dampen signal fluctuations, and permanent dipole moment was determined to be the most important factor when choosing a gas for temporal homogenization.

2.4.2 Axial field electrode potential optimizations

Axial field electrodes surround the DRC quadrupole and counteract space charge effects from constraining a large number of ions in the DRC at one time. The electrodes are held at positive voltages, tapered and increase ion transmission and sensitivity. The tapered shape of the electrodes force ions towards the exit of the DRC which counteracts attempts at temporal homogenization. A reduction of the axial field electrode potentials should increase ion residence time in the cell. Figure 2.5 shows the effect of applied axial field voltage on a $^{208}$Pb signal when the reaction cell is pressurized with NH$_3$ using the same pulsed ion optics system as described previously.
Figure 2.5: Effect of axial field voltage on ion packet broadening from a 10 ppm Pb solution using NH$_3$ collision gas. 300 V (green), 200 V (orange), 100 V (purple), 0 V (blue) and -100 V (red) potentials are shown.

The time it takes the signal to fall 50% increases from 540 $\mu$s (+300 V) to 1690 $\mu$s (-200 V) as the axial field voltage decreases. However, the increase in ion packet broadening is accompanied by a decrease in sensitivity due to lower ion transmission efficiency. The sensitivity decreases by approximately 50% when a -200 V bias is applied to the axial field electrodes compared to +300 V. When no bias is applied (0 V), the ion packets are broadened by 1320 $\mu$s (50% signal level) and sensitivity only decreased by about 10%. By applying a negative bias to the axial field electrodes,
temporal homogenization of the ion beam improves greatly but decreases the sensitivity significantly. Simply removing the positive potential improves ion beam density and reduces sensitivity only slightly.

Figure 2.6 shows a clear summary of temporal homogenization of the ion beam by pressurizing the reaction cell with NH$_3$ and removing the positive potential on the axial field electrodes.

**Figure 2.6:** Comparison of signal behavior from 5 ppm Ag solution in an evacuated (red) and pressurized (blue) reaction cell when the flow of ions is instantaneously stopped. Pressurized cell filled with 8 mTorr NH$_3$.
The signal in figure 2.6 falls in 60 μs after the lens voltage is turned off in the vented (evacuated chamber, no gas) mode, but exponentially decays in the pressurized mode. Ions take approximately 10 ms to “wash out” of the reaction cell when it is pressurized with NH₃. Flicker noise fluctuations are significantly dampened in the pressurized mode.

2.5 Precision dependence on dwell time

The effect of dwell time on isotope ratio precision was systematically studied to determine the range of dwell times at which the counting statistics limit could be reached. Precision is expected to be limited by counting statistics if the measurement time is faster than the flicker noise fluctuations, and is expected to worsen as dwell time increases. Because different isotopes are measured sequentially in a peak hopping mode, a longer dwell time results in a longer time between hops from measurement of one isotope to the other. If the fluctuations are dampened, then longer dwell times may be used. Figures 2.7a – c show the precision of the $^{107}$Ag/$^{109}$Ag ratio measured as a function of dwell time using no gas, Ne and NH₃.
Figure 2.7: $^{107}$Ag/$^{109}$Ag isotope ratio precision as a function of dwell time with a) no gas flow and RPq = 0.25, b) 2.8 Ar equivalent mL min$^{-1}$ Ne and RPq = 0.25 and c) 1.35 Ar equivalent mL min$^{-1}$ NH$_3$ RPq = 0.65. Both the experimental (● with 95% confidence intervals shown) and counting statistics limited %RSD (□) are shown.

At the shortest dwell time (0.2 ms), the experimental isotope ratio precision equals the theoretical counting statistics precision in all cases. As dwell time is increased, measured precision begins to deviate from the counting statistics limit. In the
vented mode, this deviation begins at 0.5 ms and worsens as dwell time increases. At the longest dwell time (100 ms), the vented mode precision is 5 times worse than the counting statistics precision. Counting statistics limited precision was reached with Ne and NH$_3$ at dwell times as long as 2 ms. These results agree with similar experiments, although those studies were performed at different cell pressures. It is important to note that in practical terms it is more important to obtain the best possible precision rather than precision close to counting statistics. However, comparing the precision measured to the theoretical counting statistics precision offers a convenient way to ascertain whether the ion beam is homogenized.

The freedom to choose a range of dwell times for each isotope allows for high precision isotope ratio measurements. Isotope ratio uncertainty is minimized when there are approximately an equal number of counts for each isotope. Many isotopic ratios of interest are composed of one major and one minor isotope (e.g. $^{44}$Ca/$^{42}$Ca). In these cases, the measurement time may be optimized to have roughly the same number of counts for each isotope, minimizing uncertainty. Pressurizing the DRC and homogenizing the ion beam allows a range of dwell times to be chosen so that high precision measurements can be made.

2.6 Laser ablation sample introduction

Although LA-ICP-MS offers minimal sample preparation, as well as lateral and depth resolution of solid samples, it is also can be a very noisy sample introduction source, particularly if the sample is heterogeneous, porous or has a rough surface. Each laser pulse may eject different amounts of mass from the sample surface, depending on
the local sample properties, which degrades precision. Variations in both particle number and size are likely responsible for the poor precision of laser ablation ICP-MS. Variations in the amount of material sampled may be compensated by using an internal standard or by measuring isotope ratios rather than attempting to calibrate based on a single isotope or elemental ion signal. For instance, signals from trace elements can be ratioed to the calcium signal when the sample is in a carbonate matrix. If the calcium concentration is constant everywhere in the matrix, then it may be representative of the total amount of mass ablated. If the elemental ratio precision of the metal/Ca measurement is poor, then the uncertainty of the trace metal concentration will also be large. Figure 2.8 shows the Ca⁺ signal from laser ablation of a carbonate sample matrix (coral) in both vented and NH₃ modes.
Figure 2.8: $^{42}$Ca$^+$ signal measured in a) vented mode and b) 1.0 Ar equivalent mL min$^{-1}$ NH$_3$ from the analog channel of the electron multiplier detector with $10^6$ gain and $\tau = 10$ µs. Laser ablation pulse repetition rate 10 Hz and XY stage speed 10 µm s$^{-1}$.

Figure 2.8a shows the very large signal fluctuations as different numbers and sizes of particles are introduced to the plasma. The relative standard deviation of the data in figure 2.8a is 51%, with signal fluctuations as much as 5x larger than the average signal. Precision might be improved if the signal fluctuations are significantly damped.

Figure 2.8b shows the effect of adding 1.0 Ar equivalent mL min$^{-1}$ NH$_3$ to the reaction cell during measurement. The average signal was decreased by approximately 25% due to transmission losses through the reaction cell. Collisions with NH$_3$ in the reaction cell sufficiently broadened the ion packets so that the measured relative standard deviation was improved from 51% to 12% and the largest signal fluctuation was only 40% larger than the average signal.
2.6.1 ICP-DRC-MS, ICP-SF-MS, ICP-OES precision comparison

ICP-quadrupole-MS, ICP-sector field-MS, ICP-DRC-MS and ICP-OES were coupled to the laser ablation system to determine which instrument could offer the best isotope ratio precision of a NIST standard reference glass. Although ICP-DRC-MS could dampen signal fluctuations, ICP-SF-MS offers higher sensitivity and flat topped peaks. Because counting statistics limits are determined by total counts, higher sensitivity from ICP-SF-MS may provide better precision even though no fluctuations are dampened. ICP-OES offers simultaneous measurement of multiple wavelengths and should be able to compensate for any flicker noise contributions. The instruments were compared using National Institute of Standards and Technology (Gaithersburg, MD) glass standards (SRM 612) with instrumental parameters which are listed in table 2.4. The Sr and Ca concentrations of SRM 612 are 78.4 ppm and 12.0% CaO, respectively. The ICP-OES read time was set to equal 1 ms (identical to ICP-MS dwell time) with the total integration time also equal to the ICP-MS integration time. The Sr and Ca ion lines at 407 and 317 nm were used because they were the most sensitive lines that did not saturate the CCD during the 1 ms read time.
Table 2.4: Instrument settings for ICP-q-MS, ICP-DRC-MS, ICP-SF-MS and ICP-OES comparison of precision for laser ablation of NIST 612 glass standard.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Dwell time (ms)</th>
<th>Time per measurement (s)</th>
<th>Time between measurements (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elan 6100 ICP-q-MS</td>
<td>1</td>
<td>1</td>
<td>2.2</td>
</tr>
<tr>
<td>Elan 6100 ICP-DRC-MS</td>
<td>1</td>
<td>1</td>
<td>2.2</td>
</tr>
<tr>
<td>Element 2 ICP-SF-MS</td>
<td>1</td>
<td>1</td>
<td>31</td>
</tr>
<tr>
<td>Optima ICP-OES</td>
<td>N/A</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

Laser ablation parameters

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Spot size</td>
<td>385 x 40 μm rectangle</td>
</tr>
<tr>
<td>Repetition rate</td>
<td>10 Hz</td>
</tr>
<tr>
<td>Stage speed</td>
<td>20 μm s⁻¹</td>
</tr>
</tbody>
</table>

The NIST 612 glass standard was analyzed by all four instruments for the Sr/Ca elemental ratio. Identical isotopes, dwell times, and laser ablation parameters were used for each ICP-MS. The DRC was pressurized with 0.5 Ar equivalent mL min⁻¹ NH₃. The sector field instrument requires a longer magnet settling time than the quadrupole mass spectrometers (29 ms for sector field, 0.2 ms for quadrupole). Figure 2.9 shows the results of 20 replicate measurements of Sr/Ca ratios on each instrument after correction for isotopic abundances (0.135% for ⁴³Ca and 8.6% for ⁸⁶Sr).
Figure 2.9: Measured Sr/Ca ratios using ICP-q-MS (left y-axis, ○), ICP-DRC-MS (left y-axis, □), ICP-SF-MS (left y-axis, ◊) and ICP-OES (right y-axis, ●). * ICP-OES are signal ratios, ICP-MS data are concentration ratios.

The precision and theoretical (counting statistics limited) precision of the data in figure 2.9 is listed in table 2.5. The CCD detector efficiency in the Optima 3000 ICP-OES is 15%\(^{44}\), therefore, signal intensity was divided by 0.15 in order to calculate the counting statistics limited relative standard deviation.
Table 2.5: Sr/Ca elemental ratio precision measured by four different ICP instrumental techniques.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Sr/Ca precision (% RSD)</th>
<th>Theoretical limit (% RSD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICP-q-MS</td>
<td>0.631</td>
<td>0.448</td>
</tr>
<tr>
<td>ICP-DRC-MS</td>
<td>0.521</td>
<td>0.497</td>
</tr>
<tr>
<td>ICP-SF-MS</td>
<td>0.596</td>
<td>0.050</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>0.334</td>
<td>0.256</td>
</tr>
</tbody>
</table>

ICP-DRC-MS precision is counting statistics limited, while the precision by ICP-q-MS is degraded from the counting statistics limit due to fluctuations from laser ablation sampling. ICP-DRC-MS has a larger theoretical precision than ICP-q-MS due to a loss in sensitivity when the DRC was pressurized. ICP-SF-MS has a much greater sensitivity than either ICP-q-MS or ICP-DRC-MS and therefore has a much lower theoretical precision. However, ICP-SF-MS is not counting statistics limited because of flicker noise during the long magnet settling times. Despite lower sensitivity and a higher background, ICP-OES with axial viewing offers the best precision. The data in table 2.5 shows that it is possible to achieve counting statistics limited precision by laser ablation ICP-DRC-MS.

2.6.2 Laser ablation ICP-DRC-MS analysis of Sr in coral skeletons

Isotope ratios are commonly used as biological proxies\(^{45}\) and when laser ablation is coupled to ICP-MS spatial measurements can be made to reconstruct historical records. For example, long-lived coral skeletons contain records of past ocean conditions in the area surrounding the coral growth.\(^{46}\) As corals grow, they extract calcium and trace elements from the surrounding seawater. The concentrations of these trace metals can be used for temperature records,\(^{47,51}\) industrial fluxes to the surface ocean,\(^{52,53}\) alkalinity and
salinity of the ocean, and pH. Measurements of a coral skeleton are difficult because the structure is not homogenous. There is compositional and structural heterogeneity and a carbonate matrix which behaves differently in the plasma than a silicate matrix, which is commonly used as a standard. In addition, a precision of better than 1% is required for most temperature reconstruction attempts and currently requires data smoothing functions. ICP-DRC-MS was investigated as a possible source of high precision measurements of a very heterogeneous sample could be achieved without data smoothing.

A *Porites lobata* skeleton was obtained from Dr. Andrea Grottoli (School of Earth Sciences, The Ohio State University, Columbus OH) and is shown in figure 2.10.

![Image of Porites lobata skeleton](image)

**Figure 2.10:** *Porites lobata* coral skeleton sample number AMB22 borrowed from Grottoli research group.

The pink stain line was stained 12 months before harvest for growth rate calibration, reported as 1.3 ± 0.3 cm year⁻¹ (3.5 μm day⁻¹). 20 μm ablation spatial...
resolution would provide time resolution of 5-6 days, which would be degraded by data smoothing. For instance, a 10 point moving average applied in the example above degrades time resolution to roughly 1.5 months. The surface heterogeneity in figure 2.10 may be responsible for the large differences in ablated material resulting in large signal fluctuations.

A single ablation scan line was used to measure the Sr and Ca signals resulting from laser ablation of corals. Laser ablation parameters were identical to those used to measure the NIST 612 SRM. $^{86}$Sr$^+$ and $^{43}$Ca$^+$ were measured in both vented and DRC mode. Repetitions of the ablation scan were alternated between vented and DRC (0.5 Ar equivalent mL min$^{-1}$ NH$_3$) modes to minimize signal fluctuations resulting from depth heterogeneity. Data was acquired with a 2 ms dwell time, 200 µs settling time, -100 V axial field electrode potential, and 100 µm spot size scanned at 20 µm s$^{-1}$. Figure 2.11 shows the recorded signals for $^{86}$Sr and $^{43}$Ca in the vented mode.
Figure 2.11: $^{43}\text{Ca}$ (red) and $^{86}\text{Sr}$ (blue) a) vented mode and b) 0.5 Ar equivalent mL min$^{-1}$ NH$_3$ signals from laser ablation of Porites lobata coral sample AMB22.

Figure 2.11 shows the very noisy signals measured by LA-ICP-MS of a coral skeleton sample. The laser began firing at approximately the 30 second mark and stopped at the 800 second mark for a total scan distance of 15.5 cm. It is unclear why the signals in figure 2.11b appear to fluctuate more than the signals in figure 2.11a, although depth heterogeneity might be a cause. The large signal fluctuations will be dampened by ratioing the Sr/Ca if measurements were taken faster than signal fluctuations. Figure 2.12 shows the ratio of both vented mode and DRC mode measurements.
Figure 2.12: Vented mode (red) and DRC mode (blue) Sr/Ca elemental ratios from laser ablation of *Porites lobata* coral sample AMB22. Vented and DRC mode measurements were alternated and made successively and offset by 0.5 each for clarity.

The vented mode Sr/Ca ratio is greater than the DRC mode Sr/Ca ratio due to higher transmission of Sr through the reaction cell than Ca.\(^{27}\) Ca count rates were approximately doubled while Sr count rates only increased by about 75% via collisional focusing.\(^{59}\) Elemental fractionation and differences in extent of collisional focusing may be corrected by external calibration using a known standard which has been shown to provide accurate results.\(^{27}\) Theoretical counting statistics limited precision assumes homogenous distribution in the sample, which is not the case in coral skeletons.\(^{50}\)
calculated precision while the laser was firing was improved from 7.62% RSD in the vented mode to 1.91% in the DRC mode. Both measured precision values were significantly higher than the theoretical counting statistics limited precisions (0.69% and 0.58% for vented and DRC modes, respectively). The precision needed to determine a 1°C change in sea surface temperature from Sr/Ca ratios in coral skeletons is about 1% RSD. Even when the reaction cell was pressurized with NH₃ and conditions were optimized for temporal homogenization of the ion beam, 1% precision could not be achieved over the distance of the coral scan. It was not possible to quantify whether the coral heterogeneity or signal fluctuations were responsible for the poor precision. By averaging the ratios resulting from two consecutive laser ablation scans, the vented and DRC mode precisions were improved to 4.87% and 1.75% respectively. Although precision was improved, it was not able to reach the counting statistics limit, possibly due to coral skeleton heterogeneity.

2.7 Conclusions

Collision gases He, Ne, Ar and the reaction gas NH₃ were studied as possible collision partners for temporal homogenization. The permanent dipole moment of NH₃ was found to be a significant factor in initiating collisions with ions, likely due to ion-dipole attraction. Ag ion packets broadened by approximately 2.5 ms with NH₃, allowing a dwell time of 1 ms to be used for precise isotope ratio methods. Counting statistics limits were reached at 1 ms dwell time in the vented mode, but were reached at a range of dwell times from 1 to 10 ms when the cell was pressurized with NH₃. The $^{107}\text{Ag}/^{109}\text{Ag}$
ratio precision was measured as low as 0.12% RSD with a “long” dwell time of 10 ms, limited only by counting statistics.

Laser ablation was used as a noisy sample introduction method to determine the extent that collisional dampening could improve measured precision. Sr/Ca ratios were measured from a homogenous silicate sample with ICP-q-MS, ICP-DRC-MS, ICP-SF-MS and ICP-OES. ICP-DRC-MS again provided counting statistics limited precision while ICP-q-MS and ICP-SF-MS were susceptible to flicker noise contributions. The continuous measurement ability of ICP-OES offered the best precision.

*Porties lobata* skeletons were used to provide a sample surface that varied in porosity and density. Measured precision of the Sr/Ca elemental ratio was improved from 4.87% to 1.75% RSD by pressurizing the reaction cell with NH₃. This improved precision corresponds to improved Sr paleothermometer performance.


3.1 Abstract

The ability of collision induced dissociation (CID) to reduce polyatomic overlaps in the ICP-DRC-MS was investigated. Scattering and collisional focusing effects on sensitivity were studied. Changes in detection limits and sensitivities for elemental ions interfered by polyatomic ions were assessed. The efficiency of CID was compared to ion-molecule reactions for the reduction of the ArN^+ overlap.

3.2 Introduction

Despite the high temperatures of inductively coupled plasmas, some molecular (polyatomic) ions survive and overlap elemental ions of interest. Polyatomic ions can form from plasma gases, matrix species, or from other trace metals in solution.¹ Some common spectral overlaps are shown in table 3.1; other sources have more complete listings of polyatomic overlaps.²⁻⁵
Table 3.1: Common spectral overlaps due to polyatomic ions.

<table>
<thead>
<tr>
<th>Elemental ion</th>
<th>m/z</th>
<th>Polyatomic ion</th>
<th>Elemental ion</th>
<th>m/z</th>
<th>Polyatomic ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg⁺</td>
<td>24</td>
<td>C₂⁺</td>
<td>Fe⁺</td>
<td>56</td>
<td>ArO⁺</td>
</tr>
<tr>
<td>Al⁺</td>
<td>27</td>
<td>HCN⁺</td>
<td>Ni⁺</td>
<td>60</td>
<td>⁴⁰CaO⁺</td>
</tr>
<tr>
<td>Si⁺</td>
<td>28</td>
<td>CO, N₂⁺</td>
<td>Cu⁺</td>
<td>63</td>
<td>OCCl⁺</td>
</tr>
<tr>
<td>Si⁺</td>
<td>30</td>
<td>NO⁺</td>
<td>Zn⁺, Ni⁺</td>
<td>64</td>
<td>SO₂⁺, S₂⁺, ArC₂⁺</td>
</tr>
<tr>
<td>P⁺</td>
<td>31</td>
<td>NOH⁺</td>
<td>Zn⁺</td>
<td>68</td>
<td>ArCO⁺, ArN₂⁺</td>
</tr>
<tr>
<td>S⁺</td>
<td>32</td>
<td>O₂⁺</td>
<td>Ga</td>
<td>71</td>
<td>MnO⁺</td>
</tr>
<tr>
<td>K⁺</td>
<td>39</td>
<td>³⁸ArH⁺</td>
<td>Ge</td>
<td>72</td>
<td>FeO⁺</td>
</tr>
<tr>
<td>Ca⁺</td>
<td>44</td>
<td>CO₂, N₂O⁺</td>
<td>As⁺</td>
<td>75</td>
<td>ArCl⁺</td>
</tr>
<tr>
<td>Se⁺</td>
<td>45</td>
<td>CO₂H⁺</td>
<td>Se⁺</td>
<td>74</td>
<td>²³Cl₂⁺</td>
</tr>
<tr>
<td>Ti⁺</td>
<td>47</td>
<td>PO⁺</td>
<td>Se⁺</td>
<td>76</td>
<td>³⁸Ar₂⁺</td>
</tr>
<tr>
<td>Ti⁺</td>
<td>48</td>
<td>SO₂⁺</td>
<td>Se⁺</td>
<td>80</td>
<td>⁴⁰Ar₂⁺</td>
</tr>
<tr>
<td>V⁺</td>
<td>51</td>
<td>ClO⁺</td>
<td>Rb⁺</td>
<td>87</td>
<td>GaO⁺</td>
</tr>
<tr>
<td>Cr⁺</td>
<td>52</td>
<td>ArC⁺</td>
<td>Sr⁺</td>
<td>88</td>
<td>GeO⁺</td>
</tr>
<tr>
<td>Fe⁺, Cr⁺</td>
<td>54</td>
<td>ArN⁺</td>
<td>Mo⁺</td>
<td>98</td>
<td>SeO⁺</td>
</tr>
<tr>
<td>Mn⁺</td>
<td>55</td>
<td>ArNH⁺, NaS⁺</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

While ion-molecule reactions that proceed under thermal conditions are most commonly used in reaction cells,⁶ collision induced dissociation (CID) may also be used to dissociate weakly bound polyatomic ions. Polyatomic ions collide with a neutral gas during which ion kinetic energy is converted to vibrational energy. If the vibrational energy is greater than the polyatomic bond dissociation energy, the bond ruptures. For example, a collision between Ar gas in the DRC and ⁴⁰Ar⁺ overlap might rupture the Ar-Ar⁺ bond. ⁸⁰Se⁺ can then be measured with reduced background at m/z 80. CID offers the potential to reduce all weakly bound (≤3 eV) polyatomic molecular overlaps, regardless of chemical reactivity and with no a priori knowledge of the sample or matrix.⁷
The first use of an ICP-MS with a reaction cell utilized CID with Xe to attenuate polyatomic overlaps, but this approach is not commonly used. Recently there has been a report that CID may be used with Ar as a collision gas in an ICP-DRC-MS. However, the authors focused only on improving $^{75}$As$^+$ detection limits and did not report on other analytes or overlaps. They also did not describe changes in sensitivity due to scattering or focusing. No study to date has been published that has examined CID’s viability for a variety of polyatomic overlaps using ICP-DRC-MS. This section aims to discover conditions that may overcome common polyatomic overlaps in ICP-DRC-MS via CID. CID will be studied as an alternative to ion molecule reactions by:

1) Determining changes in sensitivity due to scattering and/or focusing from Ar and Xe
2) Determining which polyatomic ions undergo CID with Ar
3) Comparing CID with ion-molecule reactions for a common overlap.

3.3 Experimental details

A PerkinElmer Sciex Elan 6100 DRC$^+$ ICP-DRC-MS was used for all experiments. A peristaltic pump (Gilson Minipuls 3) delivered solution into a quartz, concentric nebulizer (TQ-30-A3, Meinhard Glass Products, Golden CO, USA) at a solution uptake rate of 1 mL min$^{-1}$. A quartz, baffled cyclonic spray chamber (Quartz Cyclonic Spray Chamber for ELAN DRC (WE025221), PerkinElmer Sciex) at ambient temperature was used with a 2.0 mm id quartz injector (WE023948, PerkinElmer Sciex). Solutions were made by serial dilution from 1,000 $\mu$g mL$^{-1}$ standard solutions (CPI International, Santa Rosa CA, USA) in deionized water (18.2 MW cm, Millipore Milli-
RO-10 and Milli-Q). HNO₃, H₂SO₄, HCl, H₃PO₄ and CH₃COOH were double distilled (GFS Chemicals, Columbus OH, USA). Collision/reaction gases introduced through Channel A via a getter to remove water and oxygen impurities included ammonia (99.999%, Scott Specialty Gases), xenon (99.999%, Praxair), and argon (99.998%, Praxair). Flows were maintained by mass flow controllers (MKS Instruments, USA) calibrated for Ar flow, with conversion factors listed in table 3.3.
Table 3.2: ICP-MS experimental parameters.

| Mass Spectrometer Parameters |  
|-------------------------------|---|
| RF power/W                   | 1250|
| Lens voltage                 | Optimized daily for m/z 115|
| Autolens                     | Off|
| Pulse stage voltage          | -2100 V|
| Analog stage voltage         | 1150 V|
| Auxiliary gas flow           | 1.2 L min⁻¹|
| Plasma gas flow              | 15 L min⁻¹|
| Nebulizer flow (optimized daily) | ~ 0.9 L min⁻¹|

**DRC Parameters**

| Entrance aperture diameter   | 2 mm|
| Exit aperture diameter       | 2.2 mm|
| Axial field voltage          | 310 V|
| RPa                          | 0.00|
| RPq                          | 0.50|
| DRC mode quadrupole rod offset | -10 V|
| DRC mode cell rod offset     | -1 V|
| RF voltage (peak to peak)    | ±200 V|
| DRC mode cell path voltage   | -19 V|

**Analyzer Parameters**

| Correction equations     | No|
| Mass resolution          | ~ 0.7 u|

**Isotope Measurement**

| Dwell time               | 100 ms|
| Sweeps                   | 2|
| Readings                 | 1|
| Replicates               | 5|
| Points per peak          | 1|
| Settling time            | 200 ms|

Table 3.3: Actual flow (mL min⁻¹) reaction gas per Ar equivalent mL min⁻¹ gas flow. Actual gas flow rate calculated by multiplying conversion factor by reported gas flow rate.

<table>
<thead>
<tr>
<th>Reaction Gas</th>
<th>Gas flow rate conversion factor¹¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>1.00</td>
</tr>
<tr>
<td>Xe</td>
<td>0.95</td>
</tr>
</tbody>
</table>
A convenient method to choose the optimum gas flow rate uses the estimated limits of detection. Estimated LOD’s assume that the standard deviation of the matrix-matched blank is due to Poisson counting statistics (shot noise).

\[
\text{Est LOD (ppb)} = 3 \times \frac{\sqrt{\text{Blank (c s}^{-1}) \times \text{time (s)}}}{\text{sensitivity (c s}^{-1} \text{ ng}^{-1} \text{ L} \times \text{time(s)}}}
\]

(3.1)

### 3.4 Changes in sensitivity due to collisional focusing and scattering

A pressurized reaction/collision cell placed between the ion source (ICP) and the mass analyzer quadrupole can change the ion transmission efficiency from the source to the detector. Sensitivity may be increased if ions are focused to the center of the cell, or reduced if ions are scattered.

Collisional focusing occurs when ion trajectories collapse towards the axis of the DRC after collisions with gas atoms or molecules. Each ion-neutral collision is accompanied by a loss in ion axial kinetic energy. The loss of axial kinetic energy dampens the ion trajectories and confines ions closer to the center line of the quadrupole. A higher percentage of the ions are then within the acceptance area of the quadrupole and ion transmission efficiency increases, resulting in higher sensitivity.

If the ion beam encounters a high density of heavy gas atoms or molecules in the reaction cell, the ions’ trajectories will become unstable after collisions with the gas and collide with the quadrupole rods or walls of the reaction cell, decreasing sensitivity. Significant improvement in detection limits via CID will only occur if the overlap ion
signal is reduced more than the analyte sensitivity. Changes in sensitivity were measured for ions with a wide range of masses (from $^7\text{Li}^+$ to $^{238}\text{U}^+$) with medium (Ar) and heavy (Xe) atomic collision gases.

### 3.4.1 Changes in sensitivity due to Ar

Ar has been suggested as a viable candidate for CID of weakly bound polyatomic overlaps in the DRC, but it was unknown which (if any) elements would be focused or scattered by Ar at different Ar flow rates. Sensitivity was measured as both a function of gas flow rate and ion mass.
Figure 3.1: Ratio of signals from 50 ppb analyte with a) 0.1, b) 0.2, c) 0.4, and d) 0.6 mL min\(^{-1}\) Ar flow rate into the reaction cell normalized to the vented mode (no collision gas) signal as a function of analyte mass with RPq = 0.50. The vertical line at m/z 40 is the mass of Ar.

Analytes with mass greater than 50 gained sensitivity when the DRC was pressurized with Ar, while ions less than m/z 40 had less sensitivity, even at the lowest flow rate of 0.1 mL min\(^{-1}\). Sensitivity increase is due to collisional focusing and a
sensitivity decrease is due to ion scattering losses. The majority of polyatomic ion overlaps occur at m/z 50 or greater (table 3.1), and Ar was shown to increase sensitivity for these ions at flow rates less than 0.5 mL min\(^{-1}\). Ions greater than the weight of the collision gas (40 amu) were focused at low and moderate flow rates (<0.5 mL min\(^{-1}\)), and ions less than the collision gas weight were scattered. Ar is therefore a possible candidate as a CID collision gas partner, especially for polyatomic ions heavier than 50 amu.

### 3.4.2 Changes in sensitivity due to Xe

Xe was used in the first ICP-reaction cell-MS study\(^8\) to attenuate Ar\(_2^+\), but the As\(^+\) analyte signal deceased almost as much so little improvement in detection limit was gained. Detection limits will only be significantly improved if the polyatomic ion signal is reduced (due to CID) much more than the analyte ion signal (due to scattering).
Figure 3.2:  Ratio of signals due to 50 ppb analyte with a) 0.04, b) 0.10, c) 0.20 and d) 0.30 Ar equivalent mL min\(^{-1}\) Xe flow rate into the reaction cell to the vented mode (no collision gas) signal as a function of analyte mass with RPq = 0.50. The vertical line at m/z 131 is the mass of Xe.

The signals for ions with a mass lower than 100 amu were decreased due to scattering when the reaction cell was pressurized with Xe at a flow rate of 0.04 mL min\(^{-1}\) or more. At flow rates greater than 0.30 Ar equivalent mL min\(^{-1}\) signals for almost all
elements are reduced (figure 3.2) The analyte ion signal loss was dependent on ion mass and was as large as a factor of 400x (figure 3.3). Collisional focusing was only observed for some analytes with mass greater than 150 amu (figure 3.2).

**Figure 3.3:** Signals due to $^7\text{Li}^+$ ($\circ$), $^{51}\text{V}^+$ ($\bullet$), $^{89}\text{Y}^+$ ($\square$) and $^{138}\text{Ba}^+$ ($\blacktriangle$) normalized to the vented mode signal as a function of Xe flow into the DRC at RPq 0.50. Linear regression lines are not shown.

The relationship between the rate signal loss per mL/min Xe (slope of lines fit to data plotted as in figure 3.3) as a function of ion mass is shown in figure 3.4.
Figure 3.4: Measured signal loss rates due to scattering from Xe as a function of analyte mass. Signal loss rate calculated by best fit of signal as a function of Xe flow rate. Linear correlation coefficient $R^2 = 0.96$. Only ions with m/z less than Xe are shown.

$^7\text{Li}^+$ sensitivity was reduced by 9 orders of magnitude per mL min$^{-1}$ Xe. Signals due to analyte ions with masses close to that of Xe (131 amu) were only scattered about 1 order of magnitude per mL min$^{-1}$ Xe flow rate. The large reduction in sensitivity from Xe may negate any reduction in molecular ion signals, and Xe is most likely not the best collision gas choice.
3.5 Collision Induced Dissociation in ICP-DRC-MS

One must consider focusing or scattering effects on analyte sensitivity (section 3.4), ion and gas masses, polyatomic bond strength and the flow rate required to cause suitable signal reduction when considering a collision gas to be used for CID. The maximum internal energy transferred to the molecular ion due to a collision with a neutral gas is given by:\(^\text{16}\)

\[
E_{\text{int, max}} = E_{\text{ion}} \times \left[ \frac{m_{\text{gas}}}{m_{\text{gas}} + m_{\text{ion}}} \right]
\] (3.2)

where \(E_{\text{int, max}}\) is the maximum energy converted to internal vibrational energy; \(E_{\text{ion}}\) is the ion’s incoming kinetic energy; and \(m_{\text{gas}}\) and \(m_{\text{ion}}\) are the masses of the gas atom/molecule and ion respectively. Ion kinetic energy varies from 6 to 10 eV.\(^\text{17-19}\)

According to equation 3.2, the maximum energy that can be converted into vibrational energy increases as collision gas mass increases. The collision gas should therefore be as large as possible, but large scattering losses could limit the effectiveness of heavy collision gases (such as Xe) in the DRC. A compromise must be found between reduction of molecular ion signals due to CID and loss of analyte ion signal due to scattering.

3.5.1 Prediction of CID for specific ions

Equation 3.2 may be used in combination with the bond dissociation energies in to predict whether or not CID occurs upon a single collision. Table 3.4 contains many bond dissociation energies from polyatomic ions that are frequently measured by ICP-
MS. Table 3.4 includes only those polyatomic ions with published bond dissociation energies.

Table 3.4: Bond dissociation energies of some common polyatomic overlaps in ICP-MS.

<table>
<thead>
<tr>
<th>Polyatomic overlap</th>
<th>Mass</th>
<th>( D_0 ) (eV)</th>
<th>Elemental analyte</th>
<th>Polyatomic overlap</th>
<th>Mass</th>
<th>( D_0 ) (eV)</th>
<th>Elemental analyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH(^+)</td>
<td>17</td>
<td>5.09(^{20})</td>
<td></td>
<td>NaAr(^+)</td>
<td>63</td>
<td>0.13(^{21})</td>
<td>Ni(^+), Cu(^+)</td>
</tr>
<tr>
<td>H(_2)O(^+)</td>
<td>18</td>
<td>5.43(^{1,22})</td>
<td></td>
<td>MgAr(^+)</td>
<td>64</td>
<td>0.14(^{21})</td>
<td>Cu(^+), Zn(^+)</td>
</tr>
<tr>
<td>H(_3)O(^+)</td>
<td>19</td>
<td>6.508(^{22})</td>
<td></td>
<td>MnO(^+)</td>
<td>71</td>
<td>3.7(^{23})</td>
<td>Ga(^+)</td>
</tr>
<tr>
<td>NO(^+)</td>
<td>30</td>
<td>10.85(^{20}), 11.76(^{1,22})</td>
<td>Si(^+)</td>
<td>ArCl(^+)</td>
<td>75</td>
<td>1.75(^{22}), 2.24</td>
<td>As(^+)</td>
</tr>
<tr>
<td>O(_2)(^+)</td>
<td>32</td>
<td>6.663(^{1,20,22})</td>
<td>S(^+)</td>
<td>Ar(_2^+)</td>
<td>80</td>
<td>1.25(^{25}), 1.21(^{22})</td>
<td>Se(^+), Kr(^+)</td>
</tr>
<tr>
<td>ArH(^+)</td>
<td>41</td>
<td>4.04(^{20}), 6.16(^{22})</td>
<td>K(^+)</td>
<td>FeAr(^+)</td>
<td>96</td>
<td>0.17(^{21})</td>
<td>Zr(^+), Mo(^+)</td>
</tr>
<tr>
<td>LiAr(^+)</td>
<td>47</td>
<td>0.28(^{21})</td>
<td>Ti(^+)</td>
<td>NiAr(^+)</td>
<td>98</td>
<td>0.55(^{21})</td>
<td>Mo(^+), Ru(^+)</td>
</tr>
<tr>
<td>ArB(^+)</td>
<td>51</td>
<td>0.269(^{25})</td>
<td>V(^+)</td>
<td>CoAr(^+)</td>
<td>99</td>
<td>0.4(^{21})</td>
<td>Mo(^+), Ru(^+)</td>
</tr>
<tr>
<td>ClO(^+)</td>
<td>51</td>
<td>4.65(^{21})</td>
<td>V(^+)</td>
<td>CuAr(^+)</td>
<td>103</td>
<td>0.4(^{21})</td>
<td>Rh(^+)</td>
</tr>
<tr>
<td>ArC(^+)</td>
<td>52</td>
<td>0.922(^{26}, 0.75^{20})</td>
<td>Cr(^+)</td>
<td>SrO(^+)</td>
<td>104</td>
<td>4.88(^{20})</td>
<td>Ru(^+), Pd(^+)</td>
</tr>
<tr>
<td>ArN(^+)</td>
<td>54</td>
<td>2.13(^{26}, 1.87^{20}, 1.866^{1,22})</td>
<td>Cr(^+), Fe(^+)</td>
<td>ZrO(^+)</td>
<td>105</td>
<td>7.85(^{20})</td>
<td>Pd(^+)</td>
</tr>
<tr>
<td>ArO(^+)</td>
<td>56</td>
<td>0.62(^{20}, 0.56^{25}, 0.312^{1,22})</td>
<td>Fe(^+)</td>
<td>LaO(^+)</td>
<td>155</td>
<td>8.23(^{20})</td>
<td>Gd(^+)</td>
</tr>
</tbody>
</table>

Figure 3.5 graphically displays the results of combining the bond dissociation energies in Table 3.4 and Equation 3.2 to show whether or not CID is predicted to occur using Ar as the collision gas assuming 8 eV KE.\(^{11}\) If a point with coordinates
(polyatomic mass, polyatomic $D_0$) lies above the line, CID is unlikely to occur because the bond strength is too large. If the point lies below the line, the bond strength is less than the maximum internal energy conversion, and bond rupture is possible.

![Graph showing maximum internal energy conversion for ions listed in table 3.4 sorted according to possibility for CID to occur (●) or not (○) upon a single collision with Ar in ICP-DRC-MS (8 eV ion kinetic energy).](image)

**Figure 3.5:** Maximum internal energy conversion for ions listed in table 3.4 sorted according to possibility for CID to occur (●) or not (○) upon a single collision with Ar in ICP-DRC-MS (8 eV ion kinetic energy).

Of the 24 polyatomic ions with known bond dissociation energies that are listed in table 3.4, 15 are predicted to dissociate upon collision with Ar (results in table 3.5). 6 ions have more than one published bond dissociation energy, but identical CID predictions were reached using equation 3.2, regardless of which bond energy was used.
Table 3.5: Predicted results from the use of Ar collision gas for CID of polyatomic overlaps in an ICP-DRC-MS.

<table>
<thead>
<tr>
<th>Polyatomic</th>
<th>Mass</th>
<th>D₀ (eV)</th>
<th>CID?</th>
<th>Polyatomic</th>
<th>Mass</th>
<th>D₀ (eV)</th>
<th>CID?</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH⁺</td>
<td>17</td>
<td>5.09²⁰</td>
<td>Yes</td>
<td>NaAr⁺</td>
<td>63</td>
<td>0.13²¹</td>
<td>Yes</td>
</tr>
<tr>
<td>H₂O⁺</td>
<td>18</td>
<td>5.43¹,²²</td>
<td>Yes</td>
<td>MgAr⁺</td>
<td>64</td>
<td>0.14²¹</td>
<td>Yes</td>
</tr>
<tr>
<td>H₃O⁺</td>
<td>19</td>
<td>6.508²,²²</td>
<td>No</td>
<td>MnO⁺</td>
<td>71</td>
<td>3.7²³</td>
<td>No</td>
</tr>
<tr>
<td>NO⁺</td>
<td>30</td>
<td>10.85²⁰, 11.76¹,²²</td>
<td>No</td>
<td>ArCl⁺</td>
<td>75</td>
<td>1.75-²⁴</td>
<td>Yes</td>
</tr>
<tr>
<td>O₂⁺</td>
<td>32</td>
<td>6.663¹,²⁰,²²</td>
<td>No</td>
<td>Ar₂⁺</td>
<td>80</td>
<td>1.25²⁵, 1.2²¹,²²</td>
<td>Yes</td>
</tr>
<tr>
<td>ArH⁺</td>
<td>41</td>
<td>4.04²⁰, 6.16¹,²²</td>
<td>No</td>
<td>FeAr⁺</td>
<td>96</td>
<td>0.17²¹</td>
<td>Yes</td>
</tr>
<tr>
<td>LiAr⁺</td>
<td>47</td>
<td>0.28²¹</td>
<td>Yes</td>
<td>NiAr⁺</td>
<td>98</td>
<td>0.55²¹</td>
<td>Yes</td>
</tr>
<tr>
<td>ArB⁺</td>
<td>51</td>
<td>0.269²⁶</td>
<td>Yes</td>
<td>CoAr⁺</td>
<td>99</td>
<td>0.4²¹</td>
<td>Yes</td>
</tr>
<tr>
<td>ClO⁺</td>
<td>51</td>
<td>4.65¹</td>
<td>No</td>
<td>CuAr⁺</td>
<td>103</td>
<td>0.4²¹</td>
<td>Yes</td>
</tr>
<tr>
<td>ArC⁺</td>
<td>52</td>
<td>0.922²⁶, 0.75²⁰</td>
<td>Yes</td>
<td>SrO⁺</td>
<td>104</td>
<td>4.88²⁰</td>
<td>No</td>
</tr>
<tr>
<td>ArN⁺</td>
<td>54</td>
<td>2.13²⁶, 1.87²⁰, 1.866¹,²²</td>
<td>Yes</td>
<td>ZrO⁺</td>
<td>105</td>
<td>7.85²⁰</td>
<td>No</td>
</tr>
<tr>
<td>ArO⁺</td>
<td>56</td>
<td>0.62²⁰, 0.56²⁵, 0.312¹,²²</td>
<td>Yes</td>
<td>LaO⁺</td>
<td>155</td>
<td>8.23²⁰</td>
<td>No</td>
</tr>
</tbody>
</table>

If Kr (84 amu) was used as a collision gas instead of Ar (40 amu), only 3 additional overlaps would dissociate (ArH⁺, ClO⁺ and MnO⁺). If Xe (131 amu) were used as a collision gas instead of Kr, only 1 additional overlap (H₃O⁺) would undergo CID, and the scattering losses would be expected to be large. There is only a moderate improvement in CID applicability by using collision gases heavier than Ar.

3.5.2 Attenuation of ArO⁺, ArC⁺, Ar₂⁺, ArN⁺, ClO⁺ and ArCl⁺ by CID

Some of the most common polyatomic overlaps arise from Ar⁺ based overlaps like ArO⁺, ArC⁺, et cetera. For example, the signal due to ArO⁺ exceeds 600,000 c s⁻¹ from a water sample (background equivalent concentration (BEC) approximately 20 ppb). A 2% CH₃COOH matrix produces ArC⁺ signal of 300,000 c s⁻¹ (BEC ~ 10 ppb) while a 2% HNO₃ matrix causes a signal on the order of 25,000 c s⁻¹ at m/z 54 from ArN⁺
(BEC ~ 1 ppb). Signals resulting from ClO$^+$ and ArCl$^+$ and a 2% HCl matrix are on the order of 250,000 (BEC ~ 10 ppb) and 25,000 c s$^{-1}$ (BEC ~ 3 ppb).

Equation 3.2 calculates the maximum possible amount of energy that may be transferred during a single collision, but ions may undergo more than one collision in the DRC$^{11}$ and it is unknown whether or not the assumption that the maximum amount of kinetic energy is transferred into vibrational energy is valid. Because the kinetic energy of an ion decreases substantially (>25% loss) after a collision,$^{27}$ it is unlikely that CID will occur after the first collision. It is also unknown if bond dissociation energy is related to the rate at which overlap signals are reduced. This subsection explores the validity of using equation 3.2 for predicting CID in ICP-DRC-MS.

5 polyatomic ions (ArO$^+$, ArC$^+$, Ar$_2$+$, ArN$^+$, ArCl$^+$) that are expected to dissociate and 1 (ClO$^+$) that is not were used to test the validity of equation 3.2 in ICP-DRC-MS. These ions are found in common acid matrices and are problematic for trace metal determinations. Figure 3.6 shows the signal of each polyatomic interference normalized to the vented (no gas) mode signal as a function of Ar flow into the reaction cell.
Figure 3.6: a) Signals normalized to vented (no gas) signals of ArO$^+$ (□) at m/z 56, ArC$^+$ (▲) at m/z 52, Ar$_2^+$ (○) at m/z 80, ArCl$^+$ (◇) at m/z 75, ArN$^+$ (▼) at m/z 54 and ClO$^+$ (●) at m/z 51 and b) amount of signal reduction plotted at 0.6 mL min$^{-1}$ Ar plotted as function of bond dissociation energy.

Figure 3.6 shows bond dissociation energy to be inversely related to the extent of signal reduction. ArO$^+$ and ArC$^+$ signals were reduced by almost 4 orders of magnitude. The Ar$_2^+$ signal decreased by about 2.5 orders of magnitude, and ArCl$^+$ and ArN$^+$ were reduced by 2 orders of magnitude. The signal due to ClO$^+$ increased at 0.1 mL min$^{-1}$ Ar flow into the cell due to collisional focusing,$^{12, 28}$ and the slight decrease in signal is likely due to scattering at high Ar flow rates.

The data also show that CID efficiency is dependent on $D_0$ (figure 3.6b), likely because weakly bound ions dissociate from collisions that do not transfer the maximum possible amount of energy. For example, a collision that passes only 50% of the maximum possible energy (e.g. 50%*3.4 eV = 1.7 eV, $m_{ion} = 54$) can dissociate ArO$^+$ ($D_0 = 0.26$ eV), but not ArN$^+$ (2.13 eV). ArN$^+$ will only be dissociated by collisions that pass...
nearly 100% of the possible energy into the vibration state. For other weakly bound ions listed in table 3.4 with bond dissociation energies less than 0.5 eV, CID can be reliably predicted to occur using Ar.

Section 3.4 showed that Ar did not cause significant losses in sensitivity for ions with masses larger than 50 amu, and section 3.5 showed that Ar was also able to dissociate the majority of common polyatomic overlaps. Ar is therefore the best collision gas for improving detection limits of analytes that suffer from polyatomic overlaps with mass greater than 50 amu and bond dissociation energies less than about 2 eV.

3.6 **Efficiency comparison of ion-molecule reactions and CID**

Ion-molecule reactions are considered much more efficient than CID, but use highly reactive gases and require knowledge of how to prevent unwanted secondary reactions. CID requires only that the spectral overlap be a weakly bound polyatomic ion regardless of sample matrix or reaction chemistry. Because CID is less efficient than ion-molecule chemical resolution, it is also susceptible to unknown changes in polyatomic signal magnitude (e.g. changes in sample matrix that form overlaps). For example, the signal due to an overlap ion sometimes depends on the amount of acid in solution. ArN$^+$ signal intensity is dependent on HNO$_3$ concentration in the sample matrix.
Figure 3.7: Relationship between measured ArN$^+$ signal at m/z 54 (●) as a function of HNO$_3$ concentration in the vented mode with RP$q = 0.25$.

ArN$^+$ formation increases from about 50,000 c s$^{-1}$ from a H$_2$O solution to about 160,000 c s$^{-1}$ from a 10% v/v HNO$_3$ solution. ArN$^+$ formation does not increase linearly due to the acids’ effect on the aerosol generation, analyte transport, plasma temperature and sample introduction efficiency.$^{31}$ Reducing the ArN$^+$ signal by 4 orders of magnitude (as would be appropriate for a 2% HNO$_3$ solution) would be insufficient for a 10% HNO$_3$ solution. An ideal reaction/collision gas will efficiently remove polyatomic ion from the measured signal and provide contamination limited detection limits, regardless of the vented mode (no gas) signal. If the removal of polyatomic overlap signal is not rapid,
then unknown changes in the sample matrix will have deleterious effects on the analysis accuracy.

According to equation 3.2 and table 3.5, ArN$^+$ bond rupture occurs upon a single collision with a gas heavier than 19 amu assuming the ion kinetic energy is 8 eV.$^{11}$ Ar will be able to dissociate ArN$^+$ upon a single collision, while NH$_3$ (17 amu) will not. ArN$^+$ signal attenuation when the DRC is pressurized with NH$_3$ can then be attributed to a reaction rather than CID. Although the ionization potential of ArN is unknown, many polyatomic overlaps have ionization potentials larger than 10 eV and the reaction between NH$_3$ and ArN$^+$ is guessed to proceed via charge transfer. Because NH$_3$ is commonly used to provide chemical resolution of Fe$^+$/ArO$^+$,$^{10}$ it is also an ideal candidate to use for Fe$^+$/ArN$^+$.

### 3.6.1 Attenuation of ArN$^+$ by collisions with Ar

Ar was investigated as a possible collision gas for CID of ArN$^+$ to improve $^{54}$Fe detection limits. Figures 3.8 a – d show signals at m/z 54 from 0, 2, 4, and 10% HNO$_3$ solutions as a function of Ar flow rate.
Figure 3.8: Signals at m/z 54 from blank (○, left y-axis), 1 ppb Fe (●, left y-axis) and calculated background equivalent concentration (solid line, right y-axis) from solutions containing a) 0, b) 2, c) 4 and d) 10% HNO$_3$ as a function of Ar flow rate.

Signals from each solution were reduced to blank contamination limited levels at 0.6 mL min$^{-1}$ Ar flow rate. At this point the signal is dominated by contributions from Fe$^+$ instead of ArN$^+$. Scattering accounts for less than one order of magnitude loss in
sensitivity. At flow rates greater than 0.6 mL min\(^{-1}\), the flow independent BEC’s indicate that the blank signals are due to Fe contamination (also confirmed by isotopic pattern matching). This indicates that Ar successfully ruptures the ArN\(^+\) bond via CID and that accurate Fe quantification can be performed regardless of HNO\(_3\) concentration.

Estimated detection limits for the 2, 5 and 10\% HNO\(_3\) solutions were improved from \(10^2\)-\(10^3\) ng L\(^{-1}\) to \(10^1\) ng L\(^{-1}\). If the blank solution could be made with less Fe contamination, then the estimated detection limits could be improved further.

3.6.2 Attenuation of ArN\(^+\) by reactions with NH\(_3\)

NH\(_3\) is used as the neutral species for many charge transfer reactions because its first ionization energy (10.07 eV) is higher than that of most of the periodic table but lower than that of many polyatomic ions of interest.\(^6\) Figures 3.9 a – d show the effect of NH\(_3\) on signals at m/z 54 from 0, 2, 4, and 10\% HNO\(_3\) solutions.
Figure 3.9: Signals at m/z 54 from blank (○, left y-axis), 1 ppb Fe (●, left y-axis) and calculated background equivalent concentration (solid line, right y-axis) from solutions containing a) 0, b) 2, c) 4 and d) 10% HNO₃ as a function of Ar flow rate.

The signal due to ArN⁺ decreases by about three orders of magnitude according to pseudo-first order reaction kinetics as the NH₃ flow rate is increased to about 0.3 Ar equivalent mL min⁻¹. At flow rates higher than 0.3 mL min⁻¹, the signal magnitude does
not significantly change indicating that the source of signals at these flow rates is blank contamination. The differences in blank signal magnitude between the different matrices can be attributed to Fe contamination from the double distilled HNO$_3$. Figure 3.10 shows the calculated background equivalent concentration of Fe as a function of HNO$_3$ concentration at 0.5 Ar equivalent mL min$^{-1}$ NH$_3$ flow into the reaction cell.

![Graph](image)

**Figure 3.10:** Calculated BEC concentrations as a function of HNO$_3$ concentration measured at 0.5 Ar equivalent mL min$^{-1}$ NH$_3$.

NH$_3$ improved detection limit of $^{54}$Fe$^+$ by about two orders of magnitude. The detection limit for the 2% HNO$_3$ solution was improved from 300 to 9 ng L$^{-1}$ and the BEC was improved from 65,000 to 75 ng L$^{-1}$. Each matrix displayed similarly improved BEC’s. The improvements in BEC and detection limits was achieved at lower NH$_3$ flow
rates in comparison to Ar, and so it is concluded that NH₃ is more efficient at reducing ArN⁺ than Ar. Table 3.6 summarizes the comparison of Ar and NH₃.

### Table 3.6: Comparison of Ar collision gas and NH₃ reaction gas for reduction of ArN⁺ in ICP-DRC-MS.

<table>
<thead>
<tr>
<th>ArN⁺ reduction mechanism</th>
<th>Ar</th>
<th>NH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Most efficient method?</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Requires secondary chemistry considerations?</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Optimized flow rate (Ar equivalent mL min⁻¹)</td>
<td>0.7</td>
<td>0.5</td>
</tr>
<tr>
<td>⁵⁶Fe⁺ BEC at optimized flow rate (5% HNO₃, ng L⁻¹)</td>
<td>144</td>
<td>140</td>
</tr>
<tr>
<td>⁵⁶Fe⁺ Sensitivity at optimized flow rate (5% HNO₃, cps/ppb)</td>
<td>515</td>
<td>1,611</td>
</tr>
</tbody>
</table>

In the case of ArN⁺/Fe⁺, NH₃ was the best option for reducing the overlap signal, but if a complex and unknown matrix were present, Ar was a suitable collision gas. It should also be noted that the bond dissociation energy of ArO⁺ (overlapping ⁵⁶Fe) is very weak and is efficiently dissociated by Ar (figure 3.6). Using Ar as a collision gas would provide access to 2 Fe isotopes.

### 3.7 Conclusions

The ability of CID to reduce polyatomic signals in ICP-MS has been investigated using Xe and Ar as possible collision gas partners. Xe was determined to cause significant losses in sensitivity due to ion beam scattering. Ar was found to offer the
most potential to attenuate polyatomic ion signals while maintaining sensitivity. Ions with a mass less than that of the collision gas were shown to scatter, while ions with mass greater than the collision gas were shown to focus in the DRC. Ions that are focused in the DRC displayed increased sensitivities at low to moderate collision gas flow rates.

A comparison of the efficiencies of CID and ion-molecule reactions to reduce ArN$^+$ was performed. Ar and NH$_3$ were used and both offered contamination limited detection limits and improvements in BEC. NH$_3$ was shown to reduce the ArN$^+$ signal more rapidly than Ar, but Ar might be a more suitable collision gas for ArN$^+$ signal attenuation from a complex matrix that might contain other ions that are reactive with NH$_3$. CID using Ar collision gas offers a generic method for weakly bound polyatomic signal reduction.


4 Chemical resolution of selenium isotopes using ICP-DRC-MS

4.1 Abstract

The reaction gases CH$_3$F, CH$_4$, CD$_4$, C$_2$H$_6$, CO, H$_2$, N$_2$, N$_2$O, NH$_3$, O$_2$, SF$_6$ and Xe were compared to determine which could best reduce the Ar$_2^+$, Ar$_2$H$^+$, Ar$_2$H$_2^+$, SeH$^+$, BrH$^+$ and ArCl$^+$ overlaps on Se$^+$ isotopes. The collision gases He, Ne and Ar were also investigated to determine the effectiveness of collision induced dissociation (CID) to improve Se$^+$/molecular ion signal ratios. The results of these experiments give a method for analyzing trace amounts of any of the six selenium isotopes.

4.2 Introduction

Accurate quantification of selenium at or below ppb concentrations is necessary for Se speciation studies.$^1$ There exists a narrow window between human dietary deficiency ($<$ 30 mg/day) and toxicity ($>$ 900 mg/day) for selenium.$^2,^3$ It has been proposed that selenium serves as a chemo preventative agent and heavy metal antagonist.$^4$ An inverse nonlinear association between selenium concentration and cancer mortality has been demonstrated.$^5$ Selenium is also a central component of thyroid hormone synthesis, activation and metabolism$^6$ and approximately 25 proteins contain the
amino acid selenocystein. Enriched stable isotope studies are necessary to quantitatively determine the fate of trace Se in biological systems.

Inductively coupled plasma mass spectrometry (ICP-MS) measurement of sub-ppb concentrations of Se is complicated by the presence of spectral interferences less than 1 amu from each of the Se isotopes (table 4.1). For example, background equivalent concentrations (BEC) of $10^4$ ppb at m/z 80 are due to the presence of $^{40}\text{Ar}_2^+$. While the BECs are in the low ppb range at m/z 77, 78 and 82, ArCl$^+$ and BrH$^+$ overlaps increase the BECs when samples contain high concentrations of Cl or Br. For example, the BEC of $^{77}\text{Se}^+$ is increased from 40 ppt in H$_2$O to 5,000 ppt in a 2% hydrochloric acid matrix. The presence of Cl$_2^+$ at m/z 74 increases the BEC from 4 ppb to 120 ppb.

Table 4.1: Selenium isotopes, abundances, and major spectral interferences.

<table>
<thead>
<tr>
<th>Se analytes</th>
<th>Isotopic Abundances</th>
<th>Major plasma ions</th>
<th>Plasma Ion BEC* (ppb)</th>
<th>Selenium hydride ions</th>
<th>Matrix ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isotope</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{74}\text{Se}$</td>
<td>0.89 %</td>
<td>$^{36}\text{Ar}$, $^{38}\text{Ar}$</td>
<td>50</td>
<td>$^{76}\text{SeH}^+$</td>
<td>$^{37}\text{Cl}_2^+$</td>
</tr>
<tr>
<td>$^{76}\text{Se}$</td>
<td>9.37 %</td>
<td>$^{36}\text{Ar}$, $^{40}\text{Ar}$</td>
<td>170</td>
<td>$^{77}\text{SeH}^+$</td>
<td>$^{40}\text{Ar}^{37}\text{Cl}^+$</td>
</tr>
<tr>
<td>$^{77}\text{Se}$</td>
<td>7.63 %</td>
<td>$^{36}\text{Ar}$, $^{40}\text{Ar}$</td>
<td>8</td>
<td>76$^{78}\text{SeH}^+$</td>
<td>$^{40}\text{Ar}^{37}\text{Cl}^+$</td>
</tr>
<tr>
<td>$^{78}\text{Se}$</td>
<td>23.77 %</td>
<td>$^{38}\text{Ar}$, $^{40}\text{Ar}$</td>
<td>11</td>
<td>77$^{77}\text{SeH}^+$</td>
<td>$^{79}\text{BrH}^+$</td>
</tr>
<tr>
<td>$^{80}\text{Se}$</td>
<td>49.61 %</td>
<td>$^{40}\text{Ar}_2^+$</td>
<td>4,900</td>
<td></td>
<td>$^{81}\text{BrH}^+$, $^{40}\text{Ar}^{42}\text{Ca}^+$</td>
</tr>
<tr>
<td>$^{82}\text{Se}$</td>
<td>8.73 %</td>
<td>$^{40}\text{Ar}_2\text{H}_2^+$</td>
<td>2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Background equivalent concentrations (BEC) estimated by blank signal divided by Se$^+$ sensitivity. Both signals measured without gas in the reaction cell using a matrix of deionized H$_2$O only.

In enriched isotope tracer studies, more than one isotope of Se must be measured. Isotope dilution analysis (IDA) requires measurement of at least two isotopes, preferably
free from overlaps. IDA can provide high accuracy by compensating for experimental variations such as plasma fluctuations, drift, and matrix effects.\textsuperscript{12} Recently, isotope pattern deconvolution (IPD) has been applied to total elemental analysis and speciation studies.\textsuperscript{13,14} IPD uses multiple enriched isotope spikes (e.g. one quantitation tracer and one metabolic tracer) to increase accuracy and reduce uncertainty. IPD measures all 6 Se isotopes and uses linear algebra deconvolution as a method of internal correction. A reaction gas is therefore needed which reduces spectral overlaps on all 6 Se isotopes in complex matrices. Fourteen reaction gases were compared to determine which, if any, could provide overlap free measurement of all 6 Se isotopes.

4.3 Experimental details

A PerkinElmer Sciex Elan 6100 DRC\textsuperscript{plus} ICP-DRC-MS was used for all experiments.\textsuperscript{15} A peristaltic pump (Gilson Minipuls 3) delivered solution into a quartz, concentric nebulizer (TQ-30-A3, Meinhard Glass Products, Golden CO, USA) at a solution uptake rate of 1 mL min\textsuperscript{-1}. A quartz, baffled cyclonic spray chamber (Quartz Cyclonic Spray Chamber for ELAN DRC (WE025221), PerkinElmer Sciex) was used with a 2.0 mm id quartz injector (WE023948, PerkinElmer Sciex) at ambient temperature. Solutions were made by serial dilution from 1,000 \(\mu\)g mL\textsuperscript{-1} standard solutions (CPI International, Santa Rosa CA, USA) in deionized water (18.2 M\(\Omega\) cm, Millipore Milli-RO-10 and Milli-Q). Hydrochloric acid was double distilled (GFS Chemicals, Columbus OH, USA). All solutions in this study included 3% v/v certified electronic grade anhydrous methanol (Fisher Scientific, Fair Lawn NJ) which has been shown to improve Se\textsuperscript{+} sensitivity by the carbon enhanced ionization effect.\textsuperscript{16} The
optimum CH$_3$OH concentration and measured sensitivity enhancement factor agreed with previous work.$^{11}$

The ICP-MS had two reaction gas introduction channels. Channel A included a getter to remove oxygen and water impurities. Collision/reaction gases introduced through Channel A included hydrogen (99.999%, Praxair), methane (99.997%, Praxair), deuterated methane (>99.9% purity, 99.7% enrichment, Cambridge Isotope Laboratory), nitrogen (99.998%, Praxair), xenon (99.999%, Praxair), argon (99.998%, Praxair), neon (99.999%, Praxair), helium (99.999%, Praxair), carbon monoxide (99.999%, Praxair), nitrous oxide (99.995%, Matheson Tri-gas), methyl fluoride (99.999%, Praxair), ammonia (99.999%, Scott Specialty Gases) and sulfur hexafluoride (99.9%, Praxair). Oxygen (99.999%, Praxair) was introduced through channel B, which did not contain a getter. Both flows were maintained by mass flow controllers (MKS Instruments, USA) calibrated for Ar flow, with manufacturer provided conversion factors listed in Table 4.3.
Table 4.2: ICP-MS experimental parameters.

<table>
<thead>
<tr>
<th>Mass Spectrometer Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF power/W</td>
</tr>
<tr>
<td>Lens voltage</td>
</tr>
<tr>
<td>Autolens</td>
</tr>
<tr>
<td>Pulse stage voltage</td>
</tr>
<tr>
<td>Analog stage voltage</td>
</tr>
<tr>
<td>Auxiliary gas flow</td>
</tr>
<tr>
<td>Plasma gas flow</td>
</tr>
<tr>
<td>Nebulizer flow (optimized daily)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>DRC Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Entrance aperture diameter</td>
</tr>
<tr>
<td>Exit aperture diameter</td>
</tr>
<tr>
<td>Axial field voltage</td>
</tr>
<tr>
<td>RPa</td>
</tr>
<tr>
<td>RPq</td>
</tr>
<tr>
<td>DRC mode quadrupole rod offset</td>
</tr>
<tr>
<td>DRC mode cell rod offset</td>
</tr>
<tr>
<td>RF voltage (peak to peak)</td>
</tr>
<tr>
<td>DRC mode cell path voltage</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Analyzer Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Correction for ⁷⁸Kr, ⁸⁶Kr, ⁸⁸Kr, ⁷⁶Ge, ⁷⁷Ge</td>
</tr>
<tr>
<td>Mass resolution</td>
</tr>
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<table>
<thead>
<tr>
<th>Isotope Measurement</th>
</tr>
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<tbody>
<tr>
<td>Dwell time</td>
</tr>
<tr>
<td>Sweeps</td>
</tr>
<tr>
<td>Replicates</td>
</tr>
<tr>
<td>Points per peak</td>
</tr>
<tr>
<td>Settling time</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mass Scan Measurement</th>
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<tbody>
<tr>
<td>Dwell time (for each isotope)</td>
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<tr>
<td>Sweeps</td>
</tr>
<tr>
<td>Replicates</td>
</tr>
<tr>
<td>Points amu⁻¹</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>3σ Detection Limit Measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dwell time</td>
</tr>
<tr>
<td>Sweeps</td>
</tr>
<tr>
<td>Replicates</td>
</tr>
<tr>
<td>Points per peak</td>
</tr>
<tr>
<td>Settling time</td>
</tr>
</tbody>
</table>
Table 4.3: Actual flow (mL min\(^{-1}\)) reaction gas per Ar equivalent mL min\(^{-1}\) gas flow. Actual gas flow rate calculated by multiplying conversion factor by reported gas flow rate.\(^{17}\)

<table>
<thead>
<tr>
<th>Reaction Gas</th>
<th>Gas conversion factor(^{17})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>1.00</td>
</tr>
<tr>
<td>C(_2)H(_6)</td>
<td>0.36</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>0.52</td>
</tr>
<tr>
<td>CD(_4)</td>
<td></td>
</tr>
<tr>
<td>CH(_3)F</td>
<td>0.40</td>
</tr>
<tr>
<td>CO</td>
<td>0.72</td>
</tr>
<tr>
<td>H(_2)</td>
<td>0.70</td>
</tr>
<tr>
<td>He</td>
<td>1.01</td>
</tr>
<tr>
<td>N(_2)</td>
<td>0.72</td>
</tr>
<tr>
<td>N(_2)O</td>
<td>0.51</td>
</tr>
<tr>
<td>Ne</td>
<td>1.05</td>
</tr>
<tr>
<td>NH(_3)</td>
<td>0.53</td>
</tr>
<tr>
<td>O(_2)</td>
<td>0.71</td>
</tr>
<tr>
<td>SF(_6)</td>
<td>0.19</td>
</tr>
<tr>
<td>Xe</td>
<td>0.95</td>
</tr>
</tbody>
</table>

A convenient method to choose the optimum reaction gas flow rate is based on estimated limits of detection. Estimated LOD’s assume that the standard deviation of the blank is due to Poisson counting statistics (shot noise):

\[
\text{Est LOD (ppb)} = 3 \times \frac{\sqrt{\text{Blank (c s}^{-1}\text{) x time (s)}}}{\text{sensitivity (c s}^{-1}\text{ ng}^{-1}\text{ L x time(s))}} \tag{4.1}
\]

When the blank signals are large (greater than 10,000 c) the estimated limit of detection is smaller than the attainable detection limit because the standard deviation of the blank signal is not dominated by the counting statistics but rather by flicker noise (~0.5 to 2% relative standard deviation). However, when the blank signal is suppressed using a reaction gas, the counting statistics detection limits provide a reasonable estimate.
An RPq of 0.60 was used for all gases. This value was chosen because it was the lowest value that prevented unwanted product ions for every gas. By using one RPq value for all gases, the transmission efficiency through the DRC was equal in all cases.

4.4 Overlap Attenuation by Ion-Molecule Reactions

ICP-MS instruments equipped with a reaction cell can use ion-molecule reactions to overcome spectral overlaps.\textsuperscript{15,17,18} The choice of an appropriate reaction gas will depend on whether or not it reacts efficiently enough with the undesired spectral overlap ion, avoids the formation of undesired product ions, and does not cause extensive loss of Se\textsuperscript{+} signal due to reaction or scattering. Thermodynamics can be used to determine if a reaction could occur but does not offer kinetic rate information. Table 4.4 lists established kinetic rate constants for the reaction of 14 gases with both Ar\textsubscript{2}\textsuperscript{+} and Se\textsuperscript{+}. Kinetic rate constants have not yet been reported for reactions with other overlap ions such as Ar\textsubscript{2}H and Ar\textsubscript{2}H\textsubscript{2}. 
Table 4.4: Ionization potentials of Se, Ar₂ and reaction gases along with previously measured kinetic rate constants.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Reaction Gas</th>
<th>Ionization Energy (eV)</th>
<th>Average Mass (amu)</th>
<th>Previously reported reaction rates (k) with Ar₂⁺ (10⁻¹⁰ cm³ molecule⁻¹ s⁻¹)</th>
<th>Reported reaction with Se⁺?</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td></td>
<td>24.59</td>
<td>4</td>
<td>ICP-SIFT-MS</td>
<td>SIFT-MS</td>
</tr>
<tr>
<td>Ne</td>
<td></td>
<td>21.55</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ar</td>
<td></td>
<td>15.76</td>
<td>40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td></td>
<td>15.58</td>
<td>28</td>
<td>2.2²⁰,0²¹</td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td></td>
<td>15.43</td>
<td>2</td>
<td>6.3²²,4.7²⁰,2.0²¹</td>
<td></td>
</tr>
<tr>
<td>Ar₂⁺</td>
<td></td>
<td>14.50²³,*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SF₆</td>
<td></td>
<td>14.40²⁴,†</td>
<td>146</td>
<td>4.2²⁵</td>
<td>No (k&lt;0.001)²⁶</td>
</tr>
<tr>
<td>CO</td>
<td></td>
<td>14.01</td>
<td>28</td>
<td>7.3²⁷,6.1²⁵,4.8²¹</td>
<td>No (k≤ 0.04)²⁷</td>
</tr>
<tr>
<td>N₂O</td>
<td></td>
<td>12.88</td>
<td>44</td>
<td>6.2²⁷,8.2²⁵</td>
<td>Yes, O-atom addition (k=0.007²⁷, 0.018²⁸)</td>
</tr>
<tr>
<td>CH₄</td>
<td></td>
<td>12.61</td>
<td>16</td>
<td>9.3²⁹</td>
<td>Yes, 0.15³⁰</td>
</tr>
<tr>
<td>CH₃F</td>
<td></td>
<td>12.47</td>
<td>36</td>
<td>9.3²⁹</td>
<td>Yes, 0.15³⁰</td>
</tr>
<tr>
<td>Xe</td>
<td></td>
<td>12.12</td>
<td>131</td>
<td>2.3²⁰</td>
<td>No (k≤ 0.001)³¹</td>
</tr>
<tr>
<td>O₂</td>
<td></td>
<td>12.07</td>
<td>32</td>
<td>0.74²⁵</td>
<td>Yes, O-atom addition³²</td>
</tr>
<tr>
<td>C₂H₆</td>
<td></td>
<td>11.52</td>
<td>30</td>
<td>10.6³³</td>
<td></td>
</tr>
<tr>
<td>NH₃</td>
<td></td>
<td>10.07</td>
<td>17</td>
<td>3.1³⁴,5.5³⁵, slow (k ≤ 0.11)³⁴</td>
<td></td>
</tr>
<tr>
<td>Se⁺</td>
<td></td>
<td>9.75*</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Energy to produce the listed ion from neutral.

† The ionization energy for SF₆ has been investigated by different research groups and methods and is still not unequivocally established. Reference 35 offers a recent summary of values.

Ion-neutral gas phase reactions can be used to selectively and efficiently reduce overlap ion signals with little effect on the Se⁺ signal. Exothermic charge transfer...
reactions can produce up to 9 orders of magnitude improvements in elemental ion to overlap ion signal ratios.\textsuperscript{15,17,18,36} For example, CH\textsubscript{4} reacts very efficiently with Ar\textsubscript{2}\textsuperscript{+} by charge transfer, but only slowly with Se\textsuperscript{+}. CH\textsubscript{4} can be used to remove the overlap Ar\textsubscript{2}\textsuperscript{+} from the signal at m/z 80, leaving \textsuperscript{80}Se\textsuperscript{+} to be measured with a much lower background but SeH\textsuperscript{+} is formed as a byproduct of the reaction. Sloth and Larsen\textsuperscript{37} reported 12\% of Se formed SeH\textsuperscript{+}, which interferes with \textsuperscript{77}Se/\textsuperscript{76}Se and \textsuperscript{78}Se/\textsuperscript{77}Se ratios. SeH\textsuperscript{+} is increasingly formed as CH\textsubscript{4} flow rate increases, indicating that SeH\textsuperscript{+} is formed in the reaction cell from a reaction with CH\textsubscript{4}. A series of mathematical correction equations are then required to correct for the SeH\textsuperscript{+} formation.\textsuperscript{38} Use of correction equations can degrade isotope ratio precision because each correction step has an associated uncertainty.\textsuperscript{39}

Atom addition reactions can be used to produce molecular ions (SeO\textsuperscript{+}) at higher m/z (using O\textsubscript{2} or N\textsubscript{2}O)\textsuperscript{32,40} to avoid the large Ar\textsubscript{2}\textsuperscript{+} signal at m/z 80. Others have used this method to generate SeO\textsuperscript{+} at m/z 96 (free from Ar\textsubscript{2}\textsuperscript{+} interference at m/z 80).\textsuperscript{41} However, the incomplete conversion of Se\textsuperscript{+} to SeO\textsuperscript{+} (10-25\%) reduced sensitivity. The most common atom addition reaction is the addition of a hydrogen atom to Ar\textsubscript{2}\textsuperscript{+} to “move” the signal by one amu.\textsuperscript{32,38,40,42-54} However, SeH\textsuperscript{+} is also produced through a side reaction, again interfering with \textsuperscript{77}Se/\textsuperscript{76}Se and \textsuperscript{78}Se/\textsuperscript{77}Se ratios.\textsuperscript{52}

4.4.1 Ar\textsubscript{2}\textsuperscript{+} charge transfer reactions

Some of the reaction gases in table 4.4 have lower ionization energies than that of Ar\textsubscript{2} (14.5 eV) and should undergo charge transfer reactions with Ar\textsubscript{2}\textsuperscript{+}. These include CH\textsubscript{4}, CO, Xe, CH\textsubscript{3}F, N\textsubscript{2}O, O\textsubscript{2} and NH\textsubscript{3}. Each of these gases also has an ionization
energy that is greater than that of Se and should not undergo a charge transfer reaction with Se$^+$ under thermal conditions. Signals at m/z 80 from a 1 ppb Se solution and from a blank solution are shown as a function of CO, CH$_4$, NH$_3$ and Xe gas flow in figures 4.1 a – d.
Figure 4.1: Reaction profile of a) CO, b) CH₄, c) NH₃, and d) Xe with RP₉ = 0.60. Blank signal (○, left y-axis, dashed line extrapolated to 0.1 c s⁻¹), 1 ppb Se standard signal (●, left y-axis) and estimated limit of detection (solid line, right y-axis) are shown. The true reaction gas flow is shown on the top x-axis.

All four gases react with Ar₂⁺, and blank signal decreases as the reaction gas flow rate is increased from 0 to 0.3 Ar equivalent mL min⁻¹. CH₄, CO, and Xe reduced the Ar₂⁺ signal by four orders of magnitude, the signal due to Ar₂⁺ is reduced to less than 0.1 ng L⁻¹.
c s\(^{-1}\) at 0.5 Ar equivalent mL min\(^{-1}\). NH\(_3\) reacts with Ar\(_2^+\) more slowly than CH\(_4\), CO and Xe, and the signal due to Ar\(_2^+\) also decreases by four orders of magnitude. However, NH\(_3\) required a 1.2 Ar equivalent mL min\(^{-1}\) flow rate to reduce the contribution of Ar\(_2^+\) to less than 0.1 c s\(^{-1}\).

Charge transfer reactions are pseudo first order. The Ar\(_2^+\) signal decreases linearly on a log(signal) as a function of gas flow rate. The slope changes when the Ar\(_2^+\) signal has been reduced enough that it is no longer the dominant source of the signal at m/z 80. In each case shown in figure 4.1, blank signals at flow rates greater than 1.2 Ar equivalent mL min\(^{-1}\) are due to Se contamination of the blank and were confirmed by matching the Se isotopic pattern to measured signals.

Ar\(_2^+\) is the dominant source of the signal at m/z 80 produced from a 1 ppb Se solution when no reaction gas is used (vented mode). A typically signal was 2 x 10\(^6\) c s\(^{-1}\) from Ar\(_2^+\) and ~10,000 c s\(^{-1}\) from the 1 ppb Se with no reaction gas. As the reaction gas flow rate is increased the 1 ppb Se signal at m/z 80 falls rapidly, just as it did for the blank. The change in slope at flow rates from 0.1 to 0.3 mL min\(^{-1}\) indicates that Ar\(_2^+\) is no longer the dominant source of signal at m/z 80. At higher reaction gas flow rates, Se\(^+\) is the dominant source of signal at m/z 80. An observed change in analyte signal magnitude might be attributed to three separate causes: analyte-gas reactions, collisional focusing, and scattering losses.

CO (figure 4.1a) does not significantly react with Se\(^+\). The observed signal decrease when the reaction gas flow rate is increased from 0.7 to 1.5 Ar equivalent mL min\(^{-1}\) is likely due to scattering losses. An observed ~10% increase in signal around 0.5
mL min\(^{-1}\) is due to collisional focusing.\(^{55}\) No product ions other than CO\(^+\) and Ar(CO)\(^+\) were observed, and none were observed containing Se (figure 2.2a).

\[
Ar_2^+ + CO \rightarrow 2Ar + CO^+ \quad 95\% \text{ (ref. } 27)\]

\[
Ar_2^+ + CO \rightarrow Ar + Ar(CO)^+ \quad 5\%
\]

The Ar(CO)\(^+\) signal at m/z 68 increases to \(\sim 15,000\) c s\(^{-1}\) at 0.1 Ar equivalent mL min\(^{-1}\) and decreases back to \(< 100\) c s\(^{-1}\) at 1.5 mL min\(^{-1}\). Formation of Ar(CO)\(^+\) would degrade the detection limits of \(^{68}\)Zn\(^+\) if a low value of RPq was used. The bandpass of the reaction cell could be used to reject \(^{40}\)Ar\(^{2+}\) during \(^{68}\)Zn\(^+\) measurement. At an RPq of 0.60 and RPa of 0.08 would reject masses greater than 70, rejecting the reactant Ar\(^2^+\) from the reaction cell during Zn\(^+\) measurement. At reaction gas flow rates where Se\(^+\) is the dominant signal, the slope of the log(signal) versus gas flow rate for the 1 ppb Se solution and the blank solution are similar. This is consistent with Se contamination being the dominant source of blank signal at m/z 80. The isotope ratios measured from the blank at reaction gas flow rates where Ar\(^2^+\) is no longer a significant contribution to the signal are consistent with the natural abundances of Se, also consistent with the remaining blank signal being due to Se contamination. The ratio of the blank signals to the signal due to the 1 ppb Se solution is consistent with 14 to 15 ppt Se in the blank. The estimated detection limit at the optimized reaction gas flow rate (0.4 Ar equivalent mL min\(^{-1}\)) was 3 ppt and the measured 3\(\sigma\) detection limit for \(^{80}\)Se\(^+\) was 4 ppt. A detection limit of 10 ppt has previously been shown using CO as the reaction gas.\(^{56}\) If the contamination of Se in the blank was lower, then the detection limits would also be lowered as long as there was no other ion at m/z 80.
The signal from the 1 ppb Se solution decreases by an order of magnitude as the CH$_4$ flow rate is increased from 0.5 to 1.5 Ar equivalent mL min$^{-1}$ (figure 4.1b). The elemental signal decrease is the result of reaction with Se$^+$ through two reaction channels. The first reaction channel clusters Se(CH$_x$)$_x^+$, which forms at m/z 90-98 with a slow bimolecular rate constant (table 4.4), and can be seen in figure 4.2b. Se(CH$_x$)$_x^+$ signals increase as CH$_4$ flow is increased.

![Mass spectra](image)

Figure 4.2: Mass spectra normalized to blank subtracted signal at m/z 80 of 100 ppb Se with a) CO and b) CH$_4$ at the minimum estimated detection limit flow rates.

The total ion signal (elemental Se$^+$ plus all Se(CH$_x$)$_x^+$) decreases slightly, indicating that signal loss at m/z 80 is due to both reaction and ion beam scattering. The amount of Se lost to clustering is approximately 25% at 0.6 Ar equivalent mL min$^{-1}$. When CH$_4$ is used as a reaction gas, SeH$^+$ is formed inside the reaction cell. The new interferences $^{76}$SeH$^+$ and $^{77}$SeH$^+$ are overlaps of $^{77}$Se$^+$ and $^{78}$Se$^+$. SeH$^+$ is increasingly
formed as the CH$_4$ flow rate is increased but no formation of SeH$^+$ is formed when CO is used (figure 4.3, blank subtracted $^{82}$SeH$^+$ signal divided by blank subtracted $^{82}$Se$^+$ signal).

**Figure 4.3:** Ratio of blank subtracted m/z 83 signal ($^{82}$SeH$^+$) to blank subtracted m/z 82 signal ($^{82}$Se$^+$) as a function of reaction gas flow (Ar equivalent mL min$^{-1}$). Reaction gas: (●) CH$_4$, (▲) CO, (♦) H$_2$, (□) N$_2$.

Larsen and Sloth previously used$^{37}$ deuterated methane to ascertain the mechanism of SeH$^+$ formation and observed an identical formation of SeH$^+$ using both CH$_4$ and CD$_4$ (D = deuterium, $^2$H). Our results using CD$_4$ show peaks at two mass units greater than the Se isotope pattern, indicating SeD$^+$ formation via abstracting a deuterium.
atom from CD₄ or CD₄⁺. Figure 4.4 shows the mass spectra normalized to the measured ⁸⁰Se⁺ signal for both CH₄ and CD₄.

![Mass spectra graphic](image)

**Figure 4.4:** Mass spectra normalized to blank subtracted signal at m/z 80 with 500 ppb Se⁺ using CH₄ (solid) and CD₄ (dashed). Spectra were measured at 0.6 Ar equivalent mL min⁻¹ CH₄ and 0.7 Ar equivalent mL min⁻¹ CD₄ respectively.

Using CH₄, there are noticeable peaks one mass unit greater than expected at m/z 75 (off scale), 79, 81 and 83 corresponding to ⁷⁴SeH⁺, ⁷⁸SeH⁺, ⁸⁰SeH⁺ and ⁸²SeH⁺ formation. Using CD₄, additional peaks are observed at m/z 79 and 84 corresponding to ⁷⁷SeD⁺ and ⁸²SeD⁺, respectively. The measured signal at m/z 82 using CD₄ is much larger than expected by Se isotopic ratio due to addition of ⁸⁰SeD⁺ at that mass. In disagreement with the work in reference 37, our work shows that the formation of SeH⁺
is due to the abstraction of a hydrogen atom from CH\(_4\) or CD\(_4\). CH\(_4^+\) and CD\(_4^+\), formed from the reaction with Ar\(_2^+\), should be efficiently rejected from the reaction cell at RPq 0.60. Formation of\(^{74}\text{SeD}^+, \, ^{76}\text{SeD}^+, \, ^{78}\text{SeD}^+, \, ^{80}\text{SeD}^+\) interferes with isotopic ratio measurements involving\(^{76}\text{Se}^+, \, ^{78}\text{Se}^+, \, ^{80}\text{Se}^+\) and\(^{82}\text{Se}^+\) respectively. The estimated detection limit at the optimum CH\(_4\) flow rate (0.6 Ar equivalent mL min\(^{-1}\)) was 3 ppt. The measured 3\(\sigma\) detection limit for\(^{80}\text{Se}^+\) was 2 ppt (integration time 10 seconds).

Larsen showed detection limits of 9 ppt using CH\(_4\) as the reaction gas, also limited by the contamination in the blank.\(^{37}\)

NH\(_3\) has also been used as a reaction gas to reduce the Ar\(_2^+\) signal by charge transfer reaction.\(^{56,57}\) Although the reaction of NH\(_3\) with Se is endothermic by 0.32 eV, the Se\(^+\) signal decreases as NH\(_3\) flow increases (figure 4.1c) when RPq is 0.6, consistent with a previous report.\(^{58}\) No Se containing product ions are observed, suggesting that NH\(_3\) charge transfers with Se\(^+\). At low and mid-range \(q\) parameters, energy contributions from the RF field of 0.4 eV have been shown.\(^{58}\) Energy transfer up to 0.8 eV is possible at high RPq values. Our work agrees with previous studies that the isotopic pattern is not matched at RPq values less than 0.40,\(^{59}\) particularly the measured signal at m/z 74. At RPq = 0.40, the bandpass cutoff rejects m/z 31 and below (rejecting\(^{12}\text{C}_2^+\), which may form \(\text{C}_2(\text{NH}_2)_3^+\) overlapping\(^{74}\text{Se}^+\)). At RPq = 0.60, the expected Se isotopic pattern is observed, but the quadrupole RF field provides sufficient energy to the Se\(^+\) for charge transfer between Se\(^+\) and NH\(_3\) to occur and sensitivity is decreased. A contamination-limited estimated detection limit of 4 ppt was achieved with NH\(_3\), this value was similar
to those obtained using CH$_4$ (EDL = 3 ppt) and CO (EDL = 3 ppt) despite the loss of Se$^+$ sensitivity when NH$_3$ was used.

Xe has previously been shown to exothermically charge transfer with Ar$_2^+$ to yield a contamination limited detection limit of 3 ppt.$^{39}$ As the Xe flow is increased from 0 to 0.15 Ar equivalent mL min$^{-1}$ (figure 4.1d), the measured Ar$_2^+$ blank signal is reduced by 5 orders of magnitude. At 0.2 Ar equivalent mL min$^{-1}$ flow, Ar$_2^+$ contributes less than 0.1 c s$^{-1}$ and $^{80}$Se$^+$ becomes the dominant signal source. The reaction of Se$^+$ with Xe is endothermic by 2.37 eV and should not occur, even after considering possible RF field energy contributions. No product ions containing Se were observed at any flow rate. The $^{80}$Se$^+$ signal loss was attributed to scattering losses due to the high mass of Xe. A contamination limited estimated detection limit of 12 ppt was achieved at 0.15 Ar equivalent mL min$^{-1}$ flow. The detection limit obtained using Xe was higher than for CH$_4$ and CO due to scattering losses.

4.4.2 Ar$_2^+$ charge transfer reactions with significant Se$^+$ reaction

CH$_3$F, N$_2$O, O$_2$ and C$_2$H$_6$ (figures 4.5 a – d) were also investigated as possible reaction gases. Each gas is predicted to exothermically undergo charge transfer with Ar$_2^+$ but not with Se$^+$. SIFT rate constants (table 4.4) have been established for the reactions of Ar$_2^+$ with N$_2$O, O$_2$, and C$_2$H$_6$ but a kinetic rate constant for the charge transfer reaction of Ar$_2^+$ and CH$_3$F has not been determined.
Figure 4.5: Reaction profiles for a) CH$_3$F, b) O$_2$, c) N$_2$O, and d) C$_2$H$_6$ with RPq = 0.60. Blank signal (○, left y-axis, dashed line extrapolated to 0.1 c s$^{-1}$), 1 ppb Se standard signal (●, left y-axis) and estimated limit of detection (solid line, right y-axis) are shown. The true reaction gas flow is shown on the top x-axis.

The slope of the 1 ppb Se$^+$ line is negative for all three gases due to both scattering and a product forming reaction involving Se$^+$. Signal losses are known to be
due to scattering because the sum of the elemental ion $\text{Se}^+$ and all Se containing product ions decreases as reaction gas flow increases.

A plot of signal versus flow using CH$_3$F is shown in figure 4.5a and the CH$_3$F clusters with Se$^+$ that form Se(CH$_2$)$_2^+$, Se(CH$_3$)$_2^+$ and react to form SeF$_2^+$ is shown in figure 4.6a. A 2 ppt $^{80}\text{Se}^+$ contamination limited detection limit was achieved at 0.40 Ar equivalent mL min$^{-1}$ CH$_3$F flow rate. The estimated detection limit using CH$_3$F is lower than that of CH$_4$ and CO (EDL = 3 ppt) because the BEC was lower (6 ppt using CH$_3$F compared to 14 ppt using CH$_4$ and CO). The differences in the extent of blank contamination were likely due to cross contamination from pump tubing, as these experiments were performed over the course of three weeks.

O$_2$ and N$_2$O undergo a charge transfer reaction with Ar$_2^+$ ($\Delta H_f = -2.43$ eV, -1.62 eV respectively). At 0.7 Ar equivalent mL min$^{-1}$ O$_2$ flow rate, a detection limit of 3 ppt was reached with a BEC of 11 ppt. N$_2$O reacts faster with Ar$_2^+$ than O$_2$, but also reacts faster with Se$^+$ than O$_2$. Using N$_2$O, the $^{80}\text{Se}^+$ contamination-limited detection limit of 5 ppt was reached at 0.4 Ar equivalent mL min$^{-1}$ flow rate with a BEC of 21 ppt. Both O$_2$ ($\Delta H = -0.25$ eV) (Figure 4.5b) and N$_2$O ($\Delta H = -3.68$ eV) (Figure 4.5c) are known to exothermically form SeO$_2^+$. The Se$^+$-containing products resulting from reaction with O$_2$ and N$_2$O can be seen in Figure 4.6b and Figure 4.6d, respectively. N$_2$O reacts with Se$^+$ to exothermically form both SeO$_2^+$ and SeN$_2^+$. The Se product ions contain $34\%$ SeN$^+$, and $49\%$ SeO$_2^+$. The remaining $17\%$ of Se product ions are SeNH$_2^+$ and SeOH$^+$. The product ions at m/z 94 (SeN$^+$) and 96 (SeO$_2^+$) can be used for Se quantification, but overlapping polyatomic product ions (e.g. $^{80}\text{Se}^{14}\text{N}$ interferes with $^{78}\text{Se}^{16}\text{O}$) make isotope
ratio measurements more difficult and require mathematical isotope deconvolution. Although both CH$_3$F and N$_2$O react significantly faster with Ar$_2^+$ than O$_2$, detection limits were not improved because the Se$^+$ sensitivity loss became significant. There is also the possibility that both N$_2$O and O$_2$ will oxidize and CH$_3$F will fluorinate other elements also present in solution. This may cause undesired overlaps or reduced sensitivity.

C$_2$H$_6$ reacts very efficiently via charge transfer with Ar$_2^+$ (figure 4.5d), but also reacts significantly with Se$^+$ to form SeH$_2^+$ (approximately 10%) and by clustering to form Se(CH$_3$)$_x^+$ at m/z 87-98. A kinetic rate constant or reaction mechanism for the addition of H$_2$ to Se$^+$ has not been published. Interestingly, the Se$^+$-H$_2$ formation is extremely efficient and effectively “moves” the Se$^+$ isotopic spectrum by two mass units (figure 4.6d). $^{80}$Se$^+$ contamination limited detection limits of 13 ppt were reached (at 0.35 Ar equivalent mL min$^{-1}$).
**Figure 4.6:** Mass spectra normalized to maximum measured blank subtracted signal of 100 ppb Se using a) CH₃F, b) O₂, c) N₂O and d) C₂H₆ at the minimum estimated detection limit flow rates.

### 4.4.3 Hydrogen atom addition reactions with Ar₂⁺ and Se⁺

A charge transfer reaction of H₂ and Ar₂⁺ is endothermic by 0.93 eV (table 4.4), which exceeds possible RF energy contributions. The average energy of Ar₂⁺ entering
the reaction cell is 8 eV\textsuperscript{17} and CID upon a single collision is unlikely. \( \text{H}_2 \) exothermically \((\Delta_rH = -0.218 \text{ eV})\) reacts with \( \text{Ar}_2^+ \) via two condensation reactions.\textsuperscript{32}

\[
\text{Ar}_2^+ + \text{H}_2 \rightarrow \text{ArH}^+ + \text{Ar} + \text{H} \quad (60\%)
\]

\[
\text{Ar}_2^+ + \text{H}_2 \rightarrow \text{ArH}_2^+ + \text{Ar} \quad (40\%)
\]

Tanner predicted the upper limit of \( \text{Ar}_2^+ \) signal decay by reaction with \( \text{H}_2 \) to be approximately 4 orders of magnitude, which is insufficient for the complete chemical resolution of \( ^{80}\text{Se}^+ \) from \( ^{40}\text{Ar}_2^+ \). Figure 4.7a shows the reaction profile for a blank and 1 ppb Se solution using \( \text{H}_2 \) as the reaction gas.

\[\text{Figure 4.7:}\] a) Reaction profile for \( \text{H}_2 \) with RPq = 0.60. Blank signal (○, left y-axis, dashed line extrapolated to 0.1 c s\textsuperscript{-1}), 1 ppb Se standard signal (●, left y-axis) and estimated limit of detection (solid line, right y-axis) are shown. The true reaction gas flow is shown on the top x-axis. b) mass spectrum normalized to blank subtracted signal at m/z 80 of 100 ppb Se using \( \text{H}_2 \) at the minimum estimated detection limit flow rate.

The \( \text{Ar}_2^+ \) signal was reduced by approximately 3 orders of magnitude but was not completely removed from the mass spectrum, which agrees with previous literature.\textsuperscript{32}
The maximum H$_2$ flow rate attainable is limited by the instrument, which is programmed to shut off the analyzer electronics above pressures of 8 x 10$^{-5}$ torr to prevent damage to the instrument. The estimated detection limit at the maximum possible flow rate (1.0 Ar equivalent mL min$^{-1}$) was 13 ppt with a corresponding BEC of 300 ppt. The extrapolated blank linear regression line shows that the Ar$_2^+$ cannot be removed by the H$_2$ condensation reaction, even at 1.5 Ar equivalent mL min$^{-1}$. Other instrument configurations have also shown that $^{40}$Ar$_2^+$ is not completely removed from the measured signal by reaction with H$_2$. Therefore, some authors have recommended that the most abundant isotope of Se ($^{80}$Se) not be used and $^{78}$Se$^+$ is usually the recommended isotope when using H$_2$.

Although the work in reference 45 states that $^{78}$Se$^+$ can be monitored interference free, we have found that $^{77}$SeH$^+$ interferes with the measurement of $^{78}$Se$^+$. The observed SeH$^+$ formation inside the reaction cell is small (figure 4.3), and is consistent with the thermodynamics of the hydrogen atom addition reaction ($\Delta H = +1.55$ eV). The observed SeH$^+$ formation did not exceed 4% at any H$_2$ flow rate.

### 4.4.4 Reaction of Ar$_2^+$ with SF$_6$

A charge transfer reaction between SF$_6$ and Ar$_2^+$ is exothermic by 0.1 eV (table 4.4). SF$_6^+$ is unstable and dissociates to SF$_5^+$ and F in approximately a picosecond. $^{35,61}$

$$ Ar_2^+ + SF_6 \rightarrow 2Ar + SF_6^+ \quad \Delta H_f = -0.1 \text{ eV} $$

$$ SF_6^+ \rightarrow SF_5^+ + F $$

The overall observed reaction between SF$_6$ and Ar$_2^+$ is shown.$^{25}$
\[ \text{Ar}_2^+ + \text{SF}_6 \rightarrow 2\text{Ar} + \text{SF}_5^+ + \text{F} \]

The appearance of \( \text{SF}_5^+ \) at m/z 127 would impede any measurement of other ions at that mass, e.g. \( ^{127}\text{I}^+ \). It is not possible to reject the precursor ion \( ^{40}\text{Ar}_2^+ \) using the bandpass of the DRC because \( ^{80}\text{Se}^+ \) is at the same nominal mass. Additionally, the production of \( \text{SF}_5^+ \) inside the reaction cell causes unwanted by-product reactions.\(^{62}\)

\[ \text{SF}_5^+ + \text{SF}_6 \rightarrow \text{SF}_3^+ + \text{F}_2 + \text{SF}_6 \]

A large signal at m/z 89 would interfere with any measurement of \( ^{89}\text{Y}^+ \). A further examination of product ions from \( \text{SF}_6 \) is covered in chapter 5.

**Figure 4.8:** Reaction profile for \( \text{SF}_6 \) with \( \text{RPq} = 0.60 \). Blank signal (○, left y-axis, dashed line extrapolated to 0.1 c s\(^{-1}\)), 1 ppb Se standard signal (●, left y-axis) and estimated limit of detection (solid line, right y-axis) are shown. The true reaction gas flow is shown on the top x-axis.
SF₆ did not react with Se⁺ and no Se containing product ions were observed, which agrees with reaction rate constants found in literature.²⁶ Extensive loss of Se⁺ signal (an order of magnitude loss in sensitivity for each change of 0.2 Ar equivalent mL min⁻¹) occurs due to the scattering of the ion beam. Contamination limited detection limits of 11 ppt were reached at a flow rate of 0.45 Ar equivalent mL min⁻¹ with a BEC of 28 ppt.

### 4.4.5 Ligand exchange reaction with N₂

The charge transfer reaction between Ar₂⁺ and N₂ is endothermic by 1.08 eV (table 4.4) which exceeds any possible RF energy contributions from the DRC. The reaction of Ar₂⁺ with N₂ proceeds by a ligand switching mechanism.²⁰

$$ (Ar - Ar)^+ + N₂ \rightarrow (Ar - N₂)^+ + Ar $$

Similarity of ionization energies of Ar (15.76 eV) and N₂ (15.58 eV) promotes charge delocalization in the (Ar • N₂)⁺ complex. The blank and 1 ppb standard signals measured at m/z 80 are shown in figure 4.9a. The measured mass spectrum normalized to the ⁸⁰Se⁺ signal at 0.7 Ar equivalent mL min⁻¹ can be seen in figure 4.9b.
**Figure 4.9:** a) Reaction profile for N$_2$ with RPq = 0.60. Blank signal (○, left y-axis, dashed line extrapolated to 0.1 c s$^{-1}$), 1 ppb Se standard signal (●, left y-axis) and estimated limit of detection (solid line, right y-axis) are shown. The true reaction gas flow is shown on the top x-axis. b) Mass spectra normalized to blank subtracted signal at m/z 80 of 100 ppb Se using N$_2$ at the minimum estimated detection limit flow rate.

Although not a charge transfer reaction, the ligand switching mechanism proceeds rapidly and the signal due to Ar$_2^+$ contributes less than 0.1 c s$^{-1}$ at 1.0 Ar equivalent mL min$^{-1}$, while the sensitivity for $^{80}$Se$^+$ remains high (about 8,000 c s$^{-1}$ ppb$^{-1}$). A contamination limited estimated detection limit of 2 ppt was achieved with BEC of 13 ppt at 0.7 Ar equivalent mL min$^{-1}$ flow rate. The measured 3σ (10 second integration) detection limit for $^{80}$Se$^+$ was 1 ppt. The formation and dissociation of (Ar ● N$_2$)$^+$ measured at m/z 68 can be seen in figure 4.10.
Figure 4.10: Measured signal from Ar•(N₂)+ compound is shown. The true reaction gas flow is shown on the top x-axis.

Signal at m/z 68 was measured as ~400 c s⁻¹ with no gas flow and increases to 700,000 c s⁻¹ before decreasing, possibly due to CID of (Ar•N₂)⁺. This dissociation can occur through two possible pathways:

\[
(Ar - N₂)⁺ \rightarrow Ar⁺ + N₂ \quad \Delta H = 1.26 \text{ eV}^{20}
\]

\[
(Ar - N₂)⁺ \rightarrow Ar + N₂⁺ \quad \Delta H = 1.08 \text{ eV}^{63}
\]

The ionization potential of the Ar•N₂ complex is 14.86 eV and can undergo an exothermic charge transfer reaction N₂.⁶⁴ Less than 0.1% SeH⁺ formation was observed (figure 4.3).
4.5 Interferent Attenuation by Collision Induced Dissociation

Collision induced dissociation (CID) has typically been considered to be ineffective to overcome spectral overlaps in ICP-MS instruments with collision/reaction cells that are not ion traps. Chapter 3 discussed what conditions are conducive to CID for polyatomic ion removal in ICP-DRC-MS.

Assuming a stationary, neutral collision gas atom, the maximum vibrational energy gained from a single elastic collision is expressed as a function of kinetic energy and the masses of the ion and the reaction gas.

\[
E_{\text{int,max}} = E_{\text{ion}} \times \left( \frac{m_{\text{gas}}}{m_{\text{gas}} + m_{\text{ion}}} \right)
\]  (4.2)

If the energy \(E_{\text{ion}}\) of \(^{40}\text{Ar}_2^+\) entering the dynamic reaction cell is estimated to be 8 eV (4 eV from the supersonic expansion in the interface, 3 eV from the plasma potential offset, 1 eV from the DRC offset), the maximum internal ion energy gained from a collision a neutral gas with mass larger than 15 amu is greater than the low bond dissociation energy of \(^{40}\text{Ar}_2^+\) (1.26 eV). The collision gases He, Ne and Ar were examined as possible CID partners to reduce the polyatomic ion interferences on Se.

4.5.1 Chemically inert collision gases: He, Ne, Ar

Under thermal conditions, He, Ne and Ar will not react with \(\text{Ar}_2^+\). He (4 amu) should be too light to cause CID of \(\text{Ar}_2^+\). Figure 4.11a shows that the \(\text{Ar}_2^+\) signal does not decrease as the He gas flow rate into the reaction cell is increased, consistent with the low atomic mass of He.
Figure 4.11b shows the effect of Ar collision gas flow rate on Ar$_2^+$ and Se$^+$. Ar$_2^+$ was not completely removed from the mass spectrum by CID with Ar at the highest flow rate attainable (0.95 Ar equivalent mL min$^{-1}$), although the signal to noise ratio was improved by approximately 4 orders of magnitude. McShane et al$^{67}$ reported some improvement measurement of $^{78}$Se$^+$ while using Ar as a collision gas. The Ar gas flow rate was optimized for measurement of $^{75}$As at 0.3 mL min$^{-1}$. The authors hypothesized that a higher Ar flow rate would more effectively remove $^{40}$Ar$_2^+$; however, they did not quantify loss of Ar$_2^+$ signal due to CID compared to the loss of Se$^+$ due to scattering. Analysis of $^{78}$Se$^+$ was recommended, due to low relative abundance (0.6%) of $^{38}$Ar$^{40}$Ar compared to $^{40}$Ar$_2$ while the abundance of $^{78}$Se is only about a factor of two less than the abundance of $^{80}$Se. In this work, a detection limit of 4 ppt were achieved for $^{80}$Se$^+$ with a BEC of 15 ppt. A flow rate of 1.5 mL min$^{-1}$ would be needed to reduce the Ar$_2^+$ signal to less than 0.1 c s$^{-1}$. Contamination limited detection limits were not reached for either $^{78}$Se$^+$ or $^{80}$Se$^+$.  

Figure 4.11: Reaction profiles for a) He, b) Ar, and c) Ne with RPq = 0.60. Blank signal (○, left y-axis, dashed line extrapolated to 0.1 c s⁻¹), 1 ppb Se standard signal (●, left y-axis) and estimated limit of detection (solid line, right y-axis) are shown. The true reaction gas flow is shown on the top x-axis.

Ne is heavy enough to dissociate Ar₂⁺ upon a single collision (equation 4.2). A higher gas flow rate was reached using Ne than Ar, and contamination limited detection limits of 2 ppt at 1.2 Ar equivalent mL min⁻¹ flow were achieved with a BEC of 5 ppt. If
instrumental electronics did not turn off at 1.0 mL min\(^{-1}\) using Ar (i.e. \(> 8 \times 10^5\) torr analyzer chamber pressure), it would be expected that contamination limited detection limits could be reached using Ar.

It should be noted that the slopes of the blank signal series as a function of gas flow rate using Ar and Ne are equal to two significant digits. CID requires only that the collision partner with \(\text{Ar}_2^+\) is a gas atom with mass larger than 15 amu for CID to occur upon a single collision. The differences in electronic configuration or reactivity between Ne and Ar do not matter, because CID is a purely physical, inelastic collision.

4.6 Singly Charged Overlaps on \(^{74}\text{Se}^+\)

The BEC’s at every flow rate for all gases are significantly higher for \(^{74}\text{Se}^+\) than for any other Se isotope. \(^{74}\text{Se}^+\) is interfered by \(^{74}\text{Ge}^+, \ 36\text{Ar}^{38}\text{Ar}^+, \text{and } 58\text{Ni}^{16}\text{O}^+.\) In this study, Ge and Ni were present from contamination only and are expected to be very low concentrations. \(^{36}\text{Ar}^{38}\text{Ar}^+\) is expected to react similarly to \(^{40}\text{Ar}_2^+\) according to pseudo first order reaction kinetics. Another possibility is formation of \(^{58}\text{Ni}^{16}\text{O}^+\) from the surface of the sampler cone. The ionization potential for \(\text{NiO}^+\) is 9.5 eV\(^{23}\) which is less than the ionization potential of Se (9.75 eV) making charge transfer an unsuitable reaction pathway for chemical resolution. Charge transfer reactions between \(\text{NiO}^+\) and all the gases listed in table 4.4 would be endothermic by at least 0.6 eV and unlikely to occur. The ground state bond dissociation energy for \(\text{NiO}^+\) is 2.78 eV\(^{68}\) and if the incoming ion kinetic energy is 8 eV, then a gas with mass greater than 40 amu could cause CID of \(\text{NiO}^+\) upon a single collision. Of the 15 gases studied, only Ar (\(> 1.0\) Ar equivalent mL min\(^{-1}\)), \(\text{N}_2\text{O} (> 1.0\) Ar equivalent mL min\(^{-1}\)), \(\text{SF}_6 (> 0.55\) Ar equivalent mL min\(^{-1}\)) and Xe
(> 0.15 Ar equivalent mL min\(^{-1}\)) were heavy enough to reduce the \(58^{\text{Ni}}16^{\text{O}}\) signal to less than 10 c s\(^{-1}\). However, although CID of \(\text{NiO}^+\) was probable, no gas was able to significantly lower the BEC and LOD to levels equivalent to the other Se isotopes. The interferent \(58^{\text{Ni}}16^{\text{O}}\) is likely formed at or near the surface of the sampler cone and cannot be chemically resolved by any of the gases studied here.

4.7 Singly charged overlaps \(\text{Ar}_2\text{H}^+\), \(\text{Ar}_2\text{H}_2^+\) on \(77^{\text{Se}}\) and \(82^{\text{Se}}\)

\(^{36}\text{Ar}^{40}\text{ArH}^+\) and \(^{40}\text{Ar}^{40}\text{ArH}_2^+\) overlap \(77^{\text{Se}}\) and \(82^{\text{Se}}\), respectively. Figure 4.12a shows a moderate decrease in signal of \(^{36}\text{Ar}^{40}\text{ArH}^+\) and \(^{38}\text{Ar}^{38}\text{ArH}^+\) with a 1 ppb Se\(^+\) matrix matched standard as a function of N\(_2\) flow rate. An estimated detection limit of 9 ppt was achieved at a flow rate of 1.1 Ar equivalent mL min\(^{-1}\).

**Figure 4.12:** Reaction profiles using N\(_2\) for a) \(\text{Ar}_2\text{H}\) at m/z 77 and b) \(\text{Ar}_2\text{H}_2\) at m/z 82 with an RPq 0.60. Blank signal (○, left y-axis, dashed line extrapolated to 0.1 c s\(^{-1}\)), 1 ppb Se standard signal (●, left y-axis) and estimated limit of detection (solid line, right y-axis) are shown. The true reaction gas flow is shown on the top x-axis.
Figure 4.12b shows a small decrease in Ar$_2$H$_2^+$ signal as a function of N$_2$ flow into the reaction cell. A detection limit of 5 ppt was achieved at 0.8 Ar equivalent mL min$^{-1}$ flow rate. If the flow rate was optimized for $^{80}$Se$^+$ (0.7 Ar equivalent mL min$^{-1}$), the estimated detection limits for $^{77}$Se$^+$ and $^{82}$Se$^+$ were 11 and 5 ppt respectively. BEC’s were 18 ppt at m/z 77 and 9 ppt at m/z 82. Without using a reaction gas, the LOD’s for $^{77}$Se$^+$ and $^{82}$Se$^+$ were 42 and 13 ppt, respectively.

Neither ionization potentials nor bond dissociation energies have been established for Ar$_2$H$^+$ or Ar$_2$H$_2^+$. Since little scattering loss is observed with the 1 ppb Se standard, it is likely that the blank signals are decreased by CID. Improvements in blank cleanliness would further improve the detection limits of both $^{77}$Se and $^{82}$Se.

4.8 Removal of Polyatomic BrH$^+$

$^{79}$BrH and $^{81}$BrH overlap $^{80}$Se and $^{82}$Se and may be a problem in biological matrices such as urine, where an abundance of Br is present. A 10 ppm Br solution produces BrH$^+$ in the plasma as high as 10,000 c s$^{-1}$ at m/z 82, compared to < 100 c s$^{-1}$ in a matrix with no Br present. For $^{82}$Se$^+$, the estimated LOD in a 10 ppm Br matrix is degraded from about 20 ppt (clean matrix) to 15,000 ppt. A reaction gas is needed that will reduce BrH$^+$ as well as argide interferences (table 4.1). Xe$^{39}$ and D$_2$$^{52}$ have been used to attenuate the Ar$_2^+$ signal while simultaneously avoiding production of BrH$^+$ inside the reaction cell. However, Xe causes significant sensitivity losses due to scattering (figure 4.1d) and D$_2$ causes $^{74}$SeD, $^{76}$SeD and $^{80}$SeD overlaps on $^{76}$Se, $^{78}$Se and $^{82}$Se. BrH$^+$ has an ionization potential of 11.66 eV$^{23}$ and has bond dissociation energy of 3.9 eV.$^{69}$ Of the gases studied here, BrH$^+$ will undergo a charge transfer reaction with
NH₃ only. Figures 4.13 a–f show the measured signal at m/z 82 from three different solutions: a 3% CH₃OH matrix (clean blank), a 3% CH₃OH matrix with 10 ppm Br (Br blank), and a 1 ppb Se matrix matched standard (Se standard). Figure 4.13a shows the charge transfer reaction between BrH⁺ and NH₃ as the flow is increased from 0 to 0.15 Ar equivalent mL min⁻¹. At 0.2 Ar equivalent mL min⁻¹, the slope changes and the estimated detection limit is blank contamination limited (8 ppt at 0.4 Ar equivalent mL min⁻¹).
Figure 4.13: Reaction profiles for a) NH₃, b) CH₄, c) H₂, d) N₂, e) CO and f) CH₃F with RPq = 0.60. ‘Clean’ blank signal (□, left y-axis), 10 ppm Br matrix blank (○, left y-axis) and 1 ppb Se standard signal in 10 ppm Br matrix (●, left y-axis) and estimated limit of detection (solid line, right y-axis) measured at m/z 82 are shown. The true reaction gas flow is shown on the top x-axis.

As CH₄ flow rate is increased from 0 to 0.2 Ar equivalent mL min⁻¹, both the blank and standard Br matrix signals increase from ~5,000 c s⁻¹ to ~30,000 c s⁻¹.
indicating that $^{82}\text{BrH}^+$ is being formed inside the reaction cell. If BrH$^+$ is formed by reaction of CH$_4$, the predicted reactants are neutral CH$_4$ and Br$^+$. An RPq of 0.95 would be required to reject $^{79}\text{Br}^+$ during measurement of $^{80}\text{Se}^+$. This condition is not practical because the transmission of the DRC is severely lowered as RPq gets very close to 1.0. At flow rates between 0.2 and 1.5 Ar equivalent mL min$^{-1}$, BrH$^+$ signal decreases. The lowest estimated detection limits from a 1 ppb Se$^+$ solution were degraded from 6 ppt (3% ‘clean’ methanol matrix at 0.6 Ar equivalent mL min$^{-1}$) to 126 ppt (10 ppm Br matrix; 1.15 Ar equivalent mL min$^{-1}$). The BEC at the optimized CH$_4$ flow rate was increased from 13 ppt (3% methanol matrix) to 714 ppt (10 ppm Br matrix) due to the presence of BrH$^+$. The use of CH$_4$ to chemically resolve Ar$_2^+$ from Se$^+$ is not recommended if Br is present, since the detection limit is never blank contamination limited. The minimum estimated detection limits of $^{80}\text{Se}^+$ were similarly increased from 3 ppt to 34 ppt due to the presence of $^{79}\text{BrH}^+$.

BrH$^+$ is also a byproduct when H$_2$ is used as a reaction gas (figure 4.13c).$^{38,54}$ In the matrix with no Br, the minimum estimated $^{82}\text{Se}^+$ LOD was 5 ppt at 1.0 Ar equivalent mL min$^{-1}$. In the 10 ppm Br matrix, the estimated $^{82}\text{Se}^+$ LOD was 619 ppt with a BEC of 36,000 ppt. Again, the detection limit was never blank contamination limited.

Using N$_2$ reaction gas, BrH$^+$ that was formed in the ICP was almost reduced to ‘clean’ matrix levels at 1.5 Ar equivalent mL min$^{-1}$ (figure 4.13d). The LOD of $^{82}\text{Se}^+$ in a 10 ppm Br matrix (18 ppt at 1.45 Ar equivalent mL min$^{-1}$) was close to the LOD in a clean matrix (5 ppt at 0.7 Ar equivalent mL min$^{-1}$). $^{80}\text{Se}^+$ estimated detection limits from the Br matrix (6 ppt) were also close to detection limits in the clean matrix (4 ppt).
CH$_3$F and CO were also examined as reaction gases for chemical resolution from BrH$^+$. The reaction profiles can be seen in figures 4.13e – f respectively. Although CH$_3$F appears to form BrH$^+$ in the reaction cell, subsequent reaction between BrH$^+$ and CH$_3$F decreases the blank signal to ‘clean’ levels at 1.5 Ar equivalent mL min$^{-1}$ flow rate. CO does not show any BrH$^+$ formation inside the reaction cell.

4.9 Removal of polyatomic ArCl$^+$ interferent with $^{77}$Se$^+$

$^{40}$Ar$^{37}$Cl$^+$ overlaps $^{77}$Se$^+$ in a matrix that contains chloride such as seawater or hydrochloric acid. A 2% HCl matrix blank and a matrix matched 10 ppb Se standard were measured as a function of reaction gas flow to determine which gases would resolve $^{77}$Se$^+$ from $^{40}$Ar$^{37}$Cl$^+$. The gas that most efficiently removed ArCl$^+$ was NH$_3$. The signal at m/z 75 was able to be reduced by about 5 orders of magnitude using NH$_3$ reaction gas (figure 4.14). The ionization potential of ArCl has not been published. NH$_3$ has the lowest ionization potential of any reaction gases studied, so it is possible that the reaction between ArCl$^+$ and NH$_3$ proceeds through a charge transfer mechanism.
Figure 4.14: Signals normalized to the vented mode (no gas) signal due to CID and reaction (NH₃ only) of ArCl⁺ observed at m/z 75. Reaction gas: Ne (○), CH₄ (□), N₂ (●), Ar (▲), CO (♦) and NH₃ (+).

If the energy (E_{ion}) of ⁴⁰Ar³⁷Cl⁺ entering the reaction cell is estimated to be 8 eV, a gas collision partner with mass larger than 25 amu can cause CID of ⁴⁰Ar³⁷Cl⁺ (upper limit D₀ = 2 eV). The ⁴⁰Ar³⁵Cl⁺ signal from a 2% HCl solution decreased from 10,000 c s⁻¹ to < 10 c s⁻¹ using both N₂ and CO, and was reduced to 15 c s⁻¹ using Ar. The reduction in ArCl⁺ signal is likely due to CID for CO, N₂ and Ar, since each of these gases is heavy enough to dissociate ArCl⁺ upon a single collision. For Ne and CH₄, the signal was only lowered 2 orders of magnitude. The bond dissociation energy of ArCl⁺ has a lower limit of 1.75 eV. If the lower limit of the bond strength of ArCl is used in equation 4.2, gases with mass larger than 22 amu will be able to cause CID upon a single collision.
collision. It can then be hypothesized that the observed signal decrease is a result of scattering. The efficiency of the reduction of ArCl$^+$ is much less than that of Ar$_2^+$ due to the higher bond dissociation energy (2 eV for ArCl$^+$ vs. 1.25 eV for Ar$_2^+$). Figure 4.15a shows the signal from a 2% HCl blank and matrix matched 10 ppb Se standard as a function of N$_2$ gas flow.

![Figure 4.15](image)

**Figure 4.15:** Reaction profile for a) N$_2$ and b) CO with ArCl$^+$ and RPq 0.60 at m/z 77. 2% HCl blank signal (○, left y-axis, dashed line extrapolated to 0.1 c s$^{-1}$), 10 ppb matrix matched Se standard signal (●, left y-axis) and estimated limit of detection (solid line, right y-axis) are shown. The true reaction gas flow is shown on the top x-axis.

The BEC and LOD were improved from 5,300 and 225 ppt to 123 and 24 ppt at 0.8 Ar equivalent mL min$^{-1}$, respectively. Figure 4.15b shows the signal from a 2% HCl blank and matrix matched 1 ppb Se standard as a function of CO gas flow. The BEC and LOD were improved from 4,850 and 170 ppt to 335 and 30 ppt at 0.6 Ar equivalent mL min$^{-1}$. Using CO and N$_2$, contamination limited detection limits were achieved in both a high concentration of Cl and Br, with no additional interferences formed.
4.10 Isotope ratio measurements

If all Se isotopes were measured free from overlaps, the relationship between systematic errors and the difference in mass from a reference isotope would be linear. The slope of this relationship is the instrument mass bias. If interferences do exist and have different magnitudes for each isotope (i.e. the magnitude of $^{76}\text{SeH}^+$ interference on $^{77}\text{Se}^+$ is different than the magnitude of $^{77}\text{SeH}^+$ interference on $^{78}\text{Se}^+$) then the relationship between the systematic errors and the difference in mass from the reference isotope is nonlinear. Reaction gas flow rates and bandpass settings are known to affect the mass bias, and mass biases will be different for each reaction gas. The linear relationship between the systematic errors of the uncorrected Se isotope ratios and the difference in mass from the $^{78}\text{Se}$ reference isotope is shown in figure 4.16. Mathematical corrections for mass bias and interferences were not performed.
Figure 4.16: Relationship between the systematic error from the uncorrected, measured selenium isotope ratios and the difference in mass from the $^{78}$Se$^+$ reference isotope using a) N$_2$ and b) CH$_4$ and RPq = 0.60.

The data points using N$_2$ lie close to the linear mass bias line, while the points from using CH$_4$ are affected by SeH$^+$ overlaps on $^{77}$Se$^+$ and $^{78}$Se$^+$. The mass bias using N$_2$ reaction gas was 2.1% per amu. After a linear mass bias correction factor was applied, the calculated error in measured isotope ratios was less than 2% for each ratio (table 4.7). The primary isotopes of interest, $^{76}$Se, $^{77}$Se, and $^{80}$Se, all had $^{78}$Se isotope ratio errors less than 1%. The small errors after mass bias correction indicate that overlaps were largely removed from the measured signal. The mass bias using CH$_4$ was 3.7% and agreed with a previous report (3.2%).$^{37}$ Errors in the $^{76}$Se/$^{78}$Se and $^{77}$Se/$^{78}$Se ratios using CH$_4$ were -4.7 % and -0.1 % respectively, even after correction for mass bias. After correction for SeH$^+$ formation,$^{37,38,72}$ errors for the $^{76}$Se/$^{78}$Se and $^{77}$Se/$^{78}$Se ratios were -1.5% and -8.7% respectively. Even after mathematical correction, the isotope ratios using CH$_4$ were worse than when using N$_2$. 

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One possible reason for the poor isotope ratio accuracy after correction for SeH\(^+\) formation might be differences in the extent of SeH\(^+\) formation which was dependent on which isotope of Se is selected for correction. Figure 4.17 shows the SeH\(^+\) formation as a function of CH\(_4\) flow into the reaction cell measured from the \(^{82}\text{SeH}^+/^{82}\text{Se}^+\), \(^{78}\text{SeH}^+/^{78}\text{Se}^+\), and \(^{80}\text{SeH}^+/^{80}\text{Se}^+\) ratios.

**Figure 4.17:** Ratio of blank subtracted SeH\(^+\) signal to blank subtracted Se\(^+\) signal as a function of CH\(_4\) gas flow (Ar equivalent mL min\(^{-1}\)). Isotope: (●) \(^{82}\text{SeH}^+/^{82}\text{Se}^+\), (▲) \(^{78}\text{SeH}^+/^{78}\text{Se}^+\), (♦) \(^{80}\text{SeH}^+/^{80}\text{Se}^+\).

At 0.6 Ar equivalent mL min\(^{-1}\) CH\(_4\), the SeH\(^+\)/Se\(^+\) ratio varies from 8.4\% \((^{82}\text{SeH}^+/^{82}\text{Se}^+)\) up to 9.9\% \((^{78}\text{SeH}^+/^{78}\text{Se}^+)\). Because the SeH\(^+\)/Se\(^+\) value is not unambiguously known, an incorrect correction factor will have deleterious effects on the accuracy of the isotopic ratios. It is much more desirable to avoid this problem altogether.
by using a reaction gas (e.g. CO or N₂) that does not produce SeH⁺ interferences in the reaction cell.

Table 4.5: Measured selenium isotope ratios by ICP-DRC-MS using N₂ reaction gas at 0.80 Ar equivalent mL min⁻¹ flow and 1 ppb Se in 3% CH₃OH. Count rates are blank corrected and errors are calculated relative to measured intensity at m/z 78. No corrections for mass bias or the spectral overlaps BrH⁺ or SeH⁺ was performed.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Counts (s⁻¹)</th>
<th>Expt. ratio/78</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>78</td>
<td>4813.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>74</td>
<td>163.36</td>
<td>0.033941</td>
<td>-9.4</td>
</tr>
<tr>
<td>76</td>
<td>1813.66</td>
<td>0.376819</td>
<td>-4.4</td>
</tr>
<tr>
<td>77</td>
<td>1500.13</td>
<td>0.312</td>
<td>-2.9</td>
</tr>
<tr>
<td>80</td>
<td>10416.75</td>
<td>2.164</td>
<td>+3.7</td>
</tr>
<tr>
<td>82</td>
<td>1903.68</td>
<td>0.396</td>
<td>+7.7</td>
</tr>
</tbody>
</table>

Table 4.6: Calculated isotope ratios by ICP-DRC-MS using a) N₂, b) CO and c) CH₄ at the optimized flow rate for minimum estimated LOD.

<table>
<thead>
<tr>
<th>Isotope ratio</th>
<th>True isotopic ratio</th>
<th>N₂</th>
<th>N₂</th>
<th>N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Before mass bias correction</td>
<td>After mass bias correction</td>
<td>% Error</td>
</tr>
<tr>
<td>74/78</td>
<td>0.037</td>
<td>0.034</td>
<td>0.0368</td>
<td>-1.678%</td>
</tr>
<tr>
<td>76/78</td>
<td>0.394</td>
<td>0.377</td>
<td>0.393</td>
<td>-0.362%</td>
</tr>
<tr>
<td>77/78</td>
<td>0.321</td>
<td>0.312</td>
<td>0.318</td>
<td>-0.847%</td>
</tr>
<tr>
<td>80/78</td>
<td>2.087</td>
<td>2.164</td>
<td>2.073</td>
<td>-0.691%</td>
</tr>
<tr>
<td>82/78</td>
<td>0.367</td>
<td>0.396</td>
<td>0.362</td>
<td>-1.423%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Isotope ratio</th>
<th>True isotopic ratio</th>
<th>CO</th>
<th>CO</th>
<th>CO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Before mass bias correction</td>
<td>After mass bias correction</td>
<td>% Error</td>
</tr>
<tr>
<td>74/78</td>
<td>0.037</td>
<td>0.035</td>
<td>0.0368</td>
<td>-1.694%</td>
</tr>
<tr>
<td>76/78</td>
<td>0.394</td>
<td>0.383</td>
<td>0.391</td>
<td>-0.915%</td>
</tr>
<tr>
<td>77/78</td>
<td>0.321</td>
<td>0.312</td>
<td>0.315</td>
<td>-1.993%</td>
</tr>
<tr>
<td>80/78</td>
<td>2.087</td>
<td>2.105</td>
<td>2.063</td>
<td>-1.156%</td>
</tr>
<tr>
<td>82/78</td>
<td>0.367</td>
<td>0.377</td>
<td>0.361</td>
<td>-1.634%</td>
</tr>
</tbody>
</table>
### 4.11 Reactions between doubly charged rare earth elements (REE\(^{2+}\)) and \(\text{NH}_3\)

High concentrations of certain rare earth elements (REE) in the +2 ionization state may lead to additional overlaps on Se. The ICP-MS was optimized daily to keep \(M^{2+}/M^+\) less than 3%.\(^{73}\) The amount of \(M^{2+}/M^+\) that form in the ICP is usually less than 0.1%.\(^{74}\) However, a matrix element (possibly a REE with low 2\(^{\text{nd}}\) ionization energy forming 1-3% doubly charged ions) may be 4 to 8 orders of magnitude greater in concentration than Se if the matrix element is present as 0.2% dissolved solid. For example, a 10 ppm matrix of \(^{160}\text{Gd}\) causes a two order of magnitude increase in the BEC of \(^{80}\text{Se}^+\).

Elements that can create +2 ions in the ICP and overlap Se are listed in table 4.7. Only the even mass rare earth elements are listed in table 4.7. Odd mass rare earth elements would produce a +2 ion at a ½ m/z ratio and can be rejected by increasing the mass analyzer resolution to less than 0.5 amu. The estimated formation efficiency of the \(M^{2+}\) ions in the ICP is also shown in table 4.7. The percent of \(M^{2+}\) ions formed was calculated according to the Saha distribution,\(^{75}\) but the estimated plasma temperature was 7,500 K, which is greater than most current ICP-MS plasma temperature estimates.\(^{76,77}\)

<table>
<thead>
<tr>
<th>Isotope ratio</th>
<th>True isotopic ratio</th>
<th>(\text{CH}_4) Before mass bias correction</th>
<th>(\text{CH}_4) After mass bias correction</th>
<th>% Error</th>
<th>After SeH Correction</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>74/78</td>
<td>0.037</td>
<td>0.030</td>
<td>0.034</td>
<td>-7.865%</td>
<td>0.03588</td>
<td>-4.172%</td>
</tr>
<tr>
<td>76/78</td>
<td>0.394</td>
<td>0.349</td>
<td>0.375</td>
<td>-4.762%</td>
<td>0.388435</td>
<td>-1.461%</td>
</tr>
<tr>
<td>77/78</td>
<td>0.321</td>
<td>0.309</td>
<td>0.321</td>
<td>-0.096%</td>
<td>0.293094</td>
<td>-8.691%</td>
</tr>
<tr>
<td>80/78</td>
<td>2.087</td>
<td>2.089</td>
<td>1.933</td>
<td>-7.392%</td>
<td>1.973795</td>
<td>-5.428%</td>
</tr>
<tr>
<td>82/78</td>
<td>0.367</td>
<td>0.413</td>
<td>0.352</td>
<td>-4.257%</td>
<td>0.356102</td>
<td>-3.041%</td>
</tr>
</tbody>
</table>
The percent of ions that exist in the +2 state in table 4.7 may be treated as a upper estimate.

**Table 4.7:** Selenium isotopes and possible doubly charged rare earth overlaps. The element and isotopes of the rare earth overlaps are listed along with first and second ionization potentials and estimated formation of $M^{2+}$.

<table>
<thead>
<tr>
<th>Analyte $^a$</th>
<th>Overlaps $^b$</th>
<th>1$^{\text{st}}$ ionization potential (eV)</th>
<th>2$^{\text{nd}}$ ionization potential (eV)</th>
<th>$% \text{ M}^{2+}/\text{M}_{\text{total}}$ $^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{74}\text{Se}^+$</td>
<td>$^{148}\text{Sm}^{++}$</td>
<td>5.64</td>
<td>11.07</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td>$^{148}\text{Nd}^{++}$</td>
<td>5.52</td>
<td>10.73</td>
<td>5.16</td>
</tr>
<tr>
<td>$^{76}\text{Se}^+$</td>
<td>$^{152}\text{Eu}^{++}$</td>
<td>5.67</td>
<td>11.24</td>
<td>5.00</td>
</tr>
<tr>
<td></td>
<td>$^{152}\text{Sm}^{++}$</td>
<td>5.64</td>
<td>11.07</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td>$^{152}\text{Gd}^{++}$</td>
<td>6.15</td>
<td>12.09</td>
<td>1.66</td>
</tr>
<tr>
<td>$^{77}\text{Se}^+$</td>
<td>$^{154}\text{Eu}^{++}$</td>
<td>5.67</td>
<td>11.24</td>
<td>5.00</td>
</tr>
<tr>
<td></td>
<td>$^{154}\text{Sm}^{++}$</td>
<td>5.64</td>
<td>11.07</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td>$^{154}\text{Gd}^{++}$</td>
<td>6.15</td>
<td>12.09</td>
<td>1.66</td>
</tr>
<tr>
<td>$^{78}\text{Se}^+$</td>
<td>$^{156}\text{Gd}^{++}$</td>
<td>6.15</td>
<td>12.09</td>
<td>1.66</td>
</tr>
<tr>
<td></td>
<td>$^{156}\text{Dy}^{++}$</td>
<td>5.93</td>
<td>11.67</td>
<td>2.98</td>
</tr>
<tr>
<td>$^{80}\text{Se}^+$</td>
<td>$^{160}\text{Tb}^{++}$</td>
<td>5.86</td>
<td>11.52</td>
<td>3.72</td>
</tr>
<tr>
<td></td>
<td>$^{160}\text{Dy}^{++}$</td>
<td>5.93</td>
<td>11.67</td>
<td>2.98</td>
</tr>
<tr>
<td></td>
<td>$^{160}\text{Gd}^{++}$</td>
<td>6.15</td>
<td>12.09</td>
<td>1.66</td>
</tr>
<tr>
<td>$^{82}\text{Se}^+$</td>
<td>$^{164}\text{Dy}^{++}$</td>
<td>5.93</td>
<td>11.67</td>
<td>2.98</td>
</tr>
<tr>
<td></td>
<td>$^{164}\text{Er}^{++}$</td>
<td>6.11</td>
<td>11.93</td>
<td>1.55</td>
</tr>
<tr>
<td></td>
<td>$^{164}\text{Ho}^{++}$</td>
<td>6.02</td>
<td>11.80</td>
<td>3.33</td>
</tr>
</tbody>
</table>

Reaction gases with ionization energies greater than that of Se (9.75 eV) and less than the 2$^{\text{nd}}$ ionization potential of the REE’s (ranging from 10.73 to 12.09 eV) should be chosen for resolution via a charge transfer reaction. NH$_3$ fits this criterion by possessing an ionization potential of 10.07 eV. Although the reactions between NH$_3$ and REE$^{2+}$ are
thermodynamically allowed, they may proceed slowly if the reaction has a small kinetic rate constant. Kinetic rate constants for the reactions of REE$^{2+}$ with NH$_3$ are currently not known. The signal to background ratio (S/B) for Se will be improved only if the +2 ions react faster with NH$_3$ than Se$^+$. Se$^+$ has previously been shown to endothermically charge transfer with NH$_3$ (figure 4.1c). Signals at all m/z between 74 and 82 were monitored from a blank solution, a solution containing 10 ppm REE, and a solution containing 10 ppm REE with 10 ppb Se. The rare earth elements Eu, Tb, Ho and Er are not discussed due to low isotopic abundance (<10%) at masses twice that of selenium.

As the NH$_3$ flow into the reaction cell increases, the signal due to REE$^{2+}$ decreases in agreement with previous studies of reactions between +2 ions and NH$_3$.

![Figure 4.18](image_url)

**Figure 4.18:** Reaction profile from 10 ppm $^{148}$Nd$^{2+}$ (□), $^{152}$Sm$^{2+}$ (○), $^{160}$Gd$^{2+}$ (●), $^{164}$Dy$^{2+}$ (▲) with NH$_3$ at RPq 0.25. The signals were measured at m/z 74, 76, 80 and 82 respectively.
Each REE\(^{2+}\) signal is decreased, but Gd\(^{2+}\) reacts fastest, followed by Sm\(^{2+}\), Nd\(^{2+}\) and Dy\(^{2+}\). The improvement in Se/REE\(^{2+}\) S/B can be seen in figure 4.19 a – d.
Figure 4.19: Ratio of 10 ppb Se\(^+\) divided by REE\(^{2+}\) signal from 10 ppm a) Sm solution measured at m/z 74 (○), 76 (●), and 77 (▲), b) Gd, c) Nd and d) Dy as a function of reported NH\(_3\) flow into the reaction cell. True NH\(_3\) flow is shown on the top x-axis.

The signal to Sm\(^{2+}\) ratios for Se and Sm were increased from 0.4 to 1.5, 8 and 8 for \(^{74}\text{Se}^+\), \(^{76}\text{Se}^+\) and \(^{77}\text{Se}^+\), respectively. Although S/B ratio is increased, the reaction of Se\(^+\) with NH\(_3\) (section 4.4.1 and figure 4.1c) is almost as fast as the reaction between
Sm\textsuperscript{2+} and NH\textsubscript{3}. Therefore the estimated detection limits were only marginally improved from 60, 41 and 46 ppt to 40, 4.5 and 11 ppt for \textsuperscript{74}Se\textsuperscript{+}, \textsuperscript{76}Se\textsuperscript{+} and \textsuperscript{77}Se\textsuperscript{+}, respectively.

The signal to Gd\textsuperscript{2+} ratio was increased from 0.25 to 2,000 and 1.4 to 100,000 for \textsuperscript{78}Se and \textsuperscript{80}Se respectively. The large increase in signal to Gd\textsuperscript{2+} ratio can be attributed to the fast reaction between Gd\textsuperscript{2+} and NH\textsubscript{3}. The estimated detection limits for \textsuperscript{78}Se\textsuperscript{+} and \textsuperscript{80}Se\textsuperscript{+} were improved from 320 and 400 ppt to 24 and 14 ppt respectively. Because neither Dy\textsuperscript{2+} nor Nd\textsuperscript{2+} reacted quickly with NH\textsubscript{3}, and due to the low isotopic abundance of \textsuperscript{74}Se and \textsuperscript{82}Se, the S/B ratios did not increase as dramatically as Gd\textsuperscript{2+}. The \textsuperscript{74}Se\textsuperscript{+}/\textsuperscript{148}Nd\textsuperscript{2+} ratio increased from 0.008 to 0.04, and the \textsuperscript{82}Se\textsuperscript{+}/\textsuperscript{164}Dy\textsuperscript{2+} ratio increased from 0.02 to 0.07. NH\textsubscript{3} provided a significant improvement in detection limits for a Gd matrix, moderate improvement for a Sm matrix, and negligible improvements for the Nd and Dy matrices.

4.12 Conclusions

14 gases were examined to determine the best possible reaction gas to overcome overlaps on all 6 Se isotopes. Sensitivities varied from 700 using Xe to >10,000 c s\textsuperscript{-1} ppb\textsuperscript{-1} using N\textsubscript{2}. CH\textsubscript{3}F, C\textsubscript{2}H\textsubscript{6}, CH\textsubscript{4}, CD\textsubscript{4}, CO, N\textsubscript{2}, N\textsubscript{2}O, NH\textsubscript{3}, O\textsubscript{2}, SF\textsubscript{6} and Xe all provided contamination limited detection limits for the major selenium isotope, \textsuperscript{80}Se\textsuperscript{+}. Although Ar and Ne improved the S/B ratio, the Ar\textsubscript{2}\textsuperscript{+} signal was unable to be reduced to less than 0.1 c s\textsuperscript{-1}.

CH\textsubscript{3}F, C\textsubscript{2}H\textsubscript{6}, CH\textsubscript{4}, N\textsubscript{2}O, NH\textsubscript{3} and O\textsubscript{2} reacted with Se\textsuperscript{+} and reduced the sensitivity. SF\textsubscript{6} and Xe are heavy gases and cause significant ion scattering, which reduces the
measured Se⁺ sensitivity. Tables 4.8 and 4.9 list the analytical figures of merit for 13 different reaction gases studied. CD₃ is not included.

**Table 4.8:** Analytical figures of merit for each reaction gas that undergoes a charge transfer reaction with Ar₂⁺ at the minimum estimated limit of detection of ⁸⁰Se. All values are taken from a 3% CH₃OH matrix and matrix matched 1 ppb Se standard.

<table>
<thead>
<tr>
<th>Flow (Ar equivalent mL min⁻¹)</th>
<th>C₂H₆</th>
<th>CH₃F</th>
<th>CH₄</th>
<th>CO</th>
<th>N₂O</th>
<th>NH₃</th>
<th>O₂</th>
<th>SF₆</th>
<th>Xe</th>
</tr>
</thead>
<tbody>
<tr>
<td>⁸⁰Se Sensitivity (cps/ppb)</td>
<td>1,929</td>
<td>6,668</td>
<td>6,620</td>
<td>9,343</td>
<td>4,404</td>
<td>2,589</td>
<td>6,370</td>
<td>966</td>
<td>766</td>
</tr>
<tr>
<td>⁸⁰Se BEC (ppt)</td>
<td>69</td>
<td>6</td>
<td>14</td>
<td>15</td>
<td>21</td>
<td>8</td>
<td>11</td>
<td>28</td>
<td>21</td>
</tr>
<tr>
<td>Measured ⁸⁰Se 3σ LOD (ppt)</td>
<td>4</td>
<td>2</td>
<td>4</td>
<td>7</td>
<td>5</td>
<td>3</td>
<td>12</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>⁷⁴Se Estimated LOD (ppt)</td>
<td>561</td>
<td>119</td>
<td>321</td>
<td>125</td>
<td>615</td>
<td>83</td>
<td>533</td>
<td>949</td>
<td>624</td>
</tr>
<tr>
<td>⁷⁶Se Estimated LOD (ppt)</td>
<td>43</td>
<td>7</td>
<td>30</td>
<td>11</td>
<td>35</td>
<td>17</td>
<td>29</td>
<td>17</td>
<td>47</td>
</tr>
<tr>
<td>⁷⁷Se Estimated LOD (ppt)</td>
<td>126</td>
<td>8</td>
<td>54</td>
<td>23</td>
<td>33</td>
<td>13</td>
<td>27</td>
<td>39</td>
<td>51</td>
</tr>
<tr>
<td>⁷⁸Se Estimated LOD (ppt)</td>
<td>20</td>
<td>4</td>
<td>7</td>
<td>4</td>
<td>9</td>
<td>5</td>
<td>6</td>
<td>6</td>
<td>10</td>
</tr>
<tr>
<td>⁸⁰Se Estimated LOD (ppt)</td>
<td>13</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>5</td>
<td>4</td>
<td>3</td>
<td>11</td>
<td>12</td>
</tr>
<tr>
<td>⁸²Se Estimated LOD (ppt)</td>
<td>9</td>
<td>7</td>
<td>9</td>
<td>6</td>
<td>12</td>
<td>9</td>
<td>7</td>
<td>14</td>
<td>16</td>
</tr>
</tbody>
</table>

**Table 4.9:** Analytical figures of merit for each reaction gas that does not undergoes a charge transfer reaction with Ar₂⁺ at the minimum estimated limit of detection of ⁸⁰Se. All values are taken from a 3% CH₃OH matrix and matrix matched 1 ppb Se standard.

<table>
<thead>
<tr>
<th>Flow (Ar equivalent mL min⁻¹)</th>
<th>Ar</th>
<th>H₂</th>
<th>He</th>
<th>Ne</th>
<th>N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>⁸⁰Se Sensitivity (cps/ppb)</td>
<td>5,225</td>
<td>7,731</td>
<td>4,455</td>
<td>5,995</td>
<td>10,809</td>
</tr>
<tr>
<td>⁸⁰Se BEC (ppt)</td>
<td>15</td>
<td>301</td>
<td>242,422</td>
<td>5</td>
<td>13</td>
</tr>
<tr>
<td>Measured ⁸⁰Se 3σ LOD (ppt)</td>
<td>5</td>
<td>16</td>
<td>4</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>⁷⁴Se Estimated LOD (ppt)</td>
<td>126</td>
<td>388</td>
<td>1185</td>
<td>276</td>
<td>155</td>
</tr>
<tr>
<td>⁷⁶Se Estimated LOD (ppt)</td>
<td>7</td>
<td>22</td>
<td>282</td>
<td>17</td>
<td>11</td>
</tr>
<tr>
<td>⁷⁷Se Estimated LOD (ppt)</td>
<td>6</td>
<td>31</td>
<td>139</td>
<td>18</td>
<td>12</td>
</tr>
<tr>
<td>⁷⁸Se Estimated LOD (ppt)</td>
<td>3</td>
<td>5</td>
<td>52</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>⁸⁰Se Estimated LOD (ppt)</td>
<td>4</td>
<td>13</td>
<td>700</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>⁸²Se Estimated LOD (ppt)</td>
<td>6</td>
<td>5</td>
<td>20</td>
<td>8</td>
<td>6</td>
</tr>
</tbody>
</table>
N₂ and CO were the best reaction gases to eliminate or severely reduce Ar₂⁺, ArCl⁺, BrH⁺, Ar₂H⁺, and Ar₂H₂⁺. CO and N₂ provided contamination limited detection limits and did not produce additional Se⁺ overlaps. Further, the generally inert nature of N₂ may allow its use in instruments that lack dynamic bandpass tuning (octopole and hexapole collision cells). N₂ should be used in future Se tracer studies because it offers access to overlap free measurement of multiple Se isotopes.

NH₃ was also investigated to provide chemical resolution of Se from doubly charged rare earth overlaps. NH₃ reacted quickly with Gd²⁺ and improved the detection limit of ⁸⁰Se⁺ by an order of magnitude. The reaction between NH₃ and Sm²⁺, Dy²⁺ and Nd²⁺ proceeded slowly and did not significantly improve detection limits of Se isotopes overlapped by these REE²⁺. It appears as though the charge transfer mechanism between the REE²⁺ matrix elements and NH₃ is a slow reaction, but SIFT-MS work is needed to confirm this suspicion.


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68. Evangelos G. Bakalbassis, Maria-Aglaia D. Stiakaki, Athanasios C. Tsipis and Constantinos A. Tsipis, Ground and excited state properties of the cationic and...


78. Deanna M. Rago Jones, *A study of ion-molecule reactions in a dynamic reaction cell to improve elemental analysis with inductively coupled plasma-mass spectrometry*. 2007, PhD, The Ohio State University.
5  $^{87}\text{Rb}$ and $^{87}\text{Sr}$ chemical resolution using SF$_6$ and ICP-DRC-MS

5.1  Abstract

ICP-DRC-MS can overcome spectral overlaps by taking advantage of differences in reactivity between a gas and the analyte/overlap. Chemical resolution of $^{87}\text{Rb}^+$ from $^{87}\text{Sr}^+$ using SF$_6$ requires a low pass filter and is believed to be the first case to do so. Reasons why a low pass filter is needed, considerations and optimization procedures for applying the filter as well as analysis results of a mixture of Rb and Sr are reported.

5.2  Introduction

$^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{86}\text{Sr}$ ratios can be used for age determination of a sample because $^{87}\text{Sr}$ forms from the $\beta^-$ decay of $^{87}\text{Rb}$ with a $\frac{1}{2}$ life of 48.8 billion years. $^{2, 3} \beta^-$ decay converts a proton to a neutron and emits an electron and an antineutrino electron ($\bar{\nu}_e$).

$$^{87}_{37}\text{Rb} \rightarrow ^{87}_{38}\text{Sr} + e^- + \bar{\nu}_e$$

Dating is performed by determining the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio of several co-genetic minerals and rocks and then plotting these as a function of corresponding $^{87}\text{Rb}/^{86}\text{Sr}$ ratios. $^{4-6}$ This plot is named an “isochron diagram” and its slope is proportional
to the age of the sample while the y-axis intercept is the initial $^{87}\text{Sr}^{86}\text{Sr}$ ratio. The age of sample can be determined according to equation 5.1.

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{\tau} = \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{0} + \lambda_{87} \tau$$  \hspace{1cm} (5.1)

where $\lambda_{87}$ is the decay constant of $^{87}\text{Rb}$; and $\tau$ is time. If $\lambda_{87}\tau$ is assumed to be small, the age of a rock may be determined by equation 5.2:

$$\tau = \frac{\left(\frac{^{86}\text{Sr}}{^{87}\text{Sr}}\right)_{\tau} - \left(\frac{^{86}\text{Sr}}{^{87}\text{Sr}}\right)_{0}}{\lambda_{87}}$$  \hspace{1cm} (5.2)

It is necessary to measure $^{86}\text{Sr}$, $^{87}\text{Sr}$ and $^{87}\text{Rb}$ from the same sample at the same time to determine the isochron slope which is proportional to the age of a sample.

Similar geochronology isotope combinations include U/Th/Pb, K/Ar, Sm/Nd, Lu/Hf, Rh/Os and K/Ca. The Rb/Sr geochronology pair is especially valued because Rb may replace K and Sr may replace Ca in biologically relevant specimens. The intensity at m/z 87 cannot be calculated from natural isotopic ratios because $^{87}\text{Rb}$ decays to $^{87}\text{Sr}$ so neither is a stable isotope. Sr must be separated from Rb through ion chromatography, electrothermal vaporization or ion-molecule reactions.

### 5.2.1 Previous Sr$^+$ – Rb$^+$ measurements

Rb-Sr geochronology is traditionally done using thermal ionization mass spectrometry (TIMS). TIMS provides a stable signal and precise isotope ratio measurements but requires separation of Sr and Rb from the sample matrix. TIMS sample preparation is laborious and requires purification steps, preconcentration and sample loading into a vacuum chamber. An ideal alternative to TIMS would provide...
similar precision, high sensitivity, simple sample preparation procedures while maintaining the accuracy and precision of TIMS.

ICP-MS offers simple sample preparation and much higher sample throughput. The Rb-Sr overlap at m/z 87 requires a resolution power of 280,000 (table 5.1) which is unattainable from any commercially available ICP-MS system without chemical resolution. Holcombe’s group has worked on volatility-based separation of Rb-Sr coupled with ICP-multicollector-MS.10 Other research groups have used ion chromatography to separate Sr and Rb before analysis.11-13 Ion chromatography pretreatment induces uncertainty from less than 100% sample recovery and extends the sample preparation time.

The uncertainty in age determination is directly dependent upon the uncertainty in the slope of the isochron.14 A 2% internal RSD using ICP-SF-MS and cation exchange chromatography was shown to have an age uncertainty of 150 Ma which was comparable to analysis of the same sample by TIMS.13

Chemical resolution of Sr and Rb in an ICP-DRC-MS has previously been achieved using ion molecule reactions using CH$_3$F.15 Sr$^+$ and Rb$^+$ have different electron configurations (Table 5.1) and therefore different reactivities.
Table 5.1: Mass, electron configuration and required resolution for measurement of \(^{87}\text{Rb}\) and \(^{87}\text{Sr}\).

<table>
<thead>
<tr>
<th></th>
<th>(^{87}\text{Sr}^+)</th>
<th>(^{87}\text{Rb}^+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass (amu)</td>
<td>86.90887</td>
<td>86.90918</td>
</tr>
<tr>
<td>e(^-) configuration</td>
<td>[Kr]5s(^1)</td>
<td>[Ar]3d(^{10})4s(^2)4p(^6)</td>
</tr>
<tr>
<td>Resolution (m/(\Delta m))</td>
<td>280,000</td>
<td>280,000</td>
</tr>
</tbody>
</table>

\(\text{Rb}^+\) has a noble gas electron configuration and is nonreactive with many gases. \(\text{Sr}^+\) has a lone electron in the 5s orbital and is very reactive with many reaction gases, forming \(\text{SrF}^+\) from a reaction with \(\text{CH}_3\text{F}\). The concentration of \(^{87}\text{Sr}^+\) may be determined from the \(^{87}\text{Sr}^{19}\text{F}^+\) signal at \(m/z\) 106.

Although \(\text{CH}_3\text{F}\) had previously been used for chemical resolution\(^\text{15}\) it was later published that internal correction for mass discrimination among \(\text{Sr}\) isotopes did not produce accurate results.\(^\text{16}\) Reaction gas flow rate, bandpass settings and matrix compositions were found to affect the accuracy of the measuring isotope ratios. It has been suggested that a reaction with a larger rate constant than with \(\text{CH}_3\text{F}\) might offer more accurate isotope ratio measurements.\(^\text{17}\) If the reaction proceeded more quickly, then conversion of \(\text{Sr}^+\) to \(\text{SrF}^+\) would be completed at a lower cell pressure and the effects of reaction gas flow rate would be lessened. Bohme’s group\(^\text{17}\) has suggested the “clear first choice” reaction gas for \(\text{Rb/Sr}\) chemical resolution to be \(\text{SF}_6\), which is nonreactive with \(\text{Rb}^+\) but reacts efficiently with \(\text{Sr}^+\) to form \(\text{SrF}^+\) (table 5.2).
Table 5.2: Rate coefficients for the reactions of Rb$^+$ and Sr$^+$ with nine neutral reaction gases.

<table>
<thead>
<tr>
<th>Neutral reaction gas</th>
<th>Reaction gas mass (amu)</th>
<th>Rb$^+$ rate coefficient$^{17,18}$ $(10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$</th>
<th>Sr$^+$ rate coefficient$^{17,18}$ $(10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$</td>
<td>32</td>
<td>$&lt; 0.0001$</td>
<td>0.0020</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>44</td>
<td>$&lt; 0.001$</td>
<td>0.63</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>28</td>
<td>$&lt; 0.005$</td>
<td>$&lt; 0.006$</td>
</tr>
<tr>
<td>CS$_2$</td>
<td>76</td>
<td>$&lt; 0.01$</td>
<td>0.11</td>
</tr>
<tr>
<td>D$_2$O</td>
<td>20</td>
<td>0.046</td>
<td>0.030</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>17</td>
<td>0.0055</td>
<td>0.0049</td>
</tr>
<tr>
<td>CH$_3$F</td>
<td>34</td>
<td>0.067</td>
<td>0.14</td>
</tr>
<tr>
<td>CH$_3$Cl</td>
<td>50</td>
<td>0.0054</td>
<td>0.39</td>
</tr>
<tr>
<td>SF$_6$</td>
<td>146</td>
<td>$&lt; 0.001$</td>
<td>5.7</td>
</tr>
</tbody>
</table>

5.2.2 Prevention of unwanted secondary reactions in the DRC

In ICP-DRC-MS, a wide mass range of ions enter the reaction cell and it is necessary to eject ions that might form product ions at the same mass as the analyte. It became apparent during method development that ions formed from reactions with SF$_6$ interfered with SrF$^+$. The DRC was used to determine the ions’ identity, and DRC bandpass conditions prevented unwanted product ion formation.

The DRC utilizes a quadrupole ion guide that is capable of rejecting reactants from the ion beam and is scanned in concert with the mass analyzer quadrupole to provide a low resolution DRC mass filter.$^{19}$ The user may define the points at which the cutoff both begins (RPq) and ends (RPa), providing an adjustable bandpass to prevent secondary chemistry. The regions of stability for a quadrupole can be described using the Mathieu parameters $a$ and $q$.$^{20}$
where \( n \) is the order of the multipole; \( e \) is the electronic charge; \( V_{DC} \) and \( V_{RF} \) are the direct current and zero to peak radio frequency amplitudes applied between pole pairs; \( m \) is the ion mass; \( \omega \) is the angular frequency and \( r_0 \) is the field radius of the multipole array. The Mathieu parameters are defined by the user by adjusting the related parameters \( R_{Pq} \) and \( R_{Pa} \).

\[
a_n = 4 \frac{e V_{DC}}{m^* \omega^2 r_0^2} \quad (5.3)
\]

\[
q_n = 2 \frac{e V_{RF}}{m^* \omega^2 r_0^2} \quad (5.4)
\]

The DRC provides a bandpass with adjustable widths that change in concert with the analyzer quadrupole. It is synchronized with the scanning mass filter quadrupole to provide optimum analyte transmission and controlled ion-molecule reaction chemistry. The DRC is typically operated in the radio-frequency mode only (RF) to provide a low mass cutoff. A low mass cutoff is often needed because reactants of unwanted secondary ion-molecule reactions are typically lower in mass than their product ions.

To date, no situation has been reported that required a low pass DRC filter (\( R_{Pa} > 0 \)). Although various cases have been suggested,\(^{19}\) no data have been produced that required for a high mass cutoff. One case was reported that required the use of a high mass cutoff but was later revealed that unwanted product ions were a result of vaporizing solvents that were used during instrument cleaning, and not from ions from the ICP.
This chapter focuses on the need to eject SF$_5^+$ while measuring SrF$^+$, examines
the effectiveness of the DRC high pass filter and suggests optimized conditions for the
chemical resolution of Rb$^+$ from Sr$^+$ using SF$_6$. This is a rare case for ICP-DRC-MS that
requires a rejection of a reactant ion with a mass higher than the analyte ion of interest.

5.3 Experimental

The PerkinElmer Sciex Elan 6100 DRC$^{\text{plus}}$ ICP-DRC-MS was used for all
experiments.$^{21}$ A peristaltic pump (Gilson Minipuls 3) delivered solution into a quartz,
concentric nebulizer (TQ-30-A3, Meinhard Glass Products, Golden CO, USA) at a
solution uptake rate of 1 mL min$^{-1}$. A quartz, baffled cyclonic spray chamber (Part
number WE025221, PerkinElmer Sciex) at ambient temperature was used with a 2.0 mm
internal diameter quartz injector (WE023948, PerkinElmer Sciex). Solutions were made
by serial dilution from 1,000 $\mu$g mL$^{-1}$ standard solutions (CPI International, Santa Rosa
CA, USA) in deionized water (18.2 MW cm, Millipore Milli-RO-10 and Milli-Q). Nitric
acid was double distilled (GFS Chemicals, Columbus OH, USA). Measurements were
made with solutions containing 2% v/v HNO$_3$.

Instrument parameters are listed in Table 5.3. Sulfur hexafluoride (99.9%,
Praxair) was introduced through a getter to remove oxygen and water vapor. Flow was
maintained by a mass flow controller (MKS Instruments, USA) calibrated for Ar flow,
with a sulfur hexafluoride conversion factors of 0.19 mL min$^{-1}$ reaction gas per mL min$^{-1}$
Ar equivalent.$^{20}$
Table 5.3: ICP-MS experimental parameters

<table>
<thead>
<tr>
<th>Mass Spectrometer Parameters</th>
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</thead>
<tbody>
<tr>
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<tr>
<td>Analog stage voltage</td>
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</tr>
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<td>1.2 L min⁻¹</td>
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<td>Plasma gas flow</td>
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</tr>
<tr>
<td>Nebulizer flow (optimized daily)</td>
<td>~ 0.8 L min⁻¹</td>
</tr>
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<td>DRC Parameters</td>
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<tr>
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<td>Exit aperture diameter</td>
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<td>RF voltage (peak to peak)</td>
<td>±200 V</td>
</tr>
<tr>
<td>DRC mode cell path voltage</td>
<td>-19 V</td>
</tr>
</tbody>
</table>

| DRC Parameters                                |       |
| Corrective equations                          | None   |
| Mass resolution                               | ~ 0.7 u |

| Signal Measurement                            |       |
| Dwell time                                    | 50 ms  |
| Sweeps                                        | 40     |
| Readings                                      | 1      |
| Replicates                                    | 3      |
| Points per peak                               | 1      |
| Settling time                                 | 200 ms |

5.4 Chemical resolution of Sr⁺ and Rb⁺ using SF₆

Rb⁺ and Sr⁺ may be chemically resolved using a fluorine atom addition reaction.

\[
\text{Rb}^+ + \text{SF}_6 \rightarrow \text{No reaction}
\]

\[
\text{Sr}^+ + \text{SF}_6 \rightarrow \text{SrF}^+ + \text{SF}_5
\]

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Experimental conditions for Rb/Sr resolution were optimized using a published method development procedure. The first step determines how fast the reaction gas reacts with the analyte and overlap ions. The second step optimizes the DRC bandpass to prevent unwanted product ions. Reaction gas flow rate is then reoptimized for the best detection limit and the bandpass is reoptimized at the new gas flow rate.

10 ppb solutions of Rb and Sr were measured separately to independently measure reaction rates and any product ions. Figure 5.1 shows the effect of SF$_6$ gas flow rate on $^{87}$Rb$^+$ and $^{87}$Sr$^+$ signals. Signals were measured at masses corresponding to $^{84}$Sr$^+$, $^{85}$Rb$^+$, $^{86}$Sr$^+$, $^{87}$Rb$^+$, $^{87}$Sr$^+$, $^{88}$Sr$^+$, $^{85}$RbF$^+$, $^{86}$SrF$^+$, $^{87}$RbF$^+$, $^{87}$SrF$^+$ and $^{88}$SrF$^+$ were measured.
Figure 5.1: Signals at m/z 87 produced from a 10 ppb Sr solution (○) and a 10 ppb Rb solution (●) as a function of SF₆ flow rate into the reaction cell at RPq = 0.25.

The Sr⁺ signal decreases by approximately 4 orders of magnitude according to pseudo first order reaction kinetics before reaching Rb contamination limited signals at 0.4 Ar equivalent mL min⁻¹ flow rate. The Rb⁺ signal decreases by only a factor of two at 0.4 Ar equivalent mL min⁻¹ and by a factor of about ten at 0.8 Ar equivalent mL min⁻¹ flow rate. No Rb containing product ions were observed which agrees with ICP-SIFT measurements,¹⁷ and signal decrease can be attributed to scattering losses.

The second step of the DRC method development procedure is to determine whether any product ions are formed at the same m/z as the analyte, and find the best low
mass cutoff (RPq) to reject the reactant ions. No product ions were observed to form at m/z 87, and $^{87}\text{Rb}^+$ may be measured at this m/z. The proposed method to resolve $^{87}\text{Rb}^+$ from $^{87}\text{Sr}^+$ is to “move” the Sr$^+$ signal to m/z 106 in the form of SrF$^+$.

![Graph](image)

**Figure 5.2:** Signals at m/z 106 produced from deionized water (○) and 10 ppb Sr solutions (●) as a function of SF$_6$ flow rate into the reaction cell at RPq = 0.25.

As the SF$_6$ flow rate is increased from 0 to 0.7 Ar equivalent mL min$^{-1}$, the blank signal at m/z 106 increases from about 100 to 30,000 c s$^{-1}$. The blank signal increase indicates an undesired product ion is formed which does not contain Sr. Mass spectra using no gas (vented mode) and 0.25 Ar equivalent mL min$^{-1}$ SF$_6$ were recorded to determine the identity of the product ions.
**Figure 5.3:** Mass spectra measured from a blank solution in the a) vented mode and b) with 0.25 Ar equivalent mL min\(^{-1}\) SF\(_6\) and an RPq of 0.25

Several undesired product ions are formed from SF\(_6\) (Figure 5.3b), including some at the same m/z as the SrF\(^+\) isotopes (m/z 103, 105, 106 and 107). The undesired product ion formation may be prevented by narrowing the bandpass of the DRC quadrupole. The low and high mass cutoffs of the DRC are defined by the RPq and RPa parameters, respectively. RPq was systematically increased to determine the m/z at which reactants were rejected.
Figure 5.4: Signals from blank (○) and 10 ppb Sr (●) as a function of RPq at m/z a) 105, b) 106 and c) 107 measured with 0.25 Ar equivalent mL min\(^{-1}\) SF\(_6\). Low mass cutoff at m/z 44 shown as vertical line.

The effect of RPq (low m/z cutoff) on the measured signal at the m/z 105, 106 and 107 is shown in Figure 5.4. The effect of the low mass cutoff is clearly observed at m/z 106 (figure 5.4b). As RPq is increased from 0.15 to 0.2 the signal increases slightly
due to increased transmission efficiency. As RPq is increased from 0.2 to 0.45 the signal falls by about an order of magnitude before leveling off again. This shoulder suggests that a reactant ion was rejected when RPq was increased from 0.2 to 0.40. At an RPq of 0.40, the low mass cutoff is 44 amu (vertical line, top x-axis) which rejects $^{40}\text{Ar}^+$ from the ion beam. However, the signal does not fall to levels suitable for trace element measurement. At RPq = 0.50 the blank signal at m/z 106 is about 10,000 c s$^{-1}$, indicating that an undesired product ion is still being produced.

A sequence of reactions may produce the undesired product ions. SF$_6$ is known to undergo an exothermic charge transfer reaction with Ar$^+$ with a rate coefficient of 9.3*10$^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.  

\[ \text{Ar}^+ + \text{SF}_6 \rightarrow \text{SF}_6^+ + \text{Ar} \]

The product SF$_6^+$ is unstable and dissociates to SF$_5^+$ and F in approximately a picosecond.  

\[ \text{SF}_6^+ \rightarrow \text{SF}_5^+ + \text{F} \]

SF$_5^+$ may react with SF$_6$ to form molecular fluorine and more product ions.  

\[ \text{SF}_5^+ + \text{SF}_6 \rightarrow \text{SF}_3^+ + \text{F}_2 + \text{SF}_6 \]

S$^+$, F$^+$, SF$^+$, SF$_2^+$, SF$_3^+$, SF$_4^+$, SF$_5^+$, SF$_4^{2+}$ and SF$_2^{2+}$ have all been observed as a result of the ionization and dissociation of SF$_6^+$. These ions may account for many, but not all, of the large signal peaks observed in figure 5.3.
Table 5.4: Observed product ion m/z, proposed ion identities and signals from 0.25 Ar equivalent mL min\(^{-1}\) SF\(_6\) flow and deionized H\(_2\)O.

<table>
<thead>
<tr>
<th>m/z</th>
<th>Proposed identity</th>
<th>Signal (c s(^{-1}))</th>
<th>m/z</th>
<th>Proposed identity</th>
<th>Signal (c s(^{-1}))</th>
<th>m/z</th>
<th>Proposed identity</th>
<th>Signal (c s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>89</td>
<td>(^{32}\text{SF}_3^+)</td>
<td>(&gt;2\times10^6)</td>
<td>104</td>
<td>(^{28}\text{SiF}_4^+)</td>
<td>500,000</td>
<td>108</td>
<td>(^{32}\text{SF}_4^+)</td>
<td>1.8\times10^6</td>
</tr>
<tr>
<td>90</td>
<td>(^{33}\text{SF}_3^+)</td>
<td>163,000</td>
<td>105</td>
<td>(^{29}\text{SiF}_4^+)</td>
<td>143,000</td>
<td>109</td>
<td>(^{33}\text{SF}_4^+)</td>
<td>20,000</td>
</tr>
<tr>
<td>91</td>
<td>(^{34}\text{SF}_3^+)</td>
<td>904,000</td>
<td>106</td>
<td>(^{30}\text{SiF}_4^+)</td>
<td>24,000</td>
<td>110</td>
<td>(^{34}\text{SF}_4^+)</td>
<td>87,000</td>
</tr>
<tr>
<td>93</td>
<td>(^{36}\text{SF}_3^+)</td>
<td>3,500</td>
<td>107</td>
<td>Unknown</td>
<td>87,000</td>
<td>112</td>
<td>(^{36}\text{SF}_4^+)</td>
<td>315</td>
</tr>
</tbody>
</table>

Possible product ions (table 5.4) for each of the major peaks in figure 5.3 were identified by matching the natural isotope patterns to the measured signals (figure 5.5). SiF\(_4\) was introduced to the DRC as an impurity in the SF\(_6\) at a concentration of less than 100 ppm. SiF\(_4\) can undergo an exothermic charge transfer reaction with Ar\(^+\) (\(\Delta H_f = -0.52\) eV).\(^{28,29}\) However, Ar\(^+\) should be ejected from the DRC when RPq is 0.4 at m/z 106, which would prevent the reaction. An endothermic charge transfer reaction between SiF\(_4\) and Ar\(_2^+\) (\(\Delta H_f = +0.74\) eV) should not occur.

Although Ar\(^+\) was rejected at RPq values greater than 0.45, signal intensity 100,000 c s\(^{-1}\) was still measured at m/z 105 from the blank solution. Ar\(_2^+\) is also known to undergo a charge reaction with SF\(_6\) (\(\Delta H_f = -0.1\) eV) to form SF\(_6^+\).

\[
\text{Ar}_2^+ + \text{SF}_6 \rightarrow \text{SF}_6^+ + 2\text{Ar}
\]
**Figure 5.5:** Mass spectrum from figure 5.3b overlaid with isotope patterns of sulfur and silicon and labeled product ion peaks.

The peak at m/z 105 was identified as $^{29}\text{SiF}_4^+$, but the silicon isotope pattern could not account for the total signal (using $^{28}\text{SiF}_4^+$ as the reference isotope), and neither sulfur nor silicon isotope patterns could account for the signal at m/z 107. The peak at this mass was unable to be identified via isotope pattern matching. A higher purity SF$_6$ reaction gas might provide a better clue to the true identity of the peak at m/z 107, or may eliminate it entirely if the peak is due to an unknown impurity.
Figure 5.6: Reactants and product ions involved in forming SrF\(^+\) overlaps. Shaded areas indicate possible unstable m/z ranges using the DRC ion rejection parameters RP\(q\) and RP\(a\). White areas indicate ion m/z with stable trajectories.

A total of four ions from the plasma, two neutral gases, and seven product ions must be considered. Figure 5.6 shows pictorially how each ion is formed and how each might be attenuated by use of the DRC bandpass.

Unwanted product ions are a result of SF\(_6\) reactions with either \(\text{Ar}^+\) and/or \(\text{Ar}_2^+\). \(\text{Ar}_2^+\) may be rejected from the ion beam with RP\(q\) greater than 0.80 which rejects ions with m/z less than 88. As RP\(q\) increases beyond 0.80, transmission efficiency through the DRC decreases and sensitivity is sacrificed. All ion trajectories become unstable as \(q\) exceeds 0.908 (RP\(q\) = 0.96).
Figure 5.7: Effect of RPq on sensitivity of $^{86}\text{SrF}$ (○), $^{87}\text{SrF}$ (◊) and $^{88}\text{SrF}$ (□) at 0.25 Ar equivalent mL min$^{-1}$ SF$_6$ flow rate. Sensitivity calculated from deionized H$_2$O blank and 10 ppb Sr standard solution.

Figure 5.7 shows a rapid reduction in sensitivity as RPq exceeds 0.6. At RPq = 0.5, the DRC rejects m/z less than 50 and sensitivity of $^{88}\text{SrF}^+$ is 5,000 c s$^{-1}$ ppb$^{-1}$. As RPq is increased to 0.7, the sensitivity decreases by an order of magnitude and more than two orders when RPq is increased to 0.8. An RPq value of 0.80 is required to efficiently reject Ar$_2^+$ from the ion beam, but SrF$^+$ sensitivity is also sacrificed. At high RPq values Sr$^+$ stability in the reaction cell decreases quickly, preventing SrF$^+$ formation. Low transmission efficiency of Sr$^+$ accounts for the low sensitivity of SrF$^+$. Ar$^+$ may be
rejected by optimizing RPq, but this optimization procedure is unable to account for Ar$_2^+$. A high mass cutoff might be able to reject SF$_6^+$ and SF$_5^+$ to prevent the formation of the overlapping SF$_4^+$ (see figure 5.6).

A low pass filter may be used by increasing RPa, which is applied by increasing the DC voltage applied to the DRC rods according to equations 5.3 and 5.4. To prevent SF$_4^+$ formation, the DRC must reject both Ar$^+$ (RPq at least 0.50) and SF$_5^+$ (RPa at least 0.053). Ions with m/z 64 to 117 have stable trajectories through the DRC at these values of RPa and RPq (Figure 5.8).

**Figure 5.8:** Stability diagram for m/z 105 with RPq = 0.50 (q= 0.475) and RPa = 0.053 (a=0.10) (●) and scan line of stable ion m/z at these values.
SrF$^+$ signals at m/z 105, 106 and 107 with 0.40 Ar equivalent mL min$^{-1}$ SF$_6$ and RPq = 0.50 are shown as a function of RPa in Figure 5.9.

**Figure 5.9:** Effect of RPa on signal of blank (○) and 10 ppb Sr (●) signals measured at m/z a) 105, b) 106 and c) 107 with RPq = 0.50 and 0.40 Ar equivalent mL min$^{-1}$ SF$_6$. High mass cutoff at m/z 124 shown as vertical line.
The optimized DRC bandpass parameters were found to be RPq = 0.50 and RPa = 0.050 which allow only ions between m/z 64 and 124 to pass. The final step to optimization of DRC conditions is an iterative optimization of reaction gas flow rate and bandpass settings for the lowest detection limit. One iteration was performed and the best conditions were determined to be 0.40 Ar equivalent mL min\(^{-1}\) SF\(_6\), RPq = 0.50 and RPa = 0.044. This DRC bandpass allowed ions from 65 to 130 amu, but it appears that SF\(_5^+\) at m/z 127 was unstable at these settings. The measured sensitivities and counting statistics limited detection limits at RPq = 0.50 and RPa = 0.044 are listed in table 5.5. Values were measured from a mixture of 10 ppb Sr and Rb.

Table 5.5: Analytical figures of merit for 10 ppb Sr and Rb mixture measured with 0.40 mL min\(^{-1}\) SF\(_6\) at RPq = 0.50 and RPa = 0.044 as SrF\(^+\) and in the vented mode as Sr\(^+\).

<table>
<thead>
<tr>
<th></th>
<th>Sensitivity (c s(^{-1}) ppb(^{-1}))</th>
<th>Estimated limit of detection</th>
<th>Vented mode estimated limit of detection</th>
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</thead>
<tbody>
<tr>
<td>(^{86})SrF(^+)</td>
<td>2,091</td>
<td>20 ng L(^{-1})</td>
<td></td>
</tr>
<tr>
<td>(^{87})SrF(^+)</td>
<td>1,344</td>
<td>22 ng L(^{-1})</td>
<td></td>
</tr>
<tr>
<td>(^{88})SrF(^+)</td>
<td>16,057</td>
<td>2.6 ng L(^{-1})</td>
<td></td>
</tr>
<tr>
<td>(^{86})Sr(^+)</td>
<td></td>
<td></td>
<td>24 ng L(^{-1})</td>
</tr>
<tr>
<td>(^{87})Sr(^+)</td>
<td></td>
<td></td>
<td>39,622 ng L(^{-1})</td>
</tr>
<tr>
<td>(^{88})Sr(^+)</td>
<td></td>
<td></td>
<td>113 ng L(^{-1})</td>
</tr>
</tbody>
</table>

This chapter has displayed, for the first time, a need for the use of a high mass cutoff in the DRC for prevention of unwanted secondary chemistry. This is an unusual case because the interfering ion is a result of one charge transfer reaction between the reaction gas and both Ar\(^+\) and Ar\(_2^+\), a spontaneous decomposition of SF\(_6^+\) and finally a reaction between SF\(_6\) and SF\(_5^+\).
Sr/Rb isotope ratios are useful in geochronology only if they can be accurately measured. The chosen gas flow rate, RPq and matrix composition are known to influence the measured isotope ratio in ICP-DRC-MS. To date, no study has examined the effect of RPa on isotope ratios. Figure 5.10 shows the blank subtracted $^{87}\text{Sr}^{+}/^{86}\text{Sr}^{+}$ ratio as a function of RPa at 0.40 Ar equivalent mL min$^{-1}$ SF$_6$ and RPq = 0.50. The natural $^{87}\text{Sr}^{+}/^{86}\text{Sr}^{+}$ isotopic ratio is 0.7099 and denoted by a horizontal line.

**Figure 5.10:** Measured $^{87}\text{Sr}^{+}/^{86}\text{Sr}^{+}$ as a function of RPa at 0.4 Ar equivalent mL min$^{-1}$ SF6 and RPq = 0.50 (○). True value shown (horizontal line, y = 0.7099).

At low RPa values, the $^{87}\text{Sr}^{+}/^{86}\text{Sr}^{+}$ ratio is too high. The backgrounds at m/z 105 and 106 change differently as RPa is increased from 0 to 0.01 (figure 5.9). Isotope
ratios become steady is the signal is dominated by SrF\(^+\) instead of background ions which occurs at RPa values greater than about 0.03. However, the \(^{87}\text{SrF}^+/^{86}\text{SrF}^+\) ratio is lower than the accepted natural isotope ratio value. This cannot be accounted for by mass bias errors, which would produce \(^{87}\text{SrF}^+/^{86}\text{SrF}^+\) ratio higher than the natural value. One explanation that has been proposed to affect the isotope ratio is a decrease of space charge effects in the DRC due to increased ion rejection.\(^{16}\) However this is unlikely to cause much effect, because \(^{87}\text{SrF}^+\) and \(^{86}\text{SrF}^+\) are close in mass to one another and should be affected almost identically from space charge effects. Currently, there is no clear explanation as to why the measured isotope ratio (0.6424) is significantly different than the natural isotope ratio (0.7099), but a lower isotope ratio was also observed using CH\(_3\)F.\(^{15,16}\) The inaccurate isotope ratio may be corrected by using a known reference material.

5.5 Conclusions

A new example of the need for a low pass filter in ICP-DRC-MS has been shown and is due to a chain of reactions that create new overlaps. The overlap is created via a charge transfer reaction between both Ar\(^+\) and Ar\(_2^+\) and SF\(_6\), a spontaneous decomposition of SF\(_6^+\) to SF\(_5^+\), and a reaction between SF\(_6\) and SF\(_5^+\) which forms the overlap SF\(_4^+\). In addition, SiF\(_4^+\) was observed to form within the reaction cell due to a charge transfer reaction with Ar\(^+\). However, the rejection of Ar\(^+\) from the reaction cell was unable to significantly reduce SiF\(_4^+\). Reducing the high mass cutoff from 270 to 130 amu sufficiently prevented the production of SF\(_4^+\) by rejecting SF\(_5^+\) from the DRC. Detection limits for both \(^{86}\text{SrF}^+\) and \(^{87}\text{SrF}^+\) were measured as approximately 20 ppt in a
10 ppb Rb matrix using SF₆. The $^{87}$SrF⁺/$^{86}$SrF⁺ ratio dependence on RPa was shown. No satisfactory explanation has been proposed for why the measured isotope ratios are less than the natural ratios. More work is needed to understand each factor that determines the isotope ratios, how each might be controlled, and how experiments may be designed to ensure quality results.

It has been proposed that SF₆ is superior to CH₃F for resolution of Rb⁺ from Sr⁺ due to a faster atom addition reaction rate with Sr⁺, and slower rate with Rb⁺. CH₃F did not require extensive DRC bandpass tuning, but does form some RbF⁺. SF₆ required an extra step to optimize the DRC bandpass, and once this was finished ppt level $^{87}$Sr⁺ detection limits were measured in the presence of 10 ppb Rb. Neither gas was able to accurately measure the $^{87}$SrF⁺/$^{86}$SrF⁺ ratio, and a known reference standard must be used with both.
Chapter 5 bibliography


11. David De Muynck, Gonzalo Huelga-Suarez, Lana Van Heghe, Patrick Degryse and Frank Vanhaecke, *Systematic evaluation of a strontium-specific extraction chromatographic resin for obtaining a purified Sr fraction with quantitative...*


6 Correlation of ICP-DRC-MS signal decays to kinetic rate constants

6.1 Abstract

Reaction gas flow rate dependent Ar$_2^+$, Ar$^+$ and Sr$^+$ signals are correlated to fundamental kinetic rate coefficients. A simple calculation, assuming that gas exits the reaction cell due only to effusion, is described to estimate the gas pressure in the reaction cell. New kinetic rate constants are determined for the reaction of CH$_3$F with Ar$^+$ and Ar$_2^+$.

6.2 Introduction

Overlaps separated by less than one mass unit from the analyte mass degrade detection limits on an ICP-MS$^1$ but can be circumvented using chemical resolution in a reaction cell.$^{2-6}$ Collision and reaction cells are not used to their full potential because operators may not sufficiently understand the reaction chemistry. Choosing an appropriate reaction gas is critical and is dictated by whether or not the gas reacts efficiently enough with either the overlapping ion by removing it or with the analyte ion to move the analyte to a new mass that does not suffer from an overlap. Thermodynamics dictate whether the reaction will proceed spontaneously, while kinetics describe the rate at which the reaction occurs. This work is meant to explain the
fundamental correlations between the signal, thermodynamics and kinetics of ion-molecule reactions.

6.3 Experimental Details

A PerkinElmer Sciex Elan 6100 DRC+plus ICP-DRC-MS was used for all experiments. A peristaltic pump (Gilson Minipuls 3) delivered liquid to a quartz, concentric nebulizer (TQ-30-A3, Meinhard Glass Products, Golden CO, USA) at a solution uptake rate of 1 mL min\(^{-1}\). A quartz, baffled cyclonic spray chamber (PerkinElmer Sciex) at ambient temperature was used with a 2.0 mm internal diameter quartz injector (PerkinElmer Sciex). Solutions were made by serial dilution from 1,000 \(\mu\)g mL\(^{-1}\) standard solutions (CPI International, Santa Rosa CA, USA) in deionized water (18.2 MW cm, Millipore Milli-RO-10 and Milli-Q). Nitric acid was double distilled (GFS Chemicals, Columbus OH, USA). Solutions used for \(\text{Ar}_2^+\), \(\text{Se}^+\) and \(\text{Ar}^+\) measurement in this study included 3% v/v certified electronic grade anhydrous methanol (Fisher Scientific, Fair Lawn NJ) in order to increase the \(\text{Se}^+\) sensitivity through the carbon enhanced ionization effect. \(\text{Sr}^+\) and \(\text{Rb}^+\) measurements were made with solutions containing 2% v/v \(\text{HNO}_3\).

The ICP-MS had two reaction gas introduction channels. Channel A included a getter to remove oxygen and water impurities. Collision/reaction gases introduced through Channel A included hydrogen (99.999%, Praxair), methane (99.997%, Praxair), nitrogen (99.998%, Praxair), xenon (99.999%, Praxair), argon (99.998%, Praxair), neon (99.999%, Praxair), helium (99.999%, Praxair), carbon monoxide (99.999%, Praxair), nitrous oxide (99.995%, Matheson Tri-gas), methyl fluoride (99.999%, Praxair),
ammonia (99.999%, Scott Specialty Gases), ethane (99.991%, Matheson) and sulfur hexafluoride (99.9%, Praxair). Oxygen (99.999%, Praxair) was introduced through channel B, which did not contain a getter. Both flows were maintained by mass flow controllers (MKS Instruments, USA) calibrated for Ar flow, with conversion factors listed in Table 6.2.

Table 6.1: ICP-MS experimental parameters.

<table>
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<tr>
<th><strong>Mass Spectrometer Parameters</strong></th>
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<tbody>
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<td>Lens voltage</td>
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<td>Analog stage voltage</td>
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<tr>
<td>Auxiliary gas flow</td>
<td>1.2 L min⁻¹</td>
</tr>
<tr>
<td>Plasma gas flow</td>
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<td>Nebulizer flow (optimized daily)</td>
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<td>Exit aperture diameter</td>
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<td>Axial field voltage</td>
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<td>RP_q</td>
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<td>RF voltage (peak to peak)</td>
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<tr>
<td>DRC mode cell path voltage</td>
<td>-19 V</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Analyzer Parameters</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Correction equations</td>
<td>None</td>
</tr>
<tr>
<td>Mass resolution</td>
<td>~ 0.7 u</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Signal Measurement</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Dwell time</td>
<td>500 ms</td>
</tr>
<tr>
<td>Sweeps</td>
<td>4</td>
</tr>
<tr>
<td>Readings</td>
<td>1</td>
</tr>
<tr>
<td>Replicates</td>
<td>7</td>
</tr>
<tr>
<td>Points per peak</td>
<td>1</td>
</tr>
<tr>
<td>Settling time</td>
<td>200 ms</td>
</tr>
</tbody>
</table>
Table 6.2: Actual flow (mL min$^{-1}$) reaction gas per Ar equivalent mL min$^{-1}$ gas flow. Actual gas flow rate calculated by multiplying conversion factor by reported gas flow rate.$^8$

<table>
<thead>
<tr>
<th>Reaction Gas</th>
<th>Conversion factors for other gases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>1.00</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>0.52</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>0.36</td>
</tr>
<tr>
<td>CH$_3$F</td>
<td>0.40</td>
</tr>
<tr>
<td>CO</td>
<td>0.72</td>
</tr>
<tr>
<td>H$_2$</td>
<td>0.70</td>
</tr>
<tr>
<td>He</td>
<td>1.01</td>
</tr>
<tr>
<td>N$_2$</td>
<td>0.72</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>0.51</td>
</tr>
<tr>
<td>Ne</td>
<td>1.05</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>0.53</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0.71</td>
</tr>
<tr>
<td>SF$_6$</td>
<td>0.19</td>
</tr>
<tr>
<td>Xe</td>
<td>0.95</td>
</tr>
</tbody>
</table>

6.4 ICP-DRC-MS ion-molecule reactions

$^{36}$Ar$^+$, $^{40}$Ar$_2^+$ and $^{88}$Sr$^+$ (table 6.3) overlaps were studied because multiple kinetic rate constants were available, the overlaps were common in ICP-MS, and signal intensities were large enough so that decay rates could be measured. Table 6.3 lists the mass, electron configuration and required mass spectral resolution if the analyte and overlap signals were equal.
Table 6.3: Masses, electron configurations, and required resolution for three pairs of analyte/overlaps.

<table>
<thead>
<tr>
<th></th>
<th>$^{40}$Ca$^+$</th>
<th>$^{40}$Ar$^+$</th>
<th>$^{80}$Se$^+$</th>
<th>$^{40}$Ar$_2^+$</th>
<th>$^{87}$Sr$^+$</th>
<th>$^{87}$Rb$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass (amu)</td>
<td>39.96259</td>
<td>39.96238</td>
<td>79.91652</td>
<td>79.92476</td>
<td>86.90887</td>
<td>86.90918</td>
</tr>
<tr>
<td>~Required</td>
<td>190,000</td>
<td>9,700</td>
<td>280,000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Resolution</td>
<td>(m/Δm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The required resolution in table 6.3 cannot be achieved by sector field instruments (m/Δm = 10,000, 10% valley definition) or kinetic energy discrimination (KED). In the case of Ar$_2^+/^{80}$Se$^+$, resolution of 10,000 is still insufficient because the wings of the intense $^{40}$Ar$_2^+$ signal overlap $^{80}$Se$^+$. Chemical resolution takes advantage of differences in chemical reactivity due to electron configurations to attenuate the spectral overlap so that the analyte may be measured with minimal background.  

6.4.1 Review of ion-molecule reaction thermodynamics

Enthalpy change dictates reaction spontaneity and is calculated by the difference in the sum of the heats of formation of the products and the sum of the heats of formation of the reactants.

$$\Delta H_{rxn} = \sum \Delta H_f(products) - \sum \Delta H_f(reactants) \quad (6.1)$$

Endothermic reactions are unlikely to occur if ions in the reaction cell are completely thermalized. However, ions enter the reaction cell with kinetic energy normally $\lesssim 12$ eV. $^8, ^{10}, ^{11}$ Ions can also gain up to 0.4 eV of kinetic energy from the RF field applied to the quadrupole inside the reaction cell. $^4, ^{12}$ Thermodynamics provide reaction specificity if gases provide spontaneous (exothermic) reactions with interfering
ions and non-spontaneous (endothermic) reactions with analyte ions. While thermodynamics predict whether or not the reaction will be spontaneous, kinetic rate constants are needed to predict the reaction efficiency or rate.

### 6.4.2 Review of ion-molecule reaction kinetics

A large number of ion-molecule kinetic rate constants have been established with some that are applicable to ICP-MS overlaps. Selected Ion Flow Technique (SIFT) mass spectrometry is adept at measuring the reaction efficiency of thermalized ions at room temperature. Recently, an ICP-SIFT-MS was built to provide a near universal source of atomic ions.

Reaction efficiency is exponentially dependent on the magnitude of the rate constant, so an established correlation between kinetic rate constants and ICP-DRC-MS signal decays is needed to clearly explain chemical resolution. Ion-molecule relative reaction rates measured by ICP-DRC-MS are often reported as a change in ln(signal) or log(signal) as a function of reaction gas flow rate (mL min$^{-1}$). These rates are helpful in reproducing previous results but do not easily translate to kinetic rate constants, expressed as cm$^3$ molecule$^{-1}$ s$^{-1}$. For an ion-molecule reaction, the reaction kinetics can be described as follows:

\[
A^+ + B \rightarrow \text{products}
\]

\[
Rate = \frac{d[A^+]}{dt} = \frac{d[B]}{dt} = -k[A^+][B] \tag{6.2}
\]

$A^+$ is constantly produced in the plasma (Ar$^+$, Ar$_2^+$, etc.) and so the $[A^+]$ concentration entering the reaction cell can be considered constant. In this case, the
reaction rate is dependent only upon the kinetic rate constant $k$ (cm$^3$ molecule$^{-1}$ s$^{-1}$), and the concentration of neutral reaction gas, $[B]$. 

\[
Rate \approx -k[B] \quad (6.3)
\]

The integrated second order rate law is as follows:

\[
\ln[A^+]_t = \ln[A^+]_0 - kt[B] \quad (6.4)
\]

The ion signal at time $t$, $[A^+]_t$, could be determined from the initial signal, $[A^+]_0$ and the kinetic rate constant multiplied by the ion’s reaction cell residence time and neutral gas density.

\[
kt[B] = (rate \ constant) \times (residence \ time) \times (gas \ density) \quad (6.5)
\]

A plot of $\ln[A^+]$, versus $[B]$ will yield a line with a slope of $-kt$ and a $y$-intercept of $\ln[A^+]_0$. The gas density $[B]$ and ion residence times are not measured on commercial ICP-MS instruments. Instead, the PerkinElmer Sciex Elan DRC instrument reports only the Ar equivalent reaction gas flow rates into the cell. A conversion from flow rate (Ar equivalent mL min$^{-1}$) to gas density (mTorr, molecule cm$^3$) is needed.

Gas density (pressure) in the cell can be estimated if the flow of reaction gas out of the cell is primarily due to effusion. Gas effusion through an orifice (gas flow out of the cell) is inversely proportional to the square root of the atomic weight of the gas (figure 6.1).26
Figure 6.1: Estimated pressure inside the dynamic reaction cell of an Elan 6100 as a function of gas atomic/molecular weight at 1 mL min\(^{-1}\) gas flow rate.

If the temperature, size of the reaction cell apertures and true gas flow rate are known, the gas density inside the reaction cell can be estimated.\(^{27,28}\) The true gas flow rate is calculated from the reported flow rate reported multiplied by the mass flow controller (MFC) calibration factors (table 6.2).

\[
\text{True flow } \left( \frac{\text{mL}}{\text{min}} \right) = \left( \text{Reported flow } \left( \frac{\text{mL}}{\text{min}} \right) \right) \text{ (Table 6.2 conversion)} \quad (6.6)
\]
Assuming ideal gas behavior and knowing that the mass flow controllers provide a volume flow rate calibrated delivery pressure $P_{\text{delivery}} = 1$ atm, the gas delivered to the reaction cell can be calculated.

$$
\text{Gas In} \left( \frac{\text{particle}}{s} \right) = \frac{m_L}{\text{min}} \times \frac{60s}{60s} = \frac{P_{\text{delivery}} \times V_{\text{delivery}}}{60s \times RT} \times A_N \quad (6.7)
$$

where $V_{\text{delivery}}$ is the corrected flow rate into the cell (mL min$^{-1}$) and $A_N$ is Avogadro’s number. If no interparticle collisions occur (mean free path of gas particle is larger than the aperture) and cell pressure is constant, the gas exiting the reaction cell is equal to the flow rate delivered to the cell. The rate of effusion from the high pressure cell to the low pressure mass spectrometer is related to cell pressure by the following:

$$
\text{Gas Out} \left( \frac{\text{particle}}{s} \right) = \frac{n \sigma}{4} \times \Delta A = \left( \frac{\text{pressure} \times \bar{c}}{4k_B T} \right) \left( A_1 + A_2 \right) \quad (6.8)
$$

$$
\bar{c} = \sqrt{\frac{8RT}{\pi \sigma m}} \quad (6.9)
$$

where, $\bar{c}$ is the calculated mean thermal gas velocity; $R$ is the ideal gas constant; $m$ is the atomic/molecular weight of the reaction gas (g mol$^{-1}$); $A_1$ and $A_2$ are the entrance and exit aperture areas; $k_B$ is the Boltzmann constant and $T$ is temperature. The number of gas particles per unit volume is then expressed by setting Gas Out equal to Gas In and rearranging to solve for $n$.

$$
\frac{P_{\text{delivery}} \times V_{\text{delivery}}}{60s \times RT} \times A_N = \frac{n \sigma}{4} \times (A_1 + A_2) \quad (6.10)
$$

$$
n = \frac{P_{\text{delivery}} \times V_{\text{delivery}}}{\bar{c} \times \Delta A \times 60s \times RT} \times 4A_N \quad (6.11)
$$

The estimated gas density (pressure) inside the reaction cell was used to correlate ICP-DRC-MS signal decays to kinetic rate constants. $^{36}\text{Ar}^+$, $^{40}\text{Ar}_2^+$ and $^{87}\text{Sr}^+$ were
reacted with several gases and ICP-DRC-MS signal decays as a function of gas density were compared to kinetic rate constants.

### 6.4.3 Reactions with $^{36}$Ar$^+$

$^{40}$Ca$^+$ is the preferred isotope for trace Ca measurement due to its high isotopic abundance (97%), but suffers from a severe $^{40}$Ar$^+$ (99% abundance) overlap so large that it produces a detector current too large to measure. $^{36}$Ar$^+$ (0.34% abundance) was measured as a surrogate for $^{40}$Ar$^+$. Reaction spontaneity can be predicted by $\Delta H_f$ using equation 6.1. An example charge transfer reaction with NH$_3$ is shown.

\[
\begin{align*}
Ar^+ + e^- &\rightarrow Ar \quad \Delta H_f = -15.76 \text{ eV} \\
NH_3 &\rightarrow NH_3^+ + e^- \quad \Delta H_f = +10.07 \text{ eV} \\
Ar^+ + NH_3 &\rightarrow NH_3^+ + Ar \quad \Delta H_f = -5.69 \text{ eV}
\end{align*}
\]

Gases with ionization energies less than that of Ar (15.76 eV) are thermodynamically allowed to undergo a charge transfer reaction with Ar$^+$. Each gas listed in table 6.4 has ionization energy greater than that of Ca (6.11 eV) so charge transfer with Ca$^+$ will be endothermic and non-spontaneous. Gases with ionization energies that are “sandwiched” above Ca$^+$ and below Ar$^+$ are all candidates to provide chemical resolution of Ca$^+$ from Ar$^+$ through a charge transfer mechanism.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Reaction Gas</th>
<th>Ionization Energy (eV)$^{29}$</th>
<th>Average Mass (amu)</th>
<th>Previously reported reaction rates ($k_{\text{ran}}$ with Ar$^+$ (10$^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$))</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td></td>
<td>24.59</td>
<td>4</td>
<td>SIFT-MS</td>
</tr>
</tbody>
</table>

Table 6.4: Properties of ions, reaction gases, previously reported Ar$^+$ reaction rates by SIFT-MS.
<table>
<thead>
<tr>
<th></th>
<th>Ne</th>
<th>21.55</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar*</td>
<td>15.76*</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>N2</td>
<td>15.58</td>
<td>28</td>
<td>0.1030, 0.31, 0.9032, 0.1233</td>
</tr>
<tr>
<td>H2</td>
<td>15.43</td>
<td>2</td>
<td>8.231, 8.634</td>
</tr>
<tr>
<td>SF6</td>
<td>14.4035†</td>
<td>146</td>
<td>9.336</td>
</tr>
<tr>
<td>CO</td>
<td>14.01</td>
<td>28</td>
<td>0.3632, 0.4037, 0.3738</td>
</tr>
<tr>
<td>N2O</td>
<td>12.88</td>
<td>44</td>
<td>2.232, 3.336</td>
</tr>
<tr>
<td>CH4</td>
<td>12.61</td>
<td>16</td>
<td>8.238, 39</td>
</tr>
<tr>
<td>CH3F</td>
<td>12.47</td>
<td>36</td>
<td>None previously established</td>
</tr>
<tr>
<td>Xe</td>
<td>12.12</td>
<td>131</td>
<td>0.004331</td>
</tr>
<tr>
<td>O2</td>
<td>12.07</td>
<td>32</td>
<td>0.5221, 0.3530, 0.5532, 0.3936, 0.38841, 0.5037, 0.4638</td>
</tr>
<tr>
<td>C2H6</td>
<td>11.52</td>
<td>30</td>
<td>11.442</td>
</tr>
<tr>
<td>NH3</td>
<td>10.07</td>
<td>17</td>
<td>17.036</td>
</tr>
<tr>
<td>Ca+</td>
<td>6.11*</td>
<td>40</td>
<td></td>
</tr>
</tbody>
</table>

SIFT-MS rate constants listed here measured at 300K unless otherwise denoted.

* Energy to produce the listed ion from neutral.
† The ionization energy for SF6 has been investigated by different research groups and methods and is still not unequivocally established. Reference 43 offers a recent summary of values.

Another possible method to overcome spectral overlaps is an atom addition reaction. Either the overlap ion or the analyte ion, but not both, abstracts an atom (usually H, O or F) from the reaction gas to form a product ion at a new, higher mass.

Reaction spontaneity can be predicted from the bond dissociation energies of the reaction gas and the final analyte-containing product ion. Ar+ reacts with H2 through two pathways.31

**Pathway 1:**

\[
Ar^+ + e^- \rightarrow Ar \hspace{1cm} \Delta H_f = -15.76 \text{ eV}
\]

\[
H_2 \rightarrow H_2^+ + e^- \hspace{1cm} \Delta H_f = +15.43 \text{ eV}
\]

\[
Ar^+ + H_2 \rightarrow Ar + H_2^+ \hspace{1cm} \Delta H_f = -0.34 \text{ eV}
\]
Pathway 2:

\[ H_2 \rightarrow 2H \quad \text{D}_0 = 4.51 \text{ eV} \]

\[ Ar^+ + H \rightarrow ArH^+ \quad \text{D}_0 = -6.16 \text{ eV}^{44} \]

\[ Ar^+ + H_2 \rightarrow ArH^+ + H \quad \Delta H_f = -1.65 \text{ eV} \]

Two reaction mechanisms in addition to charge transfer have been identified by SIFT-MS for the reaction of Ar\(^+\) with CH\(_4\):\(^{36,39}\)

\[ Ar^+ + CH_4 \]

(1) \[ Ar + CH_2^+ + H_2 \quad (11\%) \]

(2) \[ Ar + CH_3^+ + H \quad (79\%) \]

(3) \[ Ar + CH_4^+ \quad (10\%) \]

SF\(_6\) reactions with Ar\(^+\) have also been identified by SIFT-MS:\(^{36}\)

\[ Ar^+ + SF_6 \rightarrow SF_5^+ + F + Ar \]

The charge transfer reactions of gases with Ar\(^+\) not described above are listed in table 6.5.

**Table 6.5:** Charge transfer reactions of Ar\(^+\) and eight neutral reaction gases.

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Products</th>
<th>( \Delta H_f ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Ar^+ + N_2 )</td>
<td>( Ar + N_2^+ )</td>
<td>-0.18</td>
</tr>
<tr>
<td>( Ar^+ + CO )</td>
<td>( Ar + CO^+ )</td>
<td>-1.75</td>
</tr>
<tr>
<td>( Ar^+ + N_2O )</td>
<td>( Ar + N_2O^+ )</td>
<td>-2.88</td>
</tr>
<tr>
<td>( Ar^+ + CH_3F )</td>
<td>( Ar + CH_3F^+ )</td>
<td>-3.29</td>
</tr>
<tr>
<td>( Ar^+ + Xe )</td>
<td>( Ar + Xe^+ )</td>
<td>-3.64</td>
</tr>
<tr>
<td>( Ar^+ + O_2 )</td>
<td>( Ar + O_2^+ )</td>
<td>-3.69</td>
</tr>
<tr>
<td>( Ar^+ + C_2H_6 )</td>
<td>( Ar + C_2H_6^+ )</td>
<td>-4.24</td>
</tr>
<tr>
<td>( Ar^+ + NH_3 )</td>
<td>( Ar + NH_3^+ )</td>
<td>-5.69</td>
</tr>
</tbody>
</table>

Figures 6.2 a – j show the attenuation of Ar\(^+\) by CH\(_4\), CO, C\(_2\)H\(_6\), H\(_2\), N\(_2\)O, NH\(_3\), N\(_2\), O\(_2\), SF\(_6\) and CH\(_3\)F, respectively. The signals fall according to pseudo first order
reaction kinetics until the slope changes as a result of Ar$^+$ is no longer the dominant source of signal. The signal in figure 6.2d (H$_2$) did not fall below 5,000 c s$^{-1}$ due to an unknown background ion.
Figure 6.2a-f: Measured signals from $^{36}$Ar$^+$ as a function of a) CH$_4$, b) CO, c) C$_2$H$_6$, d) H$_2$, e) N$_2$O and f) NH$_3$ flow into the reaction cell with RPq = 0.60. Bottom x-axis is the reported flow uncorrected for mass flow controller calibration and top x-axis is...
estimated gas density inside the reaction cell. Measured (●) and extrapolated signal (-) are shown.

![Graphs showing m/z 36 signal as a function of N₂, O₂, SF₆, and CH₃F flow into the reaction cell with RPq = 0.60.](image-url)

**Figure 6.2g-j:** Measured signals from ³⁶Ar⁺ as a function of g) N₂, h) O₂, i) SF₆ and j) CH₃F flow into the reaction cell with RPq = 0.60. Bottom x-axis is the reported flow uncorrected for mass flow controller calibration and top x-axis is estimated gas density inside the reaction cell. Measured (●) and extrapolated signal (-) are shown.

Table 6.6 lists the measured signal decay rates (slopes of the extrapolated series in figures 6.2 a – j) as a function of reaction gas density (top x-axis, molecule cm⁻³).

196
<table>
<thead>
<tr>
<th>Reaction Gas</th>
<th>SIFT rate constant ((10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})) from table 6.4</th>
<th>ICP-DRC-MS measured signal decay – (\ln(\text{signal})) (10^{-14} \text{ molecule cm}^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{C}_2\text{H}_6)</td>
<td>11.4 (^{42})</td>
<td>12.6</td>
</tr>
<tr>
<td>(\text{CH}_3\text{F})</td>
<td>None listed</td>
<td>10.6</td>
</tr>
<tr>
<td>(\text{CH}_4)</td>
<td>8.2 (^{36,39})</td>
<td>9.33</td>
</tr>
<tr>
<td>(\text{CO})</td>
<td>0.36 (^{32}), 0.40 (^{37}), 0.37 (^{38})</td>
<td>2.14</td>
</tr>
<tr>
<td>(\text{H}_2)</td>
<td>8.2 (^{31}), 8.6 (^{34})</td>
<td>9.90</td>
</tr>
<tr>
<td>(\text{N}_2\text{O})</td>
<td>2.2 (^{32}), 3.3 (^{36})</td>
<td>3.10</td>
</tr>
<tr>
<td>(\text{NH}_3)</td>
<td>17.0 (^{36})</td>
<td>16.9</td>
</tr>
<tr>
<td>(\text{N}_2)</td>
<td>0.10 (^{30,31}), 0.90 (^{32}), 0.12 (^{33})</td>
<td>1.87</td>
</tr>
<tr>
<td>(\text{O}_2)</td>
<td>0.52 (^{21}), 0.35 (^{40}), 0.55 (^{32}), 0.39 (^{36}), 0.388 (^{41}), 0.50 (^{37}), 0.46 (^{38})</td>
<td>2.16</td>
</tr>
<tr>
<td>(\text{SF}_6)</td>
<td>9.3 (^{36})</td>
<td>10.2</td>
</tr>
</tbody>
</table>

Signal decays measured by ICP-DRC-MS are plotted as a function of reported flow rate and reaction gas density in figure 6.3. Reactions with more than one rate constant are shown with open symbols; all others have closed symbols.
Figure 6.3: Measured Ar$^+$ signal decays rates plotted as a function of a) reported flow and b) estimated gas density. Reaction gases shown include CH$_4$ (▲), CO (Δ), C$_2$H$_6$ (●), H$_2$ (○), N$_2$O (▽), NH$_3$ (+), N$_2$ (◊), O$_2$ (□) and SF$_6$ (■). Error bars at 95% confidence level are smaller than symbols.

There appears to be some correlation between the DRC measured signal decays and kinetic rate constants in figure 6.3a ($R^2 = 0.78$) but this is not observed for every gas. For example, consider the reaction of Ar$^+$ with H$_2$ and CH$_4$. H$_2$ attenuates $^{36}$Ar$^+$ much more slowly than CH$_4$ even though the kinetic rate constants are very similar. Figure 6.3b ($R^2 = 0.99$) shows a good correlation between DRC measured decays and kinetic rate constants. It is also interesting to note that the series shown in 6.3b does not pass through the origin. Scattering of the ion beam might cause the offset if all gases produced identical scattering losses. However, scattering losses increase as reaction gas mass increases and should vary according to gas mass. The signal decay rates were not ratioed to a nonreactive internal standard such as $^{40}$Ca$^+$ to correct for scattering losses, so it is not possible to conclude if the offset is due to scattering.
When the measured signal decay rates (cm$^3$ molecule$^{-1}$) are plotted as a function of rate coefficients found in literature (cm$^3$ molecule$^{-1}$ s$^{-1}$), the slope of the series (92 µs) acts as a calibration factor. The series in figure 6.3b is linear because the y-axis values of each point in figure 6.3b represent both the rate of signal decay ($\Delta \ln(A^+)_k$) as a function of gas pressure, and the rate coefficient multiplied the ion residence time ($-k_{\text{rxt}}t$ in equation 6.6). The relationship between signal decay rates and kinetic rate constants is linear only if the residence time increases linearly with reaction gas flow rate (gas pressure). Ion residence time in the reaction cell will be addressed using ion trajectory simulations in chapter 7.

There is no previously reported kinetic rate constant for the reaction of CH$_3$F and Ar$^+$, but after calibration using known kinetic rate constants, a kinetic rate constant of 9.6 x 10$^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ was calculated. Although there is a very large database of rate constants for bimolecular ion-molecule reactions, almost all (> 99%) rate constants are for elemental singly charged ions and the database does not include most of the polyatomic overlaps found in ICP-MS. Using ICP-DRC-MS and the calibration method described here, it may be possible to estimate previously unknown kinetic rate constants of interest. ICP-DRC-MS signal decay rates must first be calibrated against at least two known bimolecular rate constants (two point calibration curve) before determining the rate constants for new reactions. The ICP is such a good ion source that it provides the possibility to quickly add to the existing database of bimolecular rate constants. The method has also effectively related signal decays from both charge transfer and atom addition reactions to kinetic rate constants.
The ICP-DRC-MS can also be used to determine the accuracy of some rate constants that have multiple values in the literature. For example, the reaction \( \text{Ar}^+ + \text{N}_2 \) has three rate constants published, but the ICP-DRC-MS data show that \( 0.10^{30, 31} \) or \( 0.12^{32} \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) fall most closely on the series in figure 6.3d.

Measurement of this bimolecular rate constant by a new experimental method offers further validation to the value of \( 0.10^{30, 31} \) or \( 0.12^{32} \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) as opposed to \( 0.90^{33} \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \).

### 6.4.4 Reactions and Collision Induced Dissociation with \(^{40}\text{Ar}_2^+\)

\(^{80}\text{Se}^+\) is the preferred isotope for trace concentration analysis because it is the most abundant isotope (49.7%) but suffers from a severe overlap of \(^{40}\text{Ar}_2^+\). The ionization energy of \( \text{Ar}_2^+ \) is 14.5 eV\(^{45}\) and reaction kinetic rate constants with a variety of different gases are listed in table 6.7.
Table 6.7: Properties of ions, reaction gases, previously reported Ar$_2^+$ reaction rates by SIFT-MS.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Reaction Gas</th>
<th>Ionization Energy (eV)</th>
<th>Average Mass (amu)</th>
<th>Previously reported reaction rates (k) with Ar$_2^+$ ($10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ICP-SIFT-MS</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>SIFT-MS</td>
</tr>
<tr>
<td>He</td>
<td></td>
<td>24.59</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Ne</td>
<td></td>
<td>21.55</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Ar</td>
<td></td>
<td>15.76</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>N$_2$</td>
<td></td>
<td>15.58</td>
<td>28</td>
<td>2.2$^{31,0^{32}}$</td>
</tr>
<tr>
<td>H$_2$</td>
<td></td>
<td>15.43</td>
<td>2</td>
<td>6.3$^{22}$, 4.7$^{31}$, 2.0$^{32}$</td>
</tr>
<tr>
<td>Ar$_2^+$</td>
<td></td>
<td>14.50$^{45,*}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SF$_6$</td>
<td></td>
<td>14.40$^{35,*}$</td>
<td>146</td>
<td>4.2$^{36}$, 4.8$^{32}$</td>
</tr>
<tr>
<td>CO</td>
<td></td>
<td>14.01</td>
<td>28</td>
<td>7.3$^{23}$, 6.1$^{36}$, 8.2$^{36}$</td>
</tr>
<tr>
<td>N$_2$O</td>
<td></td>
<td>12.88</td>
<td>44</td>
<td>6.2$^{23}$, 9.3$^{39}$</td>
</tr>
<tr>
<td>CH$_4$</td>
<td></td>
<td>12.61</td>
<td>16</td>
<td>9.3$^{39}$, 9.2$^{36}$</td>
</tr>
<tr>
<td>CH$_3$F</td>
<td></td>
<td>12.47</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>Xe</td>
<td></td>
<td>12.12</td>
<td>131</td>
<td>2.3$^{31}$, 2.5$^{32}$</td>
</tr>
<tr>
<td>O$_2$</td>
<td></td>
<td>12.07</td>
<td>32</td>
<td>0.74$^{36}$, 0.73$^{36}$</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td></td>
<td>11.52</td>
<td>30</td>
<td>10.6$^{42}$, 10.5$^{43}$</td>
</tr>
<tr>
<td>NH$_3$</td>
<td></td>
<td>10.07</td>
<td>17</td>
<td>3.1$^{20}$, 5.5$^{36}$</td>
</tr>
<tr>
<td>Se$^+$</td>
<td></td>
<td>9.75$^{*}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Energy to produce the listed ion from neutral.
† The ionization energy for SF$_6$ has been investigated by different research groups and methods and is still not unequivocally established. Reference $^{43}$ offers a recent summary of values.

Gases with ionization energies that are “sandwiched” between the ionization energies to create Ar$_2^+$ and Se$^+$ are eligible to provide chemical resolution of Se$^+$ by an exothermic charge transfer reaction. Table 6.8 lists the reactants and products for the reactions that occur via a charge transfer mechanism.
Table 6.8: Charge transfer mechanisms for the reaction of Ar$^+$ and eight neutral reaction gases.

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Products</th>
<th>$\Delta H_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Ar_2^+ + CO$</td>
<td>$2Ar + CO^+$</td>
<td>-1.75 eV</td>
</tr>
<tr>
<td>$Ar_2^+ + N_2O$</td>
<td>$2Ar + N_2O^+$</td>
<td>-2.88 eV</td>
</tr>
<tr>
<td>$Ar_2^+ + CH_3F$</td>
<td>$2Ar + CH_3F^+$</td>
<td>-3.29 eV</td>
</tr>
<tr>
<td>$Ar_2^+ + Xe$</td>
<td>$2Ar + Xe^+$</td>
<td>-3.64 eV</td>
</tr>
<tr>
<td>$Ar_2^+ + O_2$</td>
<td>$2Ar + O_2^+$</td>
<td>-3.69 eV</td>
</tr>
<tr>
<td>$Ar_2^+ + C_2H_6$</td>
<td>$2Ar + C_2H_6^+$</td>
<td>-4.24 eV</td>
</tr>
<tr>
<td>$Ar_2^+ + NH_3$</td>
<td>$2Ar + NH_3^+$</td>
<td>-5.69 eV</td>
</tr>
</tbody>
</table>

Gases with ionization energies greater than the ionization energy for Ar$_2^+$ (14.5 eV) are not thermodynamically allowed. However, Ar$_2^+$ reacts with H$_2$ through H-atom addition. $^{31}$ Ar$_2^+$ reacts with N$_2$ occurs through a ligand switching mechanism.$^{31}$

\[(Ar - Ar) + N_2 \rightarrow (Ar - N_2) + Ar\]

Figures 6.4 a – f and 6.5 g – k show the attenuation of $^{40}$Ar$_2^+$ signal by CH$_4$, CO, C$_2$H$_6$, H$_2$, N$_2$O, NH$_3$, N$_2$, O$_2$, SF$_6$, Xe and CH$_3$F reaction gases respectively.
**Figure 6.4:** Measured signal from $^{40}$Ar$_2^+$ as a function of a) CH$_4$, b) CO, c) C$_2$H$_6$, d) H$_2$, e) N$_2$O and f) NH$_3$ flow into the reaction cell (●). Bottom x-axis is the software reported gas flow rate uncorrected for mass flow controller calibration, and top x-axis is
the estimated gas density inside the reaction cell. Solid line is the extrapolated signal to 0.1 \text{ c s}^{-1}.

![Graphs showing measured signal from $^{40}\text{Ar}^+$ as a function of different gases: N$_2$, O$_2$, SF$_6$, Xe, and CH$_3$F flow into the reaction cell.](image)

**Figure 6.5:** Measured signal from $^{40}\text{Ar}^+$ as a function of g) N$_2$, h) O$_2$, i) SF$_6$, j) Xe and k) CH$_3$F flow into the reaction cell (●). Bottom x-axis is the software reported gas flow.
rate uncorrected for mass flow controller calibration, and top x-axis is the estimated gas
density inside the reaction cell. Solid line is the extrapolated signal to 0.1 c s$^{-1}$. The
heavy reaction gases SF$_6$ and Xe have the blank subtracted signal due to 1 ppb Se at m/z 80 displayed (○) for scattering corrections.

$^{80}$Se$^+$ was used as an internal standard to correct for scattering losses from the heavy reaction gases SF$_6$ and Xe. A charge transfer reaction of Se$^+$ with each gas was endothermic and the scattering loss of $^{40}$Ar$_2^+$ signal was assumed to be equal to the scattering loss of blank subtracted Se$^+$. This assumption may not be accurate if the collision cross sections of $^{40}$Ar$_2^+$ and Se$^+$ are different. The polyatomic Ar$_2^+$ cross section should be larger than monoatomic Se$^+$, but has not yet been published. Standardization to Se$^+$ was deemed the best alternative to correct for scattering losses, which were significant. Figures 6.5 i and 6.5 j show the decrease in blank subtracted 1 ppb Se$^+$ signal as a function of gas flow rate into the reaction cell. Sensitivities using both SF$_6$ and Xe are significantly lowered due to scattering losses. The corrected Ar$_2^+$ decay rate was calculated as the observed Ar$_2^+$ rate minus the observed Se$^+$ signal decay rate. Only SF$_6$ and Xe were observed to significantly scatter Ar$_2^+$ and Se$^+$ based on the blank subtracted signals measured from a 1 ppb Se solution.

Reduction of Ar$_2^+$ signal might be achieved through collisional dissociation instead of a chemical reaction, if the ion has a sufficient kinetic energy and the gas has enough mass. Although others have suggested the use of CID for polyatomic attenuation (chapter 3),$^{46,47}$ there has not been a study that quantified the contribution of CID to signal decay using gases that also react.
Collisional dissociation occurs when kinetic energy is transferred into vibrational energy which exceeds the bond strength of the polyatomic ion. Assuming a stationary neutral molecule, the maximum internal energy conversion from a single collision can be calculated from the mass of the neutral gas molecule and both the kinetic energy and mass of the ion.\(^8,12,48\)

\[
E_{\text{int,max}} = E_{\text{ion}} \times \left[ \frac{m_{\text{gas}}}{m_{\text{gas}} + m_{\text{ion}}} \right] \quad (6.12)
\]

The bond strength of Ar\(_2^+\) is 1.26 eV.\(^44\) If the average kinetic energy of the incoming \(^{40}\)Ar\(_2^+\) is estimated to be 8 eV,\(^8\) then a neutral gas with a mass larger than 15 amu may cause bond rupture upon a single collision. All gases listed in table 6.7 are able to dissociate Ar\(_2^+\) upon a single collision except for H\(_2\) and He assuming that the maximum energy is transferred to the internal vibrational energy of the polyatomic ion. \(^{40}\)Ar\(_2^+\) signal as a function of He, Ne and Ar gas flow rate is shown in Figures 6.6 a – c.
Figure 6.6: Measured $^{40}\text{Ar}_2^+$ signal (●) as a function of a) He, b) Ne, and c) Ar flow into the reaction cell. Bottom x-axis is the software reported gas flow rate uncorrected for mass flow controller calibration, and top x-axis is the estimated gas density inside the reaction cell. Solid line is the extrapolated signal to 0.1 $\text{c s}^{-1}$.

Both Ne and Ar were able to reduce the measured signal due to $^{40}\text{Ar}_2^+$ by 4 orders of magnitude through CID. CID is generally believed to be much less efficient than ion-molecule reactions, but blank contamination limited detection limits were achieved using
the inert collision gas Ne because weakly bound Ar$_2^+$ readily dissociates upon collisions. He was too light to cause CID and did not reduce the measured Ar$_2^+$ signal, even at 3.0 mL min$^{-1}$ (data not shown).

Signal decay rates (slope of the extrapolated series in figures 6.5 and 6.6) were measured as a function of reaction gas density (table 6.9).

Table 6.9: Kinetic rate constants (previously measured by SIFT-MS) and ICP-DRC-MS measured Ar$_2^+$ signal decays as a function of reaction gas reported flow, reaction gas true flow, estimated reaction cell pressure, and estimated reaction gas density.

<table>
<thead>
<tr>
<th>Reaction Gas</th>
<th>SIFT rate constant (10$^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) from table 6.7</th>
<th>ICP-DRC-MS measured signal decay – ln(signal) 10$^{-14}$ molecule cm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>0</td>
<td>1.79</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>10.6$^{42}$</td>
<td>17.8</td>
</tr>
<tr>
<td>CH$_3$F</td>
<td>None listed</td>
<td>17.4</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>9.3$^{39}$</td>
<td>16.5</td>
</tr>
<tr>
<td>CO</td>
<td>7.3$^{23}$, 6.1$^{36}$, 4.8$^{32}$</td>
<td>12.6</td>
</tr>
<tr>
<td>He</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>H$_2$</td>
<td>6.3$^{22}$, 4.7$^{31}$, 2.0$^{32}$</td>
<td>8.19</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>6.2$^{23}$, 8.2$^{36}$</td>
<td>11.5</td>
</tr>
<tr>
<td>Ne</td>
<td>0</td>
<td>2.37</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>3.1$^{20}$, 5.5$^{36}$</td>
<td>6.51</td>
</tr>
<tr>
<td>N$_2$</td>
<td>2.2$^{31}$, 0$^{32}$</td>
<td>4.78</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0.74$^{36}$</td>
<td>2.89</td>
</tr>
<tr>
<td>SF$_6$</td>
<td>4.2$^{36}$</td>
<td>7.45</td>
</tr>
<tr>
<td>Xe</td>
<td>2.3$^{31}$</td>
<td>5.32</td>
</tr>
</tbody>
</table>
Figure 6.7: Measured signal decays rates plotted as a function of a) Ar equivalent flow rate and b) estimated gas density. Reaction gases shown include CH$_4$ (▲), CO (∆), C$_2$H$_6$ (●), H$_2$ (○), N$_2$O (▽), NH$_3$ (□), N$_2$ (◇), O$_2$ (+), SF$_6$ (■), Xe (▼) and three collision gases He, Ne, and Ar (♦). Two best fit lines are shown in figure 6.7 d for gases that cause CID and that cannot (He and H$_2$ only). 95% confidence intervals smaller than plot symbols.

When the signal decays are plotted as a function of estimated reaction gas density (6.7b) there is a good correlation ($R^2 > 0.98$) with the literature kinetic rate constants but the regression line does not pass through the origin. This is likely because the observed signal decays result from both ion-molecule reactions and CID. SIFT-MS kinetic rate constants do not include contributions from collision induced dissociation because ions are thermalized by collisions with a buffer gas before colliding with the reaction gas.$^{21-23}$ The offset in figure 6.7b suggests that CID is a binary “go” “no-go” process, i.e. CID rates are similar for all gases that can provide $E_{\text{int, max}} > D_0 (\text{Ar}_2^+)$.

Gases with a high enough mass to dissociate Ar$_2^+$ upon a single collision are CH$_4$, CO, C$_2$H$_6$, N$_2$O, NH$_3$, N$_2$, O$_2$, SF$_6$, Xe, CH$_3$F, Ne and Ar but not He nor H$_2$ (equation
While $\text{H}_2$ is too light for CID, it reacts with $\text{Ar}_2^+$ via H-atom addition and charge transfer. Two different regression lines were drawn: one through the points for He and $\text{H}_2$, which do not undergo CID and one line through the remaining points that can undergo CID. The contribution of CID to signal attenuation relative to the overall signal decay can be observed by the y-axis offset of the two series in figure 6.7b. The top regression line in figure 6.7b is fit to gases that can cause CID of $\text{Ar}_2^+$ upon a single collision, while the bottom line is fit to He and $\text{H}_2$. The slopes of these series are approximately equal because the calibration between kinetic rate constants and signal decay due only to reactions does not depend on whether or not CID is occurring.

The $\text{Ar}_2^+$ signal decay due only to ion-neutral gas chemical reactions may be determined by accounting for the contribution of CID (measuring using Ne and Ar) from the measured signal decay rates. $\text{Ar}_2^+$ signal decays ($k_{\text{CID}}$) due to Ne and Ar were 1.79 and $2.37 \times 10^{-14}$ cm$^3$ molecule$^{-1}$ respectively. The average of the two values was subtracted from the observed $\text{Ar}_2^+$ signal decay rate.

$$k_{\text{observed}} = (k_{\text{reaction}}) + (k_{\text{CID}}) \quad (6.13)$$

$$k_{\text{reaction}} = (k_{\text{observed}}) - (k_{\text{CID}}) \quad (6.14)$$

He and $\text{H}_2$ are too light to cause dissociation of $\text{Ar}_2^+$ upon a single collision, so no correction is made to the calculated rate constants for these gases.

$$k_{\text{He, H}_2} = (k_{\text{observed}}) \quad (6.15)$$

The transfer of kinetic energy from the collision event to internal vibrational energy is dependent only on the ion and reaction gas masses for a given ion kinetic energy and does not depend on reaction gas reactivity or electron configuration. Although
it is intuitive to assume CID efficiency increases as collision gas mass increases, it appears that as long as the collision gas is heavier than the threshold required for CID, then the gas mass is not significant. Subtraction of Ar and Ne CID rates will correct for the CID contribution to observed signal decay for the gases CH₄, CO, C₂H₆, N₂O, NH₃, N₂, O₂, SF₆, Xe, CH₃F, Ne and Ar. After correction for CID contributions, the correlation between the DRC measured signal decays and the SIFT-MS kinetic rate constants is shown in figure 6.8.
Figure 6.8: Measured signal decay rates corrected for collision induced dissociation plotted against SIFT kinetic rate constants. Only ICP-SIFT-MS rate constants are shown if more than one rate constant was available. Reaction gases shown include CH₄ (▲), CO (∆), C₂H₆ (●), H₂ (○), N₂O (▼), NH₃ (□), N₂ (◊), O₂ (+), SF₆ (■), Xe (▼) and three collision gases He, Ne, and Ar (♦).

The kinetic rate constants obtained using an ICP-SIFT-MS correlate very well with the signal decays that are observed using an ICP-DRC-MS. The slope of the series in figure 6.8 is 152 µs with a 0.991 coefficient of determination (R²). The slope of figure 6.8 is a calibration factor only; ICP-DRC-MS signal decay rates must be calibrated against known bimolecular rate coefficients.
It is possible to convert signal decay rates measured on the DRC to kinetic rate constants if at least two points can be plotted as in figure 6.8. After accounting for CID, dividing the reaction rates from equation 6.14 by the calibration factor (152 $\mu$s for $\text{Ar}_2^+$) will yield a kinetic rate constant in terms of cm$^3$ molecule$^{-1}$ s$^{-1}$. There is no previously published rate constant for the reaction between $\text{Ar}_2^+$ and CH$_3$F. Using the cross calibration method described, the kinetic rate constant for this reaction was determined to be $1.03 \times 10^{-9}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

It appears that when more than one rate coefficient was published the ICP-SIFT-MS value agreed better than values obtained by other types of measurement. These rate coefficients were used in figure 6.8 and table 6.10. It is unclear why the ICP-SIFT-MS data agree with the ICP-DRC-MS data better than other ionization source SIFT-MS data (see table 6.7 for all rate coefficients), since the ions should be thermalized before entering the flow tube regardless of ionization source. The ICP-SIFT-MS measurements were all measured by a single research group and their methods may be more accurate than others$^{20}$. All of the calibrated ICP-DRC-MS rate coefficients are within the published uncertainty except $\text{Ar}_2^+ + \text{N}_2$. Residuals from ICP-DRC-MS calibrated rate constants and the regression line, and sources of the figure 6.8 data are listed in table 6.10.
Table 6.10: SIFT ionization sources, uncertainties and rate constants for the reaction of Ar^+ with 14 neutral gases with DRC signal decays calibrated to SIFT rate constants, residuals and % differences.

<table>
<thead>
<tr>
<th>Reaction Gas</th>
<th>SIFT rate constant (10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})</th>
<th>Method*</th>
<th>Published Uncertainty</th>
<th>DRC rate constant (10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})</th>
<th>Residual (10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>0</td>
<td></td>
<td></td>
<td>0.00637</td>
<td>0.00637</td>
<td></td>
</tr>
<tr>
<td>C_{2}H_{6}</td>
<td>10.6^{42}</td>
<td>EI SIFT</td>
<td>30%</td>
<td>10.5</td>
<td>0.0307</td>
<td>-1%</td>
</tr>
<tr>
<td>CH_{3}F</td>
<td>None found</td>
<td></td>
<td></td>
<td>10.3</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>CH_{4}</td>
<td>9.3^{39}</td>
<td>EI SIFT</td>
<td>30%</td>
<td>9.68</td>
<td>0.495</td>
<td>4%</td>
</tr>
<tr>
<td>CO</td>
<td>7.3^{23}</td>
<td>ICP-SIFT</td>
<td>30%</td>
<td>7.11</td>
<td>-0.100</td>
<td>-3%</td>
</tr>
<tr>
<td>He</td>
<td>0</td>
<td></td>
<td></td>
<td>0</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>H_{2}</td>
<td>6.3^{22}</td>
<td>ICP-SIFT</td>
<td>30%</td>
<td>5.38</td>
<td>-0.847</td>
<td>-15%</td>
</tr>
<tr>
<td>N_{2}O</td>
<td>6.2^{23}</td>
<td>ICP-SIFT</td>
<td>30%</td>
<td>6.4</td>
<td>0.276</td>
<td>3%</td>
</tr>
<tr>
<td>Ne</td>
<td>0</td>
<td></td>
<td></td>
<td>0.386</td>
<td>0.386</td>
<td></td>
</tr>
<tr>
<td>NH_{3}</td>
<td>3.1^{20}</td>
<td>ICP-SIFT</td>
<td>None provided</td>
<td>3.1</td>
<td>0.041</td>
<td>0%</td>
</tr>
<tr>
<td>N_{2}</td>
<td>2.2^{31}</td>
<td>EI SIFT</td>
<td>5%</td>
<td>1.97</td>
<td>-0.203</td>
<td>-10%</td>
</tr>
<tr>
<td>O_{2}</td>
<td>0.74^{38}</td>
<td>EI SIFT</td>
<td>30%</td>
<td>0.725</td>
<td>-0.00654</td>
<td>-2%</td>
</tr>
<tr>
<td>SF_{6}</td>
<td>4.2^{36}</td>
<td>EI SIFT</td>
<td>30%</td>
<td>3.72</td>
<td>-0.428</td>
<td>-11%</td>
</tr>
<tr>
<td>Xe</td>
<td>2.3^{31}</td>
<td>EI SIFT</td>
<td>5%</td>
<td>2.32</td>
<td>0.0495</td>
<td>1%</td>
</tr>
</tbody>
</table>

* Electron Impact ionization

6.4.5 Reactions with Sr^+

Sr and Rb can be used for magmatic age determination.\textsuperscript{49-53} A reaction gas must be chosen to take chemically separate Sr^+ from Rb^+ and allow nearly simultaneous measurement.\textsuperscript{51} An atom addition reaction “moves” one of the analytes to a new, higher mass enabling both resolution and measurement of both elements. A mono-isotopic element is ideal for atom addition so that the isotopic pattern of the analyte will be simply
shifted and no isotope deconvolution procedures will be necessary. $^{19}$F is an ideal candidate for this type of atom addition reaction. If isotope ratio measurements are not required and only concentration information is desired, then a monoisotopic atom addition would suffice.

Table 6.11: Properties of ions, reaction gases, previously reported $\text{Ar}_2^+$ reaction rates by SIFT-MS.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Reaction Gas</th>
<th>Ionization Energy (eV)$^{29}$</th>
<th>Average Mass (amu)</th>
<th>Previously reported ICP-SIFT-MS reaction rates (k) with $\text{Ar}_2^+$ reaction rates ($10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\text{Sr}^+$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$5.7^{15}$</td>
</tr>
<tr>
<td>SF$_6$</td>
<td></td>
<td>$14.40^{35}$†</td>
<td>146</td>
<td>$0.63^{18}$</td>
</tr>
<tr>
<td>N$_2$O</td>
<td></td>
<td>$12.88$</td>
<td>44</td>
<td>$0.14^{17}$</td>
</tr>
<tr>
<td>CH$_3$F</td>
<td></td>
<td>$12.47$</td>
<td>36</td>
<td>$0.002^{54}$</td>
</tr>
<tr>
<td>O$_2$</td>
<td></td>
<td>$12.07$</td>
<td>32</td>
<td>$0.0049^{54}$</td>
</tr>
<tr>
<td>NH$_3$</td>
<td></td>
<td>$10.07$</td>
<td>17</td>
<td>$5.69$</td>
</tr>
<tr>
<td>Sr$^{+*}$</td>
<td></td>
<td></td>
<td></td>
<td>$4.18$</td>
</tr>
</tbody>
</table>

* Energy to produce the listed ion from neutral.

† The ionization energy for SF$_6$ has been investigated by different research groups and methods and is still not unequivocally established. Reference $^{43}$ offers a summary of values.

Bohme’s group recently published work on the search for the optimum reagent for chemical resolution of Sr$^+$ from Rb$^+$. The resolution of Sr$^+$ from Rb$^+$ relies on the respective differences in electron configuration and subsequent differences in reactivity. Rb$^+$ has a noble gas electron configuration and is generally inert. Sr$^+$ has a lone electron in the 5s orbital and is reactive to many neutral gases. Bohme’s ICP-SIFT-MS study displayed the differences in reactivity between Sr$^+$ and Rb$^+$ very clearly.$^{54}$
In general, atom addition reactions have rate coefficients less than charge transfer reactions. For the case of Ar$_2^+$, 8 of the 9 charge transfer reactions had a kinetic rate constant greater than $10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ versus 1 of 5 for Sr$^+$. CH$_3$F, SF$_6$ and N$_2$O were the only gases studied because reactions with kinetic rate constants less than $10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ are difficult to separate from ion beam scattering by ICP-DRC-MS.

ICP-DRC-MS chemical resolution of $^{87}$Rb$^+$ from $^{87}$Sr$^+$ has previously been achieved by using CH$_3$F.$^{51}$

$$Sr^+ + CH_3F \rightarrow SrF^+ + CH_3$$

$$Rb^+ + CH_3F \rightarrow No reaction$$

The bond dissociation energy of the CH$_3$-F bond is 110.0 $\pm$ 2.0 kcal mol$^{-1}$, while the bond strength of the Sr$^+$-F bond is 144 $\pm$ 7 kcal mol$^{-1}$. The extraction of a fluorine atom from CH$_3$F by Sr$^+$ is exothermic by 34 kcal mol$^{-1}$. $^{88}$Sr$^+$ reacts with CH$_3$F as indicated by the decrease in $^{88}$Sr$^+$ signal and increase in $^{88}$Sr$^{19}$F$^+$ at m/z 107, as seen in Figure 6.9a. No Rb-F$^+$ was observed to form when a 10 ppb solution of Rb was measured with CH$_3$F in the reaction cell.
Figure 6.9: Measured signal from 10 ppb $^{88}$Sr$^+$ as a function of a) CH$_3$F, b) SF$_6$ and c) N$_2$O flow into the reaction cell with RPq 0.45. Signals at m/z 88 ($\bullet$), 104 (□) and 107 (○) shown. Bottom x-axis is the reported flow uncorrected for mass flow controller calibration and the top x-axis is the estimated gas density inside the reaction cell. The solid line is the extrapolated signal down to 0.1 c s$^{-1}$. 
The production of SrF$^+$ is spontaneous while the production of RbF$^+$ either does not occur or is very slow. $^{87}$Rb$^+$ may be measured at m/z 87 while $^{87}$Sr$^+$ can be measured at m/z 106 as $^{87}$Sr$^{19}$F$^+$. A similar fluorine atom extraction can be achieved using SF$_6$.

$$Sr^+ + SF_6 \rightarrow SrF^+ + SF_5^+$$

$$Rb^+ + SF_6 \rightarrow \text{Slow reaction}$$

The bond dissociation energy of the SF$_5$-F bond is 93.6 kcal mol$^{-1}$, while the bond strength of the Sr$^+$-F bond is 144 ± 7 kcal mol$^{-1}$. The extraction of a fluorine atom from SF$_6$ by Sr$^+$ is exothermic by 50 kcal mol$^{-1}$. The reaction between $^{88}$Sr$^+$ and SF$_6$ is shown in Figure 6.9b. No atom transfer reaction is observed with Rb$^+$ suggesting that the F-atom affinity of Rb$^+$ is less than 94 kcal mol$^{-1}$. $^{54}$SrF$^+$ formation occurs at a rate more than 40 times faster when using SF$_6$ than by CH$_3$F based on the kinetic rate constants.

The signal loss of $^{85}$Rb$^+$, which is unreactive with SF$_6$, was equal to roughly 20% of the signal loss of $^{88}$Sr$^+$. If $^{85}$Rb$^+$ may be treated as an internal standard, then measured signal decay of $^{88}$Sr$^+$ can be attributed to 80% due to reaction with SF$_6$ and 20% due to scattering losses.

The atom addition reaction between N$_2$O and $^{87}$Sr$^+$ forms $^{87}$SrO$^+$ enabling trace measurement of $^{87}$Sr$^{16}$O$^+$ at m/z 103 and $^{87}$Sr$^{18}$O$^+$ at m/z 105.

$$Sr^+ + N_2O \rightarrow SrO^+ + N_2$$

$$Rb^+ + N_2O \rightarrow RbO^+ + N_2$$

The bond dissociation energy of the N$_2$-O bond is 39.3 ± 0.1 kcal mol$^{-1}$. The bond dissociation energies of the Sr$^+$-O and Rb$^+$-O bonds are 71.4 ± 0.5 and 7.0 kcal mol$^{-1}$ respectively. The extraction of an oxygen atom from N$_2$O by Sr$^+$ is exothermic by 32
kcal mol\(^{-1}\) while the same reaction by Rb\(^+\) is endothermic by 32 kcal mol\(^{-1}\). The reaction between \(^{88}\)Sr\(^+\) and N\(_2\)O can be seen in Figure 6.9c. However, because oxygen has more than one isotope, SrO isotope ratio measurements require deconvolution. For instance, \(^{86}\)Sr\(^{18}\)O\(^+\) interferes with the measurement of \(^{88}\)Sr\(^{16}\)O\(^+\). This may complicate experiments that rely on high precision measurements since any deconvolution or correction procedures induce additional uncertainty.

Like the previous studies, there is no clear correlation between ICP-DRC-MS signal decay rates as a function of flow rate and kinetic rate constants (6.10a). A direct correlation is observed when the signal decay is plotted as a function of reaction gas density (Figure 6.10b).

**Table 6.12:** Kinetic rate constants previously determined by ICP-SIFT-MS and ICP-DRC-MS measured signal decays as a function of Ar-equivalent reaction gas flow rate, true reaction gas flow rate, estimated reaction cell pressure, and estimated reaction gas density.

<table>
<thead>
<tr>
<th>Reaction Gas</th>
<th>SIFT rate constant ((10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})) from table 6.11</th>
<th>ICP-DRC-MS measured signal decay (-\ln(\text{signal})) ((10^{-14} \text{ molecule cm}^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)F</td>
<td>0.14(^{17})</td>
<td>4.17</td>
</tr>
<tr>
<td>N(_2)O</td>
<td>0.63(^{18})</td>
<td>4.52</td>
</tr>
<tr>
<td>SF(_6)</td>
<td>5.7(^{15})</td>
<td>8.25</td>
</tr>
</tbody>
</table>
Figure 6.10: Measured signal decays rates plotted as a function of a) reported flow, b) true flow, c) estimated pressure and d) estimated gas density. (▲) CH$_3$F, (●) N$_2$O and (♦) SF$_6$. 95% confidence intervals smaller than plot symbols.

It is still unclear why the series plotted in figure 6.10b does not pass through the origin. Attempts at correcting for scattering losses by using $^{85}$Rb$^+$ as an internal standard did not bring the series through the origin. The blank subtracted rate of $^{85}$Rb$^+$ signal decay was used to correct the $^{88}$Sr$^+$ signal decays in the same method that Ar$_2^+$ scattering losses were corrected by $^{80}$Se$^+$. A similar study using another elemental ion might help elucidate the reason the series does not pass through the origin. Sc$^+$ and Y$^+$ have been shown to be extremely reactive with numerous rate coefficients greater than 10$^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. More gases could be tested and additional ICP-DRC-MS versus SIFT-MS plots might be constructed.
6.5 Conclusions

For the first time, a simple calculation procedure has been shown to provide direct correlation between the observed signal decays measured by ICP-DRC-MS and fundamental kinetic rate constants regardless of reaction mechanism, reaction gas identity, or if the overlap is monatomic or polyatomic. When signal decays were plotted against estimated gas density, a direct correlation to the SIFT-MS kinetic rate constants was shown for the reactions of Ar⁺, Ar₂⁺ and Sr⁺ with various neutral species. All ions showed excellent correlation, but the Sr⁺ linear regression line did not pass through the origin as expected. Reactions with Sr⁺ were only performed with three gases, and more gases should be used in order to determine possible reasons why the line does not pass through the origin.

The kinetic rate constant database¹⁴ offers reaction rates and efficiencies for possible solutions to singly charged elemental overlaps, but many polyatomic overlaps in ICP-MS do not appear in the database. If rate constants using at least two reaction gases are known, then other kinetic rate constants may be determined by calibrating ICP-DRC-MS signal decays to SIFT-MS rate constants. For the first time, kinetic rate constants were determined for reactions between CH₃F, Ar⁺ and Ar₂⁺ as 9.59 x 10⁻¹⁰ and 1.03 x 10⁻⁹ cm³ molecule⁻¹ s⁻¹ respectively. The ability of ICP to efficiently produce many polyatomic and metallic ions, combined with the above method to calculate kinetic rate constants, might allow the bimolecular rate constant database to significantly expand. Many of the problematic polyatomic ions in ICP-MS do not have known kinetic rate
constants with any gases. This method provides a way to simultaneously overcome spectral overlaps in ICP-MS while adding to the kinetic rate constant knowledge base.


52. Adam Rowland, Todd B. Housh and James A. Holcombe, *Use of electrothermal vaporization for volatility-based separation of Rb–Sr isobars for determination of


7.1 Abstract

The ion trajectory modeling program SIMION 8.0 is used to show how simple simulations of ion-gas collisions can add insight into the processes that occur in the reaction cell. A hard sphere collision model written using the ion trajectory simulation program SIMION 8.0 was used to explore ion-neutral collisions, collisional focusing and scattering.

7.2 Introduction

Computer simulations offer an easy way to visualize focusing, scattering and collisions in the Dynamic Reaction Cell (DRC) which is used for ion-molecule reactions to overcome spectral overlaps in ICP-MS. A computer simulation was written in SIMION 8.0 to study the effect of reaction gas on ions passing through the DRC. A combination of thermodynamics and computer simulations should allow a researcher, analyst or student to understand many of the ion-molecule processes occurring inside the instrument without stepping foot inside the laboratory.

The simulation was written in the ion optics program SIMION 8.0. SIMION is a 32-bit virtual DOS program that utilizes potential arrays to simulate ion trajectories. Geometry and arrangement of electrodes are defined followed by assigning voltages to
the electrodes. SIMION then calculates the electrostatic potential at each point in space between the electrodes as well as the fields defined by the gradient of those potentials. The electrostatic potentials are calculated by solving the Laplace equation by the finite difference method called over-relaxation.  

The motion of ions through a quadrupole mass filter has been previously simulated using the custom in-house software, MathCad and SIMION. Ion trajectories through pressurized regions have also been previously simulated with a quadrupole ion trap and linear quadrupole ion guides, as well as through octopole and hexapole ion guides. One group has published simulation results from a proprietary program but only showed the effects of the pressurized reaction cell on ion trajectories and RF-energy contributions. To date, no published study has attempted to use simulations to predict ICP-DRC-MS signals.

7.3 Experimental

Computer simulations were performed on a personal computer running SIMION 8.0 (Scientific Instrument Services, Ringoes NJ and Idaho National Laboratory, Idaho Falls ID). Data were analyzed with Microsoft Excel (Redman, WA).

7.4 Dynamic Reaction Cell design in SIMION 8.0

The dynamic reaction cell (DRC) is composed of an encased quadrupole which both transports ions to the analyzer quadrupole and can be used to prevent unwanted secondary chemistry. The DRC quadrupole high pass filter selectively allows only ions of greater m/z than a user defined limit to pass while causing unstable trajectories for all
other ions.\textsuperscript{14-16} The m/z range of ions that have stable trajectories through the DRC depend on the RF amplitude and frequency applied to the quadrupole rods. Equations 7.1 and 7.2 show the relationship between RF amplitude, frequency and ion m/z for a stable trajectory through the DRC:

\begin{align*}
a_n &= 4 \frac{e \cdot V_{DC}}{m \cdot \omega^2 \cdot r_0^2} \quad (7.1) \\
q_n &= 2 \frac{e \cdot V_{RF}}{m \cdot \omega^2 \cdot r_0^2} \quad (7.2)
\end{align*}

where \( n \) is the order of the multipole, \( e \) is the electronic charge, \( V_{DC} \) and \( V_{RF} \) are the direct current and peak to peak radio frequency amplitudes applied between pole pairs, \( m \) is the ion mass, \( \omega \) is the angular frequency and \( r_0 \) is the field radius of the multipole array. The DRC is operated in a frequency scanning mode in an attempt to avoid any RF contributions to the ion kinetic energy.\textsuperscript{17,18} Pairs of rods are connected electronically as seen in figure 7.1.
Figure 7.1: General schematic diagram of the quadrupole mass filter observed axially indicating potentials of the electrode surfaces.

The potentials applied to the quadrupole rods are shown in figure 7.1 where $U$ is the DC potential, $V_{RF}$ is the peak to peak RF amplitude, $\omega$ is the RF frequency in radians/s, and $t$ is the flight time in seconds. The rods are coupled so that there is a $\pi$ radian phase difference between the x and y pairs. At a fixed frequency, the RF and DC potentials act as low and high mass cutoff parameters, respectively. Ions outside the stability region of the quadrupole have unstable trajectories in the x-direction ($m/z$ too small) or y-direction ($m/z$ too large). The DRC almost always acts as a high pass filter because secondary reaction chemistry almost always produces products at a larger m/z than the reactants. Product formation at the same mass as the analyte can be prevented.
by rejecting low mass reactants. This allows the DRC to act as a RF only quadrupole with the voltage applied to the quadrupole rods $V = V_{RF}\cos(\omega t)$.

7.4.1 DRC design using SIMION 8.0

The SIMION potential array was designed to emulate the instrument by matching the dimensions, voltages, RF frequencies and amplitudes, offsets and spacing as closely to possible to the Perkin Elmer Elan 6100 DRC$^{\text{PLUS}}$. The major omission is the absence of axial field electrodes. These tapered electrodes lie between the quadrupole rods and compensate for space charge effects inside the reaction cell by adding a positive potential to move ions towards the outlet of the DRC. SIMION did not include space charge effects from ion beam repulsion, so axial field electrodes were not expected to impact the number of predicted collisions. However, the positive voltage on the tapered axial field electrodes likely affects the flight time of ions through the reaction cell.

Four quadrupole electrodes ($r_0 = 3.55$ mm, length = 12 cm) were modeled as those in the DRC and its RF frequency was automatically adjusted according to the specified low mass cutoff and equation 7.1 with a peak to peak magnitude of 200 V. Electrically isolated electrostatic lenses were placed at the entrance and exit of the “cell,” 0.4 millimeters before and after the quadrupole rods respectively. The entrance and exit lenses were modeled as rectangular plates perpendicular to the quadrupole rods with a circular orifice through which ions could pass into and out of the DRC. The Elan 6100 ICP-DRC-MS has circular entrance and exit lenses, but the difference in modeled shape was not expected to have an impact because ions flew through the center of the lenses and did not come close to the edges. In reality, the entrance and exit lenses also serve to
enclose the reaction cell so that reaction gas can only escape by effusing through the lens orifices. A “detector” was placed 1 mm outside the exit lens and held at -150 V to provide ions with a location to terminate after passing through the exit lens. A total of seven potential arrays (4 rods, 2 lenses, 1 detector) were generated, each containing approximately 160,000 adjustable points called grid units. SIMION then calculated the electric fields in the space between the electrodes by solving the Laplace equation (7.3).

\[
\nabla^2 V = \nabla \cdot \nabla V = 0 \quad (7.3a)
\]

\[
\nabla V = \left( \frac{\partial V}{\partial x} \right) i + \left( \frac{\partial V}{\partial y} \right) j + \left( \frac{\partial V}{\partial z} \right) k = E \quad (7.3b)
\]

\[
\nabla^2 V = \nabla \cdot E = \frac{\partial E_x}{\partial x} + \frac{\partial E_y}{\partial y} + \frac{\partial E_z}{\partial z} = 0 \quad (7.3c)
\]

SIMION uses a finite difference technique named “over-relaxation” to solve the Laplace equation. The relaxation technique uses successive approximations to give a best estimate of the electric field at every non-electrode point in 3D space. The electric field is calculated as the average value of its nearest six neighbors. This process is repeated unless the changes are small enough that the potential array can be said to be refined. Non-electrode points change by smaller and smaller amounts during each iteration, until a suitable solution is arrived upon and the refined arrays provide a potential energy field. The over-relaxation method has the advantages that numerical computation errors are minimized, solutions are stable, and computer memory requirements are minimized.

The total SIMION workspace area was 16 mm wide by 16 mm tall, with a length of 123 mm and spatial resolution of 5 grid units mm\(^{-1}\). Table 7.1 shows the dimensions
of the DRC modeled in SIMION. To reduce the dimensionality of the simulation, only the inner halves of the quadrupole rods were modeled.

**Table 7.1:** Geometry and potentials used to create a replica of the dynamic reaction cell using SIMION 8.0.

<table>
<thead>
<tr>
<th>Dynamic Reaction Cell Geometry</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrode</td>
<td>Dimension</td>
<td>Grid Units</td>
</tr>
<tr>
<td>Quadrupole rod length</td>
<td>12 cm</td>
<td>600 g.u.</td>
</tr>
<tr>
<td>Quadrupole rod diameter</td>
<td>8 mm</td>
<td>40 g.u.</td>
</tr>
<tr>
<td>Quadrupole rod spacing</td>
<td>$r/r_0 = 1.127$; $r_0 = 3.55$ mm</td>
<td>17.75 g.u.</td>
</tr>
<tr>
<td>Entrance lens aperture diameter</td>
<td>2.2 mm</td>
<td>11 g.u.</td>
</tr>
<tr>
<td>Exit lens aperture diameter</td>
<td>2.0 mm</td>
<td>10 g.u.</td>
</tr>
<tr>
<td>Distance from entrance lens to exit lens</td>
<td>0.4 mm</td>
<td>2 g.u.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Dynamic Reaction Cell Electrode Potentials</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Quadrupole rod RF amplitude</td>
<td>200 V peak to peak</td>
</tr>
<tr>
<td>Quadrupole rod RF frequency</td>
<td>Adjusted based on user determined lowest mass allowed to pass through the quadrupole</td>
</tr>
<tr>
<td>Quadrupole rod DC offset</td>
<td>- 8 V</td>
</tr>
<tr>
<td>Entrance lens voltage</td>
<td>-10 V</td>
</tr>
<tr>
<td>Exit lens voltage</td>
<td>-10 V</td>
</tr>
<tr>
<td>Detector Voltage</td>
<td>-150 V</td>
</tr>
</tbody>
</table>

A user program (Appendix A) was written that automatically adjusted voltages applied to the quadrupole. The portion of the program that handled collisions was written by David Manura and modified for the DRC simulation. The program was written in the programming language Lua and contained subroutines that controlled all simulation parameters. For example, if a user set the RF peak to peak voltage at 200V, and wanted to reject ions less than m/z 40 from the quadrupole, the user program automatically calculated the RF frequency to be 2.09 MHz.
The ions were flown through the virtual DRC with a Gaussian kinetic energy distribution centered at 8 eV with a width of 1 eV (full width at half maximum; $\sigma \approx 0.42$ eV). The initial directions and angles of ions flown into the DRC were randomly varied in a circle distribution of radius 1 mm with a conical distribution of 10° half angle.

Another quadrupole simulation used a beam divergence of 6° and radius of 0.6 mm, although the ion source and optics, interface region and quadrupole dimensions were different in that study. The starting beam radius and divergence values used were determined to provide 100% transport efficiency through the quadrupole in the vented (no gas) mode. When applicable, groups of ions were flown separated in time by 1 μs (simulated signal $10^6$ c s$^{-1}$) so that the phase of the RF cycle on the quadrupole rods would be different for each ion as long as the calculated frequency was not a multiple of $10^6$ Hz (it was not in this work). The 3D SIMION model is shown in figure 7.2. The entrance and exit lenses are removed and the quadrupole rods only are shown in figure 7.3.
Figure 7.2: 3D model of the dynamic reaction cell oriented 35° from the horizontal. The entrance lens is shown in the bottom left of the cell, with the exit lens at the top right.
Figure 7.3: 3D representation of the simulated DRC with entrance and exit lenses removed for clarity.

Figure 7.4: Axial view of the simulated DRC with entrance and exit lenses removed for clarity.

The specific ion flight conditions for each experiment will be described in the relevant sections. Unless noted otherwise, all user input variables and the values used are listed in table 7.2 with a short explanation of each.
### Table 7.2: Simulation variables, values used and short explanation of each.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value used (unless otherwise noted)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Entrance lens voltage</td>
<td>-10 V</td>
<td>Bias applied to entrance lens</td>
</tr>
<tr>
<td>Exit lens voltage</td>
<td>-10 V</td>
<td>Bias applied to exit lens</td>
</tr>
<tr>
<td>Bandpass cutoff</td>
<td>Varies according to experiment</td>
<td>Mass used to calculate quadrupole RF frequency</td>
</tr>
<tr>
<td>Percent tune</td>
<td>0</td>
<td>Per cent of maximum (a = 0.908) on stability diagram (set to 0 for RF only mode)</td>
</tr>
<tr>
<td>Quadrupole rod offset</td>
<td>-8 V</td>
<td>DC bias applied to rods</td>
</tr>
<tr>
<td>Detector voltage</td>
<td>-150 V</td>
<td>Slight negative voltage to provide ions a place to terminate</td>
</tr>
<tr>
<td>Effective radius (cm)</td>
<td>0.4 cm</td>
<td>Radius of quadrupole rods</td>
</tr>
<tr>
<td>RF voltage</td>
<td>200 V</td>
<td>Peak to peak RF amplitude</td>
</tr>
<tr>
<td>PE update (μsec)</td>
<td>0.05</td>
<td>Potential energy surface refresh rate (not used in this work)</td>
</tr>
<tr>
<td>Phase angle (degree)</td>
<td>0º</td>
<td>Phase of RF cycle</td>
</tr>
<tr>
<td>Gas mass (amu)</td>
<td>Varies according to experiment</td>
<td>Mass of reaction gas</td>
</tr>
<tr>
<td>Mean free path</td>
<td>-1</td>
<td>When set to -1, user program automatically calculates according to equation 5.27</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>298</td>
<td>Temperature of gas</td>
</tr>
<tr>
<td>Pressure (mTorr)</td>
<td>Varies according to experiment</td>
<td>Pressure of gas</td>
</tr>
<tr>
<td>Cross section</td>
<td>Varies according to experiment</td>
<td>Hard sphere cross section of ion and gas</td>
</tr>
<tr>
<td>( v_x ) (mm μs(^{-1}))</td>
<td>0</td>
<td>Gas velocity in x direction</td>
</tr>
<tr>
<td>( v_y ) (mm μs(^{-1}))</td>
<td>0</td>
<td>Gas velocity in y direction</td>
</tr>
<tr>
<td>( v_z ) (mm μs(^{-1}))</td>
<td>-0.1</td>
<td>Gas velocity in z direction (towards outlet)</td>
</tr>
<tr>
<td>Steps per mean free path</td>
<td>20</td>
<td>How many times the ion’s position is calculated per mean free path length</td>
</tr>
<tr>
<td>Mark Collisions</td>
<td>1</td>
<td>Mark ion trajectory with a red dot when collision occurs (1) or no mark (0)</td>
</tr>
</tbody>
</table>

Figure 7.5 shows an example \(^{115}\)In\(^+\) trajectory with no gas present and the DRC operated with a low mass cutoff of 100 amu. The ion traverses the DRC in a “weaving”
pattern that is typical of RF only quadrupole ion guides.\textsuperscript{8, 9, 12, 13, 20} The initial ion position was 1 mm immediately preceding the entrance lens (removed in figure 7.5 for clarity) offset +1 mm from the central axis in the x-direction and -1 mm in the y-direction.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure7.5.png}
\caption{Example of a RF only simulated ion trajectory through the SIMION designed DRC when no gas is present. A 3D perspective view (a) of the ion trajectory and close up of the axial view (b) in the lower right hand corner inset. The simulated ion was m/z 115 and the quadrupole rejected ions less than m/z 100 (RPq = 0.83).}
\end{figure}

A hard sphere collision model was also used to simulate the interactions of ions with gas in the reaction cell. The hard sphere model was used for its simplicity and typical kinetic energy of ions extracted from the ICP. At high kinetic energies (>1 eV) the ion-gas interactions can be treated as purely elastic collisions with no significant ion-
dipole interactions. The hard sphere cross section of any ion and gas pairing can be calculated if both the individual ion and gas cross sections are known.

\[ \sigma = \pi (r_{ion} + r_{gas})^2 \]  
(7.4)

where \( r_{ion} \) and \( r_{gas} \) are the collision radii of the ion and gas species respectively. The user program calculates the mean free path of the ions in the reaction cell. The ion-gas collisions are treated as elastic and energy transfers occur solely through these collisions. The background gas is assumed to be neutral in charge, with a Maxwell-Boltzmann velocity distribution. The reaction gas velocity was provided by the manufacturer (0.1 mm \( \mu s^{-1} \) from front to back of the cell) and did not depend on gas flow rate into the cell. SIMION predicted the collision probability so that each ion would undergo one collision per mean free path on average. For an infinitesimal distance (dx) traveled, the increase in the fraction (f) of collided particles relative to the number of yet uncollided particles (1-f) is equal to the distance traveled (dx) over the mean free path (l)\(^1\)

\[ \frac{df}{(1-f)} = \frac{dx}{l} \]  
(7.5)

\[ f = 1 - \exp\left(\frac{-dx}{l}\right) = 1 - \exp\left(\frac{-vdt}{l}\right) \]  
(7.6)

where \( v \) is the ion velocity; and \( dt \) is the time between computations. \( f \) can be interpreted as the probability that a single particle undergoes a collision in the distance calculated. As the distance traveled (\( v * dt \)) approaches the mean free path, the probability of a collision occurring approaches 1. The collision impact angle and offsets were randomized by SIMION. The impact offset describes whether or not the ion and gas collide head on, glancing, or nearly miss. After the collision, depending on the impact
offset and angle, new ion velocities and trajectories are calculated. Any change in ion kinetic energy is also re-calculated using equation 5.14.

7.4.2 Effect of low mass cutoff on ion trajectories

The simulation’s quadrupole frequency is set to provide a low mass cutoff where ions below this mass have unstable trajectories. The low mass cutoff provides a way to prevent unwanted secondary chemistry due to atom or molecule addition or condensation/clustering reactions with an ion that has a lower mass than the analyte ion. The effect of the low mass cutoff on ion trajectories is shown in figures 7.6 a-d.
Figure 7.6: Simulated $^{115}\text{In}^+$ trajectories through the no gas mode DRC as a function of low mass cutoff. The low mass cutoffs of a) 25, b) 50, c) 75 and d) 100 amu are shown.

Figures 7.6 a-d show how the trajectory of $^{115}\text{In}^+$ changes at different low mass cutoff values. As the quadrupole low mass cutoff increases, the frequency of the quadrupole decreases. Table 7.3 shows the calculated RF frequencies for the cutoffs shown in figure 7.6.
Table 7.3: Calculated quadrupole RF frequencies and $^{115}\text{In}^+$ flight distances for 25, 50, 75 and 100 m/z low mass cutoff and 200 V peak to peak amplitude.

<table>
<thead>
<tr>
<th>Largest m/z allowed to pass the quadrupole (low mass cutoff)</th>
<th>Corresponding RPq for $^{115}\text{In}^+$</th>
<th>Calculated frequency assuming 200 V peak to peak RF amplitude</th>
<th>Distance traveled (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.21</td>
<td>2.65 MHz</td>
<td>13.7</td>
</tr>
<tr>
<td>50</td>
<td>0.42</td>
<td>1.88 MHz</td>
<td>15.8</td>
</tr>
<tr>
<td>75</td>
<td>0.62</td>
<td>1.53 MHz</td>
<td>20.6</td>
</tr>
<tr>
<td>100</td>
<td>0.83</td>
<td>1.32 MHz</td>
<td>26.3</td>
</tr>
</tbody>
</table>

When the DRC was programmed to reject ions less than 25 amu, the $^{115}\text{In}^+$ ion traveled a total distance of 13.7 cm as it traversed the 12.5 cm quadrupole. When the DRC rejected ions less than 100 amu, the $^{115}\text{In}^+$ ion traveled a total distance of 26.3 cm. The ion passes through the XZ plane 8 times and never travels more than 2 mm from the center of the quadrupole when the low mass cutoff is 25 amu, but crosses the XZ plane 21 times and is at times as far as 4 mm from the quadrupole center when the cutoff is 100 amu. Ions experience increased force as they fly closer to the electrodes, increasing their kinetic energy which also increases the possibility for endothermic reactions to occur. The forces that ions experience may be expressed by Coulomb’s Law

$$ F = k_e \frac{q_1 q_2}{r^2} $$

(7.7)

where $F$ is the force experienced when the ion of charge $q_1$ comes within distance $r$ of the electrode with charge $q_2$; and $k_e$ is Coulomb’s constant. This increase in kinetic energy has been estimated to be no more than 0.4 eV using a thermodynamic ladder, meaning that a reaction that is endothermic by 0.4 eV or less may still occur inside the DRC.
Ion trajectories presented here agree well with the general trajectory patterns of previous ion flight simulations through RF-only quadrupoles.\textsuperscript{4, 6, 11, 12, 14, 20, 21, 23} The examples here were for $^{115}$In$^+$ traversing the reaction cell with no gas present, but the simulation can be extended to any of the other elements in the periodic table and any specific instrument electrode voltages and frequencies.

### 7.4.3 Simulation of collisional focusing and ion beam scattering

An increase in sensitivity up to a factor of 6 can be achieved due to loss of axial kinetic energy, resulting in ions being ‘focused’ to the center of the reaction cell.\textsuperscript{24} Collisional focusing occurs at low to medium (typically < 0.5 mL min\textsuperscript{-1}, less than 10 mTorr) collision/reaction gas flow rates for ions that have greater mass than the gas atom or molecule. Significant signal loss may occur due to ion beam scattering if the mass of the gas atom or molecule is much greater than the ion mass.

Ions were flown into the virtual reaction cell at varying pressures and the spread of ions exiting the DRC was recorded. $^{115}$In$^+$ was used as a mid-mass representative ion with RPq = 0.25 (low mass cutoff 30 amu). Eleven ions were spaced 0.35 mm apart along the XZ plane from -1.75 mm to +1.75 mm. Figure 7.7 shows the trajectories of the eleven ions when no gas is present.
Figure 7.7: Simulation of the ion trajectories of eleven $^{115}$In$^+$ ions displaced along the XZ plane in the no gas mode with RPq = 0.25.

When the reaction cell is pressurized under the right conditions, the ions may be collisionally focused to the center of the quadrupole and transmission through the cell is increased. Chapter 3 described which conditions where collisional focusing or scattering predominately occurs. The trajectories of the same eleven ions in figure 7.7 were simulated while the virtual DRC was pressurized with NH$_3$ at a flow rate of 1.0 Ar equivalent mL min$^{-1}$ (~6 mTorr). The centering of ions are shown radially (figure 7.8) and axially (figure 7.9).

Figure 7.8: Radial view of simulated trajectories of eleven $^{115}$In$^+$ through a DRC pressurized with 6 mTorr NH$_3$ and RPq = 0.25.
The initial spread of ions entering the DRC was 3.5 mm and the ions were spaced evenly from at x values +1.75 mm to -1.75 mm (y = 0 mm, z = -125 mm for all ions). After collisional focusing, the ions were spaced from -0.21 mm to +0.25 mm, which translates roughly to a 10x focusing. The reduction in radial spatial distribution shows how the transmission of ions through the exit lens may increase sensitivity.
Simulated trajectories from $^{115}$In$^+$ with no gas (blue) and 6 mTorr NH$_3$ (red) at RPq = 0.25. Starting ion position for both no gas and pressurized simulation was (-2.0 mm, -1.0 mm, -125 mm).

The boundaries of the ion paths with no gas in the cell are bound by an outside and inside surface, due to conservation of total energy and the angular momentum, respectively. When the cell is pressurized appropriately, the ion trajectories collapse towards the central axis as radial energy is decreased. SIMION is able to calculate the kinetic energy of ions as they traverse the reaction cell. Figure 7.11 shows the calculated
kinetic energy of the two ions in figure 7.10 as a function of distance traveled in the reaction cell.

Figure 7.11: Calculated kinetic energy of an example of one particular $^{115}\text{In}^+$ ion as a function of distance traveled into the quadrupole for a) no gas and b) 6 mTorr NH$_3$. For clarity figure 5.21b shows the average kinetic energy between collisions.
In most collisions the ion transfers a portion of its kinetic energy to the neutral collision gas. The ion in figure 7.11a undergoes no collisions and its kinetic energy varies due to the oscillating RF field. Figure 7.11b shows the average kinetic energy between collisions so that the decrease in kinetic energy after each collision may be observed. The trace in 7.11b shows the average kinetic energy between collisions to show the step down in energy after each collision. The ion’s kinetic energy decreases from 8 to 6.1, 4.2, 3.1 and 1.0 eV after 1, 2, 3, and 4 collisions, respectively. As the total kinetic energy decreases the ion’s trajectory collapses to the central axis as shown in figure 7.10. The radial spread of ions decrease and the transmission through the reaction cell is enhanced.

If the pressure of the reaction gas is too high or the gas mass too large, it becomes more likely that the ions will be scattered. When the reaction cell is filled with Xe at 6 mTorr (~0.2 Ar equivalent mL min\(^{-1}\)) the \(^{115}\)In\(^+\) ion transmission decreases by a factor of 2 compared to the vented mode (chapter 2). Figure 2.17 shows the normalized transmission efficiency under these conditions.
Figure 7.12: Simulated trajectories of a) eleven ions evenly spaced along the vertical axis and b-d) individual ion trajectories through a DRC pressurized with 6 mTorr Xe and RPq = 0.25.

When the DRC was pressurized with 6 mTorr Xe, only three ions out of eleven passed through the exit lens (7.12a). Five ions exited back out through the entrance lens, and three ions collided with the quadrupole electrodes. This transmission efficiency (3/11 = 27%) is within a factor of 2 with the sensitivity loss when the cell is pressurized at 6 mTorr with Xe flowing at 0.2 Ar equivalent mL min⁻¹. In contrast, when the cell was pressurized with 6 mTorr NH₃, all 11 ions in the SIMION simulation were transmitted through the exit lens.

SIMION randomized the number of collisions, collision angle and time of collision (or distance into the quadrupole when the collision occurs) as illustrated in
figures 7.12 b – d. The simulated trajectories of three individual ions introduced at exactly the central axis are unique from each other. The collisional focusing and scattering simulations were intended to provide a qualitative and pictorial explanation of why signal varies according to gas flow rate, even if no reaction is occurring.

### 7.5 Signal simulations using SIMION 8.0

Predictions of the collision rate combined with second order kinetic rate laws were related to experimental measurements. If successful, this would allow researchers to simulate the best reaction gas flow rate to reduce the ion signal by a given or desired factor assuming 100% reaction efficiency. The simulation might also be used to calculate reaction efficiency without SIFT-MS by comparing the experimentally measured signal decrease as a function of reaction gas flow rate to the signal decrease predicted by the SIMION model assuming a reaction during every collision.

SIMION can only predict the number of collisions that an ion undergoes while traveling through the reaction cell. The simulation cannot predict any secondary ion chemistry, although it does account for the influence of the low mass cutoff (RPq).

#### 7.5.1 Second order kinetic rate laws as applied to SIMION

The SIMION model can estimate the number of collisions ions undergo while traveling through the reaction cell. Alternatively, the model can estimate the fraction of ions that will pass through the cell without undergoing a collision, although that would require that the trajectories of a very large number of ions be simulated. The fraction of ions that are unreacted ([A⁺]₀/[A⁺]) is estimated to be 1/exp(kt[B]).²¹

kt[B] is sometimes
called the “number of reactive collisions” which is equal to the number of collisions multiplied by the efficiency \( \frac{k_{\text{rxn}}}{k_{\text{coll}}} \).

\[
kt[B] = \left( \frac{\text{cm}^3}{\text{molecule}\cdot\text{s}} \right) \ast (s) \ast \left( \frac{\text{molecules}}{\text{cm}^3} \right) = \# \text{ reactive collisions} \quad (7.8)
\]

\[
[A^+] = \frac{[A^+]_0}{\exp(\# \text{ collisions})} \quad (7.9)
\]

SIMION will be used to predict the average number of ion-neutral gas collisions at various gas concentrations in the cell. Equation 7.9 could then be used to predict the signal at that particular reaction gas flow rate, assuming that the ion residence time is independent of the gas flow rate. The validity of this assumption, as well as a study to determine the effect of gas flow rate on ion residence time will be discussed.

7.5.2 Simulating the number of collisions from kinetic gas theory

As a simple alternative to the SIMION simulation, the number of ion-gas collisions was roughly estimated by assuming that the ion passed down the middle of the reaction cell in a straight line. The mean free path of the ion was calculated assuming that the ion-gas collision cross section did not change as a function of changes in kinetic energy.

Ion-molecule interactions can safely be treated as hard sphere collisions when the ion kinetic energy is greater than 1 eV.\(^{21}\) The number of collisions could be estimated by dividing the length of the reaction cell (12.5 cm) by the ion-gas mean free path (a function of the reaction gas pressure in the reaction cell). This estimate was expected to be too low because the length of the reaction cell is less than the distance traveled by any ion that does not enter the reaction cell exactly on the z-axis. When the DRC was
programmed to reject ions less than 25 amu, the $^{115}\text{In}^+$ ion traveled a total distance of 13.7 cm when no gas was present. When the DRC rejected ions less than 100 amu, the $^{115}\text{In}^+$ traveled a total distance of 26.3 cm when no gas was present. It was therefore expected that simply dividing the length of the DRC by the mean free path would underestimate the number of collisions.

The mean free path of an ion-gas pair was calculated according to equation 7.10 where gas density is in molecules cm$^{-3}$, and $\sigma$ is the collision cross section.

$$mean\ free\ path = \frac{1}{\sqrt{2}(\text{gas density})\sigma} \quad (7.10)$$

The collision cross section for Ar$^+$ with NH$_3$ was assumed to be $6.39 \times 10^{-19}$ m$^2$. Using equation 7.9 and the signal with no gas present as $[\text{Ar}^+]_0$, the signal as a function of reaction gas flow rate can be estimated. The number of reactive collisions between Ar$^+$ and NH$_3$ was estimated from the number of collision times $k_{\text{rxn}}/k_{\text{coll}}$ (0.89, measured by SIFT-MS).
Figure 7.13: Overlay of simulated signals (□) and experimentally measured signal intensities (●) at m/z 36 as a function of NH₃ reaction gas flow.

The simulated signals agree within a factor of 4 with the experimental data at flow rates from 0.15 to 0.50 Ar equivalent mL min⁻¹. Because the method assumes ions fly down the center of the reaction cell, it underestimates both the total distance the ion travels and the number of collisions that the ion undergoes, which in turn overestimates signal.

Although this simplified method provides a reasonable estimate, it does not yield information about the distribution of the number of collisions. It is important to
understand at what flow rates there is acceptable probability that an ion will undergo zero collisions as it traverses the DRC. SIMION was used to correct for changes in ion trajectory and to determine a collision distribution.

7.5.3 Simulating the number of collisions with SIMION 8.0

For any given ion-molecule pair and gas pressure, the user program in Appendix A offers a quick method to predict the number of ion-molecule collisions. By extension, the program also can calculate the probability of an ion undergoing no collisions (and no reactions) as it traverses the DRC. The only prerequisite knowledge required is the ion-molecule hard sphere collision cross section calculated using equation 7.4 and the reaction gas pressure calculated using equation 6.11. These two factors vary according to the reaction gas choice, and if it is assumed that every collision results in a reaction, then these factors are responsible for the difference in observed signal decays. The simulation was first tested by using $^{36}$Ar$^+$ and CH$_4$ and NH$_3$ as reaction gases. The hard sphere collision cross sections for Ar$^+$ with NH$_3$ and CH$_4$ are 6.39 and 4.91 ($10^{-19}$ m$^2$) respectively, calculated using equation 7.4.\textsuperscript{13}

Ions were flown into the reaction cell with a Gaussian kinetic energy distribution centered at 8 eV and 1 eV FWHM. The ions’ initial position was randomized within a 1.5 mm of the center axis and with initial trajectories distributed in a half angle of 10°. 500 ion flights were simulated at each gas flow rate. The low mass cutoffs for NH$_3$ (19 amu, RPq 0.50) and CH$_4$ (32 amu, RPq 0.85) were determined experimentally on the ICP-DRC-MS. These values were sufficient to prevent any secondary chemistry from occurring.

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Figure 7.14: Histogram of the simulated number of $^{36}\text{Ar}^+$ collisions with a-c) NH$_3$ and d-f) CH$_4$ at 0.1 (top), 0.2 (middle) and 0.3 (bottom) Ar equivalent mL min$^{-1}$ flow rates.

Perhaps surprisingly, the distribution of the number of collisions is quite wide, with RSD values routinely greater than 100%. The probability of an ion passing through the reaction cell without undergoing a collision decreases as the gas flow rate is increased and mean free path is decreased. The probability of Ar$^+$ passing through the DRC...
without undergoing a collision decreases from 18% to 0.2% as the NH\textsubscript{3} gas flow rate is increased from 0.1 to 0.3 Ar equivalent mL min\textsuperscript{-1}. The non-zero probability of no collisions is one reason why signals are still measured at higher flow rates, even when the average number of collisions is much greater than 1. If it is assumed that every single collision results in a reaction, then the probability of zero collisions may be treated as the probability of an ion successfully exiting the DRC. For a no gas mode signal of 362,720 c s\textsuperscript{-1} and an 18% simulated probability of an ion undergoing zero collisions (i.e. 18% chance an ion makes it out of the cell into the mass analyzer), a signal may be simulated to be 0.18*372,720 = 65,289 c s\textsuperscript{-1}. This value agrees within a factor of 2 of the experimentally measured signal at 0.1 Ar equivalent mL min\textsuperscript{-1} NH\textsubscript{3} flow rate and within a factor of 3 at 0.3 Ar equivalent mL min\textsuperscript{-1} NH\textsubscript{3} flow rate. This is the simplest way to use SIMION to predict the number of ions exiting the DRC. Equation 7.11 shows one general method to predict the measured signal using SIMION.

\[ \text{Signal (c s}^{-1}) = (\text{Signal}_{\text{no gas}})(\text{Probability of zero collisions}) \]  \hspace{1cm} (7.11)

A second way to predict signals is to simulate the average number of collisions an ion undergoes and use equation 7.9 to predict signal. This method also assumes 100% reaction efficiency. The zero collisions method (equation 7.11) considers only trajectories with zero collisions, and all other ions are ignored. So it is irrelevant if the ion undergoes 1, 10, or 100 collisions on average; only the probability of zero collisions matters. The average number of collisions method (equation 7.9) considers all ion trajectories, so the distribution width and the overall average number of collisions are important.

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Table 7.4: Results from Ar⁺ simulation of reactions with NH₃ and CH₄.

<table>
<thead>
<tr>
<th>Reaction gas flow rate (Ar equivalent mL min⁻¹)</th>
<th>³⁶Ar⁺ + NH₃</th>
<th>³⁶Ar⁺ + CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average number of collisions</td>
<td>Standard deviation of number of collisions</td>
<td>Probability of zero collisions</td>
</tr>
<tr>
<td>Average number of collisions</td>
<td>Standard deviation of number of collisions</td>
<td>Probability of zero collisions</td>
</tr>
<tr>
<td>Probability of zero collisions</td>
<td>Probability of zero collisions</td>
<td></td>
</tr>
<tr>
<td>0.00</td>
<td>0</td>
<td>100%</td>
</tr>
<tr>
<td>0.10</td>
<td>2.41</td>
<td>18.0%</td>
</tr>
<tr>
<td>0.15</td>
<td>3.76</td>
<td>6.6%</td>
</tr>
<tr>
<td>0.20</td>
<td>5.93</td>
<td>3.0%</td>
</tr>
<tr>
<td>0.25</td>
<td>8.87</td>
<td>1.6%</td>
</tr>
<tr>
<td>0.30</td>
<td>12.07</td>
<td>0.2%</td>
</tr>
<tr>
<td>0.35</td>
<td>15.35</td>
<td>0.4%</td>
</tr>
<tr>
<td>0.40</td>
<td>18.14</td>
<td>0.0%</td>
</tr>
<tr>
<td>0.45</td>
<td>20.60</td>
<td>0.0%</td>
</tr>
</tbody>
</table>

Table 7.4 shows the very large standard deviations of the average number of collisions that an ion might undergo. The data in table 7.4 are graphically shown in figure 7.15.
Figure 7.15: Probability of zero collisions (○, left y-axis) and simulated average number of collisions (●, right y-axis) for a) NH₃ and b) CH₄ as a function of reaction gas flow into the cell.

The only difference between NH₃ and CH₄ is the slight difference in pressure due to MFC calibration, 1 amu difference in mass and the difference in collision cross sections. At the highest reaction gas flow rate simulated (0.45 Ar equivalent mL min⁻¹),
Ar$^+$ undergoes 8 more collisions on average with NH$_3$ than with CH$_4$. Figure 7.16 shows the simulated signal of $^{36}$Ar$^+$ as a function of reaction gas flow using both methods overlaid with the experimentally measured signals.

**Figure 7.16:** Overlay of simulated signals (○) and experimentally measured signal intensities (●) at m/z 36 as a function of a – b) NH$_3$ and c – d) CH$_4$ reaction gas flow.
The data in figures 7.16b and 7.16d use equation 7.11 and the probability of zero collisions to calculate the signals at each flow rate. There is agreement within a factor of 1.5 at flow rates less than 0.15 mL min\(^{-1}\). As flow rate is increased to 0.3 mL min\(^{-1}\), the agreement between simulated and experimental signals only agree within a factor of 10. The number of ions that make it out of the DRC with zero collisions is small (2 out of 500 at 0.35 mL min\(^{-1}\)), and so the uncertainty in the simulated signal is quite large. For the case of 0.35 mL min\(^{-1}\) and assuming counting statistics, the number of ions that make it out of the DRC with zero collisions is \(2 \pm \sqrt{2}\) (1 standard deviation).

The data in figures 7.16a and 7.16c use equation 7.9 and the average number of collisions to predict signals. At flow rates less than about 0.20 mL min\(^{-1}\), the simulated data and experimental data agree within a factor of 2. As the flow rate is increased beyond 0.25 mL min\(^{-1}\), SIMION predicts signals too low. At 0.30 mL min\(^{-1}\), SIMION cannot predict signals to be within a factor of 100 of the experimental signals using the average number of collisions method. At these higher flow rates, and when the gas mass is close to the ion mass, the ions sometimes become ‘trapped’ in the DRC and undergo many collisions. The collision histograms in figures 7.14 show the effect of increasing gas flow on the distribution width. As NH\(_3\) or CH\(_4\) gas flow rate increases, the SIMION predicted Ar\(^+\) signals deviate further from the experimentally measured signals. This deviation becomes exponentially worse as the flow rate increases.

Equation 7.9 is valid as long as the reaction time (ion residence time) is constant. As pressure inside the reaction cell is increased, ions are expected to take a longer time to make it through the cell, and the number of collisions increases exponentially.
$^{36}$Ar$^+$ ions were flown with varying pressures of NH$_3$ and identical initial conditions and DRC parameters as previously described.

**Figure 7.17:** Histogram of simulated $^{36}$Ar$^+$ flight times through the DRC pressurized with a) 0, b) 0.1, c) 0.2, d) 0.3 and e) 0.4 Ar equivalent mL min$^{-1}$ NH$_3$ with RPq 0.50. Y-axis scaling changes with each histogram.
The average ion residence time in the DRC based on the SIMION model increases by 94 μs for every 1 mTorr increase in pressure. Figure 7.17d shows the linear increase in residence time as a function of cell pressure. Equation 7.8 and 7.9 show how the predicted signal is exponentially dependent upon the residence time of ions in the cell, and so the accuracy of the predicted signals in figure 7.16 grow exponentially worse as residence time changes. For the case of Ar⁺ reacting with NH₃ and CH₄, SIMION was unable to accurately predict signals using derivations of second order kinetic rate laws.

Both SIMION based simulation methods assume every collision results in a reaction, (100% efficiency) and can be treated as a collision rate. Reaction efficiencies, k_{rxn}/k_{coll}, for Ar⁺ with NH₃ (89%) and CH₄ (75%) have been measured by ICP-SIFT-MS. The uncertainties in the measured efficiencies are large (from 10-30%, see table 6.10). For example, the reaction efficiency of Ar₂⁺ and N₂O was reported to be 110%²⁵, which is impossible. These uncertainties are likely due to inaccuracies in the estimated location dependent reaction gas concentration in the flow tube as well as uncertainty in the reactive cross section calculations.

The combination of SIMION simulations and experimental data may be used to estimate the efficiency of the reactions (# of measured reactions divided by # of simulated collisions). Because the zero collision probability method was shown as the best option to simulate signal, the data from figures 7.16b and 7.16d are used.
**Figure 7.18:** Simulated (blue) and experimental (red) $^{36}\text{Ar}^+$ signals with linear regression fit lines and best fit equations using a) NH$_3$ and b) CH$_4$ reaction gases.

The slope of the simulated data assumes that every collision results in a reaction, it underestimates the number of ions that make it out of the DRC. The collision rate and the number of uncollided ions are inversely related. When the slope of the experimental intensities (proportional to the reaction rate) is divided by the slope of the simulated intensities (representative of the collision rate) the resulting ratio is the reaction efficiency.

$$\text{Reaction Efficiency} = \frac{\text{Slope of log (intensity}_{\text{exp}}}{\text{Slope of log (intensity}_{\text{sim}}}) \quad (7.13)$$

For the case of Ar$^+$ reacting with NH$_3$ and CH$_4$, the ICP-SIFT-MS reaction efficiencies are $89\%^{25}$ and $75\%^{26}$, respectively. The ICP-DRC-MS measured efficiencies using SIMION to model the collision rate yield reaction efficiencies of $108\%$ and $123\%$.
for NH$_3$ and CH$_4$, respectively, which is impossible. The efficiencies will be too high if the number of simulated collisions is too low. This could be due to underestimation of the collision cross section in the hard sphere collision model. Depending on the specific ion-gas pair, an increase in collision cross section of less than 20% has shown results that agree with the experimental data better than those shown in figure 7.18. If another collision model were used such as the Langevin or Average Dipole Orientation that account for ion-dipole interactions, then the efficiencies are expected to be increased due to increased cross section at low kinetic energies. The hard sphere collision model is valid at kinetic energies greater than 1 eV. However, ions that undergo unreactive collisions may lose kinetic energy and fall below the 1 eV threshold. When ions fall below this threshold the reactive cross section increases due to ion-dipole interactions. Because the user program written for SIMION does not change the cross section as a function of kinetic energy, it will underestimate the collision rate for any ions that have low kinetic energy.

The agreement between simulated signals (zero collision method) and experimental signals was not significantly improved in comparison to when the cell length was simply divided by the mean free path in section 7.5.2. Both methods were able to simulate the signal to within a factor of 10 of the experimental signals. However, SIMION allows a user to visualize fundamental processes of chemical resolution in ICP-DRC-MS.
7.5.4 Simulations of reactions significantly less than 100% efficient

Section 7.5.3 showed the ability of SIMION to predict the number of ions that exit the DRC without undergoing a collision, which can be used to estimate signal within a factor of 10 if the reaction efficiency is at or near 100%. However, many reactions do not proceed with 100% efficiency. In these cases, it is not possible to use the number uncollided ions to calculate a simulated signal, unless the reaction efficiency is previously known. For example, consider the reaction between \( \text{Ar}_2^+ \) and \( \text{H}_2 \) (table 6.7 and figure 6.4). Previously reported SIFT-MS measurements determined a reaction efficiency of 31%, i.e. only 3 in 10 collisions result in a reaction. It may be possible to determine the reaction efficiency from ICP-DRC-MS data without SIFT-MS if the number of collisions is determined by SIMION simulation.

\( \text{Ar}_2^+ \) was simulated to fly through the DRC while it was pressurized with \( \text{H}_2 \). The collision cross section of \( \text{Ar}_2^+ \) is not known and had to be estimated. The bond length in a neutral Ar-Ar molecule is 372 pm.\(^{28}\) In the cationic form, an electron is removed from the molecule and the bond length is expected to decrease and the cross section is expected to be dominated by each \( \text{Ar}^+ \) radius. The radius of each \( \text{Ar}^+ \) is \( 1.54 \times 10^{-10} \text{ m} \)\(^{29}\) and the radius of \( \text{H}_2 \) is \( 2.71 \times 10^{-10} \text{ m} \).\(^{30}\) The length of the (Ar-Ar)^+ bond was unknown and therefore not included in the calculation. The resulting cross section for \( \text{Ar}_2^+ \) and \( \text{H}_2 \) was calculated as \( 1.05 \times 10^{-18} \text{ m}^2 \) using equation 7.4. 500 \( \text{Ar}_2^+ \) flights were simulated with random initial position and kinetic energy distribution centered at 8 eV, and the DRC quadrupole set to reject m/z less than 50 amu (RPq = 0.60). Figure 7.19 shows the
simulated signals with results from both zero collision probability method and average number of collisions method overlaid with the experimentally measured Ar$_2^+$ signals.

![Graph](image.png)

**Figure 7.19:** Overlay of simulated signals (○ using average collision method and □ using zero collision probability method) and experimentally measured signal intensities (●) at m/z 80 as a function of H$_2$ reaction gas flow.

Unlike the simulation for Ar$^+$ with NH$_3$ and CH$_4$, the decrease in estimated Ar$_2^+$ due to reaction with H$_2$ is similar for the average collision and zero collision approaches. In the case of Ar$^+$, the ion residence time was not constant but when Ar$_2^+$ was simulated, its high mass (80 amu) and low mass of H$_2$ (2 amu) very rarely caused a dramatic increase in the residence time.
Figure 7.20: Histogram of simulated $^{36}$Ar$^+$ flight times through the DRC pressurized with a) 0, b) 0.1, c) 0.2, d) 0.3 and e) 0.4 Ar equivalent mL min$^{-1}$ NH$_3$ with RPq 0.50. Y-axis scaling changes with each histogram.

Whereas the average ion residence time of Ar$^+$ in the DRC increased by 93 µs for each 1 mTorr of NH$_3$, the average residence time of Ar$_2^+$ only increased by 8 µs for every 1 mTorr H$_2$ (figure 7.20d). The signals calculated by both the average collision and zero
probability methods agree well, in contrast to the results for Ar$^+$. At flow rates greater
than 0.45 mL min$^{-1}$, none of the 500 ions were simulated to pass through the DRC
without undergoing a collision. Therefore, many more ion paths must be simulated to
accurately estimate the probability of a single ion passing through the DRC at high
pressures without a collision.

The simulated Ar$_2^+$ signals fall much more quickly as a function of H$_2$ flow rate in
to the cell than the experimentally measured signals, as expected for reaction efficiencies
much less than 100%. The SIFT-MS recorded reaction efficiency was 31%$^{27}$ and the
efficiency based on the experimentally measured rate divided by the SIMION model
collision rate ($k_{\text{ex}}/k_{\text{coll}}$) was 35%, which agrees within experimental uncertainty. This
agreement indicates that any underestimation of the collision rate by the hard sphere
collision model is not significant for Ar$_2^+$ and H$_2$. The hard sphere collision model is
expected to be better for Ar$_2^+$ and H$_2$ because the maximum energy that can be
transferred is smaller for a H$_2$ collision than for NH$_3$ or CH$_4$. The simulation provides a
remarkable estimate for the ion-molecule collision rate and the ability to determine
reaction efficiency without SIFT-MS.

It is important to understand that the ions undergo random numbers of collisions,
each collision with its own chance to result in a reaction, and that the distribution of
numbers of collisions is quite wide. An ICP-DRC-MS user with access to the SIMION
simulation will have a deeper understanding of the principles of chemical resolution.
7.6 Conclusions

A computer simulation was used to show that the simple hard sphere collision model could be used to simulate collisions that an ion will undergo as it traverses the DRC, as well as the qualitative effect of these collisions for collisional focusing and scattering. Future work might include a systematic study to determine the gas masses and flow rates at which any particular analyte’s signal is optimized, as well as the point when collisional focusing shifts to collisional scattering.

The SIMION model was then used to compare simulated signals of both Ar$^+$ and Ar$_2^+$ to the experimental results. Two methods were used to simulate signals: the zero collision probability method and the average collision probability method. The zero collision probability method provided signals within a factor of 10 to the experimental signals, but did not correctly predict the Ar$^+$ reaction efficiency. The average collision method did not provide accurate answers for Ar$^+$ because the constant residence time assumption was not observed in the simulation. In the case of Ar$_2^+$/H$_2$, residence time was roughly constant and the simulated efficiency matched closely to the SIFT-MS measured efficiency.

The hard sphere collision model underestimates the collision rate which tends to lead to an overestimate of the reaction efficiency. The SIMION model could be modified to use either the Langevin or ADO based collision cross sections at low kinetic energies. It would be very interesting if the user program that was written for SIMION included an “if-then” loop that recalculated the cross section after each collision depending on the ion’s kinetic energy. This type of modification might provide reaction efficiencies much
closer to the accepted efficiencies by dynamically correcting the cross sections for changes in kinetic energy.


8 Nanoparticle characterization by ICP-MS

8.1 Abstract

This study was intended to determine if nano- and microparticle size, number and composition could be measured using ICP-MS. SiO₂ and Au nanoparticles were introduced to the ICP and signals were calibrated to mass and correlated to particle mass distributions. Many of the challenges to analyzing nanoparticles by ICP-MS and the means to overcome these challenges are discussed.

8.2 Introduction

ICP-MS provides a linear response to particle mass if each particle is identically vaporized, atomized, ionized and a constant percentage of the resulting elemental ions are sampled by the mass spectrometer. Particles were introduced one at a time to an ICP and signals were related to particle mass. To do this, very dilute solutions of nanoparticles were introduced in the form of an aerosol to the ICP. If large dilutions were performed, most of the aerosol droplets would contain no particle, some would contain one particle, and almost none would contain two particles or more. The aerosol passed through an evaporation chamber where the particles dried before exiting. Finally, dry particles entered the ICP and were atomized and ionized. The ions (mainly elemental ions) are sampled into the mass spectrometer. ICP-MS can then measure particle mass, size
distributions (assuming spherical particles) and elemental composition of nanoparticles from both single size standards and mixtures.

8.2.1 Previous nanoparticle measurements using ICP

Niemax et al.\textsuperscript{1-4} have introduced nanoparticles into an ICP in individual, isolated monodisperse water droplets and detected optical emission (OES) signals. The “droplet on demand” micropump used to produce monodisperse droplets is sold mainly to deliver precisely controlled small (sub-nL) volumes of solution.\textsuperscript{3} By delivering a single drop of known size at a repeatable rate, the time that it takes to vaporize the droplet (and begin nanoparticle vaporization) can be precisely controlled. A very similar device was previously used as part of a monodisperse dried microparticulate injector (MDMI)\textsuperscript{5} to introduce individual, isolated droplets of user selectable size into an ICP.\textsuperscript{6} The MDMI was originally used to investigate the processes that droplets and desolvated particles undergo as they pass through the plasma.\textsuperscript{7-12} Monodisperse droplet introduction has at least two advantages: (1) Droplets can be injected into the plasma at well controlled, consistent intervals separated in time to ensure that only one droplet is in the ICP at a time and (2) each droplet will complete desolvation at the same location in the plasma (if the trajectories and velocities are constant).

In the recent work by the Niemax group, ICP-OES signals were calibrated as a function of mass by measuring the signal produced when individual, isolated monodisperse droplets that contained a known amount of the analyte element in solution were introduced into the ICP. They assumed that the vaporization of the nanoparticle and the desolvated particle produced from a droplet of solution were the same. Garcia et al.\textsuperscript{2}
found that a droplet with no particle containing an amount of dissolved Si similar to an 830 nm diameter SiO$_2$ particle and a droplet of water containing an 830 nm diameter SiO$_2$ particle produced similar signals. The signal produced by a droplet that contained one 830 nm SiO$_2$ particle and an equivalent amount of Si in solution produced a signal that was approximately twice as large. The advantage of this approach is that standard size nanoparticles are not required for calibration. A similar approach was used for Au nanoparticles down to 250 nm.

In a related study, the relative standard deviations (RSD) of SiO$_2$ nanoparticles masses measured by ICP-OES were similar to those measured by SEM for particles greater than 1 µm in diameter. For example, 2.06 µm diameter SiO$_2$ particles were measured with 7.6% RSD (N=1,847) by SEM, and 6.2% RSD (N=118,076) by ICP-OES. However, the smallest SiO$_2$ nanoparticle size that could be measured by ICP-OES was 1 µm in diameter. SEM measurements of 1.06 µm particles yielded 10.9% RSD (N=3,019), but the precision of ICP-OES was 16% RSD (N=51,105). The poor precision of the small particle masses was attributed to low signal to background (S/B) ratio of the Si I 288.16 nm emission line. At this size limit, the relative mass distributions measured by ICP did not match with the absolute mass distributions measured by SEM.

Another attempt at characterizing nanoparticles by ICP-MS injected diluted nanoparticle colloids into the ICP and measured the signals spikes, correlating the frequency of signal spikes to the number of Au nanoparticles per mL in solution. This study estimated the Au nanoparticle signal detection limit to be approximately one 25 nm Au particle per mL. The same group has used ICP-MS to analyze colloid suspensions of
TiO$_2$, Al$_2$O$_3$, $^{14}$ZrO$_2$, $^{15}$ThO$_2$, $^{16}$ and UO$_2$. $^{17}$ Although these ICP-MS studies have been classified as “time-resolved,” the time constant was 10 ms, which is significantly longer than the time required for a single particle to vaporize in the ICP. $^{18}$ To date, no study has systematically developed and validated a routine method for nanoparticle characterization by ICP-MS.

8.3 Experimental details

A PerkinElmer Sciex Elan 6100 DRC$^{\text{plus}}$ ICP-DRC-MS was used for all experiments. $^{19}$ A syringe pump (KD Scientific, Holliston MA) delivered solution to a Teflon parallel path nebulizer (AriMist, Burgener Research, Inc., Ontario CN). The AriMist nebulizer was used because it reportedly $^{20}$ operated at a liquid uptake rate down to 50 $\mu$L min$^{-1}$ with suspended particles up to 150 $\mu$m in diameter. A Burgener MiraMist CE nebulizer was also used for some measurements. A quartz, 40 mL conical evaporation chamber at ambient temperature was used with a 2.0 mm inner diameter quartz custom made sheath flow injector (Precision Glassblowing, Centennial CO). The injector was designed so that auxiliary gas could be added to the center gas channel without changing the nebulizer gas flow rate. The auxiliary gas was added as a sheath surrounding the gas exiting the evaporation chamber.

Solutions were made by serial dilution from nanoparticles suspensions (Corpuscular, Cold Spring NY) in deionized water (18.2 M$\Omega$ cm, Millipore Milli-RO-10 and Milli-Q). The stock nanoparticle suspensions were placed in a sonic bath for at least 2 hours before dilution to break up any agglomerated particles and to form a homogeneous suspension. Diluted nanoparticle suspensions were also placed in a sonic
bath for at least 2 hours immediately before measurement to reduce agglomeration. When not in use, solutions were kept on a shaker table at 100 revolutions per minute.

Instrument parameters are listed in Table 8.1. Ammonia (99.999%, Scott Specialty Gases) was used as a reaction gas for some experiments. The reaction gas was introduced through channel A which contained a getter to remove oxygen and water impurities. The Elan DRC 6100Plus uses a dual mode electron multiplier. The two modes (pulse and analog) were not able to be automatically cross-calibrated on this instrument because the lens voltage was manually controlled (a D/A converter to control the lens voltage through the instrument software malfunctioned) and detector cross calibration was performed offline.

Scanning electron microscope images were taken with a Quanta 200 SEM (FEI, Hillsboro OR) at the Ohio State University Campus Electron Optics Facility and recorded using an Everhart-Thornley detector. Images were analyzed (sizes of individual particles determined) using the software package ImageJ version 1.44a.\textsuperscript{21}

Two approaches were used to collect data: 1) recording using a digital oscilloscope and 2) using the Elan software. The digital oscilloscope was triggered when a particle entered the ICP and recorded data on a $\mu$s timescale. The Elan software data recording is a more traditional approach and recorded data on a ms timescale (integrated an entire signal peak). Pros and cons of each approach are reviewed.

Digital oscilloscope measurements were made by directly measuring current from the analog output of the electron multiplier. The current was amplified and converted to voltage, (Keithley 428, Cleveland OH). Voltages were recorded by a digital oscilloscope
(LeCroy 9450A, Chestnut Ridge NY). Data were retrieved from the oscilloscope using ScopeExplorer version 2.21.0 (LeCroy, Chestnut Ridge NY over an IEEE interface).

**Table 8.1:** ICP-MS experimental parameters.

<table>
<thead>
<tr>
<th>Mass Spectrometer Parameters</th>
<th>Oscilloscope data recording</th>
<th>Elan software data recording</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF power/W</td>
<td>1350</td>
<td></td>
</tr>
<tr>
<td>Lens voltage</td>
<td></td>
<td>Optimized daily</td>
</tr>
<tr>
<td>Autolens</td>
<td>Off</td>
<td></td>
</tr>
<tr>
<td>Pulse stage voltage</td>
<td>-2100 V</td>
<td>-2100 V</td>
</tr>
<tr>
<td>Analog stage voltage</td>
<td>3000 V</td>
<td>1150 V</td>
</tr>
<tr>
<td>Auxiliary gas flow</td>
<td>1.2 L min⁻¹</td>
<td></td>
</tr>
<tr>
<td>Plasma gas flow</td>
<td>15 L min⁻¹</td>
<td></td>
</tr>
<tr>
<td>Nebulizer flow</td>
<td>0.6 L min⁻¹</td>
<td></td>
</tr>
<tr>
<td>Sheath flow</td>
<td>0.1 – 0.5 L min⁻¹</td>
<td></td>
</tr>
</tbody>
</table>

**DRC Parameters**

<table>
<thead>
<tr>
<th>NH₃ flow (Ar equivalent mL min⁻¹)</th>
<th>0.00</th>
<th>0.40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Entrance aperture diameter</td>
<td>2 mm</td>
<td></td>
</tr>
<tr>
<td>Exit aperture diameter</td>
<td>2.2 mm</td>
<td></td>
</tr>
<tr>
<td>Axial field voltage</td>
<td>310 V</td>
<td></td>
</tr>
<tr>
<td>RPa</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>RPq</td>
<td>0.25</td>
<td>0.60</td>
</tr>
<tr>
<td>DRC mode quadrupole rod offset</td>
<td>-10 V</td>
<td></td>
</tr>
<tr>
<td>DRC mode cell rod offset</td>
<td>-1 V</td>
<td></td>
</tr>
<tr>
<td>RF voltage</td>
<td>200 V</td>
<td></td>
</tr>
<tr>
<td>DRC mode cell path voltage</td>
<td>-19 V</td>
<td></td>
</tr>
</tbody>
</table>

**Analyzer Parameters**

<table>
<thead>
<tr>
<th>Correction equations</th>
<th>None</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass resolution</td>
<td>~ 0.7 u</td>
</tr>
</tbody>
</table>

**Signal Measurement**

<table>
<thead>
<tr>
<th>Dwell time</th>
<th>1000 ms</th>
<th>2 – 20 ms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sweeps</td>
<td>1000</td>
<td>1</td>
</tr>
<tr>
<td>Readings</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Replicates</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Points per peak</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Settling time</td>
<td>200 ms</td>
<td>200 μs</td>
</tr>
</tbody>
</table>
8.4 Scanning Electron Microscopy of nanoparticles

Particles were analyzed by scanning electron microscopy (SEM) to confirm the sizes reported by the manufacturer. SEM images small objects by using low energy primary electrons to scan the object in a raster pattern while detecting secondary electrons. The reported SiO$_2$ sizes and distributions are shown in table 8.2.

### Table 8.2: SiO$_2$ particles purchased from Corpuscular Inc. listed with average diameter and % coefficient of variation from the manufacturer.

<table>
<thead>
<tr>
<th>Ordered diameter (nm)</th>
<th>Reported diameter (nm)</th>
<th>Reported % RSD</th>
<th>Dilution factor for SEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>319.5</td>
<td>&lt; 2.2 %</td>
<td>1000x</td>
</tr>
<tr>
<td>500</td>
<td>545</td>
<td>&lt; 2.2 %</td>
<td>1000x</td>
</tr>
<tr>
<td>600</td>
<td>620</td>
<td>&lt; 4 %</td>
<td>1000x</td>
</tr>
<tr>
<td>700</td>
<td>725</td>
<td>&lt; 4 %</td>
<td>500x</td>
</tr>
<tr>
<td>800</td>
<td>840</td>
<td>&lt; 4 %</td>
<td>500x</td>
</tr>
<tr>
<td>900</td>
<td>952</td>
<td>&lt; 4 %</td>
<td>100x</td>
</tr>
<tr>
<td>1,000</td>
<td>1,020</td>
<td>&lt; 3 %</td>
<td>100x</td>
</tr>
<tr>
<td>1,500</td>
<td>1,470</td>
<td>&lt; 2 %</td>
<td>100x</td>
</tr>
<tr>
<td>2,000</td>
<td>2,010</td>
<td>&lt; 2 %</td>
<td>50x</td>
</tr>
<tr>
<td>5,000</td>
<td>4,740</td>
<td>&lt; 2 %</td>
<td>40x</td>
</tr>
</tbody>
</table>

Nanoparticles arrived as 1% solids in a H$_2$O suspension and were diluted by the values listed in table 8.2. 10 μL of the diluted suspensions were dropped onto aluminum SEM mounting stubs and allowed to dry at ambient temperature and pressure. The stubs were then Au sputter coated for 50 s to prevent charging during SEM imaging. Au sputter coating for less than 1 minute adds less than 10 nm to the surface.
8.4.1 SEM imaging of SiO$_2$ nanoparticles

Images of each nanoparticle size were collected by SEM. Parameters were optimized so that images would be in focus as much as possible while contrast and brightness were chosen so that the particle edges would appear as sharply as possible against the background. Magnification was chosen so that each image contained less than 25 particles. Typical working conditions were 30 kV acceleration voltage and 3 $\mu$m spot size. The Ohio State Campus Electron Optics Facility staff calibrated the SEM for size using a silicon wafer$^{22}$ (Planotec wafer 615, Ted Palla. Inc., Redding CA) etched by electron beam lithography with guaranteed 1% accuracy. The etched wafer consisted of a square pattern of repeating lines 2 $\mu$m wide every 10 $\mu$m. The accuracy of the SEM calibration was not verified. A sample image of the nanoparticles reported to be 1,470 nm in diameter is shown in figure 8.1.
Figure 8.1: Example image of SiO$_2$ nanoparticles drop deposited on an aluminum SEM mount and sputter coated with Au.

The image analysis method followed previous particle sizing methods using SEM$^4$ and TEM$^{23}$ and at the National Institute of Standards and Technology (NIST, Gaithersburg MD) for Au nanoparticle size characterization (SRM 8011, 8012 and 8013).$^{24}$ Images were analyzed using the open source software package ImageJ (National Institutes of Health, Bethesda MD). This software package allows the user to edit, analyze, process, save and print 8-bit, 16-bit and 32-bit images. ImageJ is also able to calculate area and pixel value statistics of intensity thresholded images.

Images (1024 x 943 pixels) were recorded as 8-bit tagged image file format (TIFF) files and opened using ImageJ. A line was drawn over the distance scale (µm) and ImageJ then calculated the image scale (pixel µm$^{-1}$). The image was thresholded to

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separate particles from background. The threshold value was chosen so that the edges of
the imaged particles acted as a boundary and was dependent on image quality, contrast
and SEM shadow effects. The images were then despeckled using a median filter which
replaces each pixel with the median value in its 3x3 neighborhood. Particles touching
each other were separated using watershed segmentation. This function calculates the
Euclidian distance map and finds the ultimate eroded points (center of the particle, far
from the edges of neighboring particles). The segmentation function then dilates the
ultimate eroded points as far as possible until either the edge of the particle or the edge of
another particle is reached. Finally, the imaging software calculated the area of each
thresholded nanoparticle with circularity (equation 8.1) greater than 0.75 (1.0 is a perfect
circle). A high degree of circularity was used to prevent image artifacts or
agglomerations of nanoparticles from being included in the image analysis results.

\[
Circularity = 4 \pi \left( \frac{\text{Area}}{\text{perimeter}^2} \right) \quad (8.1)
\]

Images were also individually examined to ensure calculated diameters were from
single nanoparticles only. A step-by-step guide to the image processing method is shown
in figure 8.2. Of the 13 whole particles shown in figure 8.2, 12 were found acceptable by
the image analysis procedure. One particle (highlighted in yellow) was not included due
either to being too close to the edge of the image or not being circular enough.
After SEM images were processed, particle areas were converted to diameters.

An example histogram for the “1,020” nm SiO$_2$ particles is shown in figure 8.3.
Figure 8.3: Calculated “1,020” nm SiO$_2$ nanoparticle diameters from SEM measured areas (N = 632). Average diameter was 1,077 ± 89 nm at the 95% confidence interval.

The manufacturer sized the nanoparticles using photon correlation spectroscopy (ZETAPALS, Brookhaven Instruments) for sizes less than 1 μm diameter, and a laser diffraction particle size analyzer (SALD-201V, Shimadzu) for sizes 1 μm and up. The manufacturer would not provide the specific standards used, so it was not possible to quantify the accuracy or uncertainty. Areas, diameters, and distributions measured by SEM are listed in table 8.3 with the manufacturer’s reported values.
Table 8.3: SEM measured areas and diameters of SiO$_2$ nanoparticles with coefficient of variation and total number of particles measured for each size. *Discussion of 875 nm particles found below.

<table>
<thead>
<tr>
<th>Reported diameter (nm)</th>
<th>Reported % RSD</th>
<th>Data from Corpuscular, Inc.</th>
<th>Data from SEM measurements</th>
<th>Comparison</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Measured Area ($\mu$m$^2$)</td>
<td>Calculated Diameter (nm)</td>
<td>N</td>
</tr>
<tr>
<td>319.5</td>
<td>&lt; 2.2%</td>
<td>0.128</td>
<td>403</td>
<td>4.2</td>
</tr>
<tr>
<td>545</td>
<td>&lt; 2.2%</td>
<td>0.211</td>
<td>518</td>
<td>4.1</td>
</tr>
<tr>
<td>620</td>
<td>&lt; 4%</td>
<td>0.311</td>
<td>629</td>
<td>4.4</td>
</tr>
<tr>
<td>725</td>
<td>&lt; 4%</td>
<td>0.437</td>
<td>744</td>
<td>3.6</td>
</tr>
<tr>
<td>840</td>
<td>&lt; 4%</td>
<td>0.602*</td>
<td>~875*</td>
<td></td>
</tr>
<tr>
<td>952</td>
<td>&lt; 4%</td>
<td>0.649</td>
<td>907</td>
<td>8.7</td>
</tr>
<tr>
<td>1,020</td>
<td>&lt; 3%</td>
<td>0.913</td>
<td>1,077</td>
<td>4.2</td>
</tr>
<tr>
<td>1,470</td>
<td>&lt; 2%</td>
<td>2.55</td>
<td>1,801</td>
<td>2.8</td>
</tr>
<tr>
<td>2,010</td>
<td>&lt; 2%</td>
<td>3.26</td>
<td>2,035</td>
<td>3.5</td>
</tr>
<tr>
<td>4,740</td>
<td>&lt; 2%</td>
<td>6.24</td>
<td>2,810</td>
<td>7.6</td>
</tr>
</tbody>
</table>

SEM measurements of each particle size except “319.5”, “1,500” and “4,740” nm agreed within 5% of the reported sizes from the manufacturer. These 3 size standards were found to be different than the reported sizes at the 99% confidence level but the reasons for this finding are not apparent. Sizes measured by SEM are used in all subsequent calculations. SEM measured sizes are plotted in figure 8.4 as a function of the reported particle sizes.
Figure 8.4: Particle diameters measured by SEM (nm) as a function of reported diameters by the manufacturer (nm). 99% confidence intervals shown for SEM diameters. Line indicates perfect agreement.

Size distribution data for the “800” nm particles were not included in table 8.3. The SEM images of these particles showed a non-monomodal distribution. Figure 8.5 shows an image of the “800” nm SiO$_2$ particles.
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Figure 8.5: SEM image of “800” nm SiO$_2$ particles mounted on an aluminum SEM stub and sputter coated with Au.

There are a large number of small particles scattered on the SEM mount, one particle approximately 2 μm in diameter, and 4 particles averaging ~875 nm in diameter. There is also an agglomerate which is composed of five or six 800 nm particles observed towards the lower left hand corner. The smaller particles averaged 305 nm in diameter (N = 538, RSD = 33%). A polymodal distribution was not observed for any other size.

8.4.2 Limitations of SEM particle size measurements

The precision of the SEM image analysis procedure was examined by analyzing each particle in the image shown in figure 8.1 10 times. This particular image was
chosen as a “best case” scenario because the particles are large and not in contact with each other.

**Table 8.4:** 10 replicates of measured diameters of 7 SiO$_2$ nanoparticles using ImageJ. Average diameters, %RSD and 95% confidence interval included. The scale was 47.4 pixels $\mu$m$^{-1}$.

<table>
<thead>
<tr>
<th>Particle ID number</th>
<th>Replicate measurement number</th>
<th>Measured diameters (µm)</th>
<th>Avg (µm)</th>
<th>95% C.I.</th>
<th>%RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 2 3 4 5 6 7 8 9 10</td>
<td>1.76 1.78 1.77 1.74 1.74 1.75 1.75 1.76 1.75 1.75</td>
<td>1.75</td>
<td>0.0260</td>
<td>0.67%</td>
</tr>
<tr>
<td>2</td>
<td>1.74 1.75 1.75 1.72 1.73 1.73 1.73 1.74 1.73 1.74</td>
<td>1.74</td>
<td>0.0207</td>
<td>0.53%</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.71 1.72 1.72 1.69 1.70 1.70 1.70 1.71 1.70 1.71</td>
<td>1.71</td>
<td>0.0226</td>
<td>0.60%</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1.78 1.80 1.79 1.76 1.77 1.77 1.77 1.79 1.77 1.78</td>
<td>1.78</td>
<td>0.0241</td>
<td>0.61%</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.82 1.83 1.83 1.80 1.80 1.81 1.81 1.81 1.82 1.81</td>
<td>1.81</td>
<td>0.0232</td>
<td>0.57%</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1.71 1.73 1.73 1.70 1.70 1.71 1.71 1.71 1.72 1.71</td>
<td>1.71</td>
<td>0.0231</td>
<td>0.60%</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>1.79 1.81 1.80 1.77 1.78 1.78 1.78 1.77 1.78 1.78</td>
<td>1.78</td>
<td>0.0246</td>
<td>0.62%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.60%</td>
</tr>
</tbody>
</table>

For the best case scenario, the precision expressed as one standard deviation is 0.6% which corresponds to an uncertainty of ±23 nm ($p = 0.025$) in the measured particle diameter. Uncertainty is expected to increase for other images where the particles are in contact or slightly out of focus. The SEM image analysis could not provide better accuracy than about ± 23 nm diameter.

250 nm Au nanoparticles were measured to be 245 nm ($N = 407$, 11% RSD). The distribution width was hindered by the uncertainty (±23 nm, ~9.2%) of the SEM image processing routine. The particles appeared to be spherical, although triangular shapes were also observed. Two triangular particles are highlighted in figure 8.6.
Figure 8.6: 250 nm Au nanoparticles mounted on an aluminum SEM stub by drop deposition with no coating.

8.5 Single nanoparticle delivery system

In order to measure ICP-MS signals from individual particles introduced as a suspension in water, the particle introduction rate must be low enough so that signals produced from two particles do not overlap, a droplet produced by the nebulizer does not contain more than one particle and particles do not become agglomerated.

A commonly used sample introduction system (pneumatic nebulizer and spray chamber) has previously been used to introduce suspensions of nanoparticles into the ICP at 300 µL min⁻¹ liquid uptake rate.¹³⁻¹⁷ This sample introduction system is available on almost all ICP-OES and ICP-MS instruments and is simpler to use and maintain than the
monodisperse, drop on demand system. However, it delivers a polydisperse aerosol into the ICP. The smallest droplets will complete vaporization before the largest droplets. As a result, the location in the plasma where the particle begins to vaporize would depend on the size of the original droplet. The extent of diffusion of analyte that occurs from the point of particle vaporization to the location of the sampling orifice of the mass spectrometer would therefore vary for particles that were originally in different size droplets. This could complicate the relationship between particle size and ICP-MS signal when signals due to individual particles are measured.25

If the water droplets evaporated before being introduced into the plasma then the problem of different size droplets completing vaporization at different locations in the plasma would be avoided. The extent of droplet evaporation depends on the time that the droplets spend in the spray chamber before entering the plasma and the humidity of the Ar carrier gas. At room temperature Ar becomes saturated with water vapor at about 25 µg L⁻¹ Ar. Therefore, if the total liquid flow rate to the nebulizer is well below the rate that results in 100% humidity, evaporation of water from the droplets should be extensive in the spray chamber. A nebulizer gas flow rate of 0.6 L min⁻¹ (used in these studies) becomes saturated with 15 µL min⁻¹ water vapor. A liquid uptake rate of 10 µL min⁻¹ and a 40 mL conical spray chamber were used to allow extensive evaporation of the droplets before they entered the ICP.

The AriMist nebulizer was chosen to convert the nanoparticle solution to an aerosol. This nebulizer is a parallel path Teflon design that reportedly allows efficient droplet formation at flow rates greater than 50 µL min⁻¹ and also has an inner bore (150
μm) large enough that clogging is unlikely and small enough to washout should occur quickly. A Burgener MiraMist CE nebulizer was also used for some measurements. The nanoparticles were diluted with deionized water, put in an ultrasonic bath to minimize agglomeration and introduced to an evaporation chamber at 10 μL min⁻¹. This uptake rate was chosen as the lowest flow rate that consistently produces an aerosol. At uptake rates less than 10 μL min⁻¹, droplet formation can be sporadic.

Once an uptake rate of 10 μL min⁻¹ was chosen, dilution factors from the stock solutions were determined. Dilutions must be large enough so that there is a low probability of more than one particle in a single droplet, and so that it is unlikely that two droplets, each containing a particle, enter the plasma within about 0.5 ms of each other or within one signal integration (dwell) time so that their signals do not overlap. The concentration of nanoparticles was 1% solids in solution (~10 mg of SiO₂ particles per mL H₂O). The number of particles per mL in the stock solutions was calculated by dividing the mass of particles (10 mg) by the density of SiO₂ (2.2 g mL⁻¹) and dividing by the average volume of each particle size. The concentration of particles was known only to one significant digit. Particles were chosen to be delivered once every 2 ms on average, which would temporally separate particles in the ICP.

The probability of finding more than one particle in a single droplet was estimated. The rate of liquid delivery may be converted to the droplet production rate if the volume of the droplets is known. Droplet sizes measurements have been recorded using a phase Doppler particle analyzer and the mean Sauter diameter from a MiraMist nebulizer operated at similar conditions was 5 μm. If the crude assumption is made that
all of the droplets have a diameter of 5 μm, then 2.5 million droplets are produced per second at a 10 μL min⁻¹ uptake rate. The Sauter mean will be higher than the arithmetic mean, so the droplet production rate (drops/sec) will be much larger than the calculated rate assuming all droplets are 5 μm in diameter. The probability of finding a particle in a droplet was calculated by dividing the particle delivery rate (particle/sec) by the droplet production rate (drop/sec). The probability of finding two particles in a single droplet was calculated by squaring the probability of finding a particle in one droplet.

Table 8.5: SiO₂ nanoparticle diameters, volumes, masses, stock concentrations, dilution factors, estimated delivery rates to the plasma and probability of finding two particles in a single droplet.

<table>
<thead>
<tr>
<th>Measured Diameter (nm)</th>
<th>Volume (μm³)</th>
<th>Mass (pg)</th>
<th>Stock Conc. (10⁹ mL⁻¹)</th>
<th>Dilution Factor</th>
<th>Delivery @ 10 μL min⁻¹ (s⁻¹)</th>
<th>Probability of 2 particles in one drop</th>
</tr>
</thead>
<tbody>
<tr>
<td>403</td>
<td>0.034</td>
<td>0.075</td>
<td>133</td>
<td>1428571</td>
<td>15</td>
<td>6.1x10⁻⁹</td>
</tr>
<tr>
<td>518</td>
<td>0.073</td>
<td>0.16</td>
<td>62.5</td>
<td>250000</td>
<td>42</td>
<td>1.6x10⁻⁸</td>
</tr>
<tr>
<td>629</td>
<td>0.13</td>
<td>0.29</td>
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<td>200000</td>
<td>29</td>
<td>1.1x10⁻⁸</td>
</tr>
<tr>
<td>744</td>
<td>0.22</td>
<td>0.47</td>
<td>21.1</td>
<td>100000</td>
<td>35</td>
<td>1.4x10⁻⁸</td>
</tr>
<tr>
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<td>0.35</td>
<td>0.77</td>
<td>13.0</td>
<td>66667</td>
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<td>11.9</td>
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<td>1.6x10⁻⁸</td>
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<td>0.391</td>
<td>400</td>
<td>163</td>
<td>6.4x10⁻⁸</td>
</tr>
</tbody>
</table>

Particles were collected on SEM mounts that were placed 1 cm beyond the nebulizer tip and at the exit of the evaporation chamber to determine if nanoparticles...
were being delivered as individual particles, agglomerates or multiple particles in one droplet. The 2,810 nm SiO$_2$ particles were used because the large particles were easiest to image. Aerosol was collected for 30 seconds at a distance 1 cm from the nebulizer tip and for 120 seconds at the exit of the evaporation chamber.

![Typical image of 2,810 nm SiO$_2$ nanoparticles collected from aerosol 1 cm from the tip of a nebulizer operating at 0.6 L min$^{-1}$ gas and 10 $\mu$L min$^{-1}$ liquid uptake rate.](image)

**Figure 8.7:** Typical image of 2,810 nm SiO$_2$ nanoparticles collected from aerosol 1 cm from the tip of a nebulizer operating at 0.6 L min$^{-1}$ gas and 10 $\mu$L min$^{-1}$ liquid uptake rate.

Particles collected 1 cm from the tip of the nebulizer (figure 8.7) were separated from each other and no agglomerates were observed (~500 particles examined). It may be possible that weakly bound agglomerates were broken up during the turbulent nebulization process where fast moving gas interacts with the liquid at the nebulizer tip.

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Nanoparticles were also collected at the exit of the evaporation chamber. Although collection on the SEM mount was done for 120 seconds, only a total of four particles could be found. If particles were completely dry at the end of the chamber, then they most likely followed the gas streamlines around the SEM mount. Alternatively, a dry particle is not expected to “stick” to the dry SEM mount so it is possible that some particles bounced off. The results suggest, but do not conclusively prove, that particles entering the ICP are not agglomerated.

8.5.1 Secondary considerations for single particle ICP-MS

Two problems with the single particle delivery system should be mentioned that do not fit within traditional analytical categories: 1) washout time and 2) data analysis requirements. These issues limited the pace at which measurements were made (samples/day) and must be addressed.

The sample introduction system began with a gastight syringe which pushed a diluted nanoparticle suspension through 20 cm of Teflon capillary to the AriMist nebulizer which converted the solution to aerosol. After one particle size’s measurements were completed, blank water with no particles was pumped to clean the system. Particles (~1/sec) were still detected for 2-3 hours afterward even after changing the gastight syringe, tubing and fittings. These particles would randomly release into the liquid stream, which is a problem if more than one particle size is to be measured. Nanoparticles may have become “stuck” in the joints and fittings used. This problem was partially overcome by back flushing the entire system with ~100 mL of water before introducing the next size standard. The back flushing procedure reduced the
washout time to 15-20 minutes. Cross contamination was avoided by back flushing for 30 minutes, followed by a flush of deionized water for 1 hour. Both steps of this procedure were repeated once for a total “cleaning” time of 3 hours. The AriMist nebulizer had severe washout problems, while the MiraMist CE nebulizer washed out within ~15 minutes instead of 2-3 hours. In future work, the MiraMist CE nebulizer should be used for shorter washout times. It is not clear why the two nebulizers had such dramatically different washout times.

Only 3-4 different particle sizes could be measured per day when the AriMist nebulizer was used because of the long washout time. Day to day variations in instrument sensitivity might therefore cause inaccurate results when constructing a calibration curve over the course of more than a few days. This was not observed for the SiO₂ particles (linear calibration curves with data over 5 days).

Time resolved measurements (section 8.6) were recorded as 50 segments in a single oscilloscope display, 1 ms wide and composed of 1,000 data points taken every 1 μs. These data files were stored as text files after transfer from the oscilloscope to the computer and then imported into Microsoft Excel. The text file data were pasted into a spreadsheet that calculated the peak height, area, FWHM, area %RSD and diameter %RSD. Because each waveform was examined to prevent inclusion of outliers, data analysis for a single particle size took about 4 hours. In total, measurement of a single particle size including washout, flushing and data analysis required approximately 8 hours. By extension, a five point calibration curve required an entire working week. The digital oscilloscope could be used to sum and average particle signal waveforms, cutting
down data analysis time drastically. The scope could average up to 10,000 waveforms, but cannot discriminate against peaks that result from two particles (e.g. figure 8.9) so this feature was not used in this work. In practice, two particles arriving simultaneously was not a large problem, but that was not known until after this work was completed.

Data analyses of time integrated measurements (section 8.7) were far less time consuming because there was no peak shape to examine. Data were analyzed in Microsoft Excel which was programmed to automatically background subtract, and calculate the average and %RSD of the signals. When time integrated signals were measured, the washout/back flushing procedure was the dominant time commitment when using the AriMist nebulizer.

8.6 Time resolved ICP-MS signals from SiO$_2$ nanoparticles

ICP-MS analysis of nanoparticles was first performed using “time resolved” μs timescale measurements on a digital oscilloscope. The oscilloscope approach has three important advantages as opposed to the traditional millisecond integration using the instrument software: (1) The scope was triggered to record data only when a randomly arriving particle entered the ICP and caused a signal peak. This enabled the entire peak to be captured every time. (2) Occurrences when two signal peaks were not resolved were easily identified and rejected from the data set. (3) μs timescale measurements showed signal peak height, width and symmetry which may be related to the extent of vaporization and diffusion of the particle in the ICP. If the fundamental vaporization, sampling and measurement process of nanoparticles by ICP-MS are understood, then analytical methodology can be improved.
A sampling rate on the order of 0.1-1 MHz was sufficient to measure droplet vaporization\(^\text{10}\) and was assumed to be sufficient for particle vaporization as well.

**Table 8.6:** Instrument and sample introduction parameters optimized for the characterization of SiO\(_2\) nanoparticles.

<table>
<thead>
<tr>
<th>ICP-MS</th>
<th>Data Acquisition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dwell time</td>
<td>Amplifier gain</td>
</tr>
<tr>
<td>Sweeps</td>
<td>Amplifier filter rise time</td>
</tr>
<tr>
<td>Readings</td>
<td>Digital oscilloscope sampling rate</td>
</tr>
<tr>
<td>Replicates</td>
<td>Measurement window</td>
</tr>
<tr>
<td>Lens voltage</td>
<td>Analog stage voltage</td>
</tr>
</tbody>
</table>

Signal was directly measured from the analog mode of the detector via an external current amplifier and digital oscilloscope. Data were recorded by setting the oscilloscope trigger to be slightly above any background on the scope. The oscilloscope recorded 50 consecutive triggered data segments, each 1 ms wide and consisting of 1,000 points. A total of 200 data segments (each containing a signal peak) were recorded at each of 15 center gas flow rates (varied as described in section 8.6.1) for each size nanoparticle. A total of 30,000 peak profiles (waveforms) were recorded and then individually characterized according to background subtracted height, area and full width and half maximum. Figure 8.8 shows typical peak profiles recorded by the digital oscilloscope in red.
Figure 8.8: Example peak profiles from a) 1,077 nm and b) 400 nm SiO$_2$ particles introduced at a center channel gas flow rate of 0.96 and 1.02 L min$^{-1}$ respectively. Signal (red, left y-axis) and digitized FWHM output (blue, right y-axis) shown.

The oscilloscope trigger was set -100 µs from the middle of the 1 ms measurement window so that the apex of the peak would fall near the middle of the window. The peak areas were calculated by first subtracting the average signal of the first and last 100 µs. The first and last 100 µs of the measurement window should contain no peak signal, and was used for background subtraction. The sum of the background subtracted signals provided the integrated peak areas.

A procedure was developed to automatically estimate the full width at half maximum (FWHM) of the signals, which were sometimes noisy (such as figure 8.8b). The blank subtracted data were transformed through an if-then statement in Excel and then summed. If the signal was equal to or greater than half the blank subtracted maximum signal, then Excel would output a “1”. If the signal was less than half the maximum, then the if-then statement output a “0.” These values were summed to
calculate the FWHM in μs. For example, if the background subtracted peak height was 1 μA, the Excel statement output a “1” for every data point equal to or greater than 0.5 μA and “0” for every data point less than 0.5 μA. The maximum signal may slightly overestimate the peak height without noise due to the presence of noise on the peak signal. Figure 8.8 shows the output of the Excel statement in blue for both 1,077 and 400 nm particles. For the 1,077 nm particle, the output transitions from 0 to 1 when the signal exceeds half the maximum and remains at one until the signal falls below half the maximum. For the 400 nm particle, the signal to noise ratio is less than the 1,077 nm particle. The noise overlaid on the peak causes the signal to dip below half the maximum, then above again before finally decreases back to the background level. The noise was random and expected to average out to zero over a large number of analyzed particles. Groups of 200 peaks were averaged in Excel and the FWHM of the averaged signals was compared to the average FWHM measurements of single peaks. No difference was found from calculating FWHM from the averaged signal or average FWHM from individual signals.

Data from 200 peaks were individually examined to assure that only one peak was recorded during the 1 ms measurement window. 1 ms measurement windows that contained either an incomplete peak or two partially or fully resolved peaks were discarded (table 8.9 lists the number of waveforms at optimized flow rates). Figure 8.9 shows an example signal recorded from what is thought to be two nanoparticles arriving to the ICP close together.
Figure 8.9: Signal recorded from 1.077 nm SiO$_2$ nanoparticles at 0.95 L min$^{-1}$ center gas flow rate that appears to contain signals from two nanoparticles.

The integrated peak area from the signal in figure 8.9 is almost exactly double the average of the peak areas from the other 199 signals recorded under the same conditions so it was concluded that the signal in figure 8.9 is likely due to two nanoparticles arriving approximately 140 μs apart.

The final data analysis step was a 95% confidence q-test to find and reject outliers. Peak areas that were twice the area of the average (as a result of two particles entering the ICP simultaneously) were divided by 2. Less than 2% of the measurements
were divided by 2 and/or rejected and the rejection/correction did not affect the means. Data were rejected/corrected to obtain more correct %RSDs of the signal distributions.

Once each peak was individually characterized with respect to height, width and area, the averages, standard deviations and confidence intervals were calculated. Average peak area was used as the instrument response in subsequent calibration curves. The area of the signal peak is proportional to the mass of the particle according to equation 8.2 assuming spherical particles.

\[
ICP\ MS\ signal\ \propto\ particle\ mass = \left(\frac{4}{3}\pi \times \text{radius}^3\right) (density) \quad (8.2)
\]

The cubed root of the signal is proportional to the particle size (expressed as radius or diameter). The %RSD of the cubed root of the ICP-MS signal areas was compared to the %RSD of particle diameters measured by SEM.

8.6.1 Effect of center channel gas flow rate on time spent in hot region of ICP

As a dry particle is introduced to the plasma, its temperature is raised to its boiling point followed by vaporization, atomization and ionization. Optimized sensitivity is achieved when the vapor produced from the particle is sampled into the mass spectrometer but before diffusion has diluted the ion cloud. Unfortunately, particles of different sizes require different amounts of time to fully vaporize in the ICP. The amount of time the particle requires to completely vaporize is dependent on the mass of the particle, the changes in enthalpy and specific heats for solid, liquid and gas phases, enthalpies of atomization and ionization, and rate of energy transfer from the ICP.\textsuperscript{29} The effect of time spent in the hot ICP was first studied as a function of particle size by varying the center channel gas flow rate.
The time spent in the plasma is directly related to the length of the plasma, which is dependent on center channel gas flow rate\textsuperscript{30} if the particle velocity is roughly constant.\textsuperscript{31} As the center channel gas flow rate is increased (more cool gas into the ICP), the length of the hot region in the radial center of the plasma decreases. This decreases the time that the nanoparticle is exposed to the hot temperature of the plasma before reaching the sampling orifice of the mass spectrometer. Center channel gas flow rate has shown a nearly perfect linear relationship to time spent in the plasma.\textsuperscript{29} Figure 8.10 shows estimated plasma lengths at four different center channel gas flow rates calculated by the program HiFi 2.0\textsuperscript{32} using a theoretical approach.\textsuperscript{33-35}
Figure 8.10: Estimated plasma length (mm) to the sampling orifice 12 mm downstream from the load coil as a function of center channel gas flow rate (L min\(^{-1}\)) for a fixed power (1,000 W) calculated using HiFI 2.0.

The modeling program HiFI 2.0 calculated that the length of the ICP (on the radial center axis) decreases by approximately 1.7 mm for every 0.1 L min\(^{-1}\) increase in center gas flow rate. A recent, different model determined the length of the ICP decreases by 2.9 mm for every 0.1 L min\(^{-1}\) increase in center gas flow rate.\(^{36}\) Using the HiFI 2.0 value and assuming a particle velocity\(^{25,37}\) of 20 m s\(^{-1}\), the particles will experience hot temperatures for 1.4 ms when the center channel gas flow is 0.25 L min\(^{-1}\) and 0.75 ms at 1.00 L min\(^{-1}\). As a point of reference, computer simulations have
estimated that ICP vaporization rates for similar sized particles to be on the order of 1,000 μm s⁻¹, which corresponds to 1 ms ICP residence time required to vaporize a 1.0 μm SiO₂ particle.³⁹

The center gas flow rate was controlled by addition of gas via a sheath flow injector. The nebulizer gas was held constant at 0.6 L min⁻¹ and the sheath flow rate was varied from 0.2 – 0.45 L min⁻¹. The additional gas was added via the sheath flow instead of changing the nebulizer gas to avoid changing any of the primary aerosol properties, which depend on nebulizer gas flow rate.³⁸

8.6.2 Effect of time in hot ICP on signal peak area and width

Signal peak shapes provide insight into the vaporization of particles and diffusion of vapor produced from the particles in the ICP. As a particle vaporizes, the volume close to the surface of the incompletely vaporized particle is dense with ions; ions that diffuse from the particle are replaced by ions from the surface of the particle. The rate of ion diffusion in an ICP is roughly 10-100 cm² s⁻¹ and inversely related to ion mass²⁸ while the rate of particle vaporization has been estimated to be on the order of 1 mm s⁻¹.²⁹ The peak is expected to be narrow due to an incompletely vaporized particle because the additional ions are being produced from the surface of the particle, maintaining a high concentration of ions near the particle. After the particle is completely vaporized, there is no longer a local source of ions and diffusion becomes the dominant factor that controls the peak width. The effect of center channel gas flow rate on 907 nm SiO₂ particles’ peak area is shown in figure 8.11.
Computer simulations by the Hieftje group have shown that 1.0 \( \mu \)m particles are completely vaporized between 20 and 30 mm beyond the load coil in a plasma operated at 1,000 W and 1.0 L min\(^{-1}\) but the exact location of vaporization depended upon the composition of the nanoparticle (CaCl\(_2\), LiCl, NaCl particles were modeled).\(^{20}\) Based on the estimated time in the ICP and simulations for complete vaporization of a 1.0 \( \mu \)m particle, 907 nm SiO\(_2\) particles do not have enough time to fully vaporize before reaching the sampling orifice of the mass spectrometer at gas flow rates greater than 1.0 L min\(^{-1}\).
(1350 W, sampling depth 12 mm, $t \approx 0.73$ ms). This conclusion is supported by maximum peak area at $0.99$ L min$^{-1}$ center gas flow rate.

When the particle is exposed to the hot ICP for short durations, incomplete vaporization and narrow peaks are expected due to the local source of ions at the particle’s surface. At long residence times in the ICP, full vaporization is expected and short, wide peaks are expected due to radial diffusion. The changes in peak width of the four example signals in figure 8.11 are shown in figure 8.12. The peak heights are normalized so changes in width are more apparent.
Figure 8.12: Normalized signal peaks from 907 nm SiO$_2$ particle introduced to the ICP at a) 1.10, b) 1.00, c) 0.90 and d) 0.80 L min$^{-1}$ flow rate. Signal (solid) and calculated full width at half maximum (dashed) lines are shown.

As the center gas flow rate decreases from 1.10 to 0.80, the width of the signal peak increases from 67 to 143 $\mu$s. At the highest center gas flow rates, diffusion is not yet the dominant source of the peak width because the particle is still vaporizing. At low center gas flow rates, the particle is likely completely vaporized and the ion cloud is diluted due to diffusion. Ion diffusion results in a decreased peak height and increased peak width (and a lower MS signal peak width assuming that only ions near the center axis pass through the skimmer cone and into the quadrupole). The peaks in figures 8.11-
8.12 are asymmetric with noticeable tailing due to ions diffusing away from the center of the ion cloud at the back end while the ions on the front end have entered the mass spectrometer.\textsuperscript{7,8} Integrated peak areas and FWHM’s at every center gas flow rate that was studied are shown in figure 8.13.

Figure 8.13: Average integrated peak area (red, left y-axis) and full width at half maximum (blue, right y-axis) as a function of center channel gas flow rate shown with 99% confidence intervals about the mean for the 907 nm SiO\textsubscript{2} particles. N=200 for each data point.

The measured peak area increases from 44 to 90 \( \mu \text{A*\mu s} \) and the FWHM decreases from 140 to 100 \( \mu \text{s} \) as the center gas flow rate is increased from 0.7 to 0.99 L min\(^{-1}\). At
0.99 L min\(^{-1}\) the ion cloud sampled into the mass spectrometer is concentrated and sensitivity is maximized. As the center gas flow rates increase beyond 0.99 L min\(^{-1}\), the concentration of ions in the ion cloud decreases, likely due to incomplete particle vaporization. If the particle is incompletely vaporized, the FWHM is expected not to change as a function of center gas flow rate\(^{6}\) because there is a local source of ions from the surface of the incompletely vaporized particle that dominate the peak width. Experimental observations (figure 8.13) did not support this hypothesis, so it is still unclear if the particle is completely vaporized at the point of maximum sensitivity. The effect of center gas flow rate on all particle peak areas and widths is shown in figure 8.14.
Figure 8.14: Average integrated peak area (●, left y-axis) and full width at half maximum (○, right y-axis) as a function of center channel gas flow rate shown with 99% confidence intervals about the mean for the a) 400, b) 518, c) 629, d) 744, e) 875, f) 1077, g) 1801, and h) 2035 nm SiO$_2$ particles.

The exact gas flow rate at which the peak area is maximized shifts as a function of the particle mass. As particle size increases, additional time is required for vaporization. The center channel gas flow rate at which peak area is maximized decreases as particle size increases.
Figure 8.15: a) Optimized center gas flow rates for maximum sensitivity as a function of particle mass and b) optimized time in hot ICP for maximum sensitivity as a function of particle diameter.

The gas flow rate at which sensitivity is maximized changes from 1.02 to 0.96 as the particle size increases from 400 to 1,077 nm. This change corresponds to only approximately 50 μs change in the time the particle spends in the ICP (1 mm at 20 m s⁻¹). The small change in time spent in the ICP has a dramatic effect on the measured signals. For example, the signal from 907 nm SiO₂ particles is 90 μA*μs at the optimized flow rate (0.99 L min⁻¹), and 70 μA*μs at 1.05 L min⁻¹. The 50 μs change in time spent in the ICP caused a 22% change in the measured signal. The 875 and 907 nm particle sizes do not follow the same trend as the other sizes. One possible explanation for this was that those two particle sizes were measured on the same day and an incorrect gas rate was being delivered. A solid line was drawn in figure 8.15 that did not include these two sizes to show the relationship between optimized center gas flow rate and particle mass.
Not all SiO$_2$ particle sizes were able to be characterized by ICP-MS under the experimental conditions used. The 2,810 nm signal peaks (an example is shown in figure 8.16) indicated that the detector may have been saturated (resulting in a flat topped peak), which is likely due to their large size. The calculated areas from the 2,810 nm particles were incorrect due to detector saturation and data were not included in subsequent calibrations. A reduction in the analog stage voltage of the detector should allow larger particles to be characterized.

**Figure 8.16:** Example signal from a 2,810 nm SiO$_2$ particle measured on the digital oscilloscope at 0.88 L min$^{-1}$ center gas flow rate.
Once signals were recorded at different center gas flow rates, calibration curves were constructed as a function of SEM measured particle sizes. Total data collection was performed over a span of five days. The 907 nm particles were measured on two separate days and the average peak area drifted by less than 12% (2.3% drift in cubed root of signals, proportional to diameter). No corrections for drift or day to day variations in sensitivity were performed. Particle masses and diameters are listed in table 8.7.

<table>
<thead>
<tr>
<th>SEM measured diameter (nm)</th>
<th>Particle Volume (attoliter)</th>
<th>Particle Mass (pg)</th>
<th>Si mass (pg)</th>
<th>Data collection date</th>
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<tbody>
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<td>11.618</td>
<td>25.559</td>
<td>11.93</td>
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</table>

Calibration curves were constructed by plotting average integrated peak area (μA*μs) as a function of nanoparticle mass (pg). SEM measured nanoparticle sizes were used rather than the manufacturer data. Calibration curves up to 2 pg Si at different flow rates are shown in figure 8.17.
Figure 8.17: SiO$_2$ nanoparticle calibration curves from 0 to 2 pg at a) optimized, b) 0.80, c) 0.90, d) 1.00 and e) 1.10 L min$^{-1}$ center gas flow rate. Integrated peak areas (○) and extrapolated linear range (solid line) shown.

If peak areas measured at the optimized flow rate for each nanoparticle size (figure 8.15) are used, the instrument response is linear from 400 to 1,077 nm (figure 8.17a). At a fixed center gas flow rate of 0.8 L min$^{-1}$, the calibration curve is linear from 518 to 1,077 nm but the sensitivity is decreased from 104 to 56 $\mu$A$\times$μs pg$^{-1}$. At 1.1 L min$^{-1}$, the linear range is only from 400 to 620 nm. The linear range is narrower at high flow rates due to insufficient time in the ICP for full vaporization of the large particles. Figure 8.18 shows the calibration curves containing all particles.
Figure 8.18: SiO$_2$ nanoparticle calibration curves at a) optimized, b) 0.80, c) 0.90, d) 1.00 and e) 1.10 L min$^{-1}$ center gas flow rate. Integrated peak areas ($\circ$) and extrapolated linear range (solid line) shown. Lines were from linear regression over linear ranges listed in Table 8.8.

The 1,810 and 2,035 nm particles’ sensitivity is less than the smaller particles at any flow rate. At 0.8 L min$^{-1}$, 1,810 and 2,035 nm SiO$_2$ particles’ sensitivities are closer to the regression line than when the optimized flow rates are used. The difference between the expected and the measured signal is improved from -30% and -36% at the optimized flow rate to -11% and -13% at 0.8 L min$^{-1}$ for the 1,810 and 2,035 nm SiO$_2$
particles, respectively. The large particles did not fall on the linear regression line at any flow rate. The reasons that the large particles’ sensitivities were too low might be attributed to incomplete vaporization, ion signal loss due to diffusion, and local cooling effects. These possibilities are discussed in section 8.6.3.

Table 8.8: Calibration curve data for SiO$_2$ characterization at optimized, 0.80, 1.00 and 1.10 L min$^{-1}$ center channel gas flow rates.

<table>
<thead>
<tr>
<th>Center channel gas flow rate (L min$^{-1}$)</th>
<th>Linear Range (nm)</th>
<th>Sensitivity ($\mu$A*μs pg$^{-1}$)</th>
<th>R$^2$ coefficient over linear range</th>
<th>% difference from expected 1,810 nm signal</th>
<th>% difference from expected 2,035 nm signal</th>
<th>Diameter difference of 2,035 nm particle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optimized</td>
<td>400 – 1,077</td>
<td>105</td>
<td>0.9999</td>
<td>-30%</td>
<td>-36%</td>
<td>-281 nm (10%)</td>
</tr>
<tr>
<td>0.80</td>
<td>518 – 1,077</td>
<td>56</td>
<td>0.9973</td>
<td>-11%</td>
<td>-13%</td>
<td>-92 nm (3.3%)</td>
</tr>
<tr>
<td>0.90</td>
<td>400 – 907</td>
<td>87</td>
<td>0.9969</td>
<td>-16%</td>
<td>-28%</td>
<td>-211 nm (7.5%)</td>
</tr>
<tr>
<td>1.00</td>
<td>400 – 907</td>
<td>99</td>
<td>0.9961</td>
<td>-54%</td>
<td>-72%</td>
<td>-704 nm (25%)</td>
</tr>
<tr>
<td>1.10</td>
<td>400 – 620</td>
<td>47</td>
<td>0.9943</td>
<td>-49%</td>
<td>-83%</td>
<td>-908 nm (32%)</td>
</tr>
</tbody>
</table>

The best fit calibration curve for particles less than 1.1 μm diameter was achieved when each particle was measured at its optimized flow rate. However, these conditions are not possible if a mixture of nanoparticle sizes was to be analyzed because it is not possible to dynamically change the center gas flow rate according to the size of nanoparticle. The next best alternative is to use a lower flow rate than the optimized flow rates. Sensitivity is lowered, but the linear range remains wide and displays small errors.
for large particles that do not lie on the calibration curve. For SiO$_2$, a center gas flow rate of 0.80 – 0.90 L min$^{-1}$ would be appropriate for mixtures between 500 and 907 nm.

The calibration curves in figure 8.17 – 8.18 show some of the problems in measuring SiO$_2$ nanoparticles by ICP-MS. The linear range for a single gas flow rate spans only 500 nm, although smaller particles than were measured here may also fall on the line. The curves also show the importance of the time spent in the plasma on sensitivity. This must be taken into account when attempting to analyze unknown mixtures of particles.

It is important to determine the smallest size single particle that can be measured. The standard deviation of a blank measurement of deionized H$_2$O with no particles is 0.0017 $\mu$A*us and corresponds to a SiO$_2$ nanoparticle detection limit of 271 nm (23 fg SiO$_2$, 11 fg Si) using sensitivity from optimized center gas flow rates. Similar measurements using ICP-OES and monodisperse droplet introduction showed a Si detection limit of 50 fg Si, equivalent to a 450 nm SiO$_2$ particle. The ICP-MS detection limits are similar to ICP-OES mainly because of a large background ($N_2^+$, $CO^+$, $Si^+$ from quartz torch and injector).

8.6.3 Nonlinear response from large nanoparticles

Why signals from large particles do not fall on the calibration curve, even when sensitivity is optimized, must be addressed. There are three possible explanations: (1) incomplete vaporization of the large particles, (2) local cooling causing a decrease in the fraction ionized and (3) ion diffusion out of the volume of plasma where ions pass into the mass spectrometer. The ICP-MS responds linearly with respect to mass if
vaporization, ionization and the amount sampled into the mass spectrometer are size independent.

A particle will be incompletely vaporized if it does not spend enough time in the ICP, due to a high center gas flow rate for instance. At high center gas flow rates, small particles have enough time to completely vaporize but large particles do not.\textsuperscript{29} The time spent in the hot ICP was varied by adjusting the center channel gas flow rate to assess if size dependent vaporization caused nonlinear response. Signals at optimized and low flow rates would display identical sensitivity and fall on the calibration curve if incomplete vaporization was the sole reason for the nonlinear response. However, even when sensitivity was optimized at 0.88 L min\textsuperscript{-1} for the 1,810 nm particle size, the signals were still 30% lower than predicted by a linear calibration of smaller particles. Lowering the center channel gas flow rate to increase the time the particles spend in the ICP did not produce signals on the linear portion of the calibration curve, even at 0.7 L min\textsuperscript{-1} center gas flow rate. Incomplete vaporization is not the sole reason for the nonlinearity at SiO\textsubscript{2} masses beyond 2 pg (1,810 nm and up).

Another possible explanation for the nonlinear response between ion signal and particle mass is particle size dependent local cooling of the plasma that results in a smaller fraction of the Si existing as Si\textsuperscript{+} in the plasma.\textsuperscript{25, 39-43} Vaporization removes energy from the local environment surrounding the droplet or particle. Small particles remove small amounts of energy, while large particles act as heat sinks by removing energy required to vaporize their large mass. If the local plasma temperature near a particle is decreased due to energy removal during vaporization, the lower temperature
may affect the fraction of atoms that are ionized. The fraction of atoms that are ionized is determined by the ionization energy of the material and the temperature of the ICP. Local cooling from droplets and particles has previously been studied,\textsuperscript{25,39-43} and was investigated as a possible cause of the non-linear response.

1,077 nm SiO\textsubscript{2} particles were introduced to the ICP to determine the volume and magnitude of local cooling. \textsuperscript{36}Ar\textsuperscript{+} was used to monitor ICP temperature because it is sensitive to small changes in temperature due to its high ionization energy. Figure 8.19 shows example measured signals from dry (no H\textsubscript{2}O) gas, 10 \(\mu\)L min\(^{-1}\) H\textsubscript{2}O aerosol, and 10 \(\mu\)L min\(^{-1}\) with 1,077 nm SiO\textsubscript{2} particles at the optimum center gas flow rate (0.95 L min\(^{-1}\)).
Figure 8.19: $^{36}\text{Ar}^+$ signal of dry (black), 10 μL min$^{-1}$ H$_2$O (blue), and 1,077 nm SiO$_2$ particles (red) as a function of time. Dry (black) and H$_2$O only (blue) data are offset by 10 and 5 μA respectively.

The signals measured with no particles showed no significant “dips” that would be representative of local cooling surrounding a particle. When 1,077 nm particles were introduced to the ICP (red series), 2 signal dips were measured in one 12 ms window. This particular case was chosen as an example, but typical measurements contained no signal dips (1 dip every ~10 sec). The number of dips observed was very infrequent (estimated 1 dip per ~100 particles) and were an average of 100 μs wide. If the particle velocity is assumed to be 20 m s$^{-1}$, then the area affected by local cooling
surrounding a 1.077 μm particle is estimated to be 2 mm. Local cooling from droplets has previously been measured within 1-2 mm of a vaporizing droplet. The fraction of Si ionized could decrease if a large particle causes the local temperature to decrease. The effect of local cooling on Si ionization may be imagined in two steps: 1) The initially cold particle absorbs energy from the plasma as its temperature rises to its melting and boiling points and the particle begins to vaporize, and 3) the inner portion of the particle is now subjected to a lower temperature, and may form fewer ions.

Temperature changes due to local cooling can be very crudely estimated by relating the Ar\(^+\) signal to the plasma temperature. Figure 8.20 shows the relationship between the estimated ICP temperature and Ar\(^+\) concentration assuming local thermodynamic equilibrium. This estimation requires an assumption of the initial ICP temperature and that the \(^{36}\)Ar\(^+\) signal measured is proportional to the concentration of Ar\(^+\) in the ICP.
If the plasma is assumed to be 6,000 K\textsuperscript{45} and the $^{36}\text{Ar}^+$ signal is proportional to the $\text{Ar}^+$ concentration in the plasma, then the temperature depression surrounding the vaporizing particle is estimated to be no greater than 500 K. Local cooling may cause a nonlinear response if large particles lower the temperature enough to reduce the fraction of ionized atoms.\textsuperscript{25} ICP temperature,\textsuperscript{46} particle vaporization\textsuperscript{29} and ion diffusion\textsuperscript{47,48} modeling was not performed in this study, and so it is difficult to estimate the effect of a 500 K temperature depression on the fraction ionized. However, the $^{36}\text{Ar}^+$ dips were measured very infrequently when compared to the signal peaks from $^{28}\text{Si}^+$, indicating that most (> 99%) 1,077 nm SiO$_2$ particles did not cause local cooling. It is not clear why the
number of $^{36}\text{Ar}^+$ dips was not equal to the number of $^{28}\text{Si}^+$ spikes, or why some particles caused $^{36}\text{Ar}^+$ dips and others did not. It could be possible that the dips were caused by agglomerates or two particles entering the ICP at once. Signal dips were not observed for any particles less than 1,000 nm in diameter. Local cooling does not appear to be the cause of the size dependent nonlinear response.

Once particles are vaporized, atomized and ionized, ion clouds are sampled into the mass spectrometer through a two stage interface composed of a sampler and skimmer cone. Almost all ions in the ICP pass through the sampler cone into the interface of the mass spectrometer.\textsuperscript{8, 49, 50} However, only ions in the center 1 mm$^2$ of the ICP make it through the skimmer cone into the mass spectrometer.\textsuperscript{51} Ions that diffuse outside of the radial center 1 mm$^2$ of the ICP will be lost.

Assuming a constant vaporization rate of 1 mm s$^{-1}$\textsuperscript{29} a 1 μm particle vaporizes in 1 ms, a 2 μm particle vaporizes in 2 ms, et cetera. The length of time beginning from the very first atom to vaporize to the point at which the entire particle is vaporized increases with particle size. As a result, the amount of time for the very first ion to diffuse out of the center 1 mm$^2$ before vaporization is complete also increases with particle size. The largest particle size with signal that falls on the linear portion of the calibration curves in figures 8.17-8.18 is 1,077 nm, indicating that Si$^+$ diffuse from the center 1 mm$^2$ of the ICP in about 1 ms.

Particles larger than about 1,077 nm have smaller than expected signals because the time for vaporization (~1 ms) exceeds the time for ions to diffuse from the center 1
mm² of the ICP. The most likely cause for the nonlinear response of large SiO₂ particles is that diffusion causes signal to be lost before vaporization is completed.

8.6.4 Measurement of particle mass distributions

Can ICP-MS be used to not only measure the average particle size but also the distribution of particle sizes? If the precision of ICP-MS measurements is sufficient, then it may be possible to accurately measure the polydispersity of particles that are nominally “monodisperse”.

Particle size distributions measured by ICP-MS were compared to size distributions measured by SEM. The calibration curves in figure 8.18 were used to convert peak area to Si mass. Assuming spherical particles the diameter of each particle was calculated from each mass determined by ICP-MS. A total of only 200 signal peaks were recorded for each size due the time required for data evaluation. At least 94% of the 200 measurements were included when calculating the size distributions. Less than 6% of the measured signal peaks were discarded because the waveforms appeared to be due to more than one peak. The ICP-MS and SEM distributions were normalized for direct comparison of the distribution widths.
Figure 8.21: Normalized histograms from 1.077 nm SiO$_2$ particles using a) SEM and b) ICP-MS at a center channel gas flow rate of 0.96 L min$^{-1}$.

The %RSDs of the 1.077 nm SiO$_2$ particles determined by ICP-MS and SEM were 4.7% and 4.2%, respectively. The precision of the two measurement techniques is the same at the 95% confidence level ($f_{\text{measured}} < f_{\text{critical}}$). Although the %RSDs of the histograms in figure 8.21 are similar, the shapes of the distributions appear to be different. Relative standard deviations of the other nanoparticle sizes measured by both SEM and ICP-MS are shown in table 8.9.
Table 8.9: SEM and ICP-MS analyzed nanoparticle peak area, peak area %RSD’s, diameter RSD’s and optimized center channel gas flow rates.

<table>
<thead>
<tr>
<th>Data from SEM measurements</th>
<th>Data from ICP-MS with oscilloscope</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated Diameter (nm)</td>
</tr>
<tr>
<td>403</td>
<td>4.2 %</td>
</tr>
<tr>
<td>518</td>
<td>4.1 %</td>
</tr>
<tr>
<td>629</td>
<td>4.4 %</td>
</tr>
<tr>
<td>744</td>
<td>3.6 %</td>
</tr>
<tr>
<td>~875</td>
<td>Not measured</td>
</tr>
<tr>
<td>907</td>
<td>8.7 %</td>
</tr>
<tr>
<td>1,077</td>
<td>4.2 %</td>
</tr>
<tr>
<td>1,801</td>
<td>2.8 %</td>
</tr>
<tr>
<td>2,035</td>
<td>3.5 %</td>
</tr>
<tr>
<td>2,810*</td>
<td>7.6 %</td>
</tr>
</tbody>
</table>

* Data from 2,810 particles are unreliable due to detector saturation.

6 of the 9 %RSDs measured by ICP-MS are greater than those measured by SEM at the 95% confidence level. This could be due to variations in particle trajectory or the effect of different particles being at different radial positions in the ICP, resulting in variations in the fraction of ions that pass through the skimmer into the MS. Ions that are not within the center 1 mm² of the ICP will be incompletely sampled into the mass spectrometer, increasing the measured RSD. Fluctuations in the center gas flow rate that cause variations in the amount of time a particle spends in the ICP also negatively affects precision.

Only the 629 nm (4.2% vs 4.4%), 907 nm (6.1% vs 8.7%) and 2,810 nm (6.5% vs 7.6%) sized particles were measured with narrower distributions by ICP-MS than SEM.

The 2,810 nm particles saturated the detector (figure 8.16); therefore, the data are
unreliable. The 629 nm particle distributions were measured equally by SEM and ICP-MS at the 95% confidence level ($f_{\text{measured}} = 1.098 < f_{196.74} = 1.40$). The 907 nm particles had a narrower distribution when measured by ICP-MS than by SEM ($f_{\text{measured}} = 2.03 > f_{199.391} = 1.21$). It is unclear why this was observed, and more data should be collected before making a definitive conclusion.

The %RSDs in table 8.9 were measured at optimized center gas flow rates for maximum sensitivity. At center gas flow rates near the optimized flow rate, signal to noise ratios were high and peak areas were insensitive to noise. For all sizes on the linear portion of the calibration curve (400 - 1,077 nm) the optimized center gas flow rates were between 0.96 and 1.02 L min$^{-1}$ (figure 8.15). ICP-MS provides precision equivalent to or only slightly larger than SEM at this range of flow rates. The %RSDs increased when the center gas flow rate was too high (insufficient time for full vaporization) or too low (signal loss due to diffusion). Table 8.10 shows the %RSD measured from the 1,077 nm particles at various center channel gas flow rates.

**Table 8.10:** Measured %RSDs of 1,077 nm SiO$_2$ particles as a function of center channel gas flow rate.

<table>
<thead>
<tr>
<th>Center channel gas flow rate (L min$^{-1}$)</th>
<th>% RSD (signal$^{1/3}$)</th>
<th>N</th>
<th>Center channel gas flow rate (L min$^{-1}$)</th>
<th>% RSD (signal$^{1/3}$)</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7</td>
<td>14.6%</td>
<td>197</td>
<td>0.96 (optimized sensitivity)</td>
<td>4.7%</td>
<td>200</td>
</tr>
<tr>
<td>0.8</td>
<td>13.6%</td>
<td>196</td>
<td>0.97</td>
<td>5.0%</td>
<td>200</td>
</tr>
<tr>
<td>0.9</td>
<td>3.2%</td>
<td>200</td>
<td>1.0</td>
<td>8.3%</td>
<td>197</td>
</tr>
<tr>
<td>0.95</td>
<td>5.4%</td>
<td>199</td>
<td>1.05</td>
<td>10.6%</td>
<td>200</td>
</tr>
</tbody>
</table>
One of the most interesting outcomes of the study involved the analysis of the polymodal 875 nm SiO$_2$ particles. The images of the particles (figure 8.5) showed sizes ranging from 200 nm up to 2,000 nm. The data in both the calibration curves and the size distributions in table 8.9 were collected when the oscilloscope trigger was set so that only signal peaks from particles larger than ~500 nm were recorded. Data were also collected with the oscilloscope triggered to collect signals from all of the particle sizes from the 875 nm particle suspension.

The distribution of ICP-MS signal peak areas was bimodal and dominated by the small particles that are numerous in the background of the image shown in figure 8.5.

![Signals from 875 nm SiO$_2$ particles and small particles](image)

**Figure 8.22:** Measured distribution of the “875” nm SiO$_2$ particle ICP-MS signals measured using the digital oscilloscope.
Particle sizes between approximately 300 and 400 nm were measured most frequently, which agrees with sizes measured by SEM. 85% of the signal peaks were due to the smaller sized particles and 15% were due to particles centered at 875 nm. The ICP-MS data provided a clear picture that the “875 nm size standard” nanoparticles were not monodisperse, contrary to the manufacturer’s claims. Though unintended, the study of this particular sized particle has shown ICP-MS to be capable of detecting when more than one size nanoparticle is present in solution.

8.6.5 Analysis of nanoparticle mixtures by ICP-MS

Two mixtures of nanoparticles were made by staff member Anthony Lutton and analyzed by ICP-MS. A center gas flow rate of 0.90 L min\(^{-1}\) was chosen for its sufficient sensitivity for all sizes of particles. The calibration curve in figure 8.17c was used to calculate particle mass and was measured one week prior to the mixture analysis measurements. 1,000 signal peaks were measured using a current amplification of \(10^6\) V/A and a filter rise time of 10 µs.
Two large peaks in figure 8.23 appear to be due to two different particle sizes. If the particles are treated as complete unknowns, using the calibration curve in figure 8.17c, 425 and 725 nm diameters are calculated. The signals at the two maxima of the histogram were used to calculate the particle sizes. These sizes are 6% (425 nm vs 400 nm) and 2.5% (725 nm vs 744 nm) different than the sizes measured by SEM. The calibration curve was made 1 week prior to the analysis of the particle mixture, and drift
in instrument sensitivity (~13% drift for the 744 nm particles corresponded to 2.5% change in diameter) likely accounts for the small differences in diameters.

The shifts in sensitivity do not have a dramatic effect on the measured particle size because the diameter is related to the cubed root of the signal. Very large inaccuracies or variations of signal would be required to produce significantly inaccurate determinations of particle size.

The 400 nm particles encompassed 30% of the measured peaks, with the remaining 70% of signal peaks corresponding to the 744 nm particles if a vertical line were drawn at 575 nm in figure 8.23. The 400 and 744 nm stock solutions had different particle concentrations (see table 8.5 for particle mL\(^{-1}\)), and after correcting for the different stock concentrations the unknown solution was determined to be made of 34/66 v/v of the 400 and 744 nm stock solution. These amounts were within a factor of 2 of the true mixture composition of 50/50. The stock solution particle concentrations were known to only 1 significant digit (1% solids in solution) and so the uncertainty may be quite large. Measurement within only a factor of 2 is therefore not entirely unexpected due to the large concentration uncertainty in the original stock solutions.

A second unknown mixture was made and analyzed identically as the previous unknown mixture. A total of 600 signal peaks were measured using an amplifier gain of 10\(^6\) V/A. The measured histogram is shown in figure 8.24.
Figure 8.24: Histogram of signal peak areas measured from a mixture of 4 unknown particle sizes (blue, left y-axis) overlaid with a linear combination of individual normalized histograms from single standard stock solutions (red, right y-axis).

3 peaks in figure 8.24 are labeled 629, 744 and 907 nm. The fourth peak, labeled 400 nm, will be addressed shortly. A qualitative estimation of the sizes of nanoparticles was made and used to determine the sizes in the mixture. The red line is linear combination of the normalized individual size standards and roughly overlays the blue peaks from the mixture. The histogram maxima lie in bins at 650, 750 and 900 nm. These sizes are all within 25 nm of the SEM measured average diameters.
A small peak thought to be due to the 400 nm particles is also observed. In order to confirm this particle size as part of the ensemble, the current amplifier gain was increased from $10^6$ to $10^7$ V/A. Most of the signals saturated the oscilloscope, which has a small dynamic range. The signals that did not saturate the scope are shown in figure 8.25.

![Diameter (nm) vs Frequency (N)](image)

**Figure 8.25:** Histogram of 400 nm signal peak areas measured from a mixture of 4 unknown particle sizes. $10^7$ V/A gain produced saturated signals for all sizes other than 400 nm (data not shown). The single size stock solution normalized histogram is overlaid in red.

The width (expressed as %RSD) of peak areas from the 400 nm particles in the unknown mixture matches the width when the particles were measured from the stock
standard solution. The particles in the ensemble mixture were correctly identified as the 400, 629, 744 and 907 nm SiO$_2$ sizes.

One method that might be used to measure a wide range of nanoparticle sizes in a mixture is to use multiple current amplifier gains, as was used for the second unknown mixture. A gain of $10^7$ V/A is required for particles less than about 500 nm, $10^6$ V/A is required for particles from 500 to 1,500 nm, and a gain of $10^5$ V/A is required for particles larger than 2,000 nm in diameter. 1,200 peaks were measured with gains of $10^6$ (600 peaks) followed by $10^7$ V/A (600 additional peaks). From the peaks measured with $10^7$ gain, 303 were too intense for the digital oscilloscope, and the remaining 297 are plotted in figure 8.25. The signals shown in figure 8.25 were then assigned to be 400 nm, and could be roughly estimated to be 50% of the total particles in solution. However, figure 8.24 ($10^6$ V/A) shows a low percentage of peaks centered at 400. A gain of $10^6$ may miss some smaller particles that may either be less than the oscilloscope trigger value or may blend into the baseline noise. Regardless of the difficulties in simultaneously characterizing both concentrations and populations in mixtures of nanoparticles, the above examples have shown that identification of nanoparticle sizes is possible.

### 8.7 Time integrated nanoparticle characterization

Time resolved data recording (section 8.6) using a digital oscilloscope is unconventional for ICP-MS instruments used for solution analyses, not controlled through the instrument software, and may be intimidating for users not accustomed to modifying instrument electronics. The digital oscilloscope continuously records data on
a µs timescale by monitoring current from the analog output of the detector only. The
instrument software integrates signal on a ms timescale, but can also use the pulse
counting mode of the detector, which displays higher signal to noise. The ability of ICP-
MS to characterize nanoparticle sizes and mass distributions using the instrument
software and a ms timescale was investigated. Nanoparticles were introduced to the ICP
via the same sample introduction system as previously described. Some of the possible
problems and solutions are described.

SiO$_2$ particles measured in pulse mode were measured using NH$_3$ reaction gas
(0.4 mL min$^{-1}$ Ar equivalent) and RPq 0.60 to simultaneously eliminate both the $^{14}$N$_2^+$
and $^{12}$C$^{16}$O$^+$ interferents on $^{28}$Si$^+$ and prevent pulse pileup. Au particles measured in
pulse counting mode used a defocused lens to avoid pulse pileup and detector saturation
(explained in further detail in section 8.7.3).

8.7.1 Effect of instrument dwell time

Measurements with the digital oscilloscope used a trigger to record data only
when a nanoparticle entered the ICP and then sampling the current every 1 µs. The ICP-
MS software has no trigger capability and integrates signal over predetermined dwell
times, typically ranging from 1 to 500 ms. Particles are introduced at random times and
signal peak from a single particle may not be completely contained in a single integration
period. In this case, signal will not be counted in a single dwell time window and the
total counts may be split between more than one integration period (yielding counts that
are too low for example), or signals from two particles may be included in a single
integration period (with counts too high). Figure 8.26 shows an example timing diagram with randomly arriving nanoparticles.

![Timing Diagrams](image)

**Figure 8.26:** Simulated example showing the effect of dwell time length on signal capture. Peak offset by 1 ms from center of measurement period in b) and d).

Figure 8.26 shows how dwell time may affect the measurements; too short and signal may be lost if the peak does not lie in the center of the dwell time, too long and signals from two particles may be included. When the arriving nanoparticle was off-centered by just 1 ms only 41% of the signal was captured using a dwell time of 2 ms while 100% of the signal was captured using a 10 ms dwell time and the same offset. The probability of part of the signal falling outside of a single dwell time will decrease as
the ratio of dwell time to peak width increases, i.e. as the dwell time is increased. However, the probability of two particles being captured in a single dwell time increases as the dwell time is increased.

Dwell time was varied from 2 to 200 ms and a suspension of 250 nm Au particles was introduced at an uptake rate of $10 \mu \text{L min}^{-1}$ and a center gas flow rate of $0.90 \text{ L min}^{-1}$. Figure 8.27 shows histograms of the cubed root of signals measured using 2, 10, and 100 ms dwell times and a summary of all dwell times tested.

![Histogram of signals](image)

**Figure 8.27:** Histogram of $(\text{signals})^{1/3}$ at a) 2, b) 10 and c) 200 ms dwell time with d) a summary of average measured signal (sensitivity) (○, left y-axis) and %RSD (●, right y-axis) as a function of dwell times.
Figure 8.27 shows how the length of dwell time impacts both the measured sensitivity and precision of nanoparticle measurements. Sensitivity (○, left y-axis) increases from 350 to 720 counts/particle as the dwell time is increased from 2 to 200 ms. As dwell time increases, the probability that signal from one particle is lost (figure 8.26b) decreases. The width of the nanoparticle size distribution, expressed as %RSD (●, right y-axis), also decreases as the dwell time is increased. The histogram in figure 8.27c shows a sloped front edge due to partial signal loss, even at 200 ms dwell time. Although the front edge is sloped, the %RSD of the cubed root of signals improved from 9.2 % (10 ms) to 6.0% (200 ms). Figure 8.27 shows why long dwell times should be used to ensure correct measurement of sensitivity and narrow signal distributions.

Although figure 8.27d shows how increasing dwell time improves precision and sensitivity, long dwell times are susceptible to containing signals from more than one particle. Increasing dilution lowers the probability of measuring two particles in a single dwell time. Even if the particle concentrations and required dilution factors are unknown, the probability of measuring more than one particle per dwell time can be calculated according to Poisson statistics:\(^1,4\)

\[
P_\lambda(x) = \frac{\lambda^x}{x!} e^{-\lambda}
\]  
(8.3)

where \(\lambda\) is the number of particles delivered divided by the number of measurement cycles, and \(x\) is the number of particles found during each measurement cycle. The Poisson distribution assumes that the particles are uniformly distributed in the suspension and that no agglomeration is present. The validity of Poisson statistics to single particle ICP-MS was examined using SiO\(_2\) particles. Signals from 1,077 nm SiO\(_2\) particles with a
dwell time of 20 ms and a center channel gas flow rate of 0.90 L min\(^{-1}\) are shown in figures 8.28 and 8.29. The liquid uptake rate was 10 \(\mu\)L min\(^{-1}\). Data were taken in 20 second groups (1,000 replicates with 20 ms dwell time). The data in figure 8.28 are shown as a single series of 6 data groups (20 s each) for a total data acquisition time of 120 seconds.

![Graph showing signal over time](image)

**Figure 8.28:** Signal recorded from 1,077 nm SiO\(_2\) particles introduced with a center gas flow rate of 0.90 L min\(^{-1}\), 10 \(\mu\)L min\(^{-1}\) liquid uptake rate and 20 ms dwell time. Signals measured in pulse counting mode with 0.4 mL min\(^{-1}\) NH\(_3\) in the DRC.

Figure 8.28 show a large number of signal spikes near 200 counts, a few near 400 counts, and a large number less than 50 counts. The data in figure 8.28 are expressed as a histogram in figure 8.29.
**Figure 8.29:** Distribution of measured signals from 1,077 nm SiO$_2$ particles measured in pulse mode on the Elan ICP-MS at center channel gas flow rate 0.90 L min$^{-1}$.

Data less than 50 counts were attributed to background (no particle) and were excluded from 8.29. Of the 10,000 measurements, 1,169 contain signal greater than 50 counts and are assumed to be due to a particle ($\lambda = 1,169/10,000$). Using equation 8.3, the theoretical probability of finding 1 and 2 particles in a dwell time window is calculated to be 10.39% and 0.61% respectively, which are very close to the experimental occurrences of signal between 100 and 300 counts (10.9%) and between 300 and 500 counts (0.63%). The probability of finding three particles in a measurement window is 0.02%, which again is close to the number of signals greater than 500 counts (0.03%). The calculated probabilities indicate that signals from 100 to 300 counts are due to 1
particle, 300 to 500 counts are due to 2 particles, and signals greater than 500 counts are due to 3 particles in a single dwell time.

The excellent agreement between the Poisson calculated probability of measuring nanoparticles in a given dwell time proves three important facts: 1) it is possible to predict how many signals will be due to more than one particle and correct for these occurrences; 2) the particles are not agglomerated; and 3) particles are uniformly distributed in solution.

A particle whose signal spans more than one dwell time will also be a problem. In this case, the counts from the particle signal will be spread over two dwell time windows, which would yield two signals that are too low. The PerkinElmer Elan 6100PLUS ICP-MS does not measure signals continuously, with a short (200 μs) settling time between each measurement cycle. Even when only one isotope is being monitored, the instrument electronics are programmed to stop counting at the end of a dwell time, re-settle and begin counting again after the settling time has passed. Because the settling time between measurement periods is greater than the typical width of the signal peak, it is not possible for one particle to span two measurement periods.

For this work, a dwell time of 20 ms was chosen. This dwell time was deemed sufficiently long to provide good sensitivity and precision while maintaining low probability of finding two particles in a single dwell time.

**8.7.2 Effect of liquid uptake rate of signal precision**

Liquid uptake rate affects the size and number of droplets exiting the spray chamber. At high liquid uptake rates, large numbers of droplets are produced and may
collide to form larger droplets. The aerosol exiting the spray chamber therefore becomes increasingly polydisperse as uptake rate increases.\textsuperscript{39-43, 53}

Before a nanoparticle can begin vaporization, the droplet that surrounds it must first be evaporated. The size of the original nanoparticle-containing droplet then dictates the point at which nanoparticle vaporization begins. Consider two nanoparticles, one in a 1 \( \mu \)m droplet and another in a 10 \( \mu \)m droplet; the nanoparticle contained in the 1 \( \mu \)m droplet will begin to vaporize at a much lower (upstream) point in the plasma than the nanoparticle in the 10 \( \mu \)m droplet. Incompletely vaporized (from the 10 \( \mu \)m droplet) and diffused particles (from the 1 \( \mu \)m droplet) will degrade precision.

To determine the effect of liquid uptake rate on the width of the signal distributions, 250 nm Au particles were introduced to the ICP at a center gas flow rate of 0.90 L min\(^{-1}\) from an AriMist nebulizer through a 40 mL conical evaporation chamber. The center gas flow rate was optimized for maximum Au sensitivity using a 100 ppb dissolved Au solution. A single gas flow rate was used although it should ideally be optimized for each liquid uptake rate. Uptake rate was varied from 5 to 500 \( \mu \)L min\(^{-1}\).

<table>
<thead>
<tr>
<th>Liquid Uptake Rate (mL min(^{-1}))</th>
<th>% RSD of total signal</th>
<th>% RSD of cubed roots of signals</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>14.8%</td>
<td>5.23%</td>
<td>297</td>
</tr>
<tr>
<td>10</td>
<td>13.5%</td>
<td>4.92%</td>
<td>309</td>
</tr>
<tr>
<td>20</td>
<td>13.2%</td>
<td>4.49%</td>
<td>395</td>
</tr>
<tr>
<td>50</td>
<td>13.4%</td>
<td>4.81%</td>
<td>675</td>
</tr>
<tr>
<td>100</td>
<td>14.9%</td>
<td>5.23%</td>
<td>867</td>
</tr>
<tr>
<td>200</td>
<td>14.9%</td>
<td>5.44%</td>
<td>565</td>
</tr>
<tr>
<td>500</td>
<td>17.4%</td>
<td>6.48%</td>
<td>364</td>
</tr>
</tbody>
</table>

Table 8.11: %RSD’s of both total signal and cubed root of signal as a function of liquid uptake rate from 250 nm Au nanoparticles with a center channel gas flow rate of 0.90 L min\(^{-1}\).
The widths of the signal distributions were not affected by the liquid uptake rate from 10-50 µL min\(^{-1}\). At 5 µL min\(^{-1}\), the AriMist nebulizer does not produce a constant aerosol and so particles may arrive in ‘bunches.’ This may have led to the slightly higher %RSD, but this observation is supported by anecdotal evidence only. The %RSD at 5 µL min\(^{-1}\) was <1% greater than when the uptake rate was 10-50 µL min\(^{-1}\). At uptake rates greater than 100 µL min\(^{-1}\), it appears that the distribution is widening. This is likely due to some particles arriving desolvated and beginning vaporization immediately while other particles arrive in large droplets and do not begin vaporization until the droplet is vaporized. A liquid uptake rate of 500 µL min\(^{-1}\) yielded a %RSD almost 50% larger than the lowest %RSD measured.

The %RSDs of the cubed roots of signal distributions correlate to the %RSD of particle diameters. For a liquid uptake rate of 10 µL min\(^{-1}\), the %RSD of the cubed root of signals measured was 4.9%. The manufacturer reported percent coefficient of variation for the 250 nm Au particles was 8%. Interestingly (and perhaps surprisingly) the ICP-MS width is significantly less than that of the manufacturer. A distribution of the 250 nm Au particles by SEM was unable to be generated because the edges of the particles in the images were too blurred for reliable analysis. Figure 8.30 shows a histogram of signals for the analysis of 250 nm Au particles with a center channel gas flow rate of 0.90 L min\(^{-1}\) introduced from a liquid uptake rate of 50 µL min\(^{-1}\).
Data were collected for 200 seconds (10,000 data measurements each 20 ms wide). 705 recorded signals from particles were greater than 100 counts. The probability of finding a single particle in a dwell time window ($\lambda = 705/10,000, x = 1$) using equation 8.3 is 6.57%. The sum of particles from 400 to 900 counts is 665 (6.65%), which is close to the theoretical probability. The probability of finding two particles ($\lambda = 705/10,000, x = 2$) is 0.23%, and again matches closely to the experimental finding of 0.28%.

Uptake rate does not appear to significantly affect precision at flow rates less than 100 µL min$^{-1}$. It should also be noted that particle delivery rate increases with liquid
uptake rate (but not linearly because the transport efficiency decreases as the uptake rate increases), and so dilution factors should be increased as uptake rate is increased to maintain constant particle delivery (particle s⁻¹).

8.7.3 Effects of short pulse widths on single nanoparticle analysis

The short pulse widths of the particle signals may have deleterious effects on measurement accuracy due to pulse pileup in the detector. The detector operates in either digital (pulse counting) or analog (current integration) modes. When the electron multiplier detector is operated in pulse counting mode, an electronic circuit counts the number of times the voltage output from the final dynode exceeds and then falls below a preset threshold. Pulse counting mode displays higher signal to noise than analog (current integration) mode because pulses are counted and noise that falls below a set discriminator threshold is excluded, whereas the analog mode integrates both pulses and noise.

The pulse width from 1 ion striking the detector is a result of the temporal spreading of the avalanche of electrons through the 19 dynodes of the electron multiplier. This width is typically on the order of several tens of nanoseconds (55 ns in the Elan used) and is termed the dead time of the detector. If two ions strike the detector separated in time by less than the detector dead time (pulse pileup), the voltage output from the final dynode does not fall below the preset discriminator threshold and only one count is recorded. This results in a nonlinear relationship at high count rates and may be corrected according to equation 8.4:

\[
I_{\text{corrected}} = \frac{I_{\text{measured}}}{(1-\tau_i I_{\text{measured}})}
\] (8.4)
where $I_{corrected}$ is the dead time corrected count rate; $I_{measured}$ is the measured count rate; and $\tau$ is the deadtime.

Figure 8.31a shows a Microsoft Excel simulation that simulated 20 ions striking the electron multiplier at random times within a 1 $\mu$s window (2 x $10^7$ c s$^{-1}$). The pulse widths were assigned a variance of 20 ns for demonstration purposes. Of the 20 ions that strike the detector, 13 ions arrived temporally resolved, 2 sets of 2 ions arrived unresolved, and 1 set of 3 ions arrived unresolved. If the discriminator threshold were set to 0.05 a.u., the count output would be 16 instead of the correct number (20). The count rate would then be corrected using equation 8.4.

**Figure 8.31:** Simulations of ICP-MS signals a) arriving randomly and b) showing the difference between steady state (red) and short pulses (blue). Time resolution is in figure a) is 1 ns/point and 2 $\mu$s/point in figure b). Note that the y-axis full scale in (b) is 24x higher for the signal from a nanoparticle (blue) than for the continuous signal (red) that produces the same total number of counts (1000).
Count rate is calculated as the total number of counts divided by the width of the integration window (dwell time). The instrument assumes that all the counts from a particle are spread over the entire dwell time, when in reality the entire signal from a particle is contained within about 100 µs. Figure 8.31b shows a graphical illustration of the differences between calculating count rates from a steady state signal (red) compared to a discrete short pulse width (blue).

In figure 8.31b, both the steady state (red) and signal from a single nanoparticle (blue) are shown and the sum of all points in each is 1,000. The steady state signal was simulated with 1% Gaussian noise distribution. The counts were distributed over a Gaussian shaped peak 100 µs wide for the discrete pulse (blue). The height of the peak is approximately 11 counts. The count rate during the 100 µs peak is the total number of counts (1,000) divided by the peak width (100 µs) and is $10 \times 10^6$ c s$^{-1}$ assuming a rectangular waveform. The counting rate of the steady state signal is calculated in the same way, but the measurement time is the entire dwell time window (20 ms) so the count rate is $0.05 \times 10^6$ c s$^{-1}$.

Dead time corrections (equation 8.4) assume a steady state signal, and underestimate the chance that 2 or more ions strike the detector temporally unresolved when the signal is a short pulse, as would be produced from a single nanoparticle. The amount of correction increases as the count rate increases. Table 8.12 shows both intensities of steady state and short pulse width with the dead time corrected signals.
Table 8.12: Differences in corrected count rates for a steady state signal and 100 µs signal. *Intensity over the time period spanning the width of the signal peak and assuming a rectangular peak shape.

<table>
<thead>
<tr>
<th></th>
<th>True total counts</th>
<th>Dwell time (s)</th>
<th>Signal pulse width (s)</th>
<th>True intensity (c s⁻¹)</th>
<th>Deadtime (ns)</th>
<th>Measured signal (c s⁻¹)</th>
<th>Measured total counts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steady state signal</td>
<td>1,000</td>
<td>0.02</td>
<td>50,000</td>
<td>55</td>
<td>49,863</td>
<td>997</td>
<td></td>
</tr>
<tr>
<td>100 µs pulse width</td>
<td>1,000</td>
<td>0.0001</td>
<td>10⁷*</td>
<td>55</td>
<td>6.45 x 10⁶*</td>
<td>645</td>
<td></td>
</tr>
</tbody>
</table>

If the true number of 1,000 counts were spread over 20 ms, the measured number of counts would be 997 only a 0.3% adjustment. The measured number is too low and will be corrected using equation 8.4. On the other hand, if 1,000 counts were confined to the 100 µs (rectangular) signal peak, the measured counts would be only 645, which is a difference of ~35%. The short pulse width results in an underestimation of the chance that 2 ions arrive temporally unresolved. Inaccurate (too low) counting rates are reported by the instrument software because it assumes a steady state signal. These deviations must be accounted for when calculating signals from single particle ICP-MS. If the signal is too large (~2 x 10⁷ c s⁻¹ during the signal pulse), the dead time correction cited (equation 8.4 and 55 ns dead time) will not work.

8.7.4 Time integrated measurement conditions

The choice of dwell time, liquid uptake rate and the effects of discrete integration times and pulse pileup have been examined. Optimum conditions included liquid uptake rates less than 50 µL min⁻¹, very dilute nanoparticle suspensions and dwell times at least 20 ms long. These conditions were chosen because they offered the best opportunity to
deliver desolvated nanoparticles one at a time while measuring nearly 100% of the signal. After many of the problems and pitfalls of analyzing nanoparticles were determined, understood and resolved, calibration curves and mass distributions of the nanoparticle size standard ensembles were measured.

8.8 Time integrated calibration curves

Instrument response was plotted against nanoparticle mass using SiO$_2$ nanoparticle size standards. SiO$_2$ nanoparticles were measured in DRC mode using 0.4 Ar equivalent mL min$^{-1}$ NH$_3$. NH$_3$ was used to reduce the $^{14}$N$_2^+$ and $^{16}$C$^{12}$O$^+$ background via a charge transfer reaction.$^{57}$ Si$^+$ should not undergo a charge transfer reaction ($\Delta$H$_{rxn}$ = +1.92 eV) and does not cluster with NH$_3$. $^{58}$ Experimental parameters are listed in table 8.13.

Table 8.13: Instrument and sample introduction parameters optimized for the characterization of SiO$_2$ nanoparticles.

<table>
<thead>
<tr>
<th>Sample introduction system</th>
<th>ICP-MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid uptake rate</td>
<td>RF Power 1350 W</td>
</tr>
<tr>
<td>Nebulizer gas flow rate</td>
<td>10 µL min$^{-1}$</td>
</tr>
<tr>
<td>Sheath flow rate</td>
<td>0.6 L min$^{-1}$</td>
</tr>
<tr>
<td>Evaporation chamber</td>
<td>0.1 – 0.6 L min$^{-1}$</td>
</tr>
<tr>
<td>Nebulizer</td>
<td>40 mL conical</td>
</tr>
<tr>
<td>Replicates</td>
<td>Burgener AriMist</td>
</tr>
<tr>
<td>Liquid pump</td>
<td>Syringe</td>
</tr>
</tbody>
</table>
Signals from each particle size were each recorded for 200 seconds at a range of center gas flow rates each. Blank signals were recorded from liquid with no particles. Nanoparticle signals were blank subtracted, and histograms were constructed. The histograms were used to discriminate against signals that resulted from two particles arriving during a single dwell time window as described in section 8.7.1. Finally, signal averages from single nanoparticles were plotted as a function of nanoparticle mass.

Between 300 and 1,100 individual signals were recorded for each size at each center gas flow rate and were dependent on the number of particles that were delivered during the measurement period. Representative examples of 20 second data intervals are shown in figure 8.32 using the 1,077 nm SiO$_2$ particles at 6 flow rates. The data in figure 8.32 were not background subtracted, so that the typical signal to background ratio might be conveyed.
Figure 8.32: Measured signals at m/z 28 from 1,077 nm SiO$_2$ particles with 0.4 Ar equivalent mL min$^{-1}$ NH$_3$ and RPq = 0.60. Center channel gas flow rates a) 0.80, b) 0.85, c) 0.90, d) 0.95, e) 1.00 and f) 1.05 are shown.

As described in section 8.6.1, the center gas flow rate is inversely related to time the nanoparticles spend in the hot region of the ICP. Figure 8.33 shows $^{28}$Si$^+$ signals from SiO$_2$ nanoparticles ranging in size from 518 to 1,077 nm diameter as a function of center channel gas flow rate.
Figure 8.33: Average signals measured at m/z 28 using 0.4 mL min\(^{-1}\) NH\(_3\) and RPq 0.60 from SiO\(_2\) nanoparticle introduction. The SiO\(_2\) nanoparticle sizes shown are 1,077 (●), 907 (Δ), 875 (○), 744 (◊), 629 (▲) and 518 (■) nm on the left y-axis and 1,810 nm (□, right y-axis) in diameter.

Figure 8.33 may be compared to a similar plot using time resolved measurements (figures 8.13 and 8.14). The data in figure 8.33 was acquired 1 month after data in figures 8.13-14 using an identical experimental setup. The 1,810 nm SiO\(_2\) signals are plotted on a separate y-axis for clarity. Data were collected at center gas flow rates separated by 0.05 L min\(^{-1}\). All particle sizes’ maximum sensitivity was measured at 0.90 L min\(^{-1}\), except for the 1,810 nm which was optimized at 0.85 L min\(^{-1}\). This is in contrast
to the time resolved measurements, where center gas flow rates were measured every 0.01 L min\(^{-1}\) and optimized gas flow rates varied for almost every particle size (figure 8.15). It is not clear why the sensitivity of time integrated measurements did not vary as it did with time resolved measurements. One possible explanation is that data were not taken with sufficient flow rate resolution. However, the 518 nm particle sensitivity was optimized at a center gas flow rate of 0.99 L min\(^{-1}\) using time resolved measurements and at a center gas flow rate of 0.90 L min\(^{-1}\) using time integrated measurements. The flow rate at which sensitivity for a particular particle size is optimized should remain unchanged regardless of the data handling. Although the reason for the behavior observed in figure 8.33 is unexplained, the signals recorded were used to construct calibrations curves.

Dead time corrections were performed by converting counts to count rates (20 ms dwell time), calculating new count rates assuming 100 \(\mu\)s pulse width, correcting for 55 ns dead time, and converting new count rates back to total counts. Signals shown in figure 8.34 were all measured at 0.90 L min\(^{-1}\) center channel gas flow rate.
Figure 8.34: Mass calibration measured with SiO$_2$ nanoparticle suspensions using size standards ranging from 518 to 1,810 nm. Raw (●) and dead time corrected (□) signals are shown with extrapolated linear regression lines from the smallest five nanoparticle masses. 8.34a includes 1,810 nm SiO$_2$ particle; 8.34b includes only up to 1,077 nm.

The uncorrected signals display a linear range from 518 nm to 907 nm. Sensitivity (signal/pg) was lower for all particles larger than 1,000 nm, even at the optimized central channel gas flow rates. It is again thought that the reason for this behavior is that the large particles vaporize slowly, and ions are lost to diffusion as discussed in section 8.6.3.

Another factor that was considered as a cause of nonlinear response was the underestimation of the true counting rate due to incorrect dead time correction (section 8.7.3). When the dead time correction is applied using 100 $\mu$s as the pulse width (and assuming a rectangular pulse shape), the difference from the linear regression line to the measured intensity is improved from -30.5% (●) to -27.8% (□) for the 1,077 nm SiO$_2$.
particle. Although the difference between the linear regression line and the experimental data was reduced, dead time correction could not explain the lower signal signal/pg. The 55 ns dead time for the Elan ICP-MS has an uncertainty on the order of 15%. This uncertainty cannot account for the remaining -27.8% reduction in sensitivity for the 1,077 nm particle size.

8.8.1 Single nanoparticle detection limits

The Au nanoparticle detection limit was determined using pulse counting mode and a two point calibration curve at a central gas flow rate of 0.85 L min⁻¹. The sensitivity, average blank signal and standard deviation were measured as 4,230 c pg⁻¹ (dwell time window), 0.018 counts, and 0.19 counts respectively. The blank intensity and standard deviation were determined by measuring the signal using a water solution with no particles. The limit of detection (3σ definition) was equivalent to a 22 nm particle (0.11 fg Au) and limit of quantification (10σ definition) was equivalent to a 33 nm particle. The background equivalent mass (background signal/sensitivity) was 4.2 attogram Au.

Previous studies of single Au nanoparticles using ICP-OES determined the detection limit to be approximately 80 fg.¹ The detection limits were improved by more than two orders of magnitude by using ICP-MS compared to ICP-OES due to the absence of a background at m/z 197.

Au sensitivity was suppressed to prevent pulse pileup. The sensitivity was suppressed by a factor of 2 by defocusing the ion optics. Au signal was measured at a range of ion optics settings to determine the effect of defocusing on sensitivity by
aspirating a 100 ppb solution of Au with no nanoparticles present. If Au sensitivity was optimized, the expected limit of detection would be equivalent to an 18 nm (59 attogram) particle assuming that the blank standard deviation remained counting statistics limited and that sensitivity of nanoparticles reacted to ion optics changes in the same way as 100 ppb Au aerosol. Smaller Au nanoparticles, closer in mass to the detection limit are needed to correctly determine the instrumental limits of detection.

Detection limits for the SiO$_2$ particles in pulse counting mode were also determined. The sensitivity with 20 ms dwell time and 0.4 Ar equivalent mL min$^{-1}$ NH$_3$ was 182 c pg$^{-1}$ (20 ms dwell time)$^{-1}$ with 13 c (20 ms dwell time)$^{-1}$ blank signal. The standard deviation of the water blank was 4.5 counts which is close to the counting statistics limited value of 3.6 counts. All measurements were taken at 0.90 L min$^{-1}$ central channel gas flow rate. Blank signal originating from CO$^+$ and N$_2^+$ were attenuated using NH$_3$. The other source of signal was $^{28}$Si$^+$ from the quartz ICP torch, injector and blank contamination. These latter sources of background could not be attenuated via DRC chemical resolution, though NH$_3$ did suppress Si$^+$ sensitivity. The limit of detection (3$\sigma$ definition) was 71 fg, equivalent to a 399 nm SiO$_2$ nanosphere and the limit of quantification (10$\sigma$ definition) was equivalent to a 597 nm diameter SiO$_2$ particle. The background equivalent mass (background signal/sensitivity) was 70 fg Si. Similar measurements using ICP-OES and monodisperse droplet introduction showed a Si detection limit of 50 fg.$^1$ It is not clear why the ICP-OES detection limits were superior to ICP-MS, although it is believed that the use of NH$_3$ to attenuate CO$^+$ and N$_2^+$ also suppressed Si$^+$ sensitivity enough to degrade the Si nanoparticle detection limit.
Detection limits measured using pulse mode and integrating for 20 ms were worse than when analog mode and the digital oscilloscope was used. 400 nm SiO$_2$ particles were observed using the oscilloscope (analog mode, figure 8.8b) but could not be detected using the Elan software (20 ms dwell time, pulse counting mode). This result was unexpected because the pulse counting mode discriminates against low amplitude noise by only counting pulses that exceed a set threshold, whereas analog mode includes all noise contributions. Because the Elan software was not triggered like the oscilloscope, long integration times (20 ms) relative to the width of signal spikes (~100 μs) were used (see figure 8.27d). As dwell time is increased, the ratio of time spent measuring signal from a particle (roughly constant, ~100 μs) to total time spent measuring background (dependent on dwell time) decreases. Analog detection using the oscilloscope collected background for 1/20 the time using pulse (counting) detection and a 20 ms dwell time. The background at m/z 28 was 105 counts ms$^{-1}$. The standard deviation of background counts increases according to $\sqrt{N}$, where N is the total number of counts.
Figure 8.35: Measured standard deviations (○, right y-axis) and % RSD (●, left y-axis) as a function of dwell time for blank m/z 28 signals measured in the vented mode.

The total number of counts from the background increases with increasing dwell time (figure 8.35). The long integration time of the instrument software includes “extra” noise and degrades detection limits from that of the digital oscilloscope despite the fact that pulse counting mode was used with the instrument detection electronics and analog measurement was used with the current amplifier/digital oscilloscope.

8.8.1 Comparison of mass distributions by single particle ICP-MS

Measured distribution widths of SiO₂ size standards imaged by SEM were compared to distributions analyzed by ICP-MS. Time integrated measurements, using the ICP-MS instrument software to obtain a single number for each 20 ms dwell time,
were able to be analyzed much more quickly than with the oscilloscope and so more particles could be analyzed with improvements in statistical confidence.

Figure 8.36: Normalized histograms from 1,077 nm SiO₂ particles using a) SEM and b) ICP-MS at a center channel gas flow rate of 0.90 L min⁻¹.

Figure 8.36 shows are histograms of the cubed roots of measured signals resulting from introduction of 1,077 nm SiO₂ particles to the ICP. The %RSD of the SEM measurements was 4.2% RSD, while the %RSD of the ICP-MS measured particle sizes from the same stock solution was 5.6%. As with time resolved measurements, the radial distribution of particles in the ICP, slight changes in particle trajectory and gas flow variations likely contribute to the increased %RSD observed for ICP-MS measurement of mass and therefore, particle diameter. The peak shape of the discrete measurements distribution (figure 8.36b) looks very similar to the shape of triggered measurements (figure 8.21b).
Dwell times that do not capture 100% of the signal from randomly arriving particles and counting statistics are also expected to increase the measured width of the nanoparticle distributions as previously described. Figures 8.26 and 8.27 show how signal may be lost if particles do not arrive near the center of the measurement period. Dwell times of 20 ms measured the diameter %RSD of 250 nm Au particles 1.8% wider than the same particles measured with dwell time of 200 ms. The contributions of counting statistics uncertainty on the width of signal distribution is equal to $\sqrt{\text{total counts}} = 7.2\%$ RSD. The counting statistics contribution to the width of the diameter distribution is 2.4%.

The ICP-MS distribution was broader (5.6% RSD) than the SEM distribution (4.2% RSD) suggesting that the ICP-MS measurement precision may be only able to provide an upper limit to the width of the nanoparticle size distribution. It appears that two most important factors limiting the precision that nanoparticle distributions may be measured are the probability that only portions of the peak signal may be measured within a single dwell time from some particles and counting statistics limitations. All nanoparticle sizes, signals and %RSDs are listed in table 8.14.
Table 8.14: Reported, SEM and ICP-MS pulse counting mode nanoparticle sizes and distributions. ICP-MS data recorded with central channel gas flow rate 0.90 L min\(^{-1}\) and is blank subtracted but uncorrected for short pulse duration. 20 ms dwell time used.

<table>
<thead>
<tr>
<th>Manufacturer Data</th>
<th>SEM measurements</th>
<th>ICP-MS measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reported diameter (nm)</td>
<td>% RSD</td>
<td>Diameter (nm)</td>
</tr>
<tr>
<td>319.5</td>
<td>&lt; 2.2</td>
<td>403</td>
</tr>
<tr>
<td>545</td>
<td>&lt; 2.2</td>
<td>518</td>
</tr>
<tr>
<td>620</td>
<td>&lt; 4</td>
<td>629</td>
</tr>
<tr>
<td>725</td>
<td>&lt; 4</td>
<td>744</td>
</tr>
<tr>
<td>840</td>
<td>&lt; 4</td>
<td>875</td>
</tr>
<tr>
<td>952</td>
<td>&lt; 4</td>
<td>907</td>
</tr>
<tr>
<td>1,020</td>
<td>&lt; 3</td>
<td>1,077</td>
</tr>
<tr>
<td>1,470</td>
<td>&lt; 2</td>
<td>1,801</td>
</tr>
<tr>
<td>2,010</td>
<td>&lt; 2</td>
<td>2,035</td>
</tr>
<tr>
<td>4,740</td>
<td>&lt; 2</td>
<td>2,810</td>
</tr>
</tbody>
</table>

The diameter %RSDs measured by ICP-MS are larger than the diameter %RSDs measured by SEM except for the 907 nm particles. Less than 400 of the 907 nm particles were measured by either SEM or ICP-MS and might explain the discrepancy. ICP-OES was unable to characterize the %RSD of SiO\(_2\) particles less than 1 \(\mu\)m in diameter\(^4\), but ICP-MS measured the %RSD of particles as low as 500 nm in diameter (8x less mass). It is not clear why ICP-MS was able to measure distributions of smaller particles than ICP-OES, even though detection limits of the two instruments are similar. It may be that ICP-OES integrated the particle ion cloud over the entire length of the ICP (axially viewed emission) while ICP-MS measured the ion cloud at one point (12 mm downstream from the load coil). Noise fluctuations may be less when measuring ion clouds at one point in the ICP, rather than integrating signal from the entire plasma.
8.9 Conclusions

This study has provided a method for characterizing size, size distribution and elemental composition of nanoparticles. Nanoparticles were delivered to the ICP randomly using a pneumatic nebulizer and evaporation chamber at a rate low enough so that it is unlikely that the signals from two different particles overlap. Signals from nanoparticle size standards were measured by ICP-MS using both a triggered digital oscilloscope (analog mode, \( \mu \text{s/data point} \)) and the instrument software (pulse counting mode, 1-100 ms dwell times). The integrated peak areas showed very linear response with respect to nanoparticle mass between 400 and 900 nm and \%RSDs were similar or slightly wider than the SEM measurements. Two unknown mixtures of nanoparticle stock solutions were analyzed and unknown sizes in the mixture were correctly identified.

It was hypothesized that the large (> 1.1 \( \mu \text{m} \)) particles were measured with lower sensitivity (counts/pg Si) because a significant fraction of ions diffuse out of the volume that makes it into the MS before particle vaporization is completed.

Future studies might include work to extend the capability of ICP-MS to characterize a wider range of nanoparticle sizes. The ICP-MS sensitivity was attenuated to prevent severe pulse pileup in the detector pulse counting mode. The minimum Au nanoparticle detection limit was determined to be 18 nm (59 attogram Au) under conditions to optimize sensitivity (at the cost of lower dynamic range).

This method of nanoparticle introduction might also be used to investigate the transport of aerosol through the evaporation/spray chamber. The frequency of signal peaks could be divided by the known delivery rate from the nebulizer tip to determine the
efficiency of nanoparticles travelling through the evaporation chamber. This method would provide a direct determination of the transport efficiency of the spray and evaporation chambers.


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A.1 Introduction and Explanation

The following appendix is the user program written in Lua using Microsoft Notepad and used in SIMION 8.0 to control the time dependent voltages on the electrodes as well as simulate the collisions between ions and gas molecules or atoms. The program that controls the RF voltages on the quadrupole rods was written specifically for the DRC. The ion-molecule collision handling segment was adapted from that of David Manura, 2006 Scientific Instrument Services©. Segments written by Manura are kept in plain type, while segments written by Patrick J. Gray are boldfaced and italicized. Statements that begin with “--” are for explanation only and do not affect the code.

A.2 SIMION 8.0 User Program

```
simion.workbench_program()
-- The following program simulates the Sciex Dynamic Reaction Cell. Time dependent
-- voltages are applied to the quadrupole rods. The user program can simulate ion
-- trajectories through the quadrupole in both vented and pressurized modes.
```
-- Written by Patrick J. Gray, The Ohio State University
Columbus OH 43210
-- 2005-2011

-- Variables adjustable during flight:
adjustable_percent_tune = 0.0 -- percent of optimum tune.
adjustable_mass_per_charge = 100.0 -- mass/charge tune point (u/e)
adjustable_entrance_lens_voltage = -10.0 -- quad entrance voltage
adjustable_quad_rod_offset = -8.0 -- quad axis voltage
adjustable_exit_lens_voltage = -10.0 -- quad exit voltage
adjustable_detector_voltage = -1500.0 -- detector voltage
adjustable_pe_update_each_usec = 0.05 -- potential energy display -- update

-- Variables adjustable only at beginning of flight:
adjustable_effective_radius_in_cm = 0.40 -- half the minimum distance between opposite rods
adjustable_phase_angle_deg = 0.0 -- quad entry phase angle of ion (deg)
adjustable_RF_voltage = 200 -- Peak to peak RF voltage applied -- to quad electrodes

-- Temporary variables used internally.
local freq_hz -- calculated frequency applied to rods electrodes
local omega -- frequency_hz (reexpressed in radians/usec)
local theta -- phase_angle_deg (reexpressed in units of radians)
local last_pe_update = 0.0 -- last potential energy surface (usec)
function segment.fast_adjust()
  if not freq_hz then

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freq_hz = ((_RF_voltage / _mass_per_charge) / (effective_radius_in_cm^2 * 7.11016e-12))^0.5
theta = phase_angle_deg * (math.pi / 180)
omega = freq_hz * (1e-6 * 2 * math.pi)

local DC_volts = -_RF_voltage * _percent_tune * (1/100) * .1678399
local tempvolts = sin(ion_time_of_flight * omega + theta) * _RF_voltage + DC_volts

-- Finally, apply adjustable voltages to rod electrodes.
adj_elect01 = _quad_rod_offset + tempvolts
adj_elect02 = _quad_rod_offset - tempvolts
adj_elect03 = _entrance_lens_voltage
adj_elect04 = _exit_lens_voltage
adj_elect05 = _detector_voltage

end

-- SIMION segment called by SIMION after every time-step.
function segment.other_actions()
  if abs(ion_time_of_flight - last_pe_update) >=
    pe_update_each_usec then
    last_pe_update = ion_time_of_flight
    sim_update_pe_surface = 1  -- Request a PE surface display update.
  end
end

-- SIMION segment called by SIMION to override time-step size on each time-step.
function segment.tstep_adjust()
  -- Keep time step size <= X usec.
  ion_time_step = min(ion_time_step, 0.1)  -- X usec
end

-- A background gas is now added.
-- In the case of the DRC, the background gas is used to estimate
-- the number and rate of collisions as function of pressure.

-- Modified from the original workbench file collision_hs1.lua
-- A hard-sphere, elastic, ion-neutral collision model for SIMION 8.
-- Modified by Patrick J. Gray, The Ohio State University.
adjustable \_mean\_free\_path\_mm = -1 \quad -- \text{Mean free path (mm) between collisions}

\text{-- Set to -1 to calculate mean free path automatically from pressure and temperature.}

adjustable \_gas\_mass\_amu = 17.0 \quad -- \text{Mass of background gas (amu)}
adjustable \_temperature\_k = 298 \quad -- \text{Background gas temperature (K)}
\text{adjustable \_pressure\_mTorr} = 0 \quad -- \text{Background gas pressure (mTorr)}

\text{(Pa/mTorr) = 0.133322.}
\text{-- Pressure can be estimated by flow rate, collision flux and aperture area}
\text{-- See Pressure estimation excel worksheet for full pressure estimation details}
adjustable \_cross\_section = 2.27E-19 \quad -- \text{Collision cross section}

\text{(pi*(r1+r2)^2) \quad -- The hard sphere collision cross section area is calculated by}
\text{-- \textit{pi times the sum of the radii squared}}
adjustable \_vx\_bar\_gas\_mmusec = 0 \quad -- \text{Mean background gas velocity (mm/usec)}
in \text{x,y,z directions.}
adjustable \_vy\_bar\_gas\_mmusec = 0 \quad -- \text{Gas is introduced in the front,}
adjustable \_vz\_bar\_gas\_mmusec = -0.1 \quad -- \text{and net flow -- in the -z direction is observed.}
adjustable _steps_per_MFP = 20.0            -- Mean number of time steps per MFP.
adjustable _mark_collisions = 1
adjustable _trace_level = 0
adjustable _trace_skip = 10

-- Internal variables
-- current running average of KE for each particle. maps ion_number --> KE.
local ke_averages = {}  
-- last collision time for each particle. maps ion_number --> time.
local last_collision_times = {}  
-- Last known ion number (-1 = undefined).
local last_ion_number = -1
-- Last known ion speed (-1 = undefined).
local last_speed_ion = -1
-- Currently used mean-free path (-1 = undefined).
local effective_mean_free_path_mm = -1
-- Count relative to _trace_skip
local trace_count = 0
-- Maximum time step (usec) that fast_adjust should permit.
local max_timestep

-- Define constants
local k = 1.3806505e-23         -- Boltzmann constant (J/K)
local R = 8.314472             -- Ideal gas constant (J/(mol*K))
local kg_amu = 1.6605402e-27   -- (kg/amu) conversion factor
local pi = math.pi            -- PI constant
local eV_J = 6.241509476e+18   -- (eV/J) conversion factor

function erf(z)
    local z2 = abs(z)
    local t = 1 / (1 + 0.32759109962 * z2)
    local res = ( - 1.061405429 ) * t
    res = (res + 1.453152027 ) * t
    res = (res - 1.421413741 ) * t
    res = (res + 0.2844966736) * t
    res =((res - 0.254829592 ) * t) * exp(-z2*z2)
    res = res + 1

    return res
end
if z < 0 then res = -res end
return res
end

-- Return a normalized Gaussian random variable (-inf, +inf).
function gaussian_random()
    -- Using the Box-Muller algorithm.
    local s = 1
    local v1, v2
    while s >= 1 do
        v1 = 2*rand() - 1
        v2 = 2*rand() - 1
        s = v1*v1 + v2*v2
    end
    local rand1 = v1*sqrt(-2*ln(s) / s) -- (assume divide by zero improbable?)
    return rand1
end

-- SIMION intitialize segment. Called on particle creation.
function segment.initialize() end

-- SIMION time step adjust segment. Adjusts time step sizes.
function segment.tstep_adjust()
    -- Ensure time steps are sufficiently small. They should be some fraction of mean-free-path so that collisions are not missed.
    if max_timestep and ion_time_step > max_timestep then
        ion_time_step = max_timestep
    end
end

-- SIMION other acIctions segment. Called on every time step.
function segment.other_actions()
    if _pressure_mTorr == 0 then -- collisions disabled
        return
    end
    -- Temporarily translate ion velocity (mm/us) frame of reference such that mean background gas velocity is zero.
    -- This simplifies the subsequent analysis.
    local vx = ion_vx_mm - _vx_bar_gas_mmusec
    local vy = ion_vy_mm - _vy_bar_gas_mmusec
    local vz = ion_vz_mm - _vz_bar_gas_mmusec
-- Obtain ion speed (relative to mean background gas velocity).
local speed_ion = sqrt(vx^2 + vy^2 + vz^2)
if speed_ion < 1E-7 then
    speed_ion = 1E-7
        -- prevent divide by zero
end
-- Compute mean-free-path.
if _mean_free_path_mm > 0 then -- explicitly specified
    effective_mean_free_path_mm = _mean_free_path_mm
else -- Only recompute mean-free-path if speed_ion has changed significantly. This is intended to speed up the calculation a bit. This code will handle flying ions by groups.
    if last_ion_number ~= ion_number or
        abs(speed_ion / last_speed_ion - 1) > 0.05
        -- changed
        then
            -- Compute mean gas speed (mm/us)
            local c_bar_gas = sqrt(8*k*_temperature_k/pi/(_gas_mass_amu * kg_amu)) / 1000
                -- Compute median gas speed (mm/us)
                local c_star_gas = sqrt(2*k*_temperature_k/(_gas_mass_amu * kg_amu)) / 1000
                -- Compute mean relative speed (mm/us) between gas and ion.
                local s = speed_ion / c_star_gas
                local c_bar_rel = c_bar_gas * (s + 1/(2*s)) * 0.5 * sqrt(pi) * erf(s) + 0.5 * exp(-s*s))
                    -- Compute mean-free-path (mm)
                    -- Conversion factor from Pa to mTorr = 0.133322 (1/7.5006)
                    effective_mean_free_path_mm = 1000 * k * _temperature_k * (speed_ion / c_bar_rel) / (0.133322 * _pressure_mTorr * _cross_section)
            -- Store data about this calculation.
            last_speed_ion = speed_ion
            last_ion_number = ion_number
print("DEBUG:ion[c],gas[c_bar],c_bar_rel,MFP=",
       speed_ion, c_bar_gas, c_bar_rel,
effective_mean_free_path_mm)
end

-- Limit time-step size to a fraction of the MFP.
max_timestep = effective_mean_free_path_mm / speed_ion / _steps_per_MFP
-- Compute probability of collision in current time-step.
local collision_prob = 1 -
    exp(- speed_ion * ion_time_step /
effective_mean_free_path_mm)
if rand() > collision_prob then -- Test for collision.
    return -- no collision
end

-- Handle collision.
-- Compute standard deviation of background gas velocity in
-- one dimension (mm/us).
-- > From kinetic gas theory (Maxwell-Boltzmann),
velocity in
-- one dimension is normally distributed with standard
-- deviation sqrt(kT/m).
local vr_stdev_gas =
    sqrt(k * _temperature_k / (_gas_mass_amu * kg_amu)) / 1000
-- Compute velocity of colliding background gas particle.
-- > For the population of background gas particles
that collide with the
-- ion, their velocities are not entirely Maxwell (Gaussian) but
-- are also proportional to the relative velocities
the ion and
-- background gas particles:
p(v_gas) = |v_gas - v_ion| f(v_gas)
-- > To generate random velocities in this distribution,
-- use a rejection method approach:
Pick a gas velocity from the Maxwell distribution.
Accept with probability proportional to its speed relative to the ion.

local vx_gas, vy_gas, vz_gas
computed velocities

scale is an approximate upper-bound for "len" calculated below.

use three standard deviations of the three dimensional gas velocity.
local scale = speed_ion + vr_stdev_gas * 1.732 * 3  -- sqrt(3)=~1.732
repeat
vx_gas = gaussian_random() * vr_stdev_gas
vy_gas = gaussian_random() * vr_stdev_gas
vz_gas = gaussian_random() * vr_stdev_gas
local len = sqrt((vx_gas - vx)^2 + (vy_gas - vy)^2 + (vz_gas - vz)^2)
assert(len <= scale)  -- true at least ~99% of the time.
until rand() < len / scale

Translate velocity reference frame so that colliding background gas particle is stationary.
vx = vx - vx_gas
vy = vy - vy_gas
vz = vz - vz_gas

Notes on collision orientation
Compute randomized impact offset [0, 1) as a fraction
of collisional cross-section diameter.
0 is a head-on collision; 1 would be a near miss.

Formally, the normalized probability density function is
f(d) = 2*d for d in [0,1]. From the fundamental transformation
law of probabilities,
integral[0..impact_offset] f(d) dd = impact_offset^2 = U,
where U is a uniform random variable.
impact_offset = sqrt(U). Decrease it it slightly to prevent overflow in asin later.
local impact_offset = sqrt(0.99999999999999 * rand())
-- Convert impact offset to impact angle \([0, \pi/2)\)
(radians).
-- 0 is a head-on collision; \(\pi/2\) would be a near
miss.
local impact_angle = asin(impact_offset)
-- The effect of the above is that impact_angle has
-- a distribution of \(p(\text{impact_angle}) = \sin(2 \times
\text{impact_angle})\).
-- Compute randomized angle \([0, 2\pi]\) for rotation of
collision
-- plane around radial axis.
-- Note: all angles are equally likely to hit.
-- The effect is that impact_theta has a distribution
-- of \(p(\text{impact_theta}) = 1/(2\pi)\).
local impact_theta = 2\pi*\text{rand}()

-- Compute polar coordinates in current velocity
reference frame.
local speed_ion_r, az_ion_r, el_ion_r =
rect3d_to_polar3d(vx, vy, vz)

-- Compute ion velocity components (mm/us).
local vr_ion = speed_ion_r * \cos(\text{impact_angle})
-- radial velocity
local vt_ion = speed_ion_r * \sin(\text{impact_angle})
-- normal velocity

-- Attenuate ion velocity due to elastic collision.
-- This is the standard equation for a one-dimensional
-- elastic collision, assuming the other particle is
initially at rest
-- (in the current reference frame).
-- Note that the force acts only in the radial
direction, which is
-- normal to the surfaces at the point of contact.
local vr_ion2 = (vr_ion * (ion_mass - \_gas_mass_amu))
/ (ion_mass + \_gas_mass_amu)

-- Rotate velocity reference frame so that original ion
velocity
-- vector is on the +y axis.
-- Note: The angle of the new velocity vector with
respect to the
-- +y axis then represents the deflection angle.
\[
\begin{align*}
\text{vx, vy, vz} &= \text{elevation}_\text{rotate}(90 - \text{deg}(\text{impact}_\text{angle}), \\
&\quad \text{vr}_\text{ion2}, \text{vt}_\text{ion}, 0)
\end{align*}
\]

-- Rotate velocity reference frame around +y axis.  
-- This rotates the deflection angle and in effect selects the 
-- randomized impact_theta.  
\[
\begin{align*}
\text{vx, vy, vz} &= \text{azimuth}_\text{rotate}(\text{deg}(\text{impact}_\text{theta}), \text{vx, vy, vz})
\end{align*}
\]

-- Rotate velocity reference frame back to the original.  
-- For the incident ion velocity, this would have the effect 
-- of restoring it.  
\[
\begin{align*}
\text{vx, vy, vz} &= \text{elevation}_\text{rotate}(-90 + \text{el}_\text{ion}_r, \text{vx, vy, vz})
\end{align*}
\]

vx, vy, vz = azimuth_rotate(az_ion_r, vx, vy, vz)  

-- Translate velocity reference frame back to original.  
-- This undoes the prior two translations that make velocity 
-- relative to the colliding gas particle. 
\[
\begin{align*}
\text{vx} &= \text{vx + vx_gas + _vx_bar_gas_mmusec} \\
\text{vy} &= \text{vy + vy_gas + _vy_bar_gas_mmusec} \\
\text{vz} &= \text{vz + vz_gas + _vz_bar_gas_mmusec}
\end{align*}
\]

-- Set new velocity vector of deflected ion.  
\[
\text{ion_vx_mm, ion_vy_mm, ion_vz_mm} = \text{vx, vy, vz}
\]

-- Compute running average of KE, for statistical reporting only.  
-- At thermal equilibrium, KE of the ion and KE of the gas would 
-- be approximately equal according to theory.  
if _trace_level \geq 1 then  
-- Compute new ion speed and KE.  
\[
\begin{align*}
\text{local speed}_\text{ion2} &= \sqrt{(\text{ion_vx_mm}^2 + \text{ion_vy_mm}^2 + \text{ion_vz_mm}^2)} \\
\text{local ke2_ion} &= \text{speed_to_ke}(\text{speed}_\text{ion2}, \text{ion_mass})
\end{align*}
\]

-- To average ion KE somewhat reliably, do a running (exponential decay) 
-- average of ion KE over time.  The reset time of the exponential decay
is set to some fraction of the total time-of-flight, so the average
will become more steady as the run progresses
(assuming this is a
system that approaches equilibrium).
Note: exp(-x) can be approximated with 1-x for small x.

time between most recent collisions
local dt = ion_time_of_flight -
(last_collision_times[ion_number] or 0)
-- average over some fraction of TOF
reset_time = ion_time_of_flight * 0.5
-- weight for averaging.
local w = 1 - (dt / reset_time) -- ~= exp(-dt / reset_time)
-- update average ion KE
ke_averages[ion_number] = w *
(ke_averages[ion_number] or ke2_ion)
+ (1-w) * ke2_ion
if _trace_level >= 2 then -- more detail
local T_ion = ke_averages[ion_number] / eV_J / (1.5 * k)
if trace_count % _trace_skip == 0 then
print(string.format(
"n=,%d,TOF=,%0.3g,ion KE (eV)=,%0.3e,ion mean KE (eV)=," ..
"%0.3e,ion mean temp (K)=,%0.3e",
ion_number, ion_time_of_flight,
ke2_ion,
ke_averages[ion_number], T_ion))
end
end
trace_count = (trace_count + 1) % _trace_skip
end
last_collision_times[ion_number] = ion_time_of_flight
end
if _mark_collisions ~= 0 then
mark() -- draw dot at collision point
end
end
-- SIMION terminate segment. Called on particle
termination.
function segment.terminate()
-- Note: At equilibrium, the ion and gas KE become roughly equal.
if _trace_level >= 1 then
    -- ion temperature
    local T_ion = ke_averages[ion_number] / eV_J / (1.5 * k)
    print(string.format(
        "n=%d, TOF=%0.3g, ion mean KE (eV)=,%0.3e, ion mean temp (K)=,%0.3e",
        ion_number, ion_time_of_flight, ke_averages[ion_number], T_ion))
end
end
--[[commented out (unused)
function segment.efield_adjust()
    -- V(x,y,z) = x*x + y*y + z*z = r*r
    -- E(x,y,z) = -(2*x, 2*y, 2*z)
    r_max = 100 -- radius
    V_max = 10 -- voltage at r_max
    a = 2 * V_max / (r_max * r_max)
    ion_d voltsx_g u = ion_px_g u * a
    ion_dvoltsy_gu = ion_py_gu * a
    ion_dvoltsz_gu = ion_pz_gu * a
end
]]}
APPENDIX B: Glossary of commonly used terms and abbreviations

The following terms and abbreviations are used throughout the dissertation and are defined here.

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank contamination</td>
<td>Blank signal dominated by analyte contamination – little or no signal from overlap ion</td>
</tr>
<tr>
<td>limited</td>
<td></td>
</tr>
<tr>
<td>Counting statistics</td>
<td>Poisson counting statistics</td>
</tr>
<tr>
<td>cps</td>
<td>Counts per second</td>
</tr>
<tr>
<td>DRC</td>
<td>Dynamic Reaction Cell</td>
</tr>
<tr>
<td>ICP</td>
<td>Inductively coupled plasma</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Inductively coupled plasma mass spectrometer</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Inductively coupled plasma optical emission spectrometer</td>
</tr>
<tr>
<td>ICP-q-MS</td>
<td>Inductively coupled plasma quadrupole mass spectrometer</td>
</tr>
<tr>
<td>ICP-SF-MS</td>
<td>Inductively coupled plasma sector field mass spectrometer</td>
</tr>
<tr>
<td>Overlap/Interference</td>
<td>Ion that is less than 1 amu from analyte ion</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>Term</td>
<td>Definition</td>
</tr>
<tr>
<td>------</td>
<td>------------</td>
</tr>
<tr>
<td>BEC</td>
<td>Blank equivalent concentration</td>
</tr>
<tr>
<td>%CV</td>
<td>Coefficient of variance</td>
</tr>
<tr>
<td>LOD</td>
<td>Limit of detection, assuming noise from Poisson counting statistics only</td>
</tr>
<tr>
<td>%RSD</td>
<td>Per cent relative standard deviation</td>
</tr>
</tbody>
</table>