Application Note: 10068

Elimination of Neutral Noise from a GC/MS Quadrupole Mass Spectrometer

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Key Words

- Mass Spectrometer
- Single Quadrupole
- Reduced Noise
- GC-MS

Overview

Purpose: Confirm background noise is due to helium. Identify methods to reduce and eliminate this noise and improve signal-to-noise ratio.
Methods: Ion source parameters such as electron energy and lens voltages were varied. Instruments were constructed with on-axis and off-axis ion sources to study the diversion of excited neutrals.
Results: Reducing lens potentials reduced neutral noise by 95% in the on-axis instrument. However, ion intensity was also reduced. The off-axis ion source reduced neutral noise by 99.98% (6,000x) with no change in ion intensity.

Introduction

An EI source creates a large flux of helium ions and energetic neutrals. The high ionization energy of helium (24.6 eV[1]) means excited helium neutrals can ionize other molecules and create secondary particles from collisions with surfaces. These secondary particles can include electrons, ions from the surface, sputtered ions from surface contamination, and photons.[2,3,4] Non-mass-selected noise results when these secondary charged particles reach the detector. Noise caused by excited helium neutrals, known as neutral noise, has been well documented.[5,6] Although an off-axis dynode/electron multiplier detector reduces the noise, it is far from eliminated. Currently, baseline subtraction is used to improve the signal-to-noise ratio by subtracting out the noise. But even so, this steady background of noise precludes the ability to detect a single mass analyzed ion; therefore, low-level detection is compromised and dynamic range is reduced. In this work, we compare non-mass-selected noise with on-axis and off-axis ion sources.[7]

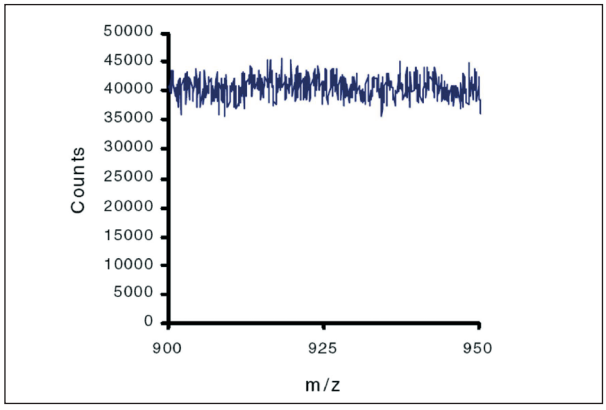

FIGURE 1: Non-mass-selected noise from on-axis instrument. This high baseline is comprised of ~124,000 ions reaching the detector per second.

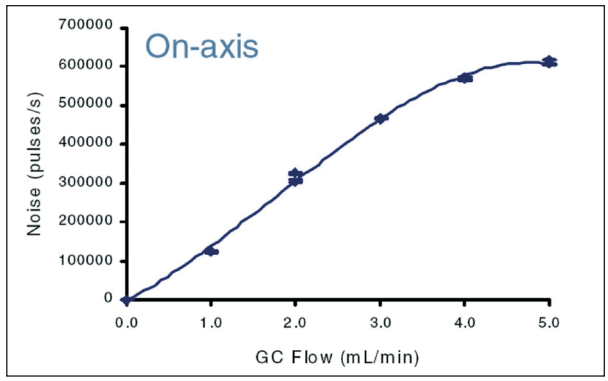

FIGURE 2:. Effect of helium flow rate into ion source. When the helium flow was turned off, the noise dropped to the same low level as when the filament was off (1 pulse/min).

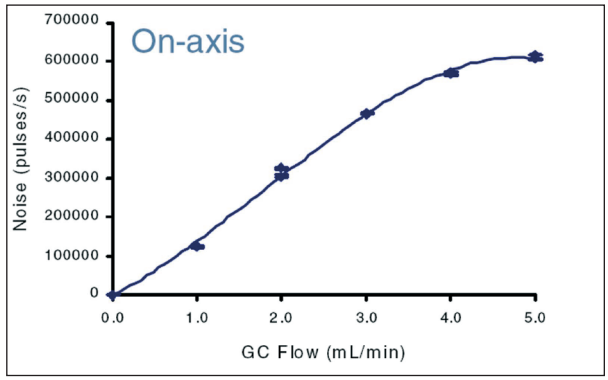

FIGURE 3: Effect of electron energy. The noise dropped dramatically as the electron energy was reduced below the ionization energy of helium. This is further evidence helium causes the noise.

Methods

Noise measurements were performed in EI with the filament set to 70 eV and 250 µA emission current. A helium flow of 1.0 mL/min into the ion source was used unless otherwise noted. The electron multiplier voltage was adjusted so that the combined gain of the dynode and multiplier was 3 x 10^5.

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Two prototype dual-stage quadrupole instruments containing the same ion source, lenses, quadrupole mass filter (Q1), and detector were compared. (Figure 7) The orientation of the ion source with respect to the mass filter and detector differed by the geometry of the RF-only quadrupole (Q0) in each instrument. The on-axis instrument used a straight Q0 to transmit ions into Q1. The off-axis instrument used a Q0 with an 11.3° bend that prevented neutrals from reaching halfway down Q1. A shield was placed around the detector on each instrument to form a physical barrier to charged particles originating outside the central ion beam.

Results

To measure non-mass-selected noise, you must first eliminate other sources of noise. To eliminate chemical noise, the quadrupole was scanned from m/z 900 to 950 in 1 s. The resolution was adjusted so that no ions should pass through the quadrupole. With the multiplier and dynode on, only 1 pulse/min of noise was measured. This includes spontaneous emission from the multiplier (dark current), stray particles, and spontaneous emission from the -10 kV dynode. Because the detector is so quiet, we can easily detect single ions striking the dynode. Therefore, the noise measurements are presented in terms of the number of pulses per second (ions per second) reaching the detector.

With the filament on, the noise jumped to ~124,000±2000 pulses/s (Figure 1). This noise is assumed to be non-mass-selected noise. To determine whether this noise was caused by helium, both the helium flow rate into the ion source (Figure 2) and the electron energy (Figure 3) were varied. When the helium flow from the GC was turned off, the noise dropped to the same level as when the filament was off (1 pulse/min).

Once we knew the noise was caused by helium, we set out to find ways of reducing it. Several alternate detector geometries and lens designs were tried (data not shown). However, none of them reduced the noise preferentially over ion current. When the excited helium neutrals strike a surface, they create secondary particles. If these particles are formed close to the detector, they can be detected. In the on-axis system, many of these excited helium neutrals strike the exit lens of Q1. The field from the -10 kV dynode extends through this aperture and can draw secondary charged particles to the dynode. The best solutions seemed to be to reduce the number of high energy helium neutrals that are formed, or prevent them from striking surfaces near the detector.

Normally, the three ion source lenses are held at -20, -100, -20 V. We discovered that lowering lens 2 from -100 to -10 V reduced noise by 95% (Figure 4a). On the other hand, ion intensity was only reduced about 68% (Figure 4b) so a 7x improvement in signal-to-noise ratio was realized. We believe that at least with this ion source, many of the excited helium neutrals are formed in the lenses rather than the ion source as one would think. We know that many helium ions are formed in the ion source. These ions travel down the lenses where they can collide with helium neutrals. When ions are accelerated to 100 eV in lens 2, these collisions can form excited helium neutrals (and ions). Reducing the kinetic energy of ions in the lenses to <40 eV, causes far fewer excited helium neutrals to be formed in the lenses. This hypothesis is also supported by the electron energy data in Figure 3. When the electron energy is reduced below the ionization energy of helium, the noise disappears indicating that helium ions play a role.

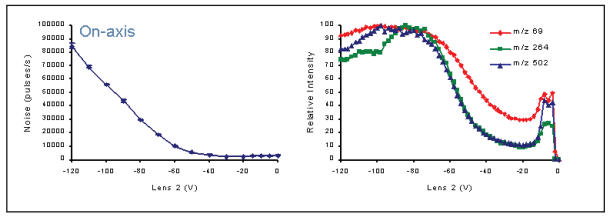

FIGURE 4: Effect of lens 2 voltage on non-mass-selected noise and ion intensity. Reducing the voltage on lens 2 from -100 V to -10 V reduced noise by 95% while ion intensity only dropped by 68%. This results in a signal-to-noise ratio improvement of 7x.

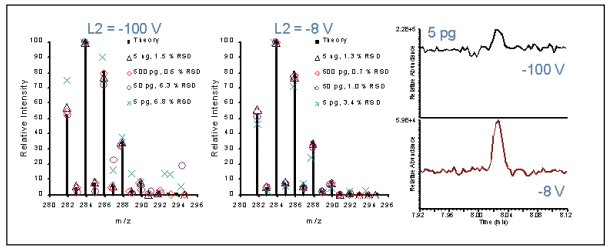

FIGURE 5: Isotope ratios and chromatograms for hexachlorobenzene on on-axis instrument. Spectra were averaged and background subtracted across the chromatographic peak. The reported RSD's represent the difference for all isotopes from the theoretical abundance. Neutral noise caused by high (-100 V) lens 2 caused poor precision and loss of some isotopes at lower sample amounts. Lowering lens 2 improved isotopic accuracy at low sample amounts. TIC chromatograms for each lens setting are shown for 5 pg injections. Neutral noise dominates the lens 2 = -100 V trace.

Another mechanism may involve helium ions colliding at high energy into the surface of the lenses. Photons formed could find their way to a surface near the detector where secondary charged particles that are formed cause noise. However, this was not investigated.

Although reducing the lens voltages significantly reduced the non-mass-selected noise, isotope ratios were still not accurate at low analyte concentrations (Figure 5). Alternatively, we studied an off-axis ion optics design that would present a physical barrier to neutrals.[7] The goal was a bend that caused all neutrals to strike a surface before reaching the midpoint of the quadrupole mass filter (Q1). By doing this, the secondary charged particles (like electrons and ions) that are formed can be eliminated by Q1 before reaching the detector.

To determine the minimum bend required, SIMION 7.0 was used. Instead of simulating ions, particles with zero charge were simulated. Concentric circles 0 to 4.9 mm from the center of the ion volume in 0.1 mm increments were defined (the ion volume has an inner diameter of 9.8 mm). On these circles, neutrals were started in 10° increments. At each of these points, a neutral particle was flown with every initial azimuth and elevation in a hemisphere (in 1° increments). The trajectories of 117,288,000 neutrals were simulated (Figure 6).

Results from the off-axis instrument are shown in Figure 8. Noise was reduced by ~6,000x compared to the on-axis instrument (Figure 2). Lowering lens 2 further reduced this noise (Figure 9), although to a lesser extent than with the on-axis instrument (Figure 4a). Figure 10 summarizes the results from the on-axis and off-axis instruments. Overall, the noise was reduced to ~2 pulses/sec. The small amount of neutral noise that is left most likely results from neutrals that bounce off of a surface and are therefore able to negotiate the bend. Increasing the bend angle or the distance between the bend and the detector should further reduce the noise. Other alternative geometries for Q0 were considered.

With the on-axis instrument, non-mass-selected noise limited detectivity. The off-axis design practically eliminates this noise. This makes isotope ratios more accurate and more precise at low analyte concentrations (compare Figure 11 to 5). Interestingly, hexachlorobenzene (HCB) does not show an improvement in the off-axis instrument when lens 2 is lowered like we saw with the on-axis instrument (Figure 5). This is because HCB is chemical noise limited at 5 pg from septum and column bleed at m/z 281-283. Octafluoronaphthalene on the other hand has lower chemical noise. Here we are able to detect 100 fg with 5 orders of linear dynamic range (Figure 12). Again though, chemical noise limits detectivity.

Reducing chemical noise, such as septum bleed, column bleed, and matrix will allow even lower limits of detection. When reducing noise is impractical, selective ionization modes like negative CI can be used to improve detection limits.

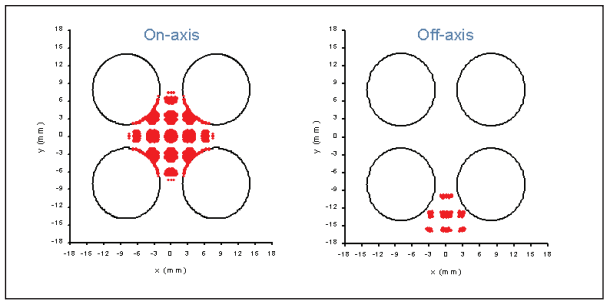

FIGURE 6: Cross-section halfway down quadrupole mass filter showing the position of neutral particles that originated from the ion source. The clusters result because ions were flown from discrete starting points in the ion source. In the off-axis instrument, only 2 ppm of neutrals even reach halfway down the quadrupole. This is 18x lower than the on-axis instrument. All of these are outside the quadrupole mass filter since they pass between the bottom rods. Therefore, they should not create secondary particles that can reach the detector.

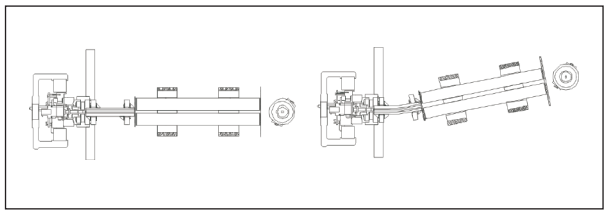

FIGURE 7: Cross-section of the on-axis and off-axis instruments. Q0 in the off-axis instrument has an 11.3° bend to prevent neutrals from reaching the detector.

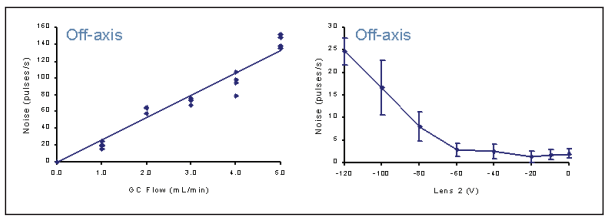

FIGURE 8: Effect of helium flow rate into ion source. With the off-axis instrument, the noise is ~6,000x lower than the on-axis instrument (Figure 2).

FIGURE 9: Effect of lens 2 voltage. Even with the off-axis instrument, reducing the voltage on lens 2 from -100 V to -10 V reduced noise by ~10x.

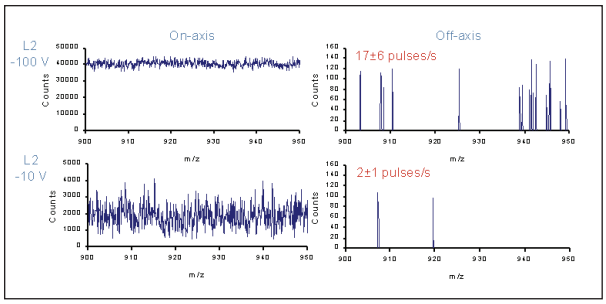

FIGURE 10: Reduction in non-mass-selected noise with off-axis instrument and lens voltages.

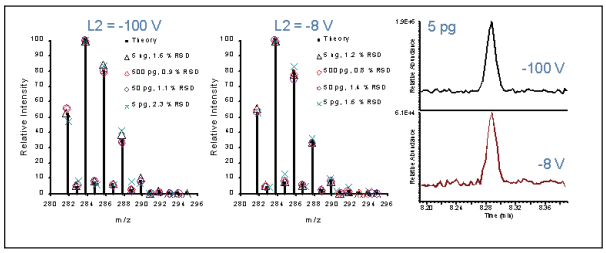

FIGURE 11: Isotope ratios and chromatograms for hexachlorobenzene on off-axis instrument. Isotopic precision and accuracy are improved. Noise is dramatically reduced compared to the on-axis instrument in the lens 2 = -100 V trace (see Figure 5). Ion intensity is not lost with the addition of the curved Q0. Signal-to-noise ratio did not improve with lower lens 2 because the noise is predominately chemical noise at m/z 281-283 from the septum and column. Analyses with lower chemical noise (like negative CI) would benefit from the dramatic reduction in non-mass-selected noise.

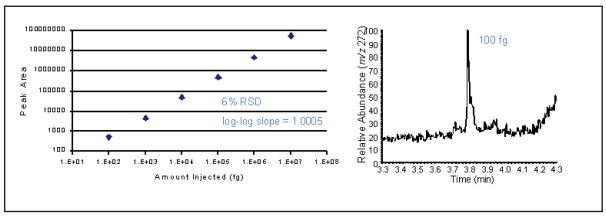

FIGURE 12: EI-SIM (1 amu, 200 ms dwell) of octafluoronaphthalene showing linear dynamic range of 5 orders of magnitude for off-axis instrument.

Conclusions

Non-mass-selected noise from excited helium neutrals limited detectivity and distorted isotope ratios in the instrument with the on-axis source.

Lowering the voltage on the ion source lenses to less than about 40 V reduced noise by 95% and ion intensity by 68%. This led to a signal-to-noise ratio improvement of 7x.

Using a curved RF-only quadrupole ion guide (Q0) before the mass filter reduced noise by 99.98% (6,000x).

Combining both of these techniques reduced noise to ~2 pulses/s. This improved low level detection and increased dynamic range. Now, chemical noise limits detectivity.

References & Acknowledgements

1. Lisa, S.G.; Bartmess, J.E.; Liebman, J.F.; Holmes, J.L.; Levin, R.D.; Mallard, W.G. J. Phys. Chem. Refer. Data 17 (1988) Supplement No. 1.

2. Kaminsky, M. ed. Atomic and Ionic Impact Phenomena on Metal Surfaces. Springer-Verlag, New York (1965) Chapter 14.

3. Beuhler, R.J.; Friedman, L. Int. J. Mass Spec. and Ion Proc. 23 (1977) 81.

4. Wang, G.H.; Aberth, W.; Falick, A.M. Int. J. Mass Spec. and Ion Proc. 69 (1986) 233.

5. Dawson, P.H. ed. Quadrupole Mass Spectrometry and Its Applications. Elsevier, Amsterdam (1976) p. 34-35.

6. Syka, J.E.P. European Patent Application.0 237 259 A2 (1987).

7. Brubaker, W.M. U.S. Patent. 3,410,997 (1968).

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