The Implications of Detector Performance in GC/MS and LC/MS Analysis – Detectors Make the Difference!

Introduction
Detector performance is critical to the success of any given chemical analysis. Two criteria by which to judge detectors are 1) linear range, and 2) lifetime, which represent instantaneous performance and long-term stability, respectively.

Linear range is determined by two competing effects, saturation and superlinearity. As analyte concentration increases, a saturation point is reached where the actual signal is lower than the expected signal. This point occurs at a concentration which leads to a response that appears larger than expected (Fig. 1). A long lifetime provides constant signal output, minimizing the need to frequently retune the instrument. Several detector types are compared to showcase these effects.

Experimental
GC/MS experiments were performed on an Agilent 5977B GC/MSD (Fig. 3). LC/MS experiments were performed on an Agilent 6410A LC/TOF (Fig. 4). Linearity results (GC/MSD only) were obtained by monitoring the ratios of PTFBA calibrant ions and their isotopes as the detector gain was increased. Because the true isotopic ratio is known, any deviation from this value arises from either saturation or superlinearity.

For GC/MS-D detector tests, Argon was introduced into the system through a mass flow controller. Data was collected in SIM mode, on that an effective duty cycle could be created by observing an ion of interest alongside a “dummy” mass which shows no signal. The signal was monitored and the detector gain was adjusted as necessary to maintain an output above a desired threshold. LC/MS lifetime tests were performed by continual introduction of Argon tune mix via an isocratic pump.

Results and Discussion – Linearity
GC/MS Linearity Results – Agilent TAD 1 vs. Agilent TAD 2
Figure 5 shows the compiled results of 14 different compounds using the Agilent TAD 1 detector. The relative response factor (RRF) should be flat across the linear dynamic range until the saturation point is reached. However, this detector is showing a compound independent superlinear response, beginning at fairly low concentration/sem.

We claim that the superlinear response is due to the voltage drop across the detector changing as a function of output current. As the output current increases, so does the local voltage. This in turn leads to an undesired increase in gain and manifests as superlinearity.

Applying a bias voltage to the anode end of the Agilent TAD 2 detector clamps the back end to a fixed voltage, thereby mitigating the superlinear effect. This is highlighted in Figure 6, which shows a superlinear response from the TAD 1 detector, while the TAD 2 detector shows only saturation. These tests, effects, saturation and superlinearity, were always at play in the TAD 1 detector. After eliminating superlinearity, only saturation diminishes at high output currents.

GC/MS Linearity Results – Agilent TAD 1 vs. OEM
The Agilent TAD 1 detector was compared to a third-party OEM detector (Fig. 7). The linear range was limited to 1000 mV due to limitations of the system. Compared to the Agilent TAD 1 detector, the OEM detector, while more linear, still shows a small deviation from the linear trend at higher concentrations.

Since the detector has been burned in, signal is stable for extended periods of time. Over a period of 4.5 days, the OEM detector showed no deviation from the 50% threshold, while the Agilent TAD 1 detector showed 10% deviation (Fig. 8).

Conclusion
Linearity
• Superlinearity can be eliminated by applying a bias voltage to the anode end of the detector.
• Linear dynamic range is limited by saturation effects.
• Agilent detectors show greater linear dynamic range than third-party OEM detectors.

LC/MS Lifetime Results
The full detector lifetime can be extrapolated based on the CEM applied voltage and the output charge at a given concentration (Fig. 9). Beginning with a charge of >20 Coulombs, the voltage was increased and the experiment was repeated. After several measurements, an extrapolated lifetime of ~200 Coulombs was calculated.

Figure 6. PTFBA mass 220/221 relative isotope ratio.

Figure 7. PTFBA mass 220/221 relative isotope ratio.

Figure 8. GC/MS detector burn-in period.

Figure 9. LC/MS signal stability & output charge over 4.5 days.

Figure 10. LC/MS burn-in period showing a signal drop of over 10% over 4.5 days of constant sample introduction (Fig. 10). During this time, well over half a Coulomb of charge was output.