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

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Introduction

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

Linear dynamic 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 linear response. Superlinearity is an observed effect which leads to a response that appears larger than expected (Fig. 1). A long lifetime provides consistent signal output, minimizing the need to frequently retune the instrument. Several detector types are compared to showcase these effects.

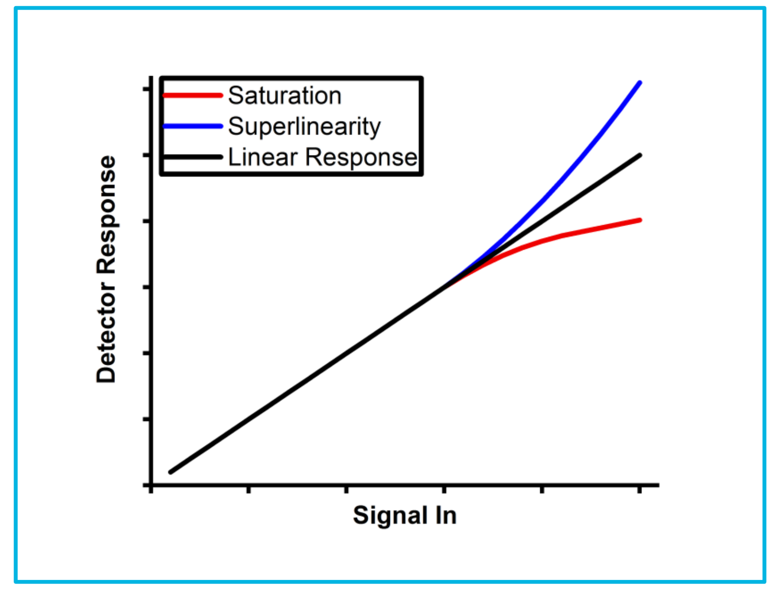

Figure 1. Saturation vs. Superlinearity.

Experimental

All detectors tested were of the channel electron multiplier (CEM) style (Fig. 2). Three types of detectors were compared for GC/MS linearity, the Agilent Triple Axis Detector 1 (TAD 1; used in the 5975 and the 5977A), Agilent TAD 2 (used in the 5977B), and a third-party OEM detector meant to replace the TAD 1. For lifetime tests, the Agilent TAD 2 was used for GC/MS and the LC/MS CEM detector was used for LC/MS.

Figure 2. Agilent GC/MSD TAD 1 Electron Multiplier.

Experimental

GC/MS experiments were performed on an Agilent 5977B GC/MSD (Fig. 3). LC/MS experiments were performed on an Agilent 6470A LC/TQ (Fig. 4). Linearity results (GC/MS only) were obtained by monitoring the ratios of PFTBA calibrant ions and their ^{13}C 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 lifetime tests, Argon was introduced into the system through a mass flow controller. Data was collected in SIM mode, so 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 Agilent tune mix via an isocratic pump.

Figure 3. 5977B GC/MSD System.

Figure 4. 6470A LC/TQ System.

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/signal.

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 too 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 two effects, saturation and superlinearity, were always at play in the TAD 1 detector. After eliminating superlinearity, only saturation dominates at high output currents.

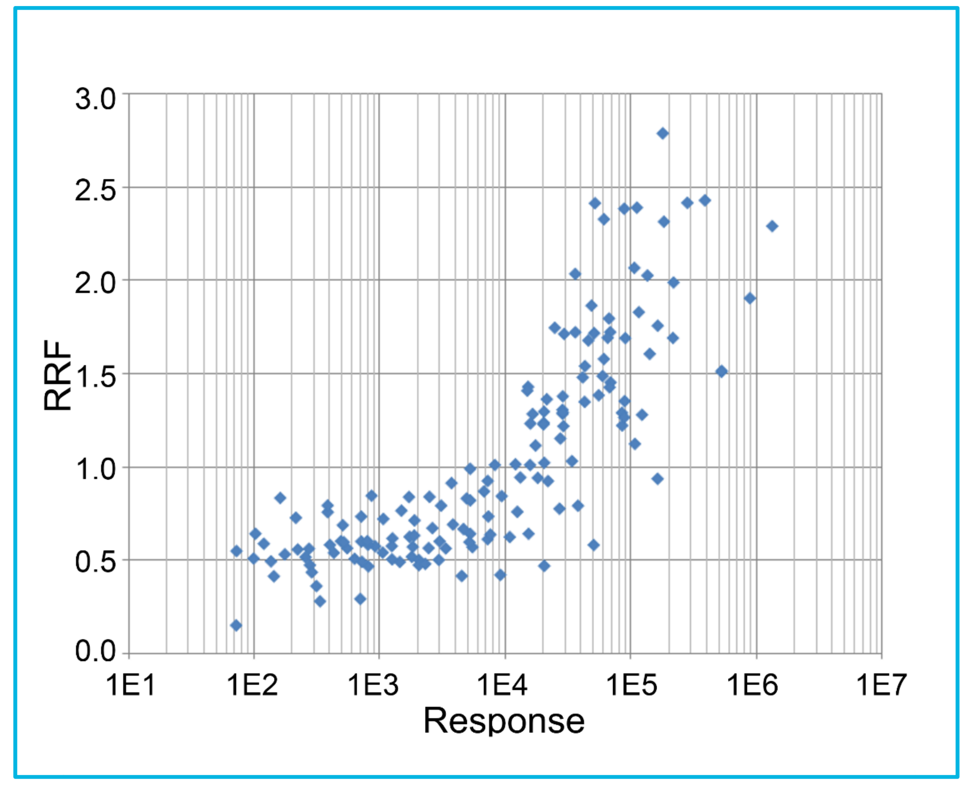

Figure 5. Superlinear response of 14 different compounds.

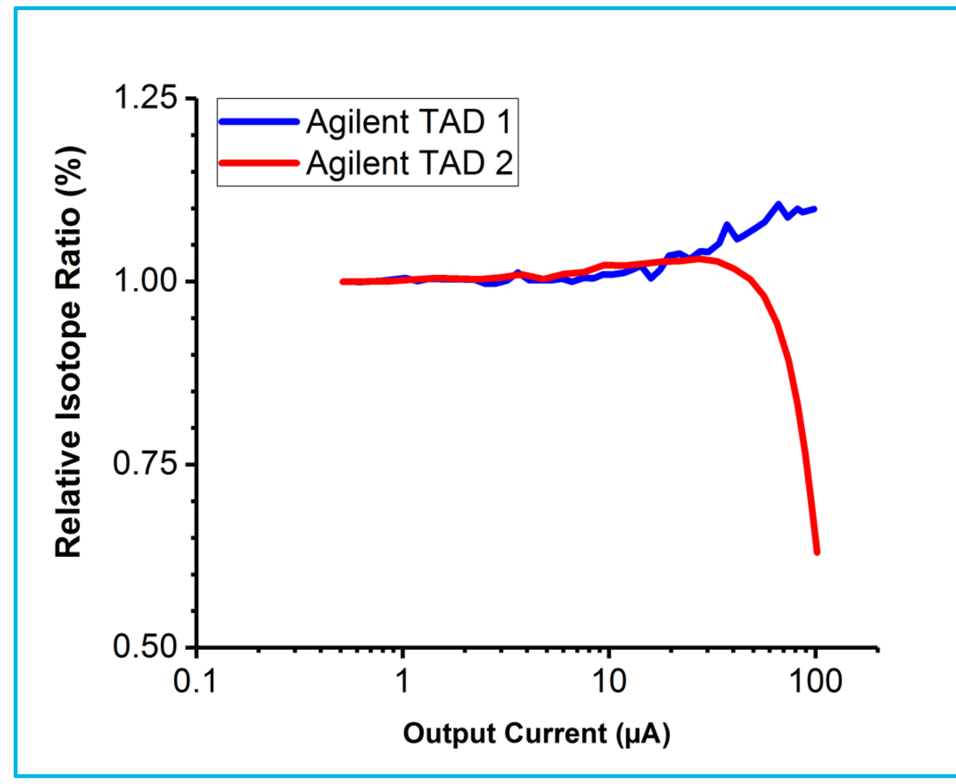

Figure 6. PFTBA mass 502/503 relative isotope ratio.

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 relative isotope ratio of PFTBA mass 219/220 should be unity over the detector's linear dynamic range. Two identical OEM detectors were tested. The first was never linear, showing an isotopic ratio drop from the very beginning, while the second was linear up to ~2-3 µA. The Agilent TAD 1 detector, on the other hand, showed linearity up to ~50 µA with <10% deviation.

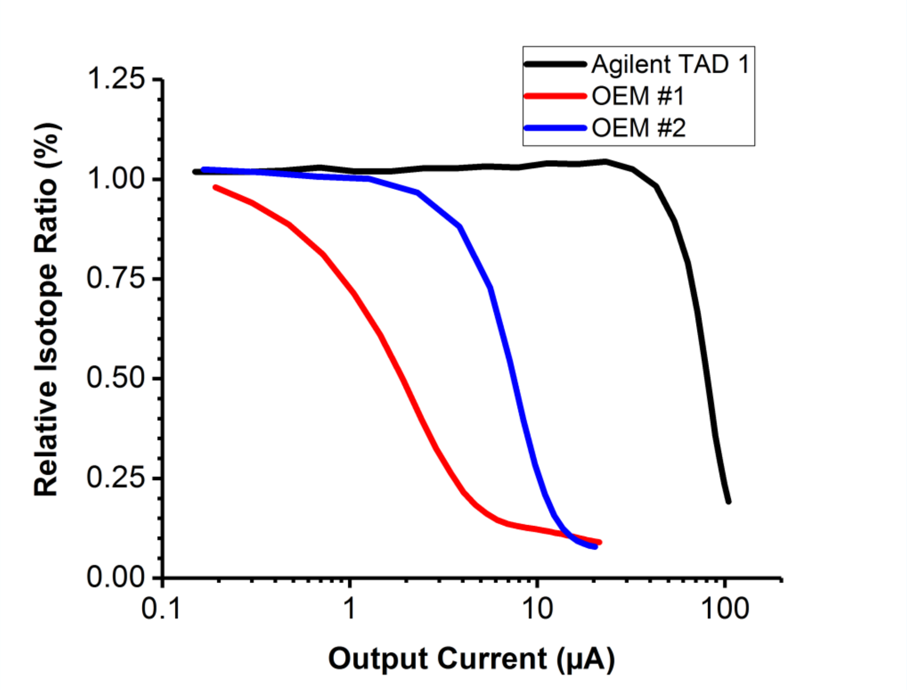

Figure 7. PFTBA mass 219/220 relative isotope ratio.

Results and Discussion – Lifetime

Detector Burn-in

It was observed that CEM detectors require a burn-in time of ~7-10 hours before stable signal can be achieved (Fig. 8). We posit that this is due to surface effects of adsorbed water on the detector which increases the observed gain. As the water is "ion scrubbed" away, the gain drops and signal stabilizes.

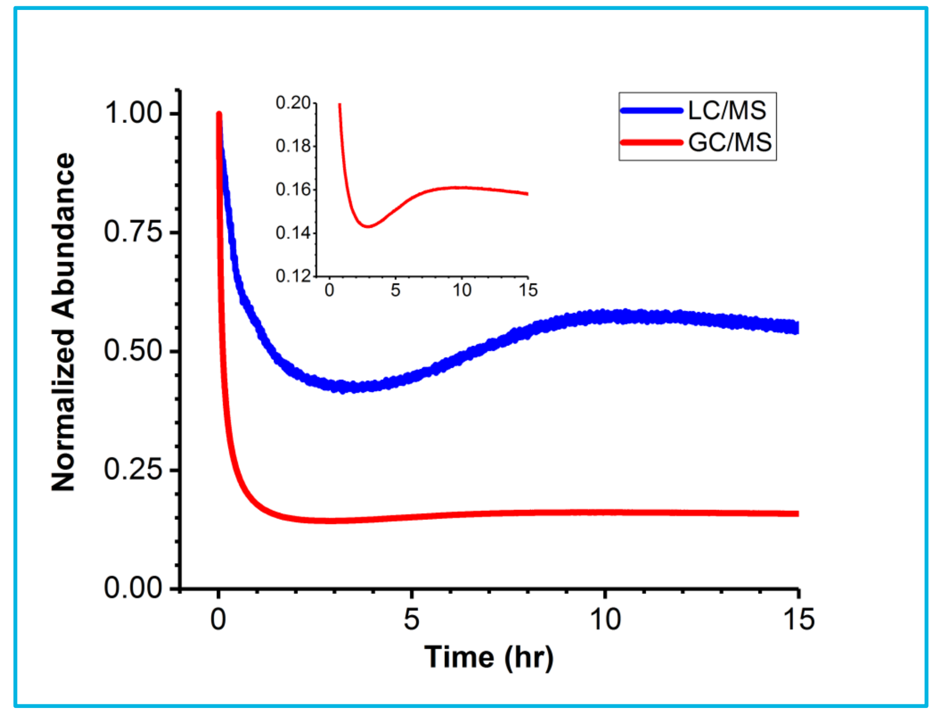

Figure 8. CEM detector burn-in period.

GC/MS Lifetime Results

Once the detector has been burned-in, signal is stable for extended periods of time. Over a period of 4.5 days of constant sample introduction, the signal only dropped by ~3%, while outputting almost an entire Coulomb of charge (Fig. 9).

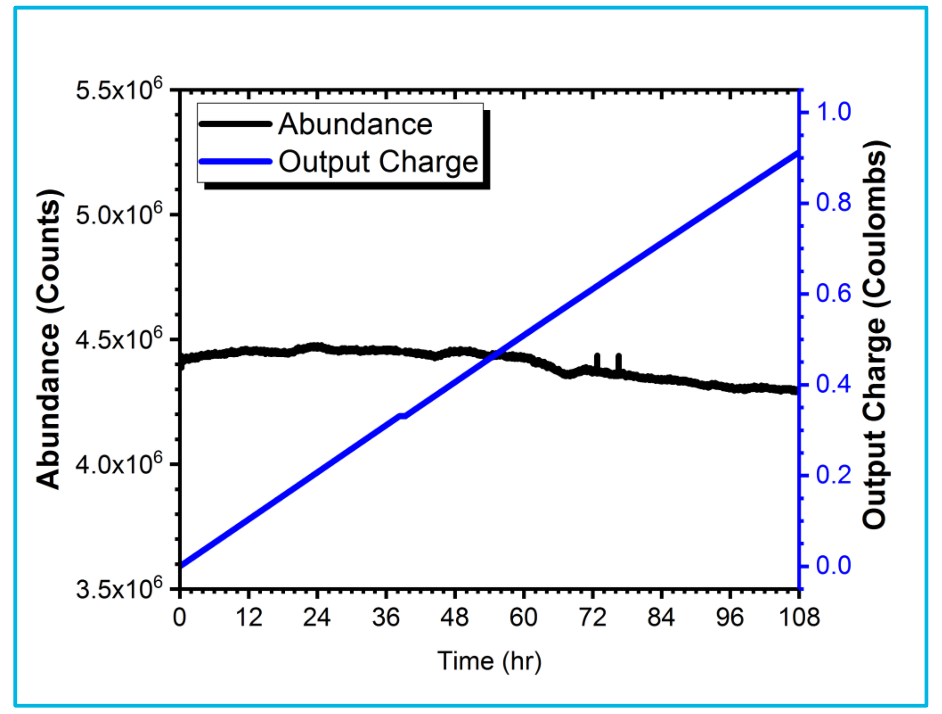

Figure 9. 5977B GC/MSD signal stability & output charge over 4.5 days

LC/MS Lifetime Results

After adequate burn-in was achieved, the LC/MS detector was also very stable, showing a signal drop of only ~8% over 4.5 days of constant sample introduction (Fig. 10). During this time, well over half a Coulomb of charge was output.

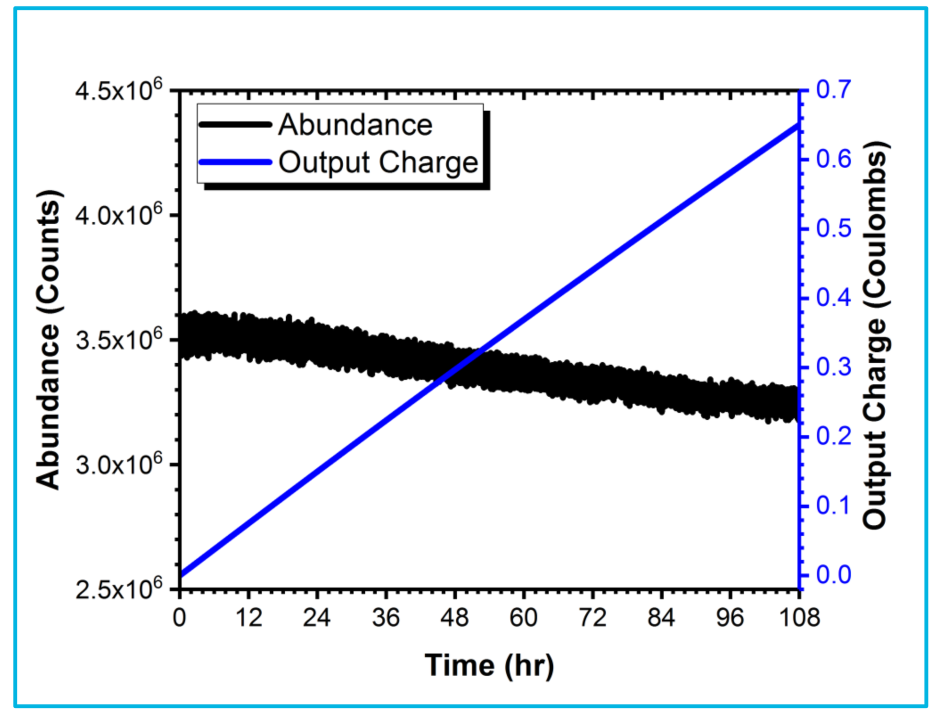

Figure 10. 6470A LC/TQ signal stability & output charge over 4.5 days.

Lifetime Extrapolation

The full detector lifetime can be extrapolated based on the CEM applied voltage and the output charge at a given voltage. When the signal decayed below a pre-determined threshold, the voltage was increased and the experiment was repeated. After several measurements, an extrapolated lifetime of >20 Coulombs was calculated.

Conclusions

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 aftermarket third party OEM detectors.

Lifetime

- Burn-in is required in order to obtain stable signal.
- Signal is stable for extended periods of time, and extrapolated lifetime charge output is >20 Coulombs.