

Supporting Information

Quantification of Isomer-Resolved Iodide CIMS Sensitivity and Uncertainty Using a Voltage Scanning Approach

Chenyang Bi¹, Jordan E. Krechmer², Graham O. Frazier¹, Wen Xu², Andrew T. Lambe², Megan S. Claflin², Brian M. Lerner², John T. Jayne², Douglas R. Worsnop², Manjula R. Canagaratna², Gabriel Isaacman-VanWertz¹

¹Department of Civil and Environmental Engineering, Virginia Tech, Blacksburg, Virginia, 24060, USA

²Aerodyne Research Inc, Billerica, Massachusetts, 01821, USA

Correspondence to: Gabriel Isaacman-VanWertz (ivw@vt.edu)

Unit conversion from ions/mole/million reagent ions to cps/ppt/million reagent ions

We convert the sensitivity measured by the TAG-CIMS/FID to a direct-air-sampling CIMS operating at an assumed condition (2 slpm sampling flow rate; 2 slpm reagent ion flow rate; and 100 mbar ion-molecule reactor (IMR) pressure; and 293K ambient temperature) to help understand the data presented.

The typical unit for CIMS sensitivity, S^{typ} , is ions per second per million reagent ions per ppt, or cps/ppt/million reagent ions, which can be written as:

$$S^{typ} = \frac{i_X}{i_P} \times \frac{1}{t} \times \frac{n_{M,samp}}{10^{12} n_{X,samp}} \quad (1)$$

where i_X/i_P is the normalized ion count, i.e., number of ions from the analyte X ratioed to the number of ions of primary reagent ions (in millions), which is usually reported per unit time, t (typically 1 second). The term on the rate is the number of moles of sample flow, $n_{M,samp}$, per trillion moles X in the sample, $n_{X,samp}$, which is equivalent to ppt⁻¹. We can multiple both sides of the equation by volumetric flow rate of the sample, Q_{samp} , which can be written as a volume, V_{samp} , of flow being sampled per unit time (units of standard cm³/s):

$$\frac{1}{Q_{samp}} S^{typ} = \frac{i_X}{i_P} \times \frac{1}{t} \times \frac{n_{M,samp}}{10^{12} n_{X,samp}} \times \frac{t}{V_{samp}} \quad (2)$$

This can be re-arranged and simplified as:

$$\frac{10^{12}}{Q_{samp}} S^{typ} = \frac{i_X}{i_P} \times \frac{1}{n_{X,samp}} \times \frac{n_{M,samp}}{V_{samp}} \quad (3)$$

The right-most term is the molar density of sample flow, which can be adjusted by Avogadro's number, A_V , to yield number density, $[M]_{samp}$, (units of molecules/cm³):

$$\frac{10^{12}}{Q_{samp}} S^{typ} = \frac{i_X}{i_P} \times \frac{1}{n_{X,samp}} \times \frac{[M]_{samp}}{A_V} \quad (4)$$

Re-arranged, we see that:

$$\frac{10^{12} A_V}{Q_{samp} [M]_{samp}} S^{typ} = \frac{i_X}{i_P} \quad (5)$$

The right-hand of this equation is normalized ions per moles, which is a unit of sensitivity conducive to GC analyses, S^{GC} . These two sensitivity units can thus be converted as:

$$S^{typ} = \frac{Q_{samp} [M]_{samp}}{10^{12} A_V} S^{GC} \quad (6)$$

Assuming a typical sample flow of approximately room temperature ambient air ($[M]_{samp} = 2.5 \times 10^{19}$ molec/cm³) and a sample flow, Q_{samp} , of 2 slpm (33.3 cm³/s, standard), the conversion is $\frac{S^{typ}}{S^{GC}} = 1.4 \times 10^{-15}$. This is the conversion factor used to relate the left and right axis of Figure 3-5 though it is dependent on operating conditions.

Calculation of maximum sensitivity

The maximum kinetically limited sensitivity in units of cps/ppt/million reagent ions, S_{kin}^{typ} , was calculated using equation S1-3 described by Isaacman-Vanwertz et al., (2018), adjusted by a factor of 10^6 to provide units of per million reagent ions:

$$S_{kin}^{typ} = \frac{10^6 [M]_{IMR} f k_{coll} t_{IMR}}{10^{12}} \quad (7)$$

Where $[M]_{IMR}$ is the number density in the IMR, calculated as $[M]_{IMR} = 2.5 \times 10^{18}$ molec/cm³ at 100 mbar. The collisional rate, k_{coll} , between the analyte molecule and the reagent ion is assumed to be 1×10^{-9} cm³ molec⁻¹ s⁻¹.

Sensitivity is dependent in part on the fraction, f , of total flow in the IMR consisting of sample, calculated as:

$$f = \frac{Q_{samp}^0}{Q_{samp}^0 + Q_{reag}^0} \quad (8)$$

the ratio of sample flow rate to the total flow rate (i.e., sample + reagent flows) entering the IMR, where ⁰ superscript denotes that both flows are referenced to a standard temperature and pressure. Under these conditions ($Q_{samp}^0 = 0.7$ sccm and $Q_{reag}^0 = 2000$ sccm), $f = 3.50 \times 10^{-4}$.

Collisions occur throughout the residence time in the IMR, t_{IMR} , which can be calculated as the time the total volumetric flow takes to sweep the physical volume of the IMR, V_{IMR} , at the adjusted from standard pressure (P^0) to the operating pressure of the IMR, P_{IMR} :

$$t_{IMR} = \frac{V_{IMR}}{(Q_{samp}^0 + Q_{reag}^0) \frac{P^0}{P_{IMR}}} \quad (9)$$

Because ratios of pressure are proportional to ratios of number density, this equation can be re-written in terms of standard and IMR number density:

$$t_{IMR} = \frac{V_{IMR}}{(Q_{samp}^0 + Q_{reag}^0) \frac{[M]^0}{[M]_{IMR}}} \quad (10)$$

The residence time of molecules in the IMR, t_{IMR} , is calculated as 0.14 s based on a pressure of 100 mbar and a volume of 47 cm³.

The kinetically limited maximum sensitivity can be calculated in units of ions per mole per million reagent ions by combining Eqs. 6 and 7:

$$S_{kin}^{GC} = \frac{10^6 [M]_{IMR} f k_{coll} t_{IMR} A_V}{Q_{samp} [M]_{samp}} \quad (11)$$

Both Q_{samp} and $[M]_{samp}$ are proportional to temperature and pressure, so the denominator of this equation is equivalent to moles/time, $\frac{V_{samp}}{t} \times \frac{n_{M,samp}}{V_{samp}} = \frac{n_{M,samp}}{t}$ (i.e., mass flow rate). This is useful, as it implies that the kinetic sensitivity is independent of the pressure and temperature of the GC effluent, which varies throughout the GC run. For use in this equation, both terms can consequently be adjusted to standard temperature and pressure, Q_{samp}^0 and $[M]^0$:

$$S_{kin}^{GC} = \frac{10^6 [M]_{IMR} f k_{coll} t_{IMR} A_V}{Q_{samp}^0 [M]^0} \quad (12)$$

Substituting Eqs. 8 and 10 into 12, a complete description of kinetically limited maximum sensitivity in GC-conductive units can be obtained:

$$S_{kin}^{GC} = \frac{10^6 ([M]_{IMR})^2 k_{coll} V_{IMR} A_V}{([M]^0)^2 (Q_{samp}^0 + Q_{reag}^0)^2} \quad (13)$$

Using the same proportionality between pressure and number density, this can be simplified as:

$$S_{kin}^{GC} = 10^6 k_{coll} V_{IMR} A_V \left(\frac{P_{IMR}}{P^0} \right)^2 (Q_{samp}^0 + Q_{reag}^0)^{-2} \quad (14)$$

Under GC-CIMS operation, $Q_{samp}^0 = 0.7$ sccm (0.012 cm³/s), $Q_{reag}^0 = 2000$ sccm (33.3 cm³/s), and $P_{IMR} = 100$ mbar, so $S_{kin}^{GC} = 2.5 \times 10^{17}$ ions/mole/million reagent ions. Using the same instrument design, Isaacman-Vanwertz et al., (2018) found

the experimentally observed maximum sensitivity to be a factor of 4 lower than calculated kinetically-limited sensitivity, so we estimate that the maximum sensitivity is within the range from 6.4×10^{16} to 2.5×10^{17} ions/mole/million reagent ions.

These values translate into $S_{kin}^{typ} = 90$ to 350 cps/ppt/million reagent ions using unit conversion described in Eq. 6. However, we note that is higher than actual kinetically-limited sensitivity calculated under typical ambient operating conditions, ($Q_{samp}^0 = 2000$ sccm) because in the GC-CIMS, there is more time for reaction in the IMR due to lower sample flows ($Q_{samp}^0 = 0.7$ sccm). Under typical ambient operating conditions at the IMR pressure used, $Q_{samp}^0 = 2000$ sccm should be used instead in Eq. 14. After unit conversion using Eq. 6, $S_{kin}^{typ} = 88$ cps/ppt/million reagent ions (Eq. 7).

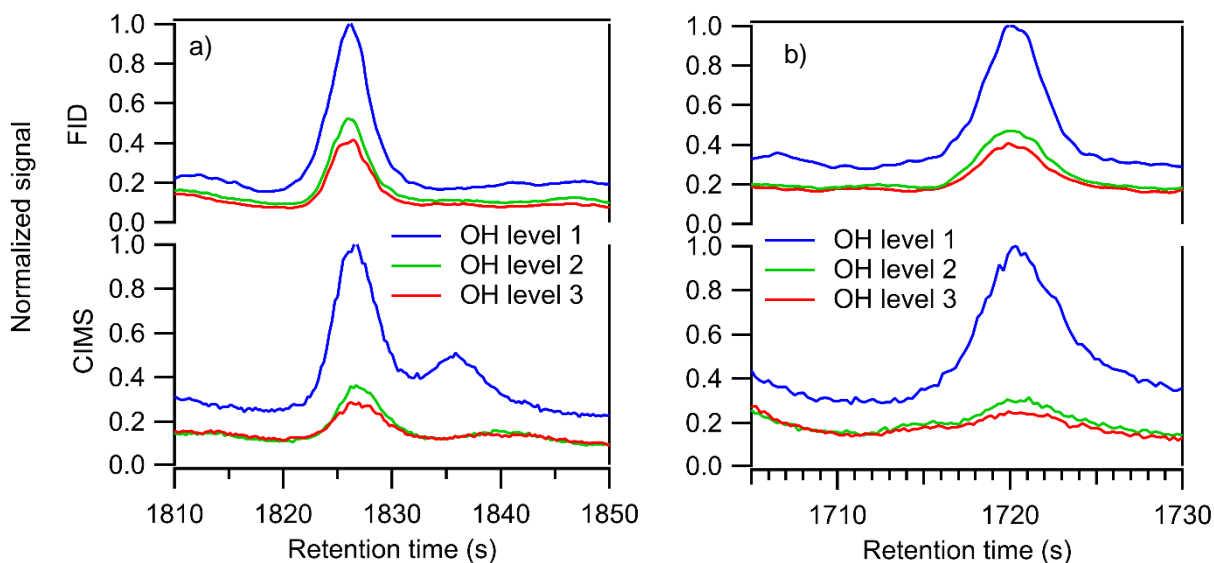


Figure S1. Comparison of CIMS and FID peaks at different OH exposure levels for a) Compound 4 and b) Compound 3.

References

Isaacman-Vanwertz, G., Massoli, P., O'Brien, R., Lim, C., Franklin, J. P., Moss, J. A., Hunter, J. F., Nowak, J. B., Canagaratna, M. R., Miszta, P. K., Arata, C., Roscioli, J. R., Herndon, S. T., Onasch, T. B., Lambe, A. T., Jayne, J. T., Su, L., Knopf, D. A., Goldstein, A. H., Worsnop, D. R. and Kroll, J. H.: Chemical evolution of atmospheric organic carbon over multiple generations of oxidation, *Nat. Chem.*, 10(4), 462–468, doi:10.1038/s41557-018-0002-2, 2018.