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Generalized Kendrick analysis for improved visualization of atmospheric mass spectral data

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S1. Mass difference expansion behavior as a function of R and X

The ability for a given X to separate ions related by certain chemical groups other than R can be calculated by Eq. (S1):

$$\Delta GKA(\Delta m/z, R, X) = \Delta m/z \frac{X}{R} - \text{round}\left(\Delta m/z, \frac{X}{R}\right) \quad (S1)$$

where $\Delta m/z$ is the mass-to-charge difference between the two ions. In this example, we calculate the resolving power between ions spaced ~1 amu apart and related by $+^{14}N - ^{12}C - ^{1}H = 0.995249$ amu. As noted in Fouquet and Sato (2017), this equation relies on anti-aliasing (i.e., wrap around correcting) to be strictly true. Figure S1 shows the separation for REKMD and GKA analysis as a function of X. Note that outside of the range of $\text{round}(\frac{2\times R}{3}) < X \leq \text{round}(2 \times \text{R})$ (the recommended range for REKMD analysis), the change in ΔREKMD(0.995249, ^{16}O, X) is no longer linear with X, whereas it is with ΔGKA(0.995249, ^{16}O, X) .

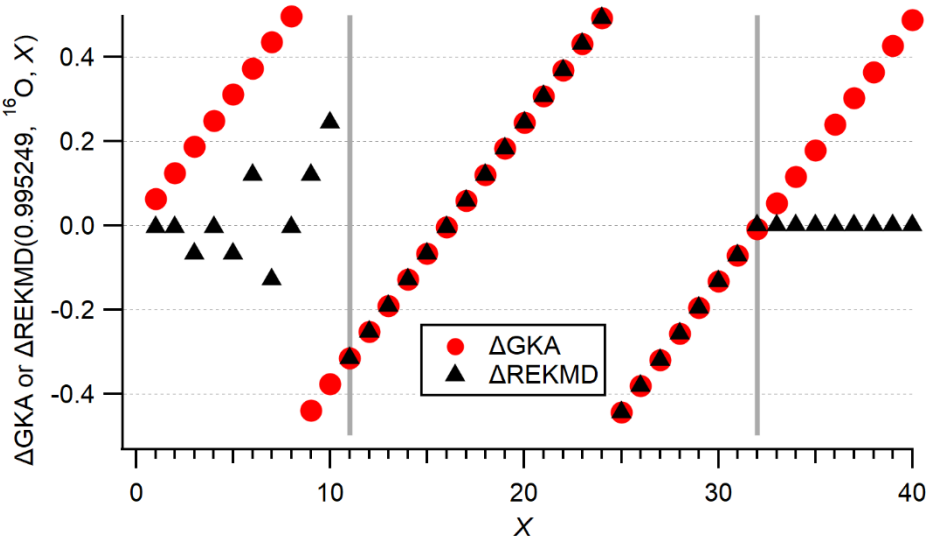

Figure S1 The difference in REKMD (Fouquet and Sato, 2017) (Eq. (3) in main text) and GKA (Eq. (4) in the main text) between ions related by the addition of one nitrogen atom and one less each of carbon and hydrogen for different X using ^{16}O as R. Note the transition from positive to negative values are an artifact from aliasing, though the absolute difference determines the separation between ions. The vertical grey lines indicate the limit of linear expansions with different X in REKMD.

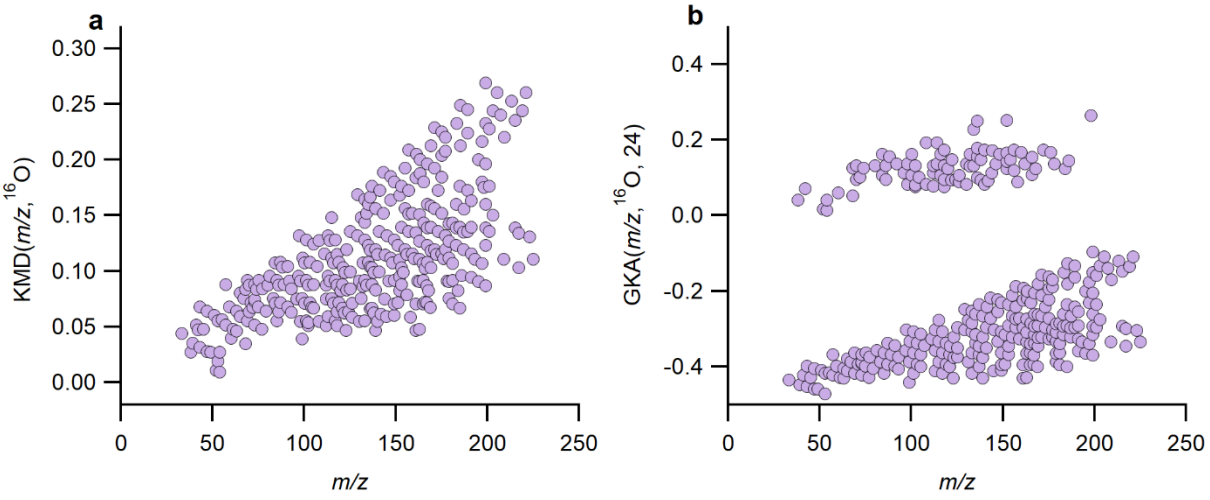

Figure S2 Reproduction of Fig. 1 from the main text with (a) a smaller y-axis range to illustrate the overlapping points do not separate well simply with zooming in and (b) Fig. 1b from the main text for comparison.

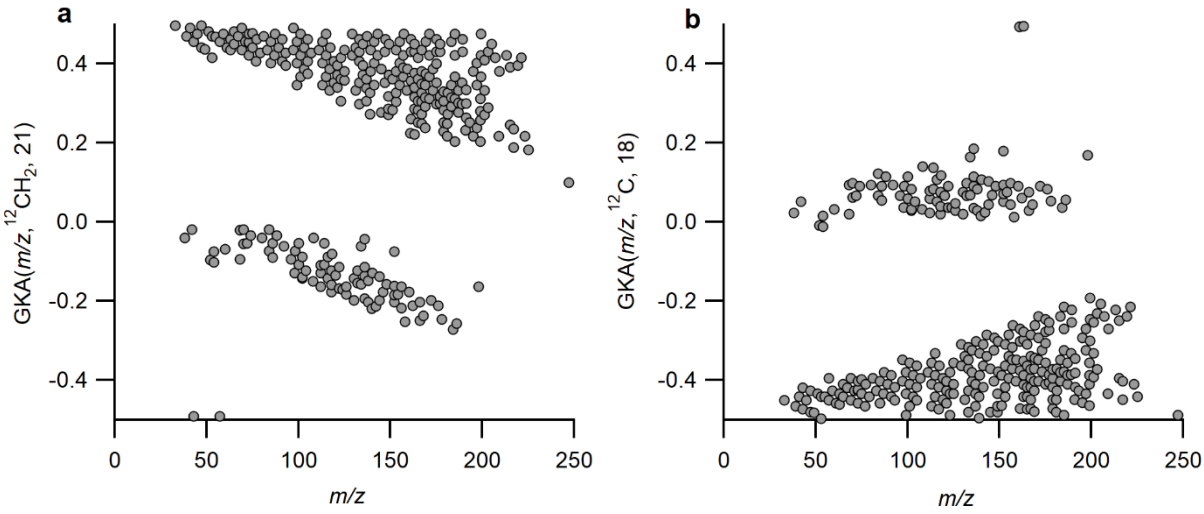

Figure S3 GKA plots with (a) $^{12}CH_2$ and (b) ^{12}C using X that leads to X/R_{IUPAC} of ~3/2 showing that the separation into the same number of groups is consistent even with different bases.

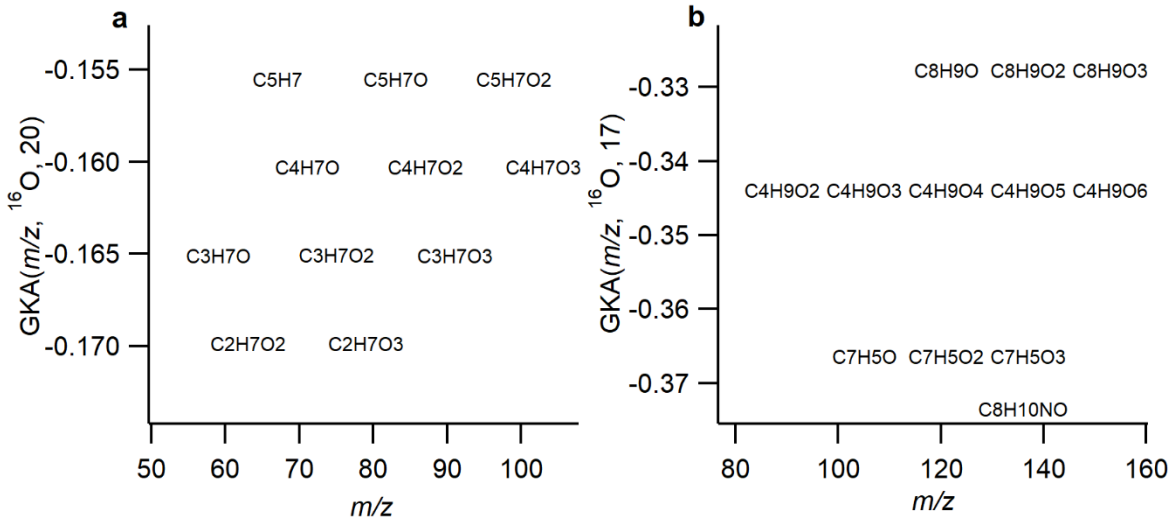

Figure S4 A reproduction of Fig. 3 in the main text, but zoomed into individual lines to show how related chemical formulas are distributed on a horizontal. Each formula has a +1 charge, not shown.

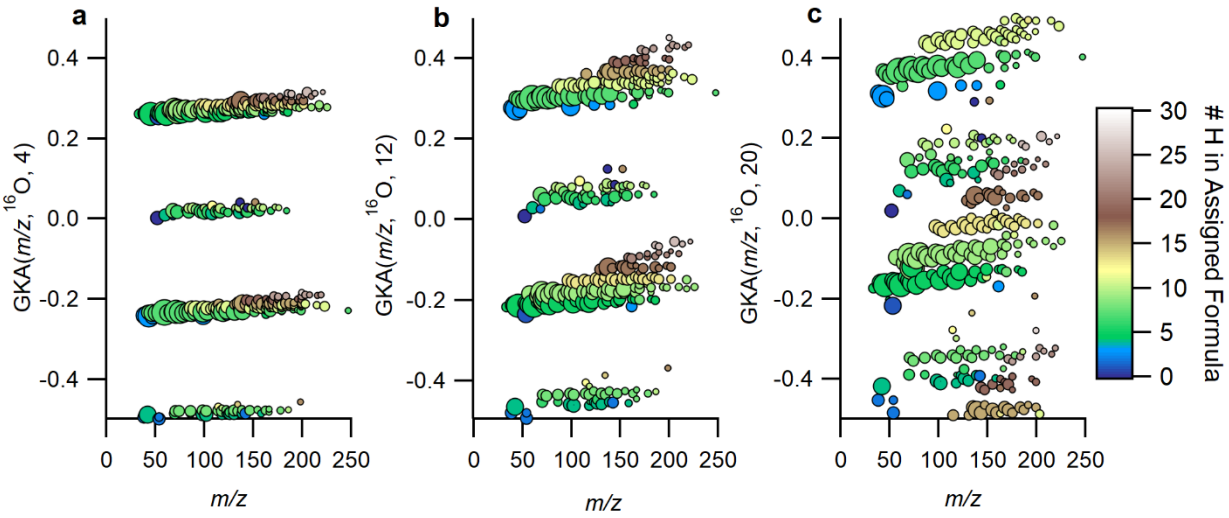

Figure S5 Similar to Fig. 4 in the main text but showing *X* values that lead to denominators of 4 for the approximate reduced fraction. R is ^{16}O in all subplots. Panel (c) illustrates how "aliasing" (0.5 to -0.5 transformation) will impact visualization. Points with the highest numbers of hydrogen atoms that appear in panel (b) with GKA(*m/z*, ^{16}O, 12) values approximately > 0.4 appear in panel (c) at GKA(*m/z*, ^{16}O, 20) values of approximately <-0.3. The points are colored by the number of hydrogens in the assigned formula and sized by the log of the measured intensity.

S2. Further explanation on groupings

Values of *X* leading to grouping by the number of hydrogen atoms are ones that minimize the absolute value of the GKA difference (Eq. (S1)) between ions that maintain the same number of hydrogen atoms. In measurements of atmospheric composition, such ions would be related, for instance, by the addition of

an oxygen atom and the loss of a carbon atom (e.g., $C_9H_{14}OH^+$ and $C_8H_{14}O_2H^+$) and would differ by 3.9942 *m/z*. As shown in Fig. S6, the absolute value of ΔGKA(3.9942, ^{16}O, *X*) is minimum for *X* divisible by 4. However, not all the *X* values fulfilling this criterion separate compounds differing by the number of hydrogen atoms equally well. In particular, $X = 16z$ for integer $z \geq 1$ will not lead to distinct regions of equal number of hydrogen atoms owing to the overlap in GKA (or KMD in the case of $X=16$) space between $C_xH_yO_z^+$ and $C_xH_yO_zN_w^+$ ions. To further refine appropriate *X* values, one should consider selections that minimize the GKA difference in ions differing by $+^{16}O - {}^{12}C$ (3.9942 amu; defined below as $\Delta m/z_1$) while maximizing the gain between ions spaced ~ 1 *m/z* apart ($\Delta m/z_2$). Here we use ions that differ by the addition of a nitrogen atom and loss of a carbon atom and a hydrogen atom ($\Delta m/z_2 = 0.9953$; e.g., $C_6H_{10}O_4H^+$ and $C_5H_9NO_4H^+$) Values of *X* satisfying these criteria will be the minima of the following quantity, termed RANK2 in (Nakamura et al., 2019).

$$RANK2(\Delta m/z_1, \Delta m/z_2, R, X) = \frac{|\Delta GKA(\Delta m/z_1, R, X)| - |\Delta GKA(\Delta m/z_2, R, X)|}{|\Delta GKA(\Delta m/z_1, R, X)| + |\Delta GKA(\Delta m/z_2, R, X)|} \quad (S2)$$

As seen in Fig. S6, values of *X* satisfying this relationship now exclude multiples of 16. The same reasoning can be followed to show that for R_{IUPAC} of ^{12}C, *X* divisible by 3 but not 12 will lead to groupings associated with the number of hydrogen atoms. Although in theory Eq. (S2) can be used to find *X* values that minimize/maximize GKA spacing for other chemical relations as has previously been shown for analysis of polymer samples (Nakamura et al., 2019), such analysis is of limited success for complex mixtures. Analysis of simpler mixtures, such as those encountered in chamber experiments, may benefit from identification of other useful groupings.

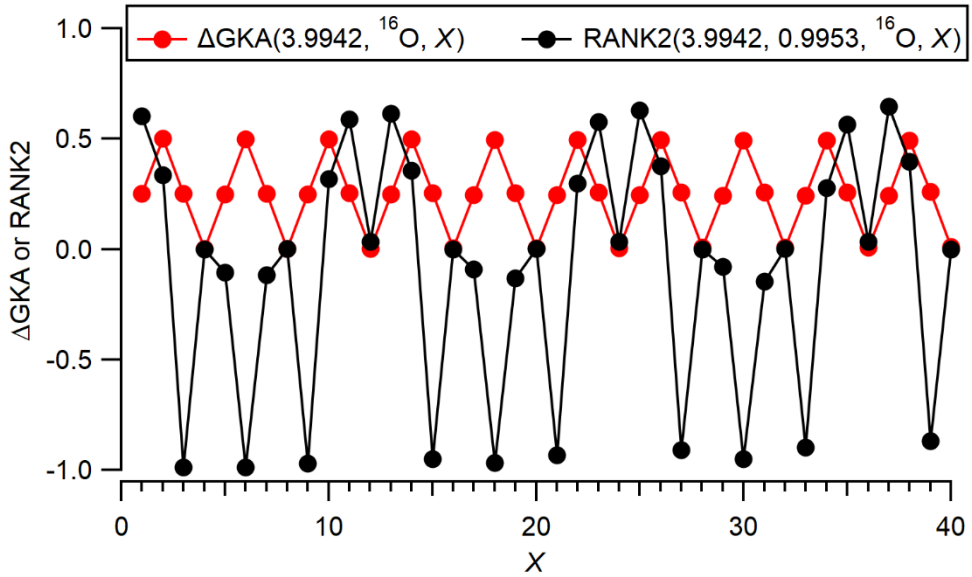

Figure S6 Change in the GKA (red) for ions differing by the addition of an oxygen atom and the loss of a carbon atom ($\Delta m/z_1$ = 3.9942) for different values of *X*. Results of RANK2 (S2; black) equation minimizing the GKA gain between ions differing by the addition of an oxygen atom and the loss of a carbon atom ($\Delta m/z_1$ = 3.9942) and maximizing the gain from ions differing by the addition of a nitrogen atom and the loss of a carbon atom and a hydrogen atom ($\Delta m/z_2 = 0.9953$).

S3. Obtaining and running the GKA panel code

The code and any future updates are available at Github at the following link: https://github.com/BrowneLab/GeneralizedKendrickAnalysis_Panel

Once the ipf is loaded into Igor Pro and compiled, a menu option will appear called “Kendrick Analysis Panel” which can be used to generate the panel shown in Figure S7.

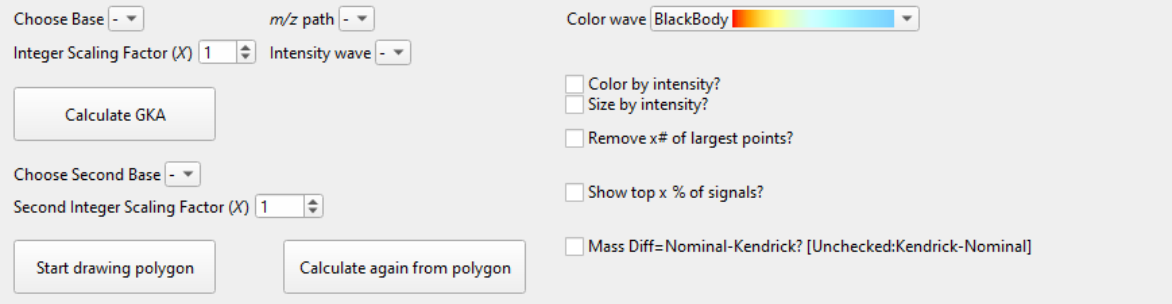

Figure S7 The main panel that is made to run the GKA analysis within Igor Pro v9 and above.

References

Fouquet, T. and Sato, H.: Improving the Resolution of Kendrick Mass Defect Analysis for Polymer Ions with Fractional Base Units, Mass Spectrometry, 6, A0055–A0055, https://doi.org/10.5702/massspectrometry.a0055, 2017.

Nakamura, S., Cody, R. B., Sato, H., and Fouquet, T.: Graphical Ranking of Divisors to Get the Most out of a Resolution-Enhanced Kendrick Mass Defect Plot, Analytical Chemistry, 91, 2004–2012, https://doi.org/10.1021/acs.analchem.8b04371, 2019.