Frame and Casciotti Supplementary Material.

Here we follow the recommendations of Westley et al (2007) and use ICON isotopomer standards to demonstrate that the yield of 31+ fragment ions per mole of parent gas molecule is about ten times higher for the 141516 isotopomer than for the 151416 isotopomer.

First, define the mixing fraction of the ICON gas and the standard tank

F = moles standard / (moles ICON + moles standard)
1 - F = moles ICON / (moles ICON + moles standard)

for the ICON + standard mixtures

$$\frac{31mix}{30mix} = \frac{F * yield31ions / mole\ standard + (1-F) * yield31ions / mole\ ICON}{F * yield\ 30ions / moles\ standard + (1-F) * yield30ions / mole\ ICON}$$

$$\frac{45mix}{44mix} = \frac{F * yield45ions / mole\ standard + (1-F) * yield45ions / mole\ ICON}{F * yield44ions / mole\ standard + (1-F) * yield44ions / mole\ ICON}$$

Using dual inlet mode, we ran the standard gas against these mixtures, so we can calculate the 31/30mix / 31/30standard ratio also. This is graphed in the excel spreadsheet included.

31standard = yield31ions / mole standard
30standard = yield30ions / mole standard

45standard = yield 45ions / mole standard
44standard = yield44ions / mole standard

If we divide 31/30mix by 31/30standard we get

$$31Rmix / 31Rstand = \frac{F + (1-F) * yield31ions / mole\ ICON * 1 / (yield31ions / mole\ standard)}{F + (1-F) * yield30ions / mole\ ICON * 1 / (yield30ions / mole\ standard)}$$

$$45Rmix / 45Rstand = \frac{F + (1-F) * yield45ions / mole\ ICON * 1 / (yield45ions/mole\ standard)}{F + (1-F) * yield44ions / mole\ ICON * 1 / (yield44ions/mole\ standard)}$$

Simplify the notation:
A = yield31ions / mole ICON * 1 / (yield31ions / mole standard)
B = yield30ions / mole ICON * 1 / (yield30ions / mole standard)
C = yield45ions / mole ICON * 1 / (yield45ions / mole standard)
D = yield44ions / mole ICON * 1 / (yield44ions / mole standard)

$$31/30mix / 31/30stand = \frac{F + (1-F) * A}{F + (1-F) * B}$$

$$45/44mix / 45/44stand = \frac{F + (1-F) * C}{F + (1-F) * D}$$

solve for F in terms of A, B, and 31Rmix / 31Rstand

$$F = \frac{A - 31Rmix/31Rstand * B}{31Rmix/31Rstand - 1 + A - 31Rmix/31Rstand * B}$$

Substitute this expression of F into the equation for 45Rmix / 45Rstand (see the column labeled calc 45R/45Rstd in the spreadsheet)

Now we have an equation for 45Rmix / 45Rstand in terms of 31Rmix / 30Rstand with unknown parameters A, B, C, and D. This equation can be applied to both 141516 and 151416 ICON standard mixtures but they will have different sets of best-fit values for A, B, C, and D. In the spreadsheet, A, B, C, and D refer to 151416 isotopomer and A', B', C', and D' refer to the 141516 isotopomer.

By definition, these parameters are all referenced to the appropriate ion yields from our standard tank, so it is possible to make direct comparisons between A and A', C and C', etc. The best fit values of A and A' (the relative yields of 31 ions) were determined by varying A, B, C, and D until the calculated slopes and intercepts of the 45Rmix / 45Rstand vs. 31Rmix / 31Rstand lines aligned with those of the actual data from the ICON mixing analyses.

We note that in this model of the 45Rmix / 45Rstand vs. 31Rmix / 31Rstand line, the best fit values of A and A' are dependent on the relative yields of 45 ions (the values of the C and C' parameters). We use values of C and C' that are essentially equal to each other and very close to values that we estimated by analyzing individual ICON standard gases using a single Faraday cup and peak jumping as discussed in Westley et al (2007).

The best fit values are A = 22.65 and A' = 217. These numbers mean that when the 151416 ICON and 141516 ICON standards are ionized, they make 22.65 and 217 times as many 31 ions per mole of parent gas than the gas in our reference tank. Their ratio (=0.104) indicates that the 141516 standard yields about ten times as many 31 ions than the 151416 standard in our ion source.

Theoretically, the best fit values of B and B' could be used to do a similar calculation for the 30 ion yields of the ICON standards referenced to our standard tank. However, the slopes of the calibration lines are not very sensitive to changes in B and B' because the gas in our standard tank also produces a large yield of 30 ions. Therefore, they may not be accurate enough to do this.