

SUPPLEMENTARY INFORMATION

for

“Using Orbitrap mass spectrometry to assess the isotopic compositions of individual components in mixtures”

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Figure S1. Comparison of Total Ion Current (TIC) profiles (gray icons) for mixtures in **(a)** ESI and **(b)** EI instruments. Points selected for analysis within the ‘para-xylene-only’ and ‘para-xylene + n-decane’ regions are shown in yellow in **(b)**.

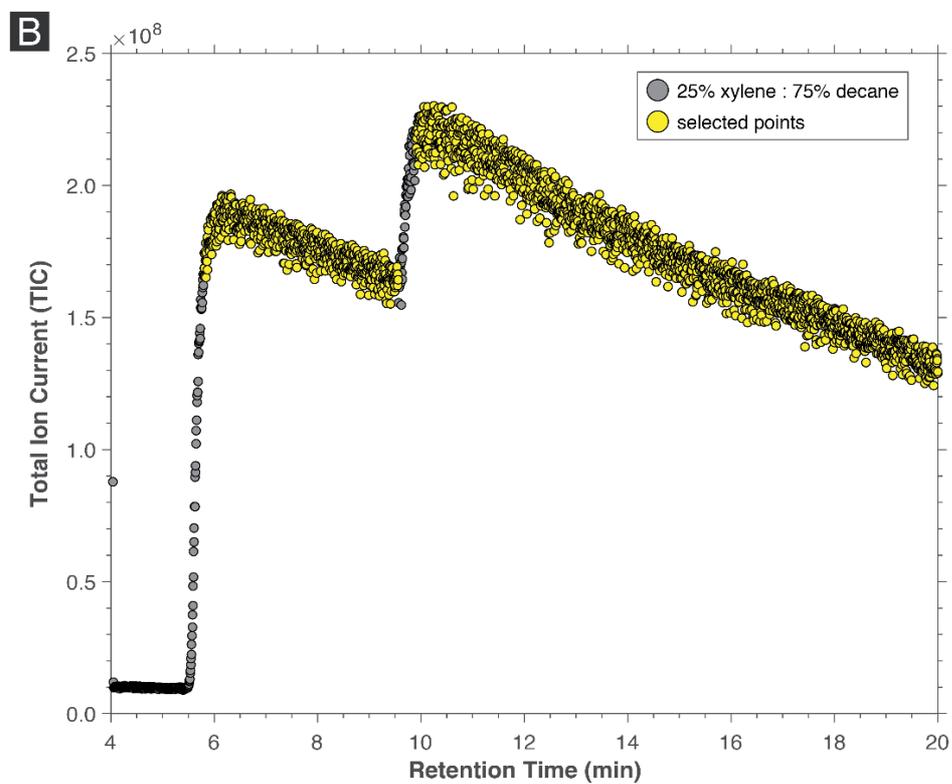
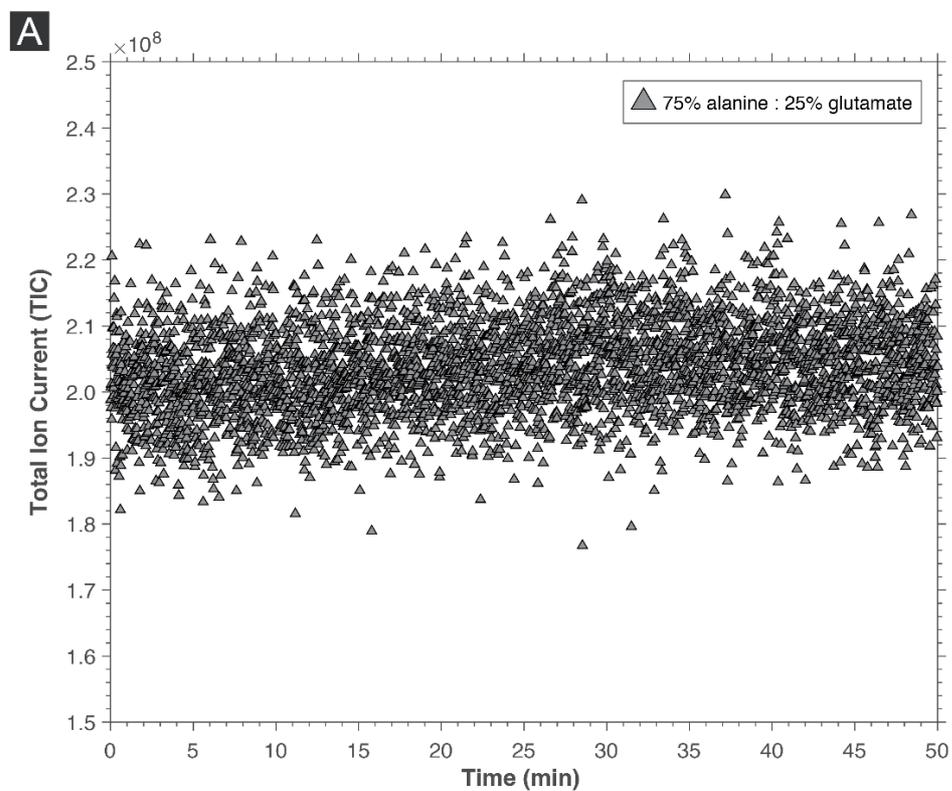


Figure S2. (a) Chromatogram from a pure para-xylene ‘peak capture’ experiment on the Q Exactive GC used in this study. Analytical and operating conditions were the same as those used in the para-xylene / n-decane experiments presented in the text. The full TIC trace is presented as gray triangles. Points selected for isotopic analysis (plotted in **(b)**) are shown in yellow. **(b)** $^{13}\text{C}/^{12}\text{C}$ ratio of para-xylene over the course of the experiment, corresponding to the yellow points in **(a)**. The red line represents the mean of a 5-minute moving window.

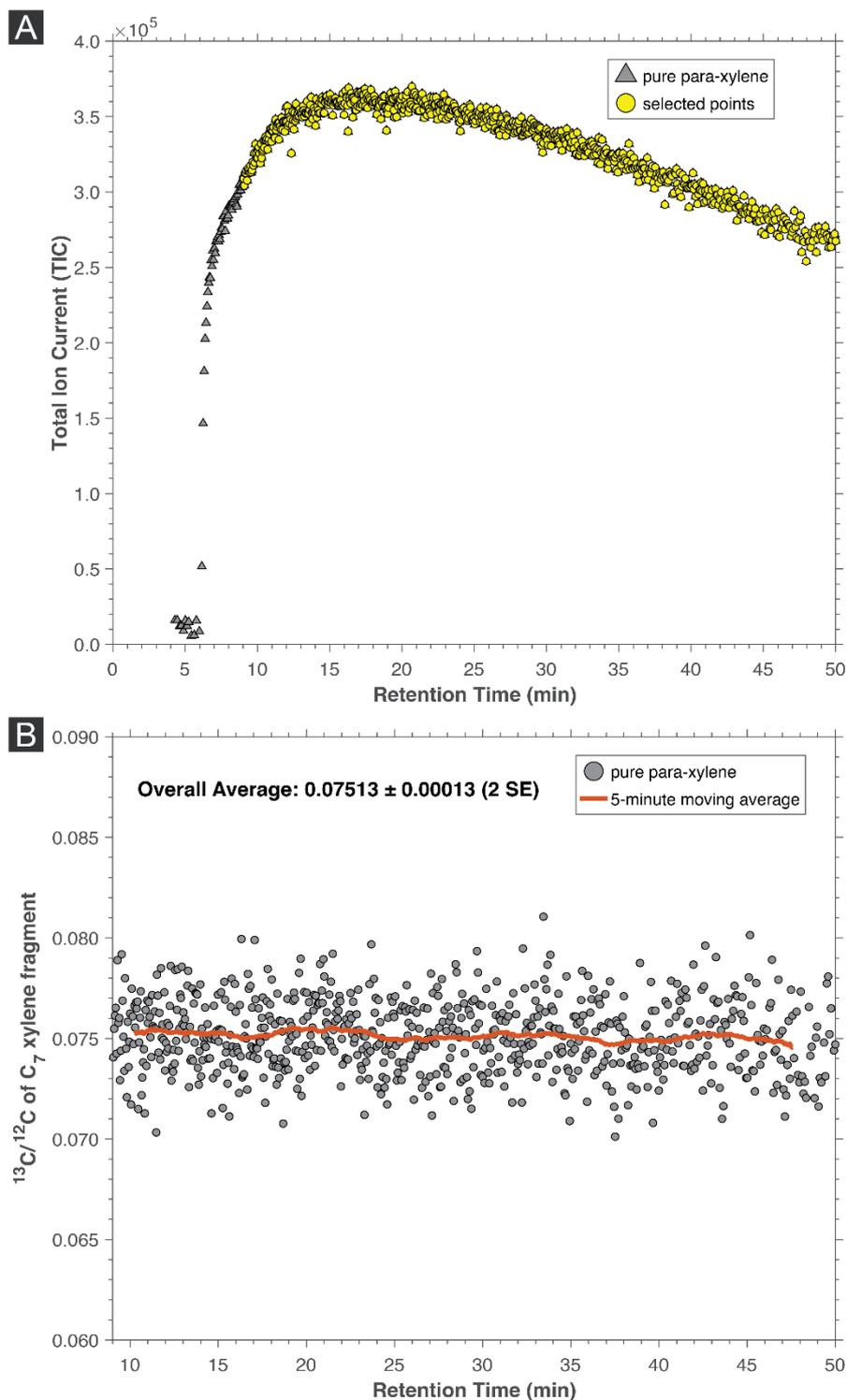


Figure S3. Comparison of mass spectra for the two nominally pure alanine solutions from the alanine / glutamate experiment set. **(a)** Alanine standard G1 with the isotopologue peaks of interest identified. **(b)** Alanine solution G2, which was prepared as a pure alanine standard, showing a higher relative abundance of contaminating species. **(c)** Zoomed-in portion of **(a)** illustrating the relative magnitude of the major peaks in the mass spectrum. **(d)** Zoomed-in portion of **(b)** showing the presence of the most abundant contaminant species.

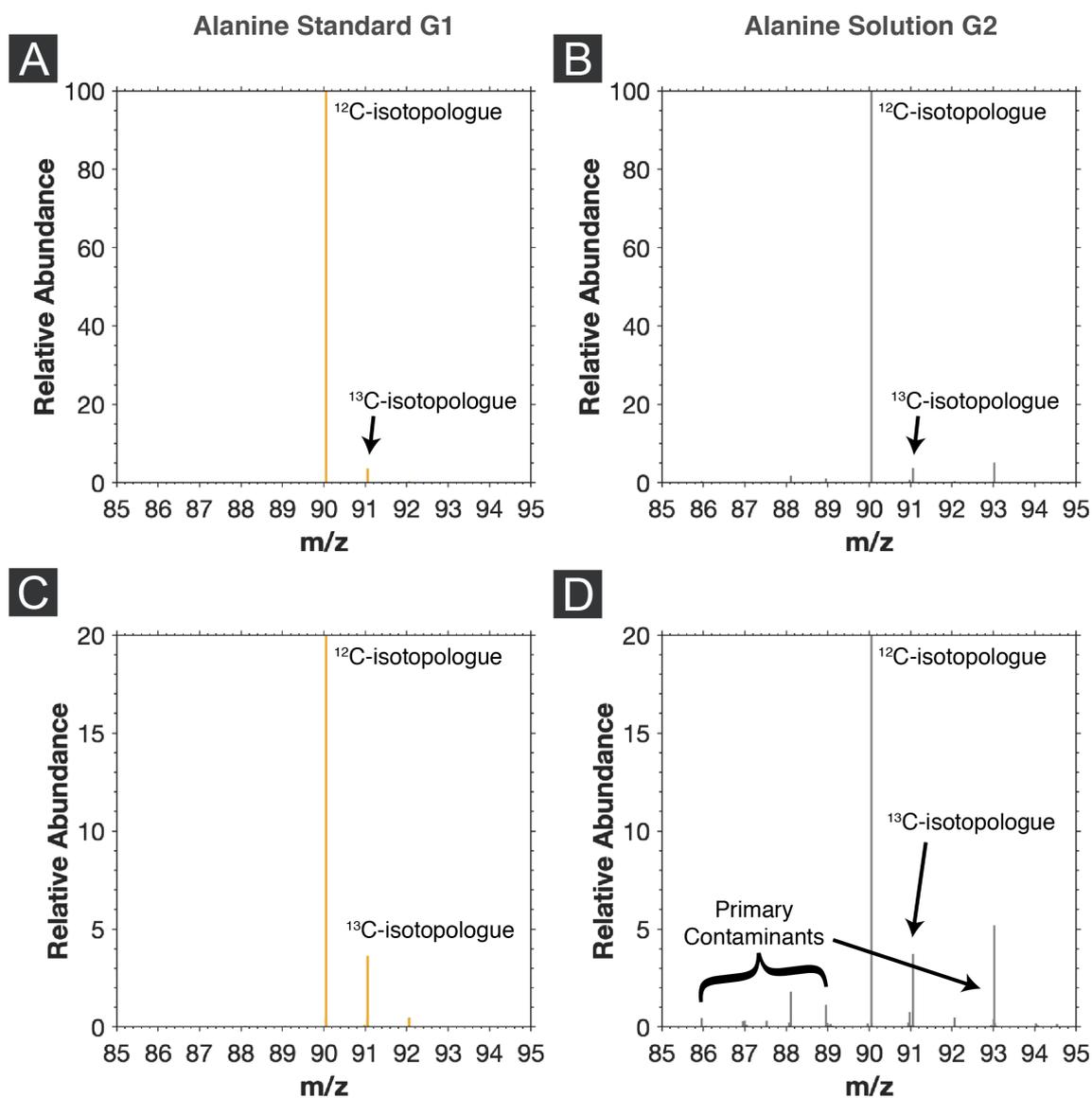


Figure S4. (a) Chromatogram from the 11152017 para-xylene + n-decane experiment. Data from the xylene + decane portion of the chromatogram were binned into 2-minute intervals, shown here as regions 1–5. **(b)** Average $^{13}\text{C}/^{12}\text{C}$ ratio of the analyte as a function of the xylene:decane mixing ratio (represented here as the absolute intensity of the ^{12}C ion beam divided by the total ion current). The red line represents a linear regression to the five regions, weighted by errors in the $^{13}\text{C}/^{12}\text{C}$ ratio of each point. The black circle is the calculated average of all five regions. Error bars represent two standard error on the $^{13}\text{C}/^{12}\text{C}$ ratio and one standard deviation on the ^{12}C Absolute Intensity / TIC ratio. Retention time as shown in **(a)** increases to the left in **(b)**. For comparison, the $^{13}\text{C}/^{12}\text{C}$ ratio for the C_7 fragment in the para-xylene-only portion of the same chromatogram is 0.07504 (Table 2) at a $^{12}\text{C}/\text{TIC}$ value of 0.39 (Table 1).

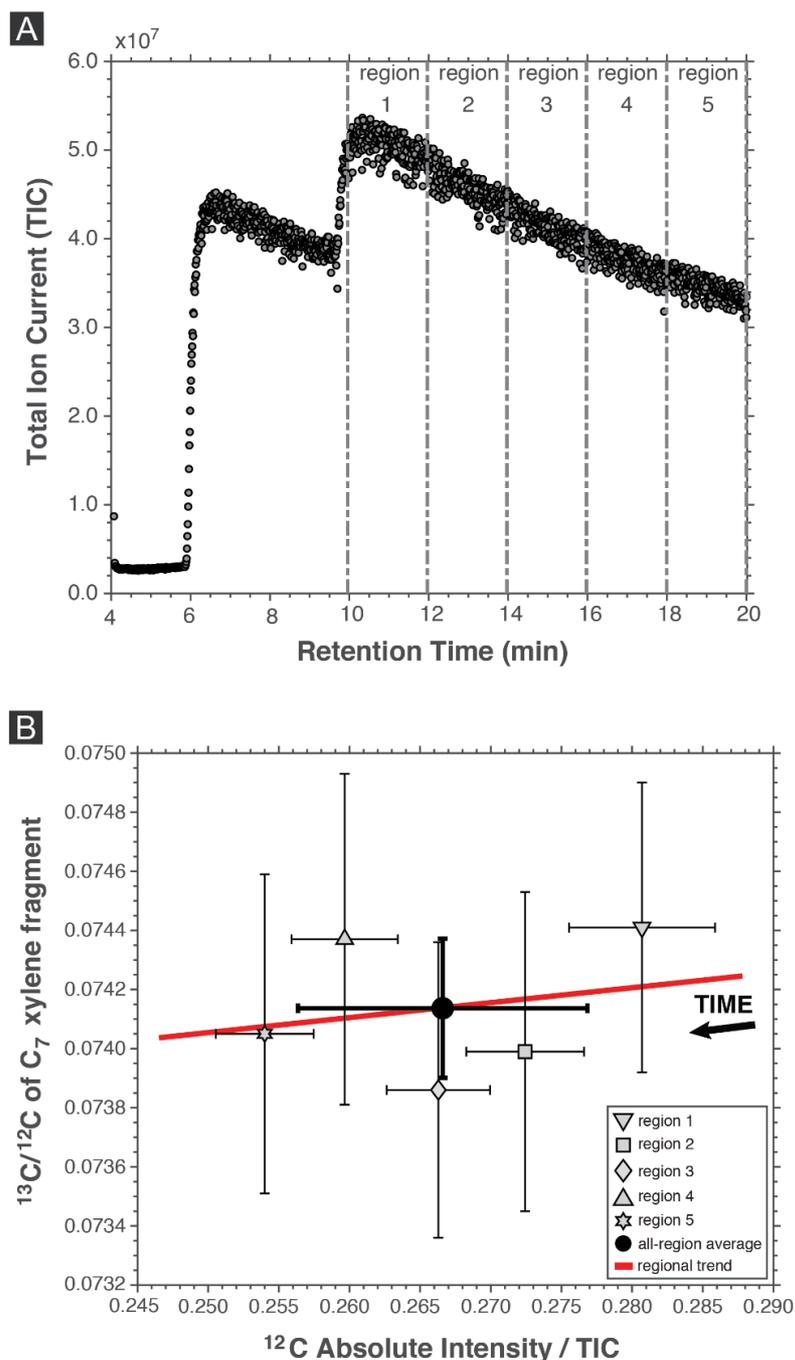


Figure S5. Comparison of spectral noise on the ^{12}C - and ^{13}C -bearing isotopologue peaks from two para-xylene / n-decane experiments performed using the same solution and the same analytical conditions except resolution. Portions of the experiment during which only para-xylene was present in the mass analyzer (corresponding to the selected analysis time windows described in Section 2.3.1) are denoted by the yellow dashed lines and labeled ‘xylene only’; the corresponding window for the para-xylene / n-decane mixture is denoted by the blue dashed lines and labeled ‘xylene + decane’. **(a)** Noise (in ion intensities) on the ^{13}C -bearing C_7 molecular ion from the 60,000 resolution experiment, showing the increase in noise when the n-decane ‘contaminant’ enters the mass analyzer. **(b)** Noise (in ion intensities) on the ^{13}C -bearing C_7 molecular ion from the 120,000 resolution experiment, showing the increase in noise when the n-decane ‘contaminant’ enters the mass analyzer. Note that the absolute magnitude of the peak noise on both the ‘xylene only’ and the ‘xylene + decane’ portions of the experiment is less than the corresponding noise magnitude in the 60,000 resolution experiment. **(c)** Noise ratio between the ^{13}C peak and the ^{12}C peak in the 60,000 resolution experiment showing greater noise on the minor (i.e., ^{13}C -bearing) species, yet an essentially constant noise ratio throughout the experiment regardless of whether para-xylene was alone in the mass analyzer or not. **(d)** Same as **(c)** but for the 120,000 resolution experiment.

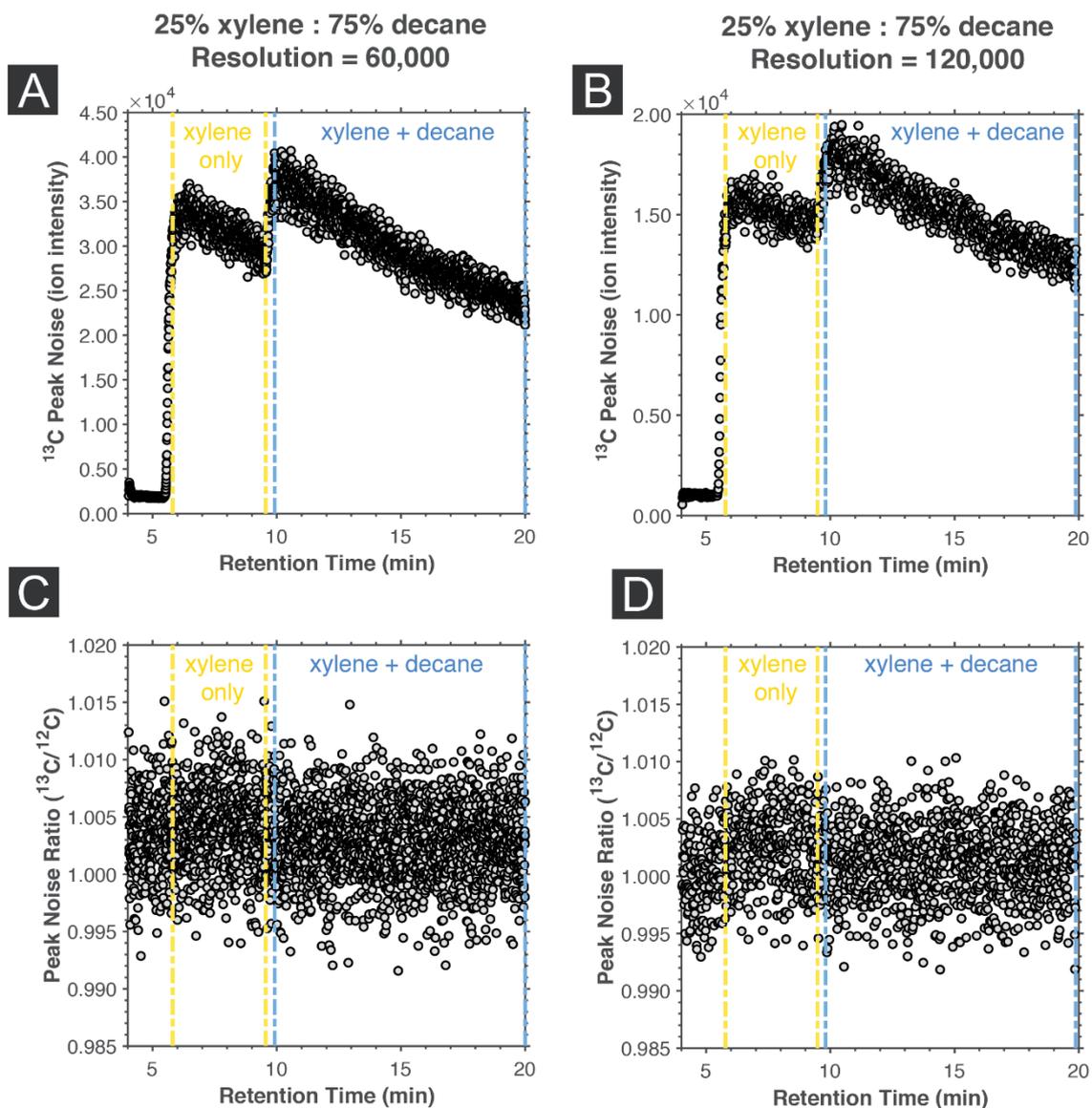


Table S1. Plateau times and parameter values for empirical fits to the para-xylene / n-decane elution curves.

Identification	Start Time (min)	End Time (min)	C	ct	m	A	w
11142017_xylene	5.96	9.40	3.98E6	5.79	3.67E5	2.25E6	0.138
11142017_xylene+decane	9.77	20.02	7.38E6	9.57	1.92E5	4.50E5	0.138
11152017_xylene	6.14	9.63	2.22E7	6.01	5.04E6	1.79E7	0.115
11152017_xylene+decane	9.96	20.02	4.50E7	9.80	-1.05E6	6.74E6	0.133
01112018_xylene	5.78	9.48	6.55E7	5.61	1.06E6	5.58E7	0.128
01112018_xylene+decane	9.80	19.88	1.31E8	9.64	-2.30E6	1.95E7	0.131
01112018_60K_xylene	5.81	9.54	9.75E7	5.66	3.41E5	8.78E7	0.127
01112018_60K_xylene+decane	9.91	20.01	1.93E8	9.73	-8.36E6	3.11E7	0.150