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Supplement of

Sensitive detection of n-alkanes using a mixed ionization mode proton-transfer-reaction mass spectrometer

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Example application of the calibrated fragment algorithm for quantifying *n*-alkanes mixtures

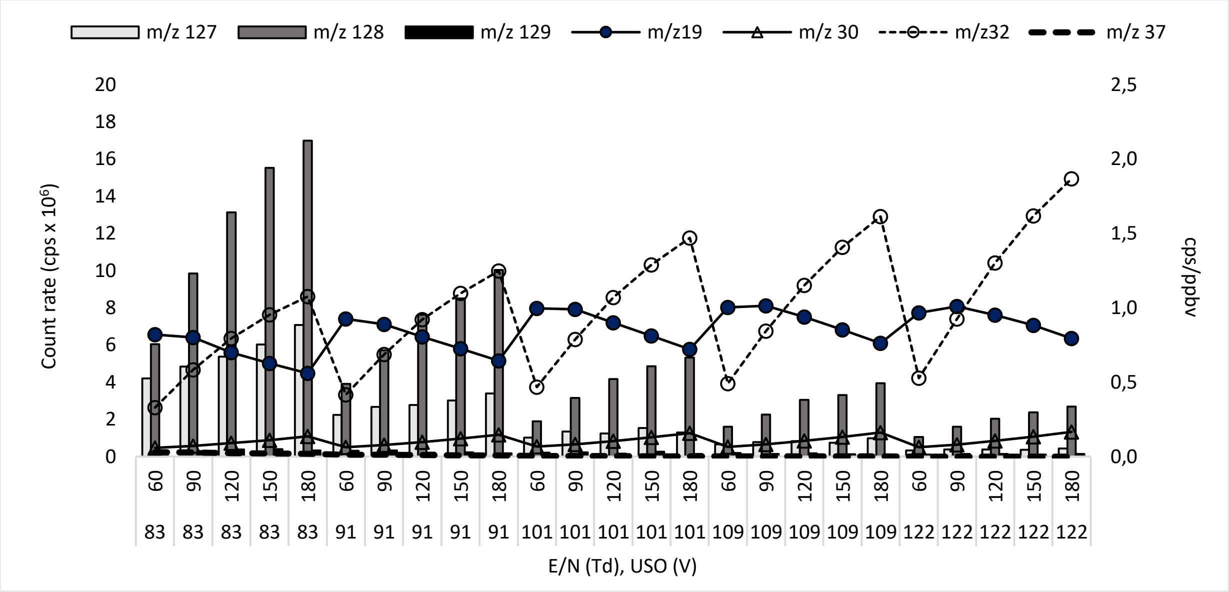
The algorithm explained in section 2.3 was applied to calculate *n*-decane (*m/z* 142) concentration, taken as an example, in a mixture created in the laboratory containing nine *n*-alkanes:

1. *wcps(*O_2^+) for *n*-decane = 77256 at 541.5 ppbv.
2. $wS(O_2^+)$ = 142.7 wcps/ppbv
3. *FCD* of *m/z* 142 on: *m/z* 156 (*n*-undecane) = 0.005, *m/z* 170 (*n*-dodecane) = 0.053 and *m/z* 184 (*n*-tridecane) = 0.059 (Table 3).
4. *Over signal* of *m/z* 142 ion: [11621 wcps * 0.005 (*n*-undecane)] + [17717 wcps * 0.053 (*n*-dodecane)] + [18887 wcps * 0.059 (*n*-tridecane)] = 2111 wcps.
5. *Pure signal* of *m/z* 142 ion: 10099 wcps - 2111 wcps = 7988 wcps.
6. $n - \text{decane concentration} = \frac{7992\ wcps}{142.7\,\frac{wcps}{\text{ppbv}}} = 57.0\ ppbv$
7. The bias with respect to the known concentration of *n*-decane (60.0 ppbv, Table S2) was -5.0 % as illustrated in table 4.

Figures

The panels in figure S1 show the variability at low water flow (2 sccm) of the key source ions comprising H_3O^+ (*m/z* 19), O_2^+ (*m/z* 32), NO^+ (*m/z* 30) and $H_2O.(H_3O)^+$ (*m/z* 37) as a function of *E/N*. Due to excessive water clusters at low *E/N* found at 6 sccm (HWF), the primary ion (H_3O^+) was saturated. The intensity of $H_2O.(H_3O)^+$ decreased, when *E/N* increased because a de-clustering effect occurs at higher electric fields (Blake et al. 2009). Higher intensities were observed at low water flow for all *n*-alkanes. Sensitivities increased when O_2^+ increased.

a



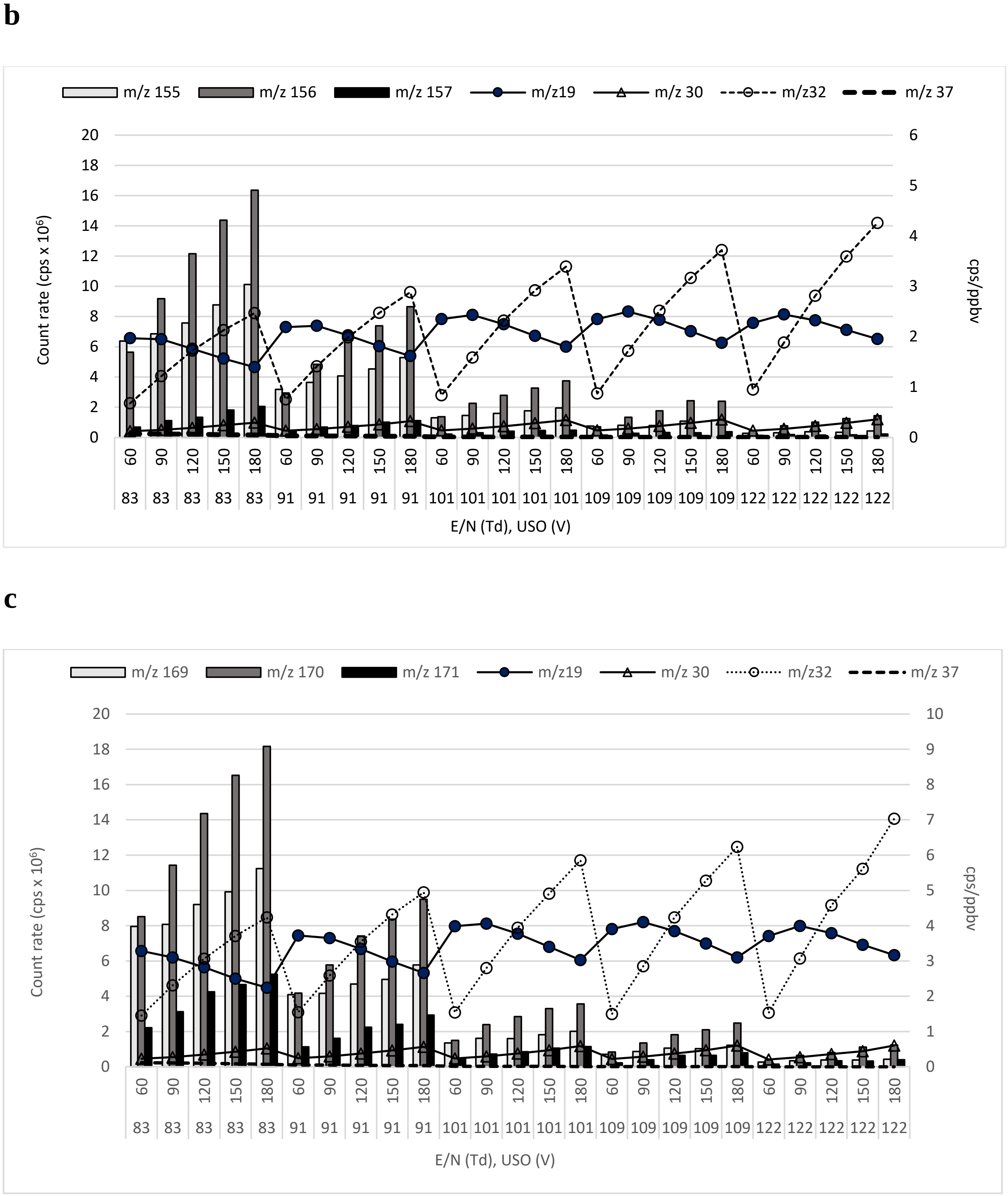


Figure S1. Intensity of signals (counts per second, cps) for H_3O^+ (*m/z* 19), NO^+ (*m/z* 30), O_2^+ (*m/z* 32), $H_2O.(H_3O)^+$ (*m/z* 37) and sensitivities (cps/ppbv) for *n*-alkanes at low water flow (2 sccm). **a.** *n*-nonane, **b.** *n*-undecane and **c.** *n*-dodecane. Data are shown for tests at five *E/N* ratios (83, 91, 101, 109 and 122 Td) and five U_{SO} voltages (60, 90, 120, 150 and 180).

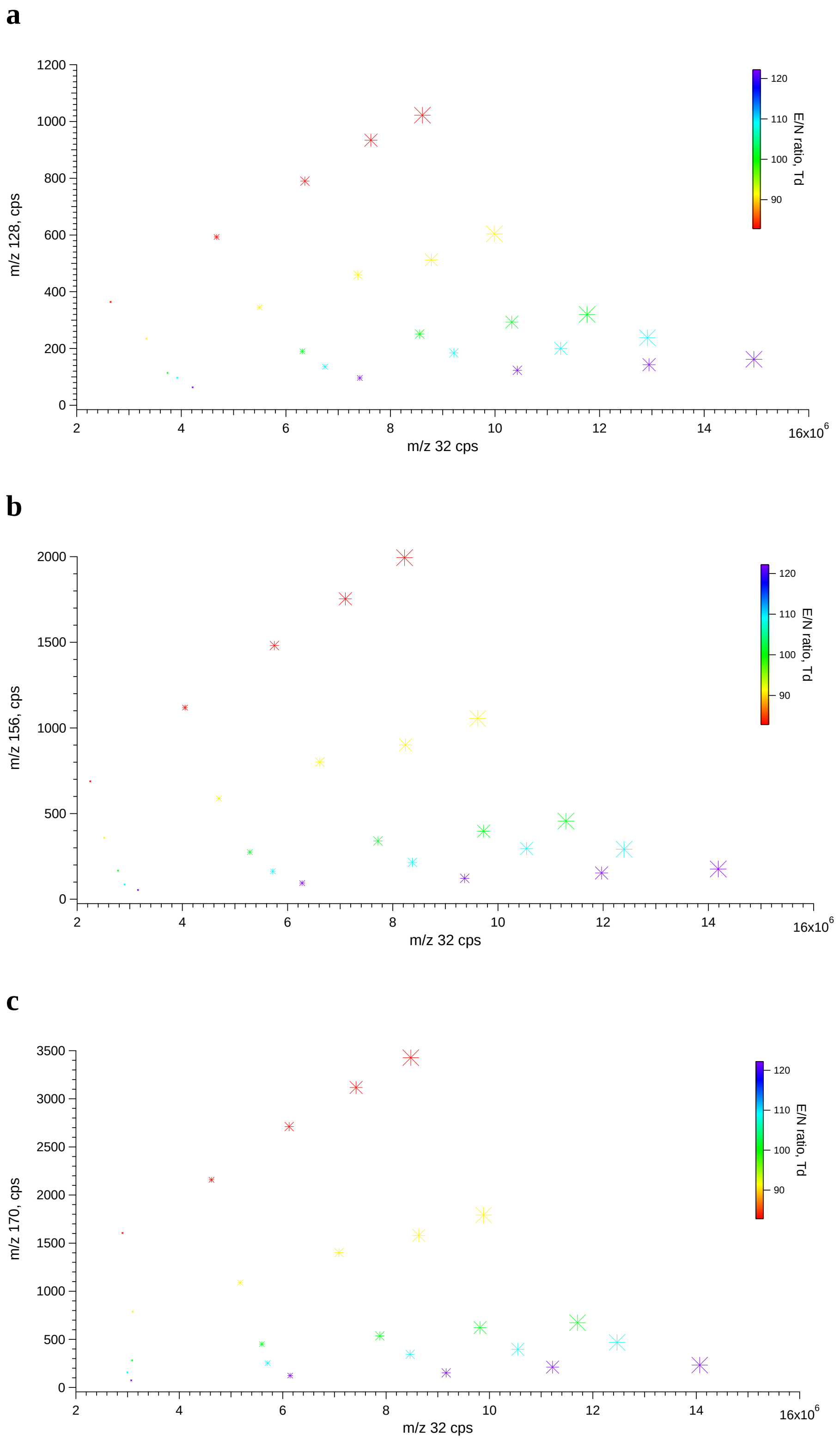


Figure S2. Intensities of *m/z* 32 (O_2^+) vs. intensities of charge transfer products for (**a**) *n*-nonane (*m/z* 128), (**b**) *n*-undecane (*m/z* 156) and (**c**) *n*-dodecane (*m/z* 170). Marker size illustrates the U_{SO}: Smallest 60 V and largest 180 V.

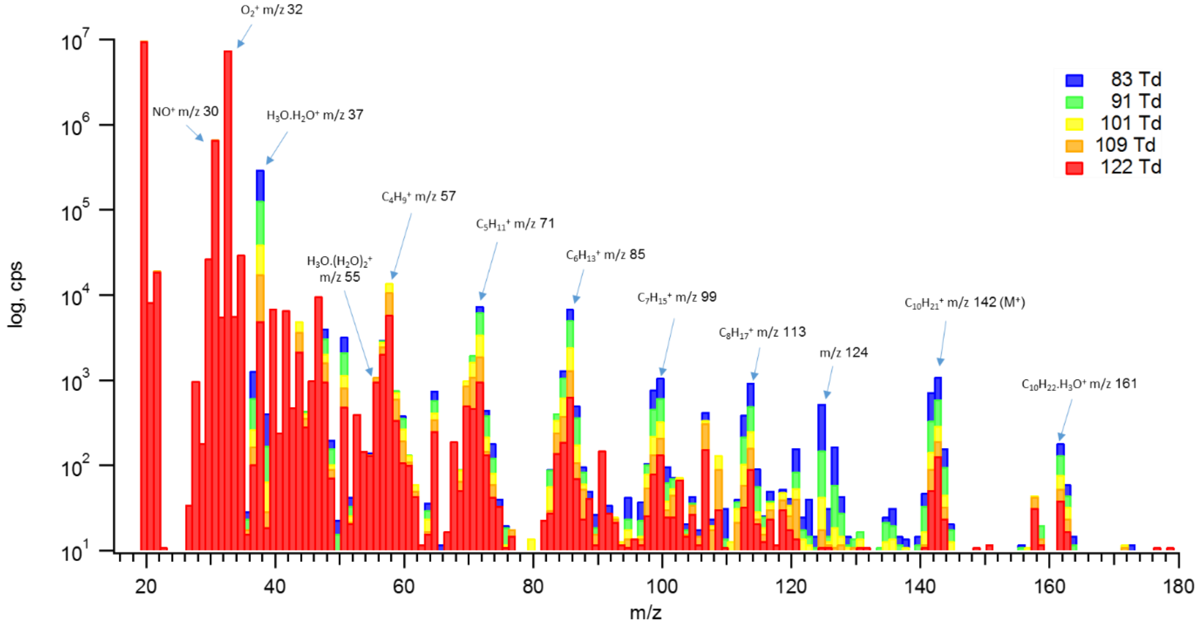


Figure S3. Mass spectra of *n*-decane. WF2, USO 60 V. *E/N* ratios from 83 to 122 Td.

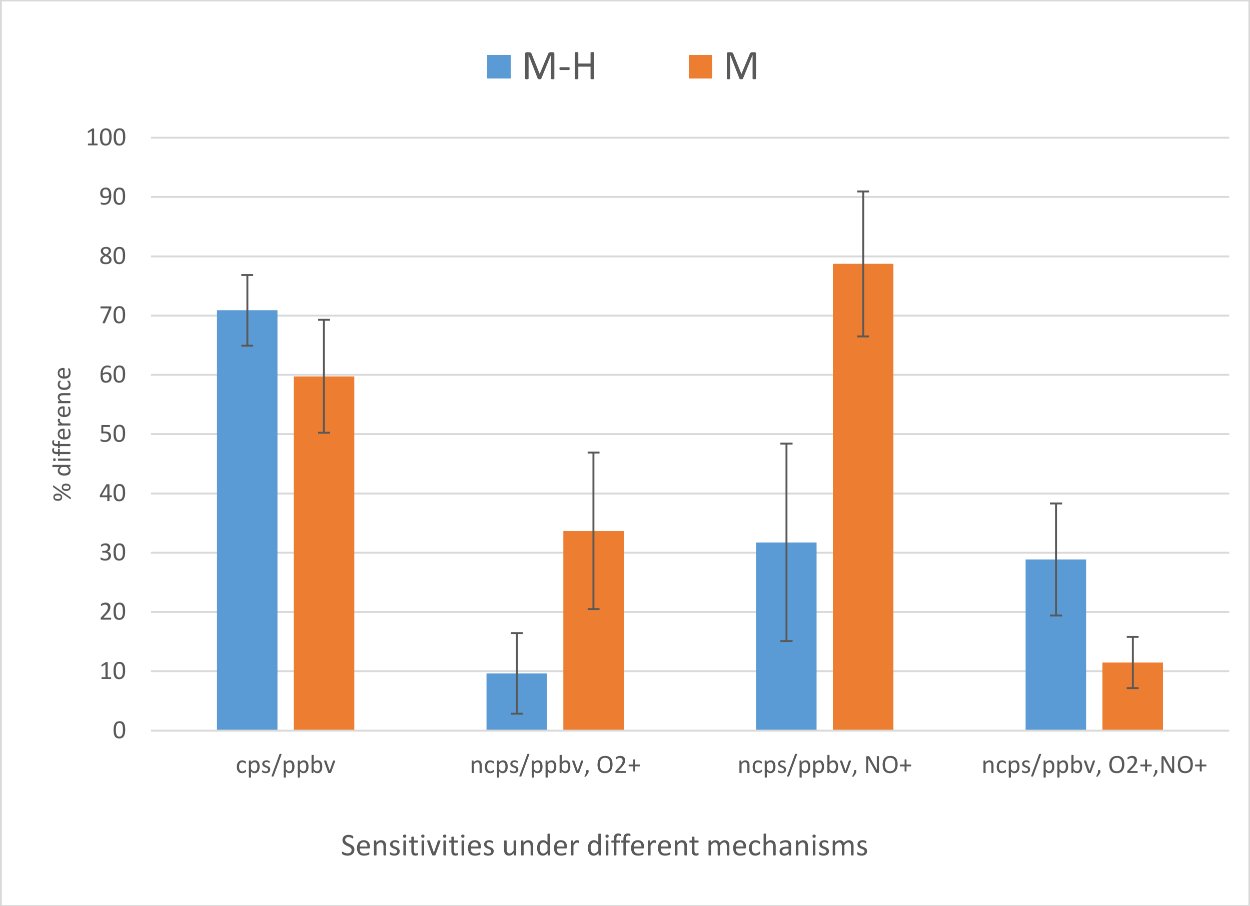


Figure S4. Difference of absolute sensitivities (cps/ppbv) and normalized sensitivities (ncps/ppbv) between two sets of experiments in percentage. Average and standard deviation (bars) shown including data for *n*-nonane, *n*-decane, *n*-undecane and *n*-dodecane. The dominant mechanism for these *n*-alkanes was CT.

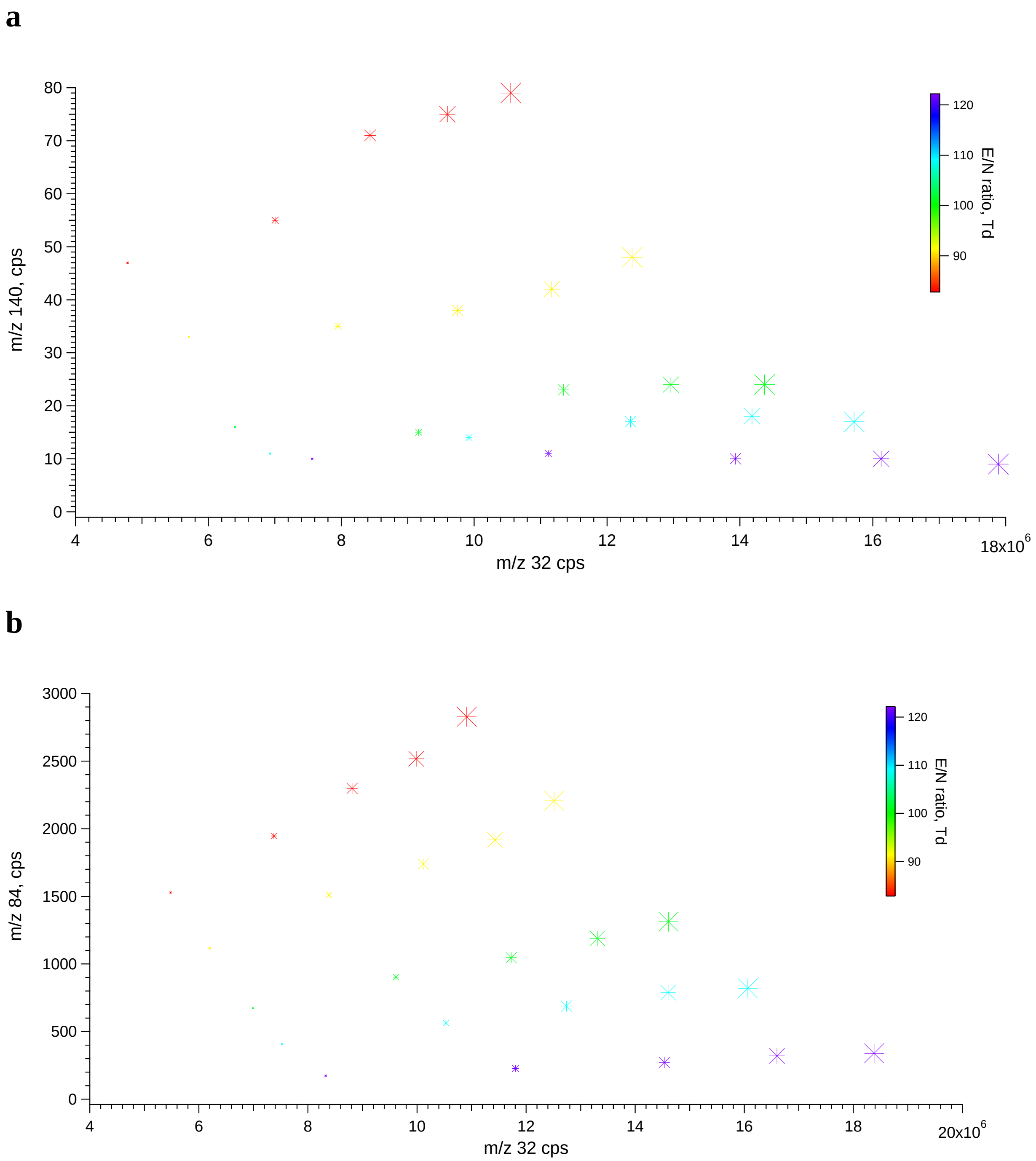


Figure S5. Intensities of double hydride abstraction for (**a**) *n*-decane (*m/z* 140) and (**b**) *n*-hexane (*m/z* 84) vs. O_2^+ (*m/z* 32). Marker size illustrates the U_{SO}: Smallest 60 V and largest 180 V.

A chromatogram of fresh liquid oil MC252 analyzed by Two-Dimensional Gas Chromatography with High-Resolution Time-of-Flight Mass Spectrometry using Vacuum UV Ionization (GCxGC/VUV-HRTOFMS) is shown in Figure S6. Oil MC252 was obtained from the Macondo well located in Mississippi Canyon lease block 252 in the Gulf of Mexico on May 20th 2010. Oil samples were diluted (500:1) in *n*-hexane. 1 µL of diluted oil was injected in splitless at 320 ºC. Analytes were transferred to the gas chromatograph (GC, Agilent 7890). Hydrocarbons were separated on a non-polar primary column (60 m × 0.25 mm × 250 µm Rxi-5Sil-MS; Restek) connected to a second-dimension polar column (1 m × 0.25 mm × 0.25 µm, Rtx-200MS, Restek Corp.) by a dual loop modulator (1.5m × 0.25 mm Rxi guard column) cooled with air from a cold finger and periodically heated by a pulse of hot air (Zoex Corp.). Helium was used as carrier gas at a flow rate of 2 mL min^{-1}. The GC temperature program was 40 °C hold for 2 min, 3.5 °C min^{-1} until 320 °C and hold for 10 min. Ionization conditions of the analytes are described in detail by Worton et al. (2015). Briefly, analytes were ionized with 10.5 electron volts (eV) vacuum ultraviolet photoionization (VUV) in a time of flight mass spectrometer (HTOF, Tofwerk). The VUV beam was generated by the Chemical Dynamics Beamline 9.0.2 of the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory. VUV ionization affords much less fragmentation than conventional electronic ionization (70 eV), increasing the molecular ion intensity.

Quantification of *n*-alkanes was made using deuterated *n*-dodecane (*n*-$C_{12}D_{26}$) at 4.9 ng µL^{-1} internal standard and relative response factor.

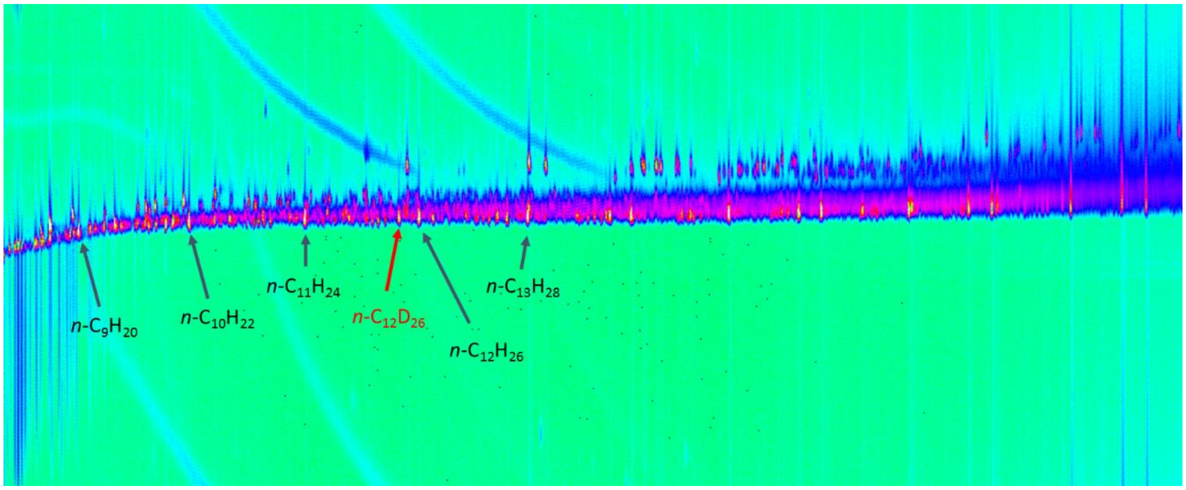


Figure S6. Two-Dimensional Chromatogram of fresh oil MC252.

Tables

Table S1. Straight chain alkanes. Concentrations to evaluate sensitivities.

#	Compound	Concentration, ppbv[a]		
		1st level	2nd level	3st level
1	*n*-Pentane	931.9	2290.7	3648.9
2	*n*-Hexane	812.4	1997.0	3181.1
3	*n*-Heptane	724.1	1179.9	2835.3
4	*n*-Octane	644.2	1583.5	2522.4
5	*n*-Nonane	586.0	1440.4	2294.5
6	*n*-Decane	541.5	1331.1	2120.3
7	*n*-Undecane	496.2	1219.8	1943.1
8	*n*-Dodecane	458.3	1126.5	1794.5
9	*n*-Tridecane	426.8	1049.2	1671.3

[a] Concentrations were calculated at 1 atm, T= 18-23 °C, R = 0.08205746 L atm/K mol.

Table S2. Straight chain alkanes. Concentrations to evaluate the algorithm.

#	Compound	Concentration, ppbv[a]		
		1st level	2nd level	3st level
1	*n*-Pentane	106.3	247.8	394.7
2	*n*-Hexane	89.0	218.7	277.6
3	*n*-Heptane	79.3	194.9	247.4
4	*n*-Octane	71.5	175.7	223.1
5	*n*-Nonane	65.0	159.8	202.9
6	*n*-Decane	60.0	147.5	187.2
7	*n*-Undecane	55.0	135.2	171.6
8	*n*-Dodecane	51.1	125.6	159.4
9	*n*-Tridecane	47.6	116.9	148.4

[a] Concentrations were calculated at 1 atm, T= 18-23 °C, R = 0.08205746 L atm/K mol.

References

Blake, R. S.; Monks, P. S. and Ellis, A. M.: Proton-Transfer Reaction Mass Spectrometry, Chem. Rev., 109, 861-896, **doi:** 10.1021/cr800364q, 2009.

Worton, D. R.; Zhang, H.; Isaacman-VanWertz, G.; Chan, A. W. H.; Wilson, K. R. and Goldstein, A. H.: Comprehensive Chemical Characterization of Hydrocarbons in NIST Standard Reference Material 2779 Gulf of Mexico Crude Oil, Environ. Sci. Technol., 49(22), 13130-13138, doi:10.1021/acs.est.5b03472, 2015.