

The MAT 253-Ultra: A New High-Resolution Gas Source Isotope Ratio Mass Spectrometer*

Alison Piasecki¹, John Eiler¹, and Daniel Stolper¹

Search and Discovery Article #40987 (2012)**

Posted August 6, 2012

*Adapted from oral presentation at AAPG Annual Convention and Exhibition, Long Beach, California, April 22-25, 2012

**AAPG©2012 Serial rights given by author. For all other rights contact author directly.

¹California Institute of Technology, Pasadena, CA (piasecki@gps.caltech.edu)

Abstract

Stable isotope geochemistry provides tools for understanding hydrocarbons and their source rocks, but interpretations are often under constrained because of the small number of measurable isotopic properties - $\delta^{13}\text{C}$ and δD values. These isotopic values reflect the biosynthetic origin of the source material and fractionations during diagenesis, catagenesis, mixing and transport. The combination of these influences makes it challenging to reach unique interpretations of data.

Stable isotopes could yield a far larger set of compositional constraints on organic compounds. For example, there are 10 isotopologues of methane, each with distinctive properties. The information recorded by this isotopic diversity is lost to conventional measurements because the analyzed molecules are destroyed through pyrolysis or combustion prior to measurement.

We have developed with Thermo Scientific a new gas source isotope ratio mass spectrometer - the MAT 253 Ultra - capable of resolving isotopologues of hydrocarbon molecules having the same cardinal mass (e.g., $^{13}\text{CH}_4$ from $^{12}\text{CH}_3\text{D}$), enabling direct isotopic analysis of a large subset of naturally occurring species of hydrocarbons, their fragments, and adducts. This machine combines the dual and carrier gas inlet systems and ion source of a MAT-253 gas source mass spectrometer with the analyzer and collector array used on the Triton and Neptune thermal and plasma source mass spectrometers. The resulting hybrid is built, functional, and has demonstrated mass resolutions greater than $\sim 25,000$. The mass range is 2-280 amu. The instrument has seven detectors (switchable between faraday and electron multipliers). Precisions in isotope ratio measurements are $\sim 0.1\%$ for weak ion beams (< 104 counts per second) measured on electron multipliers. Taken together, these capabilities will allow for unprecedented exploration of the isotopic anatomy of organic compounds.

We are exploring the multiply substituted isotopologues of methane, N_2 , N_2O and longer chain alkanes (e.g., ethane and propane). To prepare for these measurements we have undertaken a set of theoretical (DFT) studies of both methane and 5-pentanone. We predict equilibrium enrichments in ^{13}C -D bonds over a random distribution by factors of 1.006 and 1.004 for methane and 5-pentanone in the gas

phase at 25° C. Such equilibrium predictions provide a basis for new types of thermometers and a reference frame for interpreting kinetic isotope effects in organic species.

Reference

Huang, D.S., S.H. Wu, C.Y. Huang, and C.Y. Lin, 1999, An exploration of intramolecular carbon isotopic distributions of commercial acetone and isopropanol: *Organic Geochemistry*, v. 30/7, p. 667-674.

The Mat 253-Ultra

A New High-Resolution Gas Source Isotope Ratio Mass Spectrometer

Alison Piasecki
John Eiler and Daniel Stolper

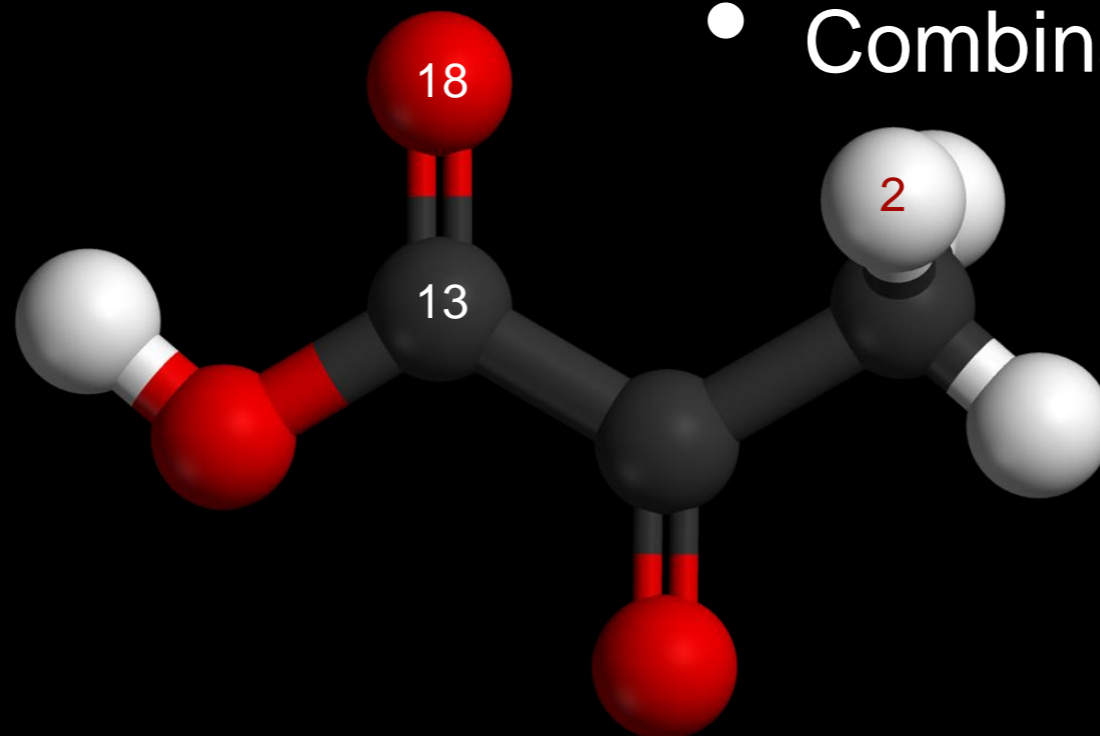
Funding: Petrobras, NSF, Caltech

Common Isotopic Geochemistry Measurements

- $\delta^{13}\text{C}$ of bulk organic molecules
- δD of bulk organic molecules
- $\delta^{18}\text{O}$ bulk
- $\delta^{34}\text{S}$ bulk
- $\delta^{15}\text{N}$

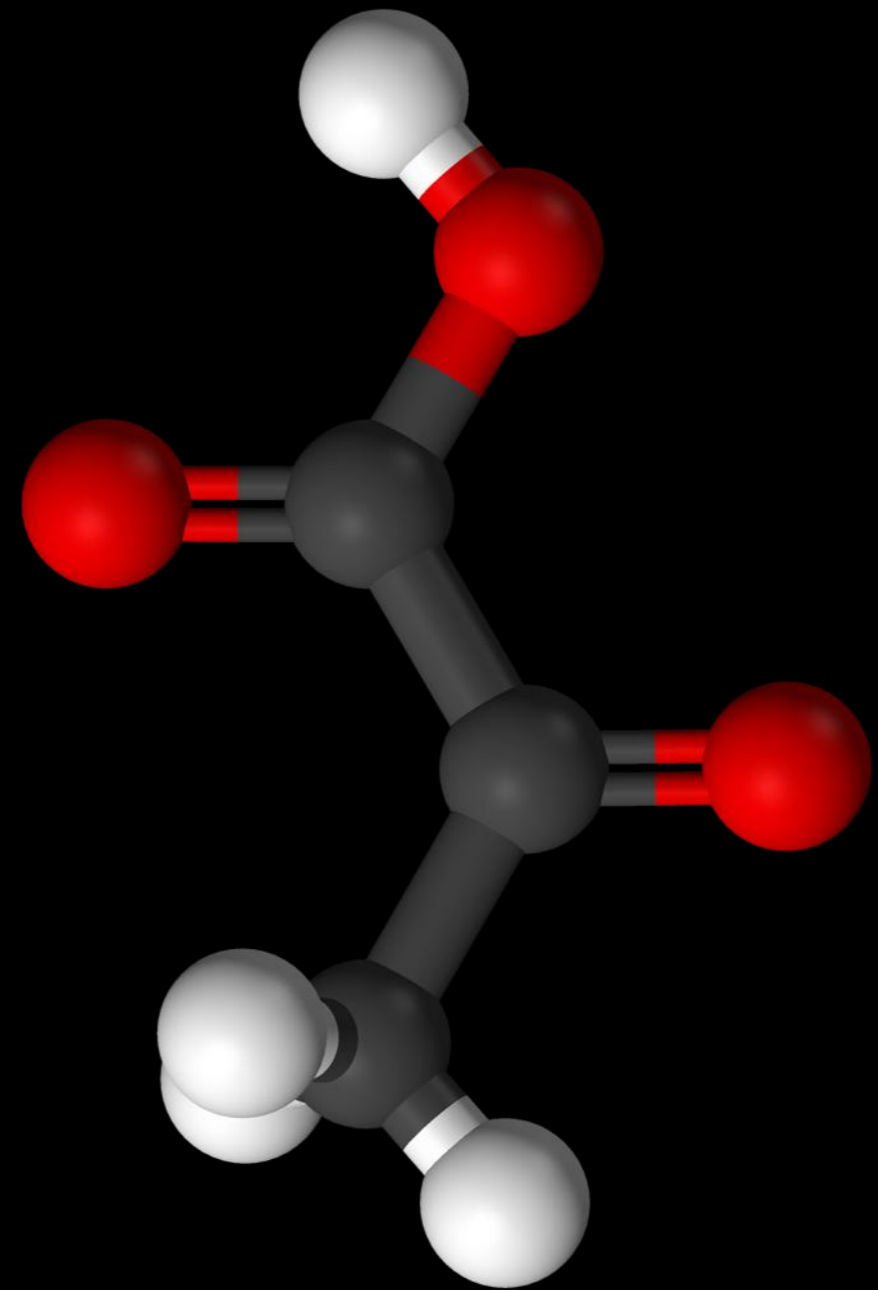
Possible Isotopic Measurements

- Site-specific (ordering of enrichment in molecules)
- Clumping (coupled isotope substitutions, currently done in CO_2)
- Combinations



Example Molecule: Pyruvic Acid

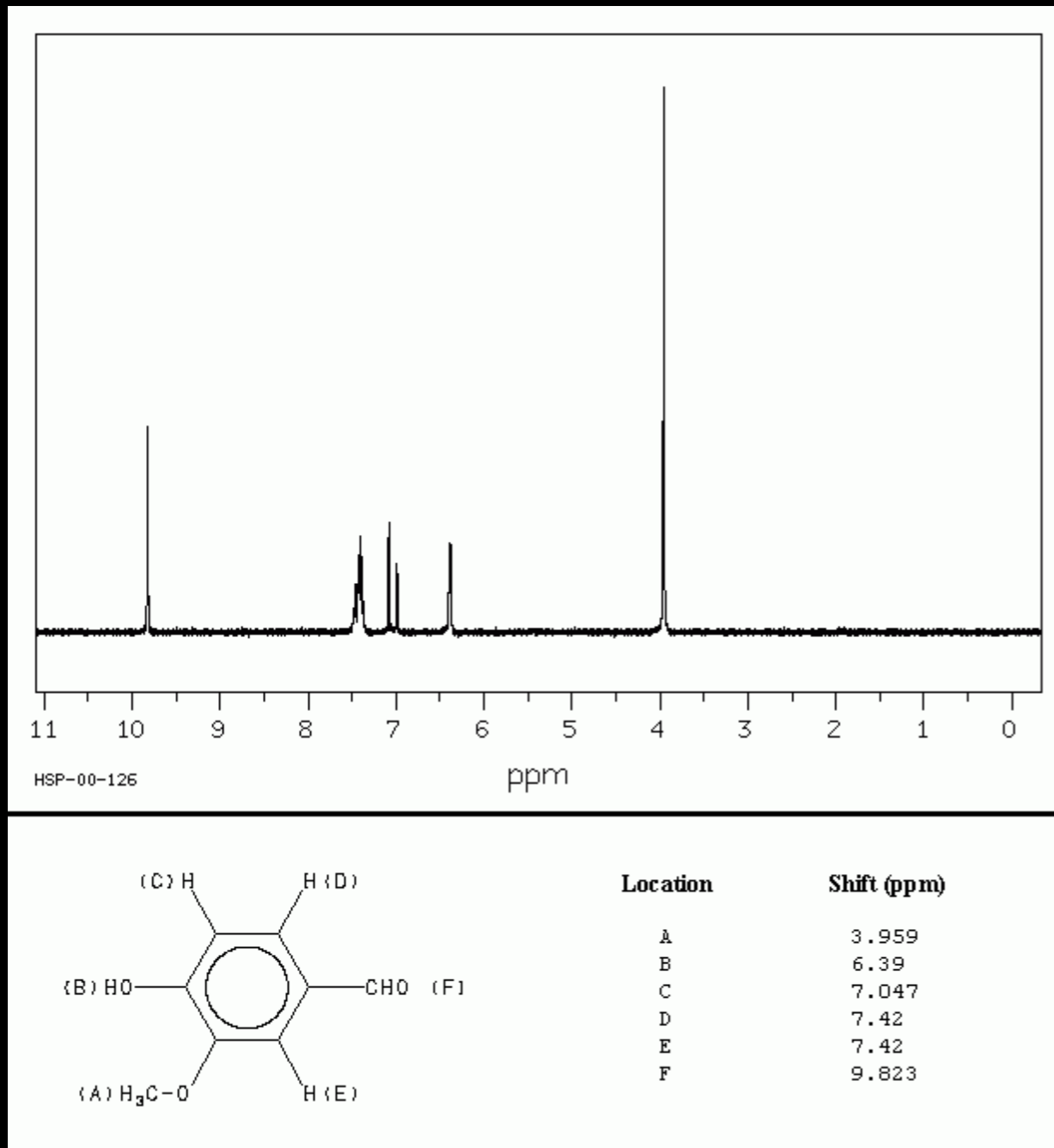
- C-H clumping in methyl group
- C-C clumping
- O-C clumping
- O-H clumping
- site specific $\delta^{13}\text{C}$
- site specific $\delta^{18}\text{O}$
- site specific δD



Natural Abundance : 3456 measurements

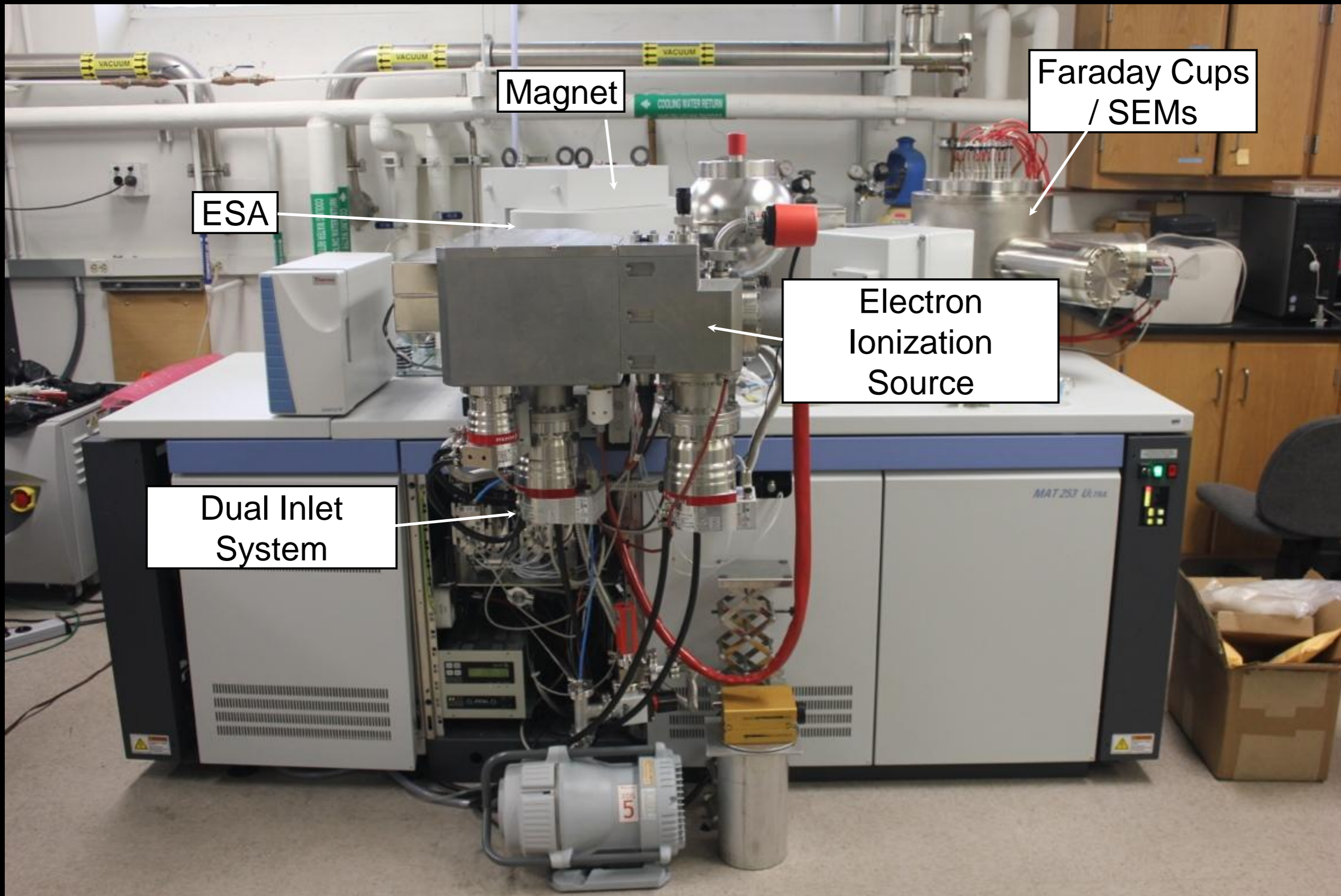
Labeled : 59049 measurements

Previous Measurement Types



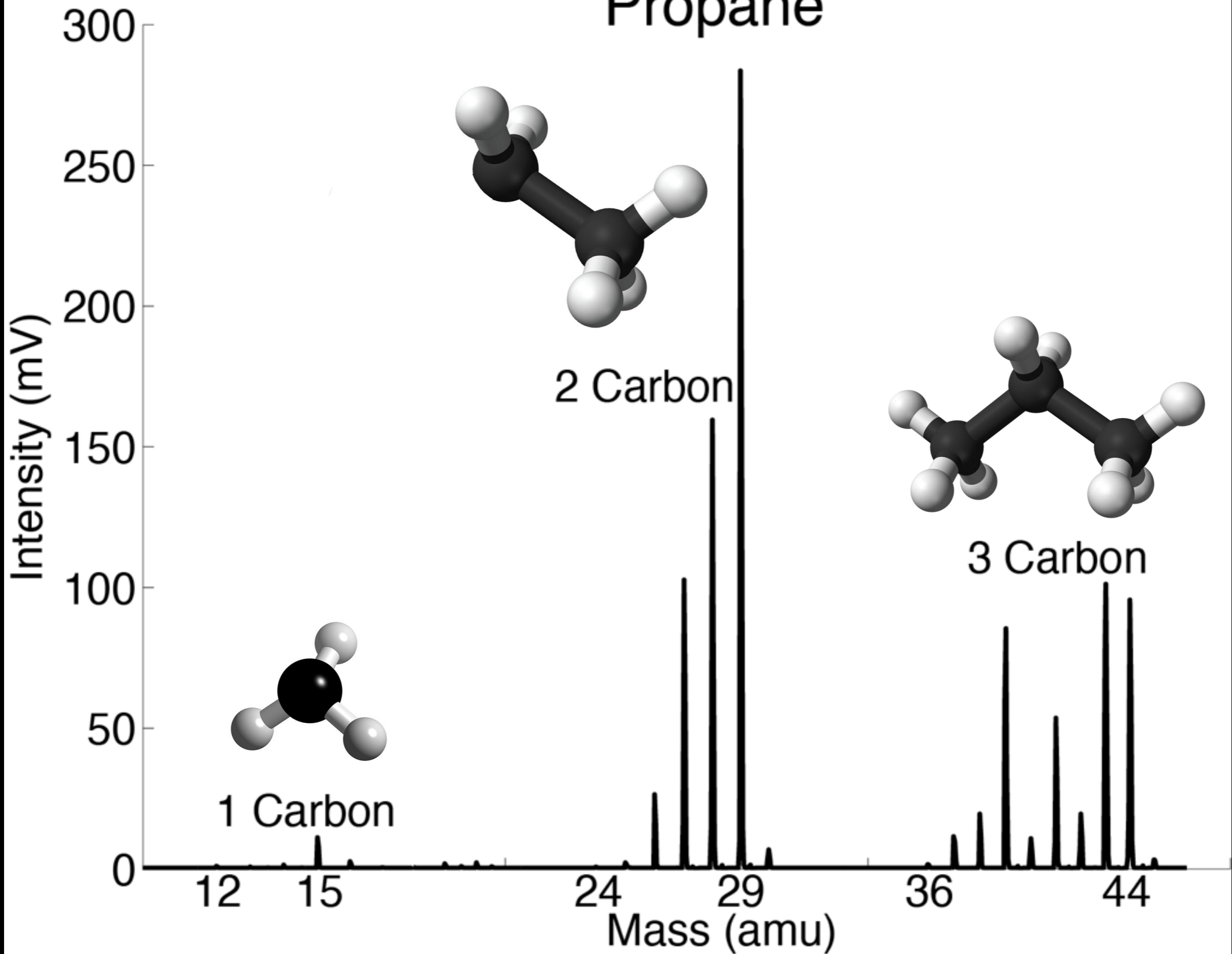
^1H (proton) NMR spectrum for 0.037 grams of vanillin in .5 milliliters of CDCl_3 (deuterated trichloromethane) taken at 89.56 MHz showing location correlated peaks.

- SNIF NMR
- Hydrogen
- Carbon
- Chemical degradation of species to measure site specific carbon
- Clumping in CO_2

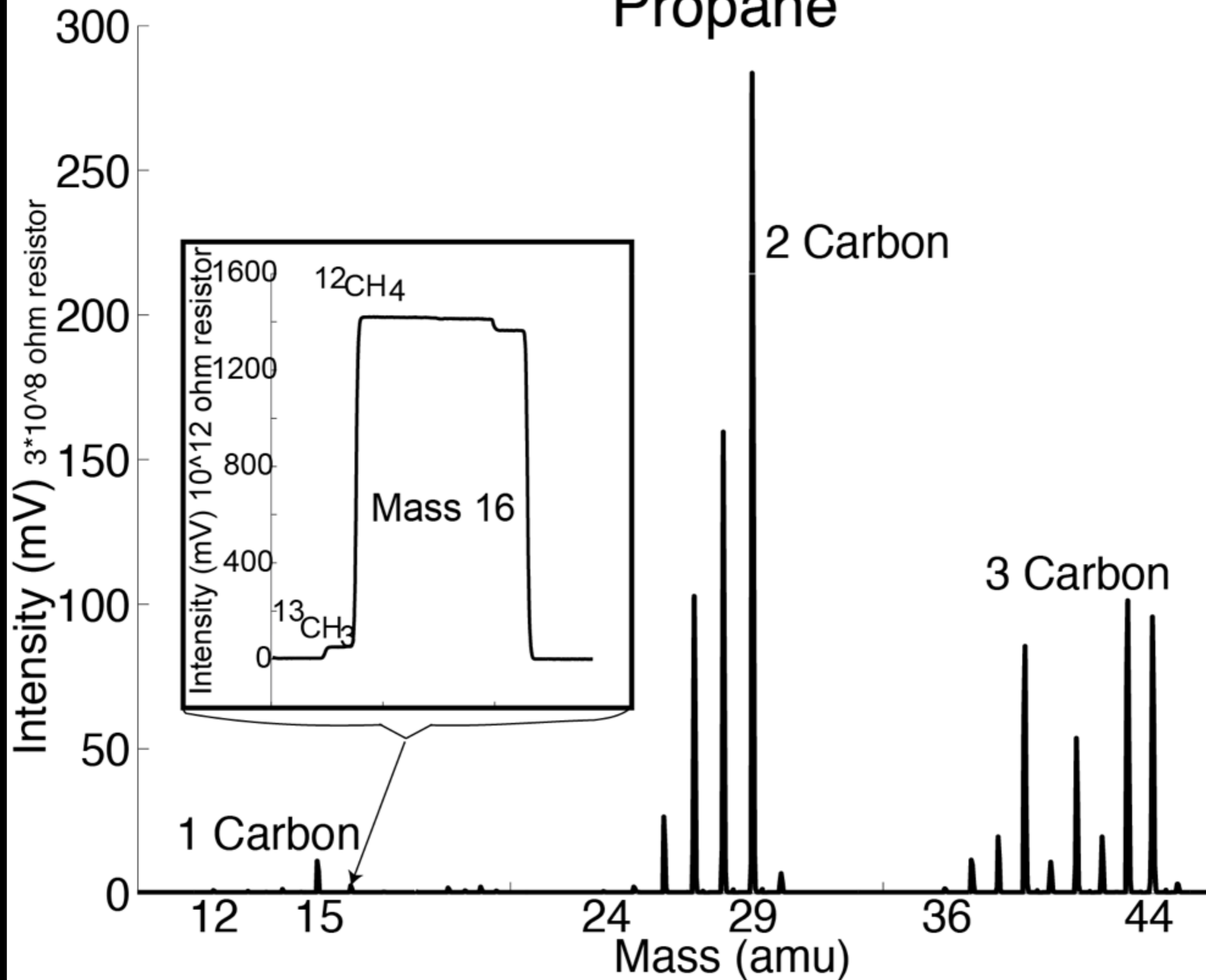


Mat 253-Ultra

Propane

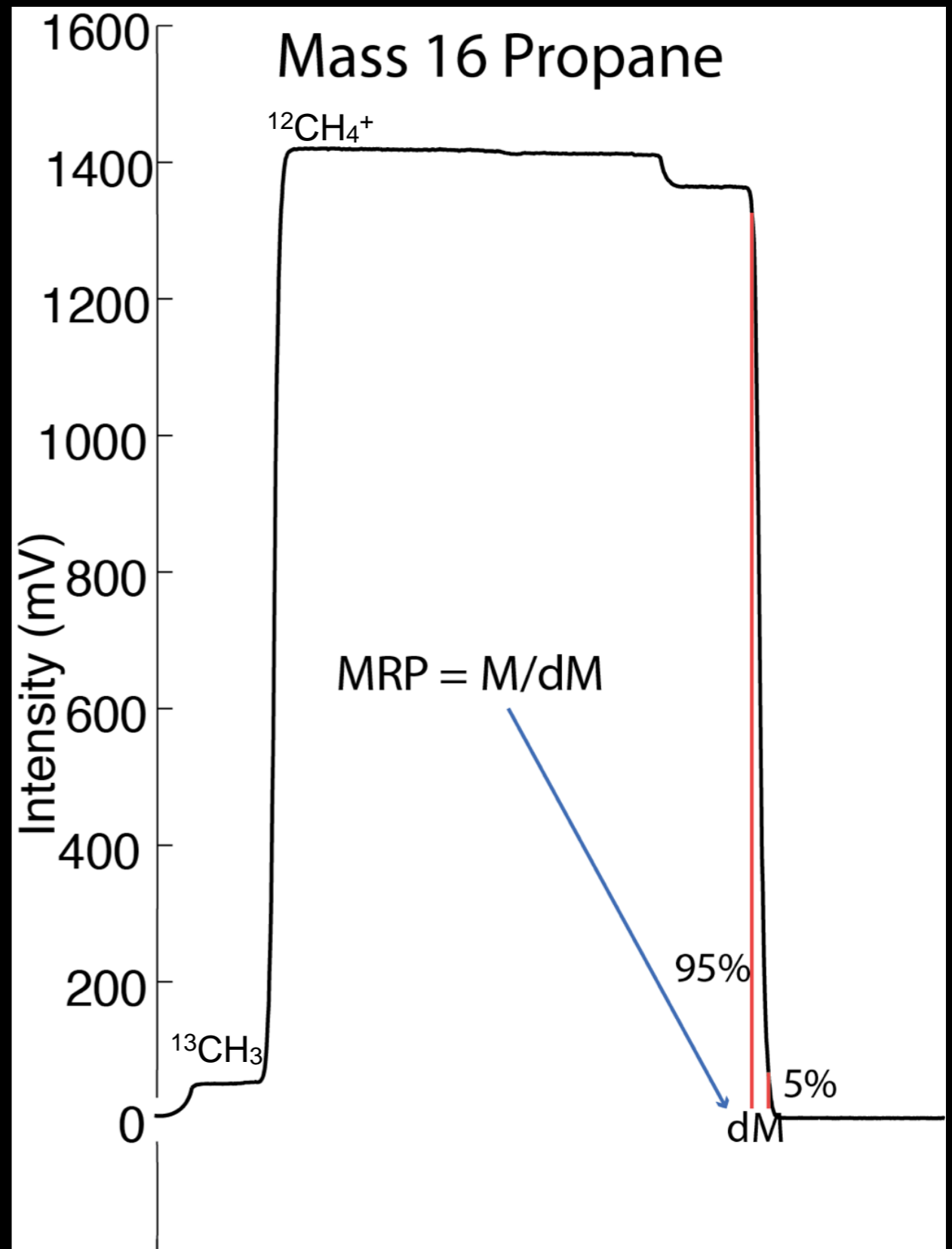


Propane

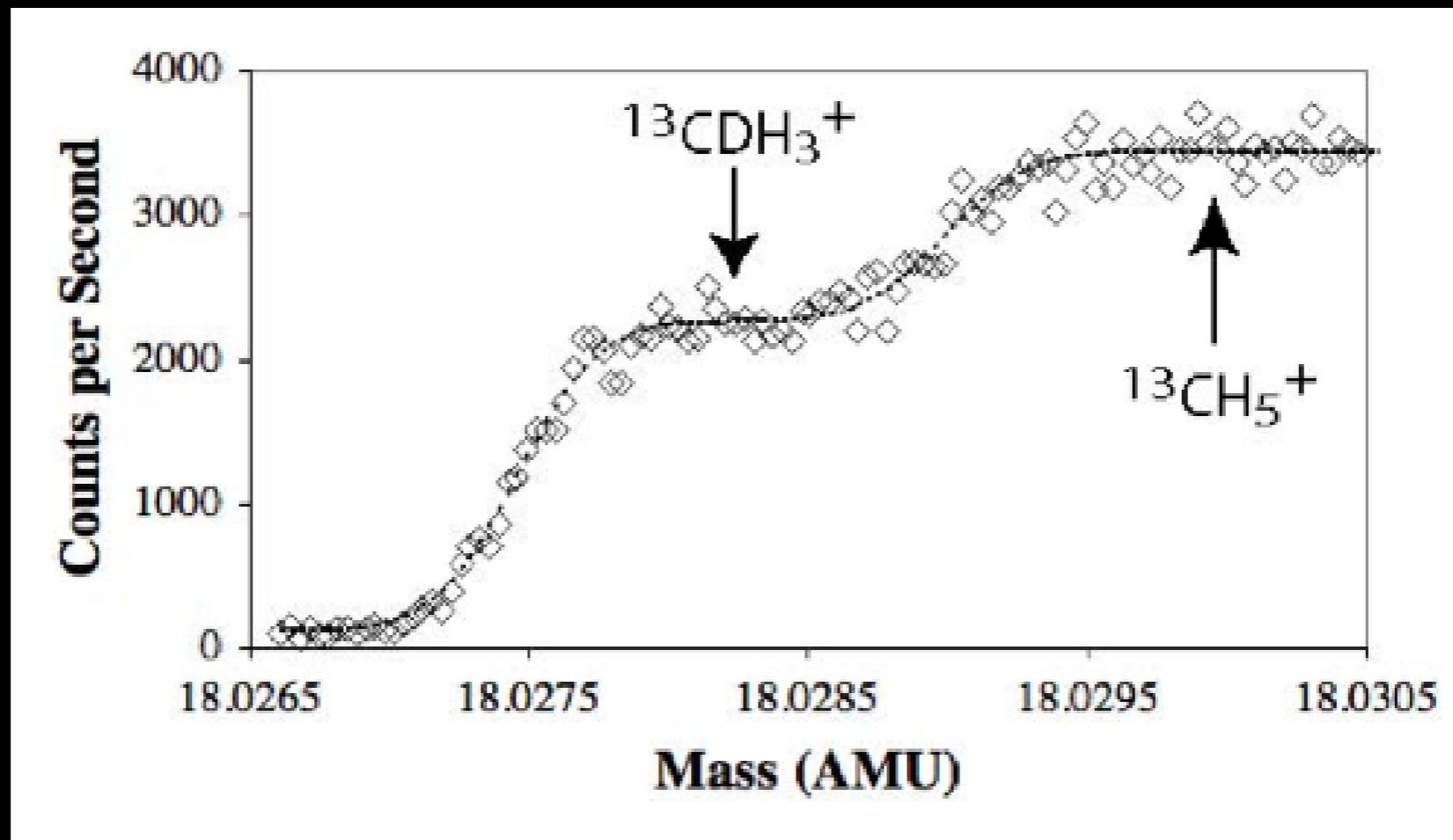


Mass Resolving Power

- Separate species of nominally same mass
- Resolving power = mass / (change in mass of 2 species)
- MRP ~24,000
- Entrance slit of 5 microns
- Measured using 10^{12} ohm resistor



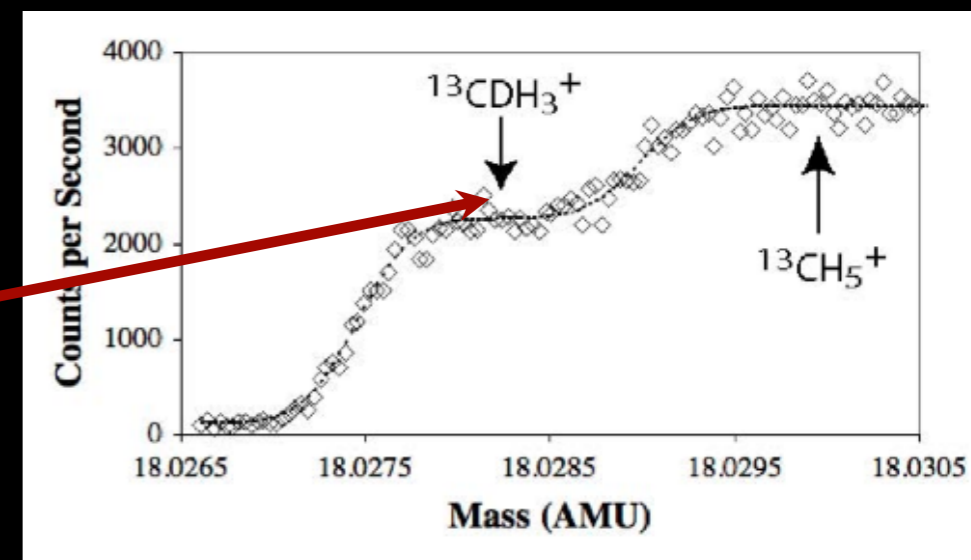
Mass Resolution



Resolving Power $\sim 24,000$

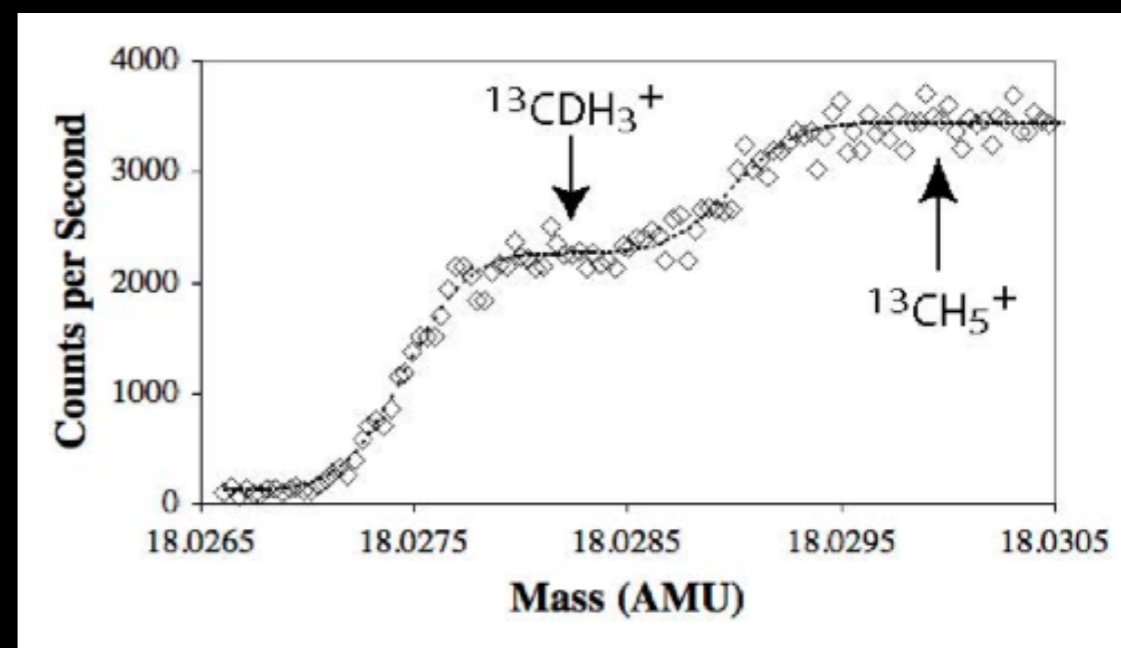
Precision (CH₄)

measurement type	standard error (per mil)	~counting statistics error	resolution
$^{13}\text{CH}_4/^{12}\text{CH}_4$	0.01	0.012	medium
$^{12}\text{CH}_5 + ^{12}\text{CH}_3\text{D}/^{12}\text{CH}_4$	0.046	0.044	high
$^{13}\text{CH}_3\text{D} + ^{13}\text{CH}_5 / ^{13}\text{CH}_4 + ^{12}\text{CH}_5$	0.404	0.346	high
$^{12}\text{CH}_3\text{D}/^{12}\text{CH}_4$	0.005	0.003	low
$^{13}\text{CH}_3\text{D}/^{12}\text{CH}_4$	0.252	0.085	low

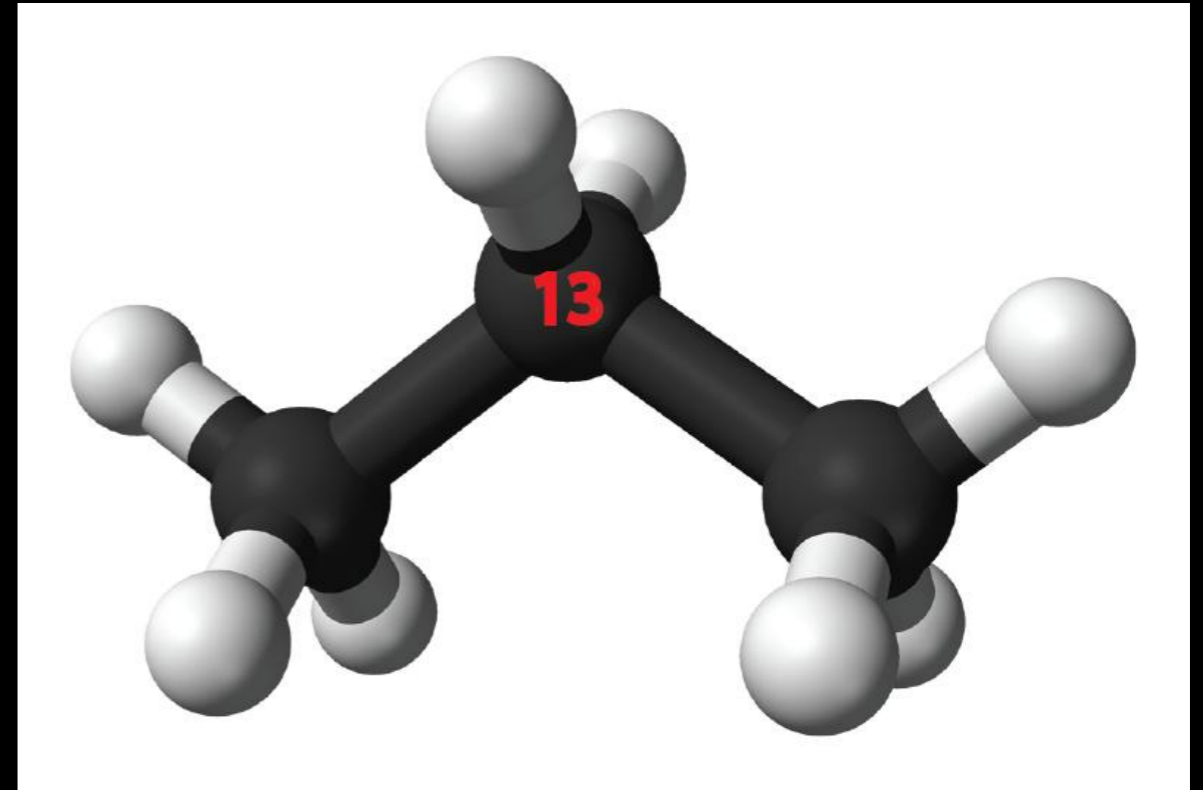
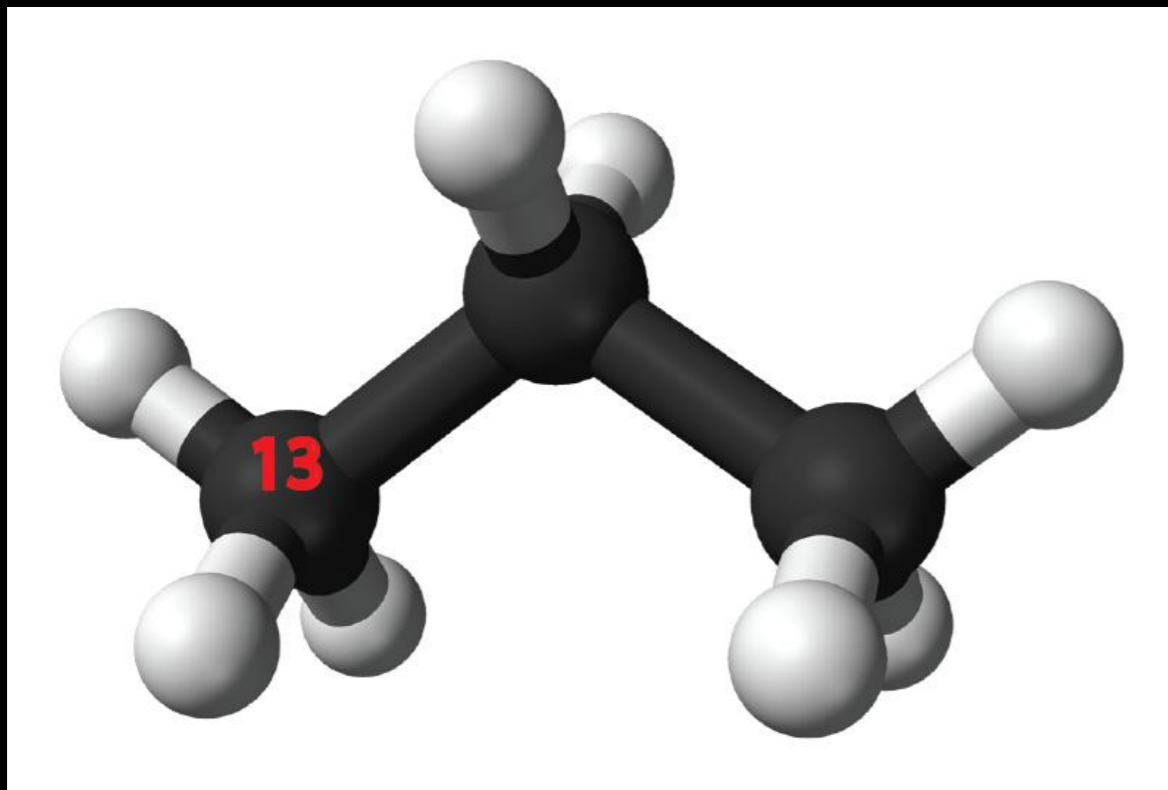


Reproducibility (CH₄)

measurement type	number of replicates	standard deviation	Standard Error 1 Measurement
$^{13}\text{CH}_4/^{12}\text{CH}_4$	2	0.029	0.01
$^{12}\text{CH}_3\text{D}/^{12}\text{CH}_4$	4	0.031	0.005
$^{13}\text{CH}_3\text{D}/^{12}\text{CH}_4$	4	0.414	0.252

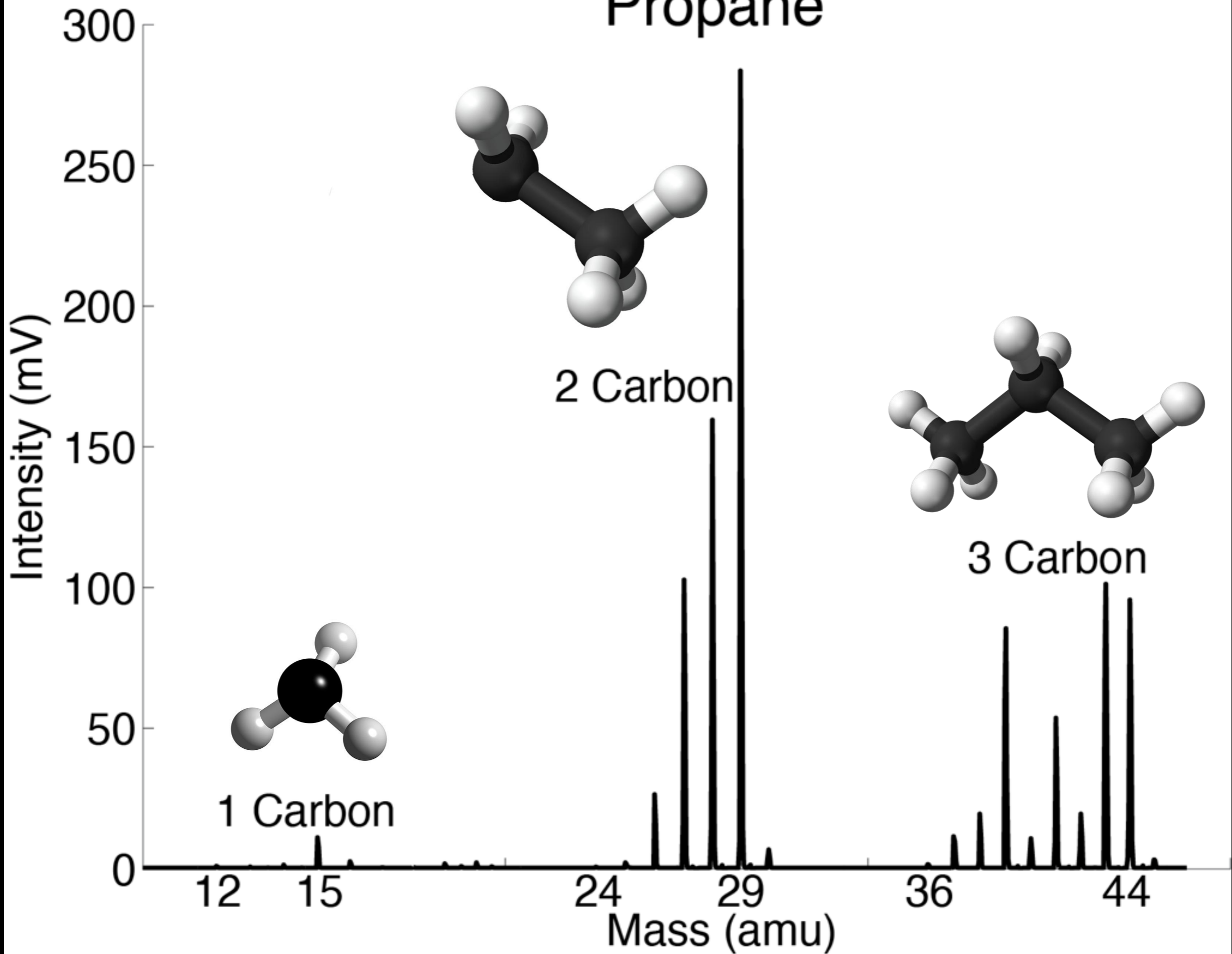


Position-Specific Propane

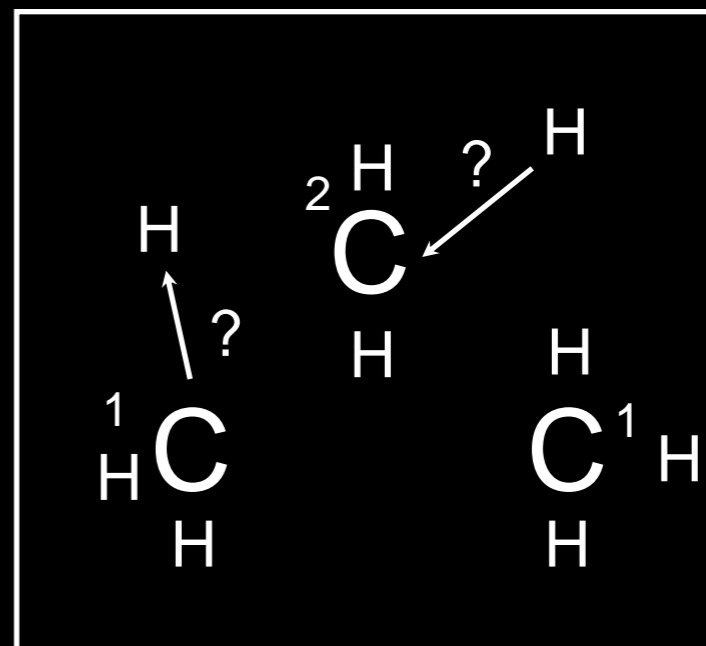
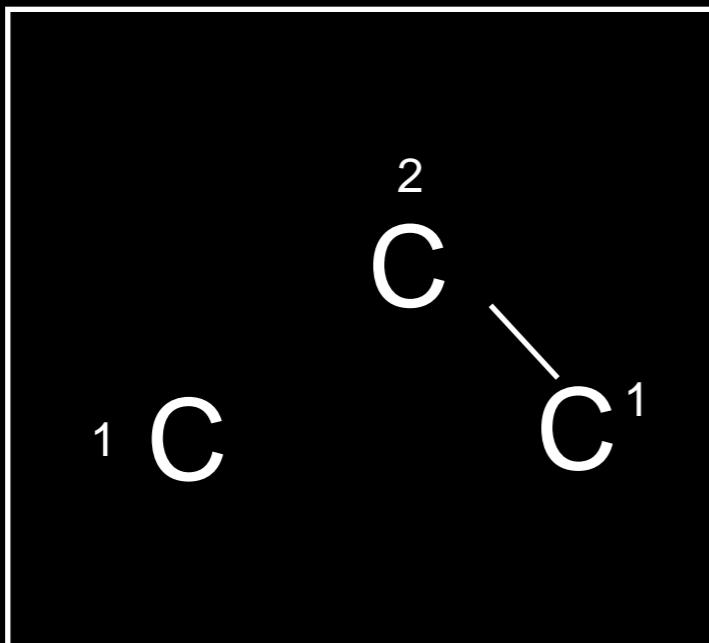
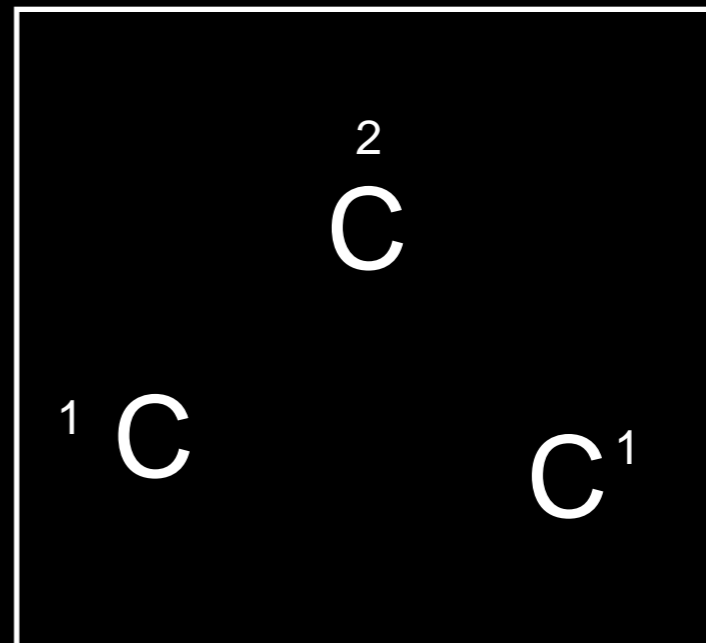
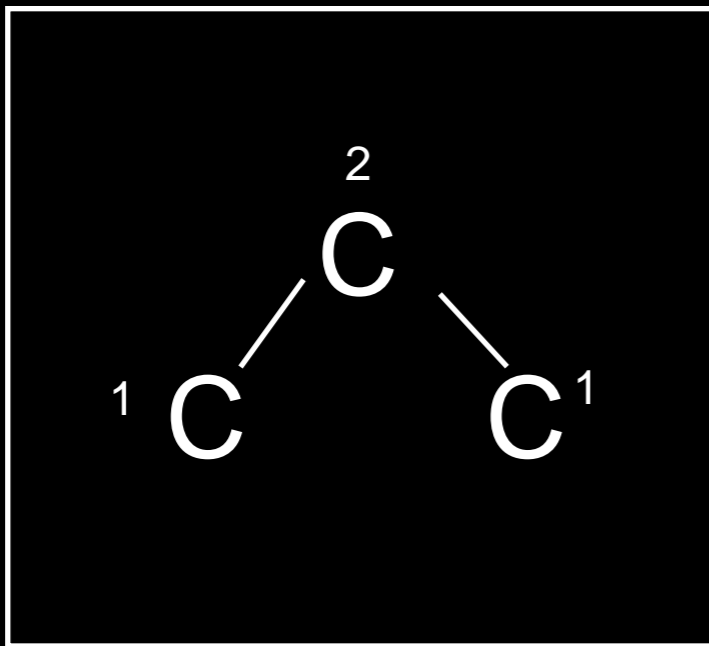


- Where do you preferentially get enrichment?
- Terminal or central carbon
- By measuring different groupings of fragments, get position specific enrichment

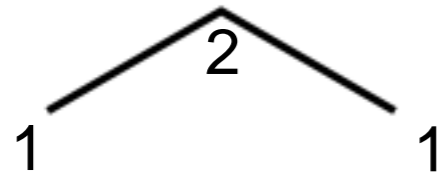
Propane



Measuring Carbon Ordering



How To Calculate Position Specific ^{13}C Content



$$[^{12}\text{C}]_1 + [^{13}\text{C}]_1 = 1$$

$$[^{12}\text{C}]_2 + [^{13}\text{C}]_2 = 1$$

$$X^{13}\text{C}_{\text{CH}_3} = \frac{^{13}\text{C}_{\text{H}_3}}{^{12}\text{C}_{\text{H}_3}}$$

$$X^{13}\text{C}_{\text{CH}_3} = \frac{[^{13}\text{C}]_1 * [\text{H}]^3}{[1 - [^{13}\text{C}]_1] * [\text{H}]^3}$$

$$X^{13}\text{C}_{\text{CH}_3} = \frac{[^{13}\text{C}]_1}{1 - [^{13}\text{C}]_1}$$

$$\text{C}_2\text{H}_5 = 2 * [\text{H}]^5 * [^{12}\text{C}]_1 * [^{12}\text{C}]_2$$

$$^{13}\text{C}^{12}\text{C}_{\text{H}_5} = 2 * [\text{H}]^5 * ([^{13}\text{C}]_1 * [^{12}\text{C}]_2 + [^{13}\text{C}]_2 * [^{12}\text{C}]_1)$$

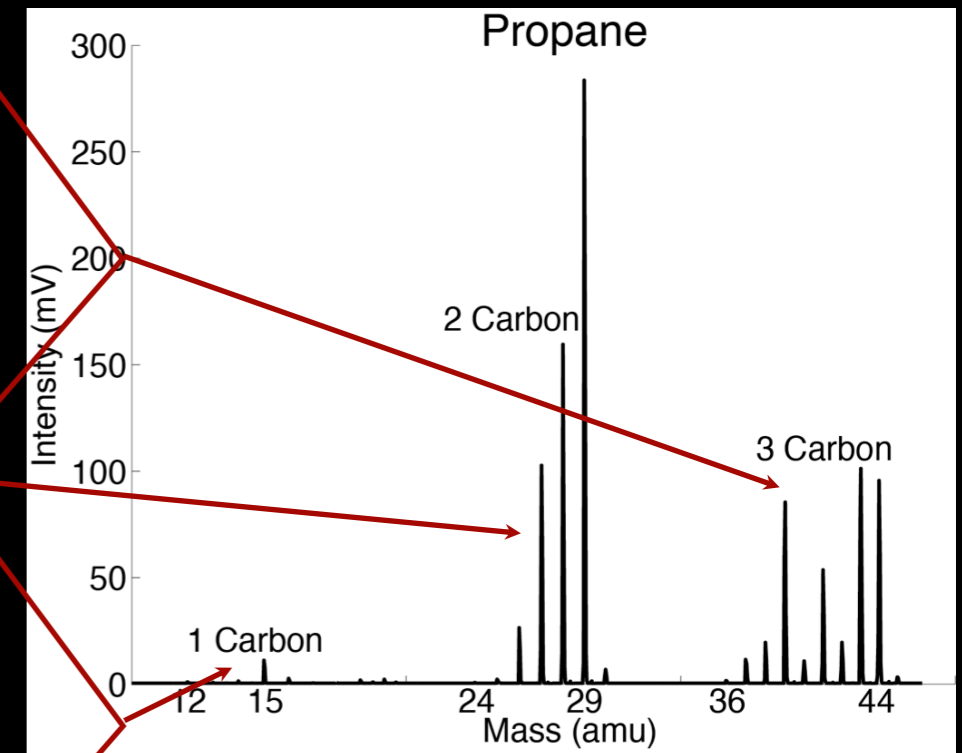
$$XC_2\text{H}_5 = \frac{[^{13}\text{C}]_1}{1 - [^{13}\text{C}]_1} + \frac{[^{13}\text{C}]_2}{1 - [^{13}\text{C}]_2}$$

$$XC_2\text{H}_5 - X\text{CH}_3 = \frac{[^{13}\text{C}]_2}{1 - [^{13}\text{C}]_2}$$

$$[^{13}\text{C}]_2 = \frac{XC_2\text{H}_5 - X\text{CH}_3}{1 + XC_2\text{H}_5 - X\text{CH}_3}$$

Preliminary Results: Propane

Species	Average	Average Standard Error
<i>45/44</i>	<i>-0.005</i>	<i>0.076</i>
<i>37/36</i>	<i>-0.471</i>	<i>0.570</i>
<i>29/28</i>	<i>-0.227</i>	<i>0.351</i>
<i>16/15</i>	<i>0.748</i>	<i>0.904</i>
<i>13/12</i>	<i>1.163</i>	<i>0.757</i>



- Zero enrichment measurements
- Most errors within 1 ‰
- Expected fractionations measuring : ~25 ‰

Previous Site Specific Measurements

Table 1
Carbon-isotope compositions of acetone and isopropanol (ppm)^a

Sample ^b	$\delta^{13}\text{C}_{\text{Pr}}^{\text{c}}$	$\delta^{13}\text{C}_{\text{EtOH}}^{\text{d}}$	$\delta^{13}\text{C}_{\text{Me}}^{\text{e}}$	$\delta^{13}\text{C}_{\text{CO}}^{\text{f}}$	Δ^{g}
A	-29.41 ± 0.15	-31.04 ± 0.31	-26.16 ± 1.06	-35.93 ± 1.68	9.77 ± 2.74
B	-28.99 ± 0.24	-30.74 ± 0.36	-25.49 ± 1.43	-35.98 ± 2.15	10.49 ± 3.58
C	-30.30 ± 0.16	-30.39 ± 0.33	-30.11 ± 1.15	-30.67 ± 1.83	0.56 ± 2.98
D	-27.49 ± 0.38	-27.61 ± 0.23	-27.46 ± 1.61	-27.95 ± 2.07	0.69 ± 3.68
E	-24.57 ± 0.31	-24.21 ± 0.29	-25.28 ± 1.52	-23.15 ± 2.10	-2.13 ± 3.61
F	-28.12 ± 0.12	-28.74 ± 0.58	-26.88 ± 1.52	-30.60 ± 2.78	3.71 ± 4.30
G	-30.75 ± 0.60	-30.77 ± 0.13	-30.73 ± 2.06	-30.80 ± 2.32	-0.07 ± 4.38
H	-29.70 ± 0.35	-33.45 ± 0.44	-22.19 ± 1.95	-44.71 ± 2.83	22.52 ± 4.78
I	-29.63 ± 0.21	-31.16 ± 0.23	-26.56 ± 1.10	-35.76 ± 1.56	9.20 ± 2.65
J	-27.10 ± 0.48	-30.21 ± 0.41	-20.87 ± 2.27	-39.56 ± 3.10	18.70 ± 5.37

^a All data are reported in $\delta^{13}\text{C}_{\text{PDB}}$ (‰) and from means of 10 determinations.

^b Samples A–E are acetone, F–J are isopropanol. Samples were obtained from Merck, Adrich, Riedel-de Haen, Tokyo, Mallinckrodt and Katayama.

^c $\delta^{13}\text{C}_{\text{Pr}}$ = measured $\delta^{13}\text{C}$ values of acetone or isopropanol = $1/3(2\delta^{13}\text{C}_{\text{Me}} + \delta^{13}\text{C}_{\text{CO}})$.

^d $\delta^{13}\text{C}_{\text{EtOH}}$ = measured $\delta^{13}\text{C}$ value of ethanol = $1/2(\delta^{13}\text{C}_{\text{Me}} + \delta^{13}\text{C}_{\text{CO}})$.

^e $\delta^{13}\text{C}_{\text{Me}}$ = calculated $\delta^{13}\text{C}$ value of methyl-carbon = $3\delta^{13}\text{C}_{\text{Pr}} - 2\delta^{13}\text{C}_{\text{EtOH}}$.

^f $\delta^{13}\text{C}_{\text{CO}}$ = calculated $\delta^{13}\text{C}$ value of oxygenated-carbon = $4\delta^{13}\text{C}_{\text{EtOH}} - 3\delta^{13}\text{C}_{\text{Pr}}$.

^g $\Delta = \delta^{13}\text{C}_{\text{Me}} - \delta^{13}\text{C}_{\text{CO}}$.

Future Work

- Measure site specific enrichment in propane and larger alkanes
- Calibrate 'clumped' thermometers for different species (with H and C enrichment)
- Calibrate recombination and fragmentation within the source