

GC/C-IRMS: Potentials and Pitfalls

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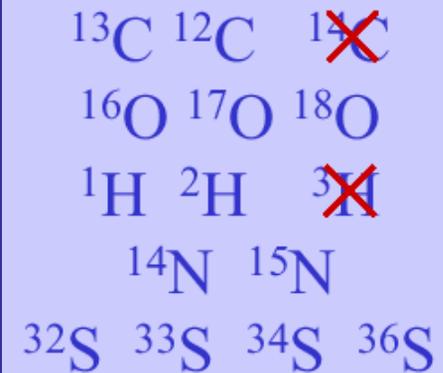
Background - I

Whole earth isotope ratios are fixed, determined at planet formation.

Fractionation processes (= mass discrimination) lead to subtle variation in isotopic abundance.

Isotope ratio mass spectrometers can measure isotopic abundance with high degree of accuracy and precision.

About 1000 labs world-wide are engaged in bulk and compound specific isotope analysis.

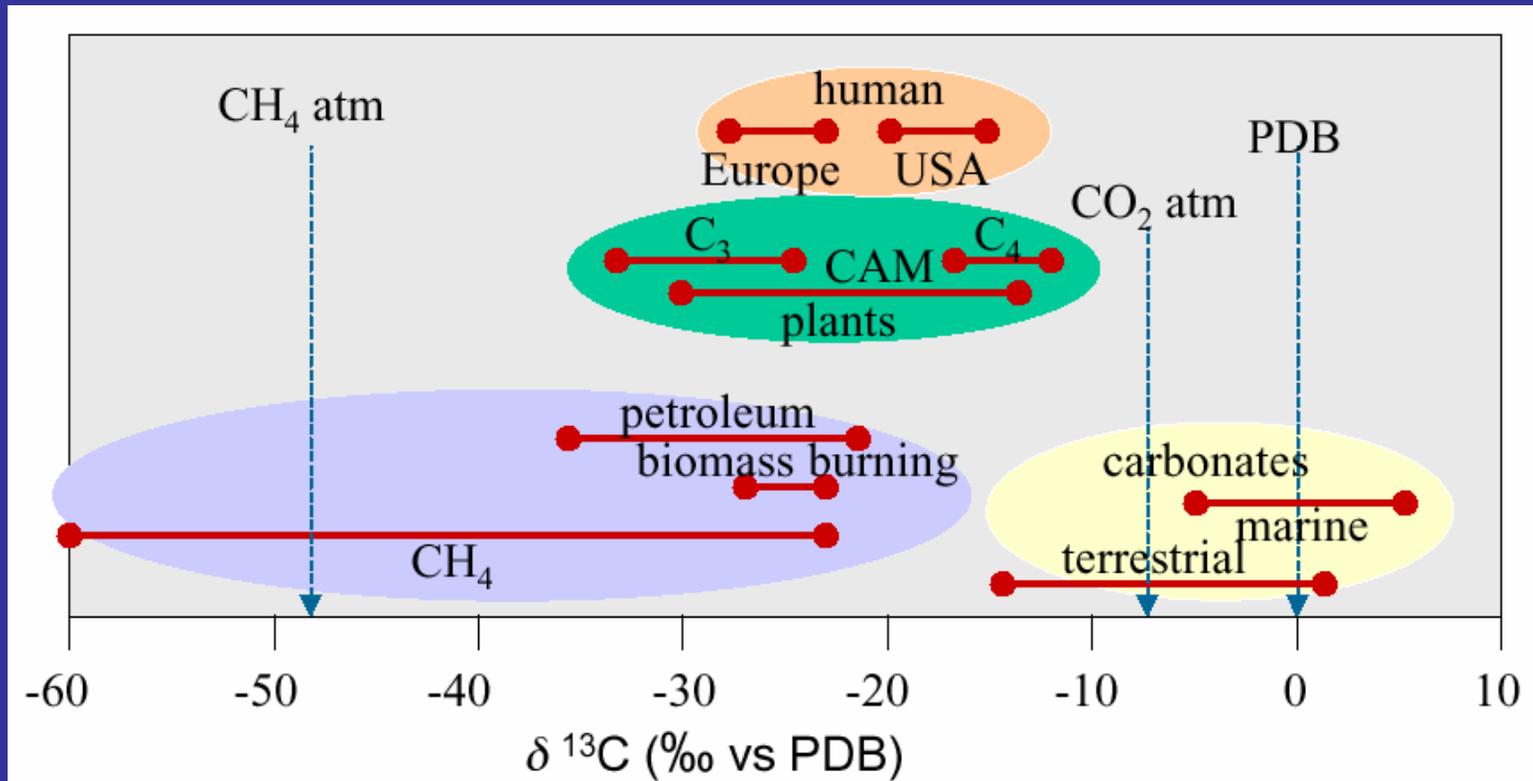


Background - II

Mass Discrimination in Nature

- For a more convenient way of expressing small variations in isotopic abundance, the δ -notation has been adopted with units of parts per mil [‰].

$$R = \frac{^{13}\text{C}}{^{12}\text{C}}$$
$$\delta^{13}\text{C}(\text{‰}) = \left[\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right] \times 10^3$$



Background - III

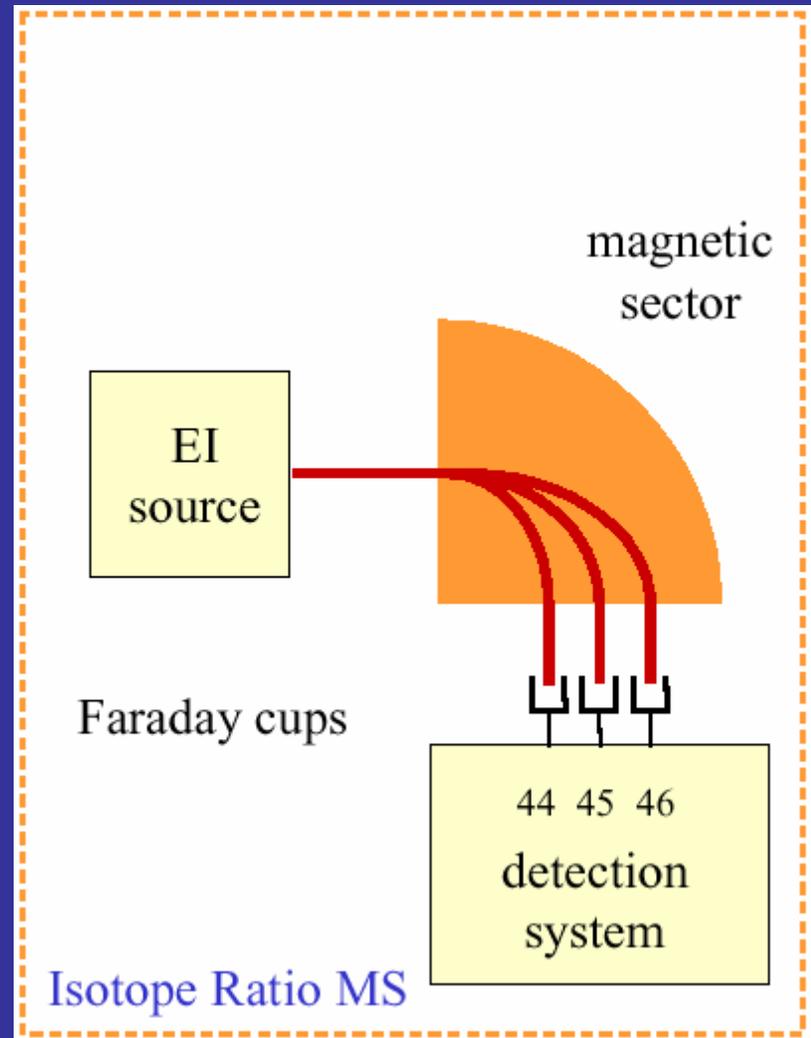
Gas Isotope-Ratio Mass Spectrometers

Single focusing magnetic sector instruments.

Isotopomers are detected by a multi-collector array continuously and simultaneously.

Isotopic abundance is measured with high degree of accuracy and precision.

Samples have to be converted into simple gases, i.e. CO_2 , N_2 , CO , H_2 and SO_2 .



Murphy's Law and related Pitfalls

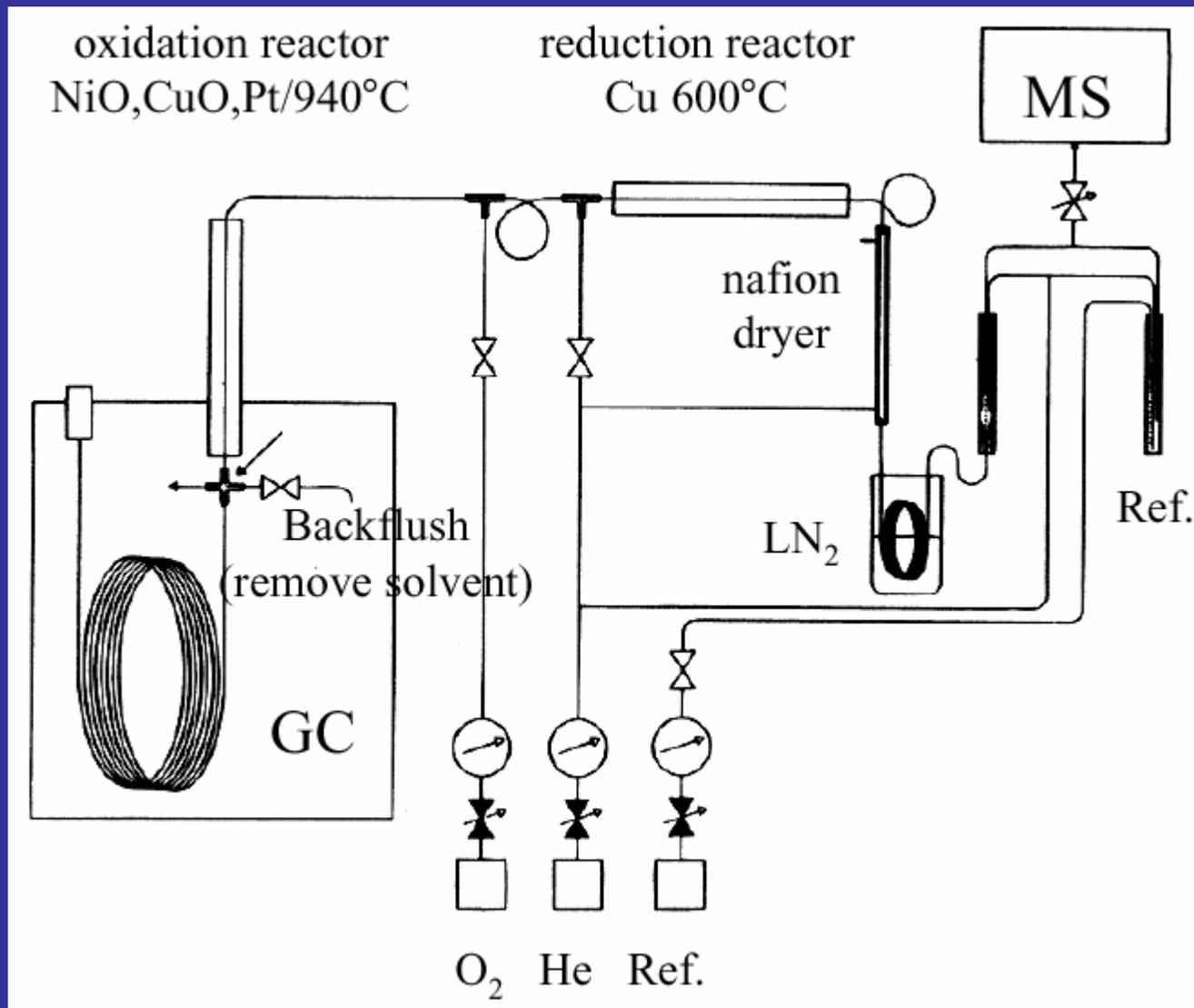
- If something can go wrong, it will.
- Any error or mistake that can creep in will do so; it will then propagate in the direction that will cause the most detrimental effect to one's IRMS analysis.
- A newly purchased IRMS instrument will meet its specification long enough, and only long enough to pass installation by the engineer.

More Pitfalls

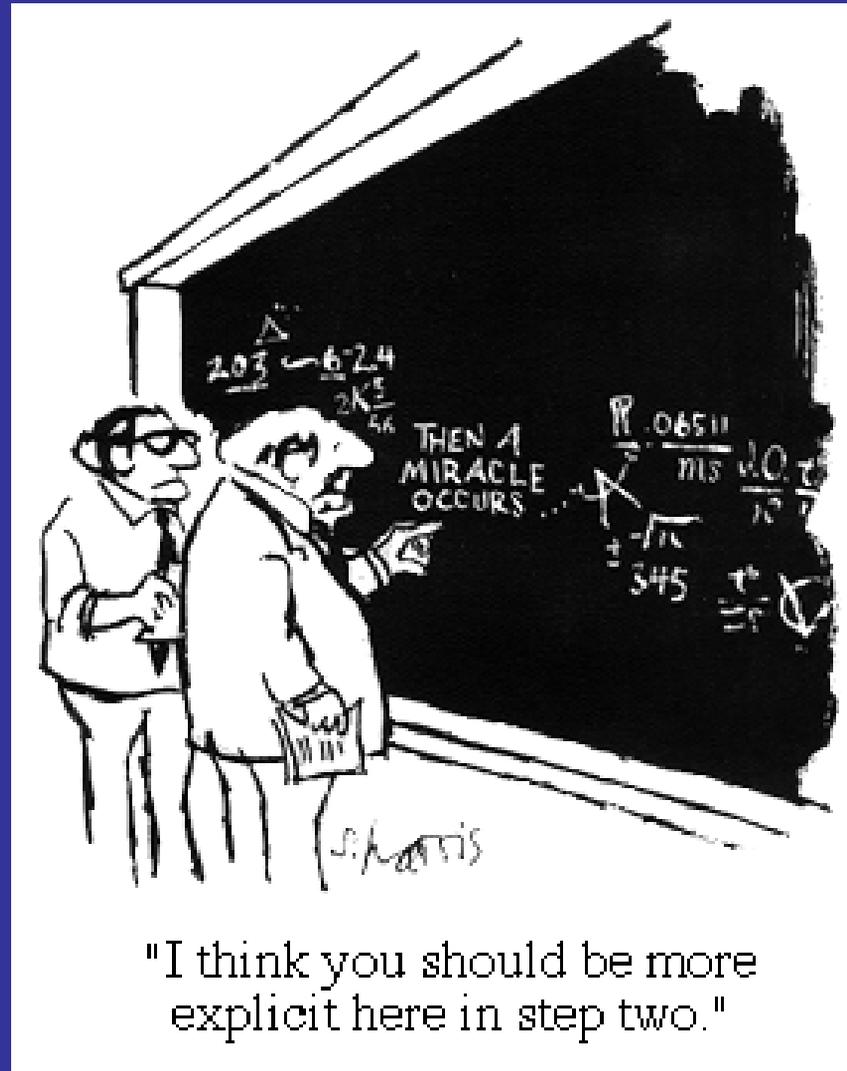
- Staff's attitude towards operation and maintenance of GC/C-IRMS instruments.
- **Your** anticipation of **ideal** staff and attitude towards operation and maintenance of GC/C-IRMS instruments.



Schematic of a GC/C-IRMS



The Missing Link



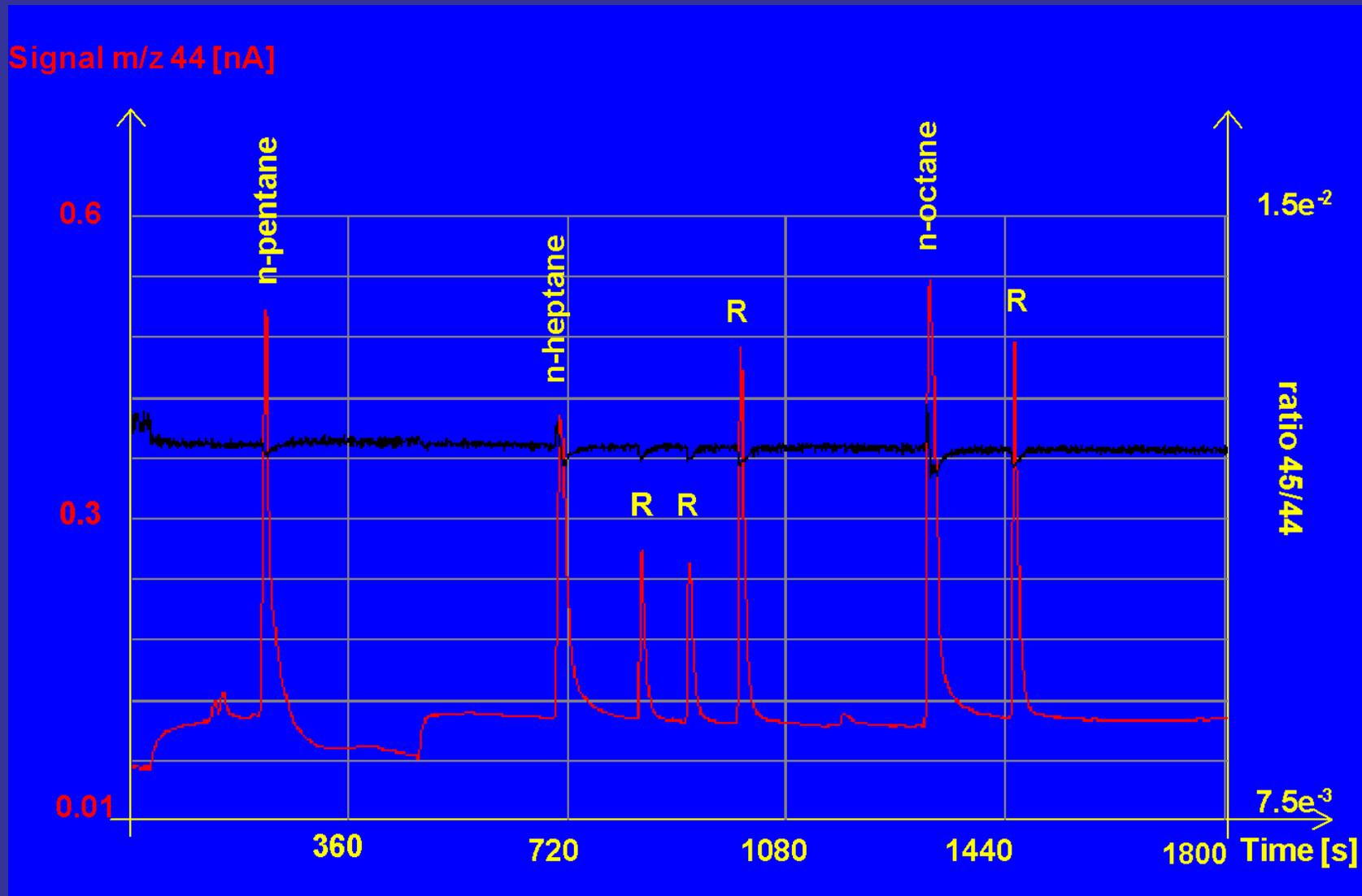
Pitfalls Hampering Accurate Compound Specific Isotope Analysis (CSIA)

- Mass discrimination (isotopic fractionation).
- Derivatisation.
- Non-representative isotopic calibration.
- Insufficient peak resolution.

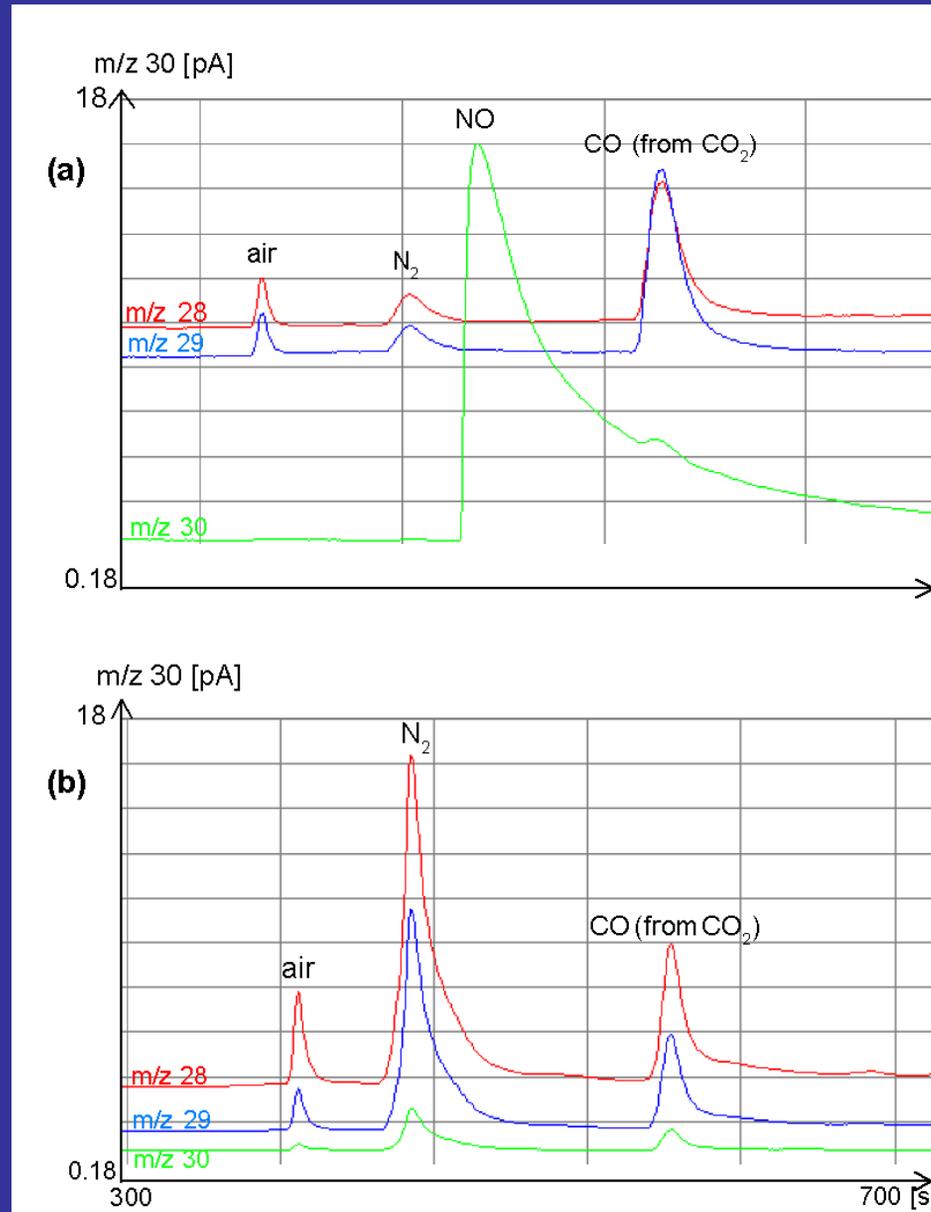
Sources of Mass Discrimination

- Sampling and sample preparation.
- Sample injection on to the GC.
- Chromatographic isotope effect.
- Non-quantitative compound conversion into CO_2 , N_2 or CO .
- Peak distortion and peak overlap as a result of passage through the combustion interface.

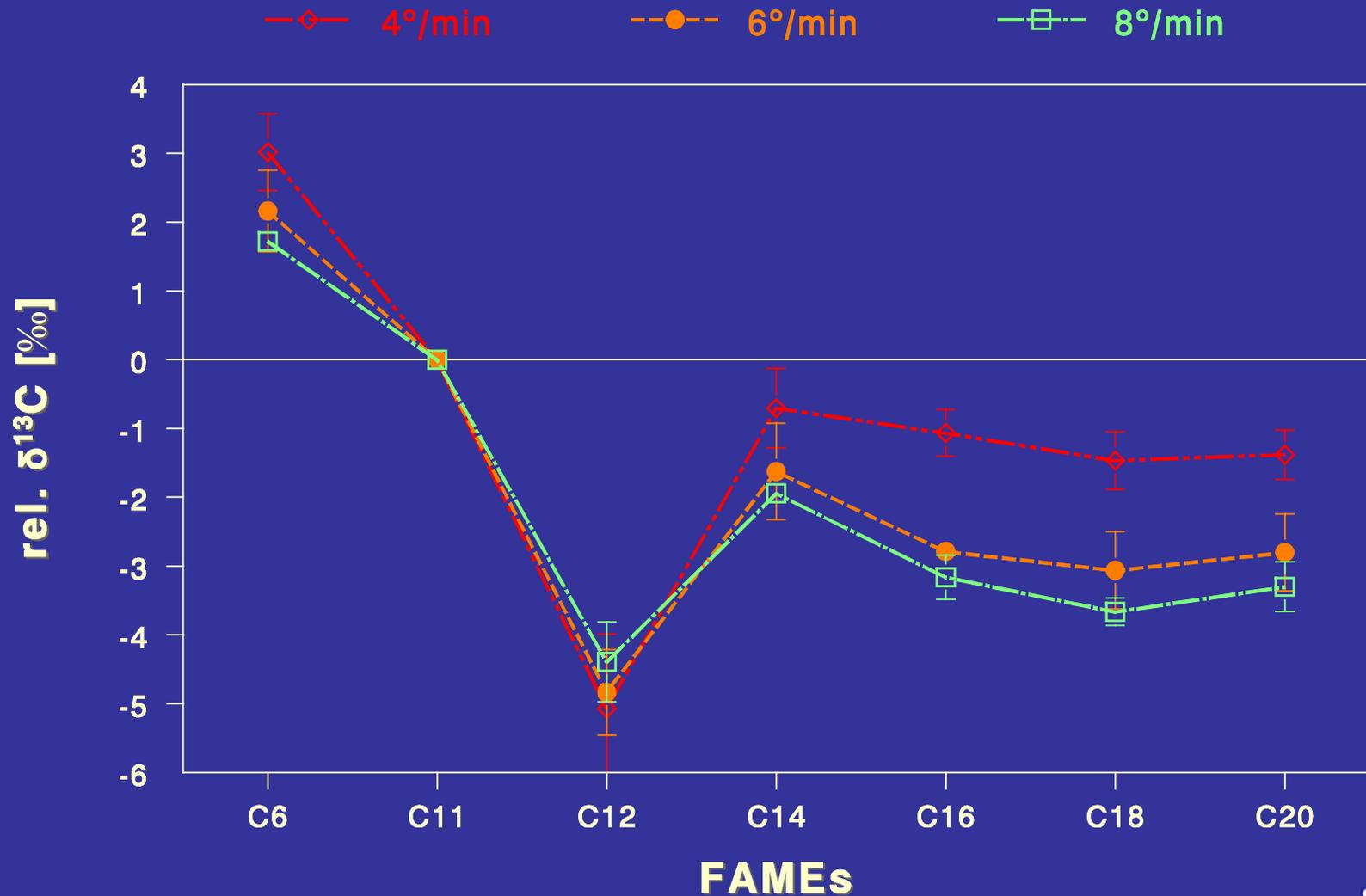
Quantitative Sample Conversion



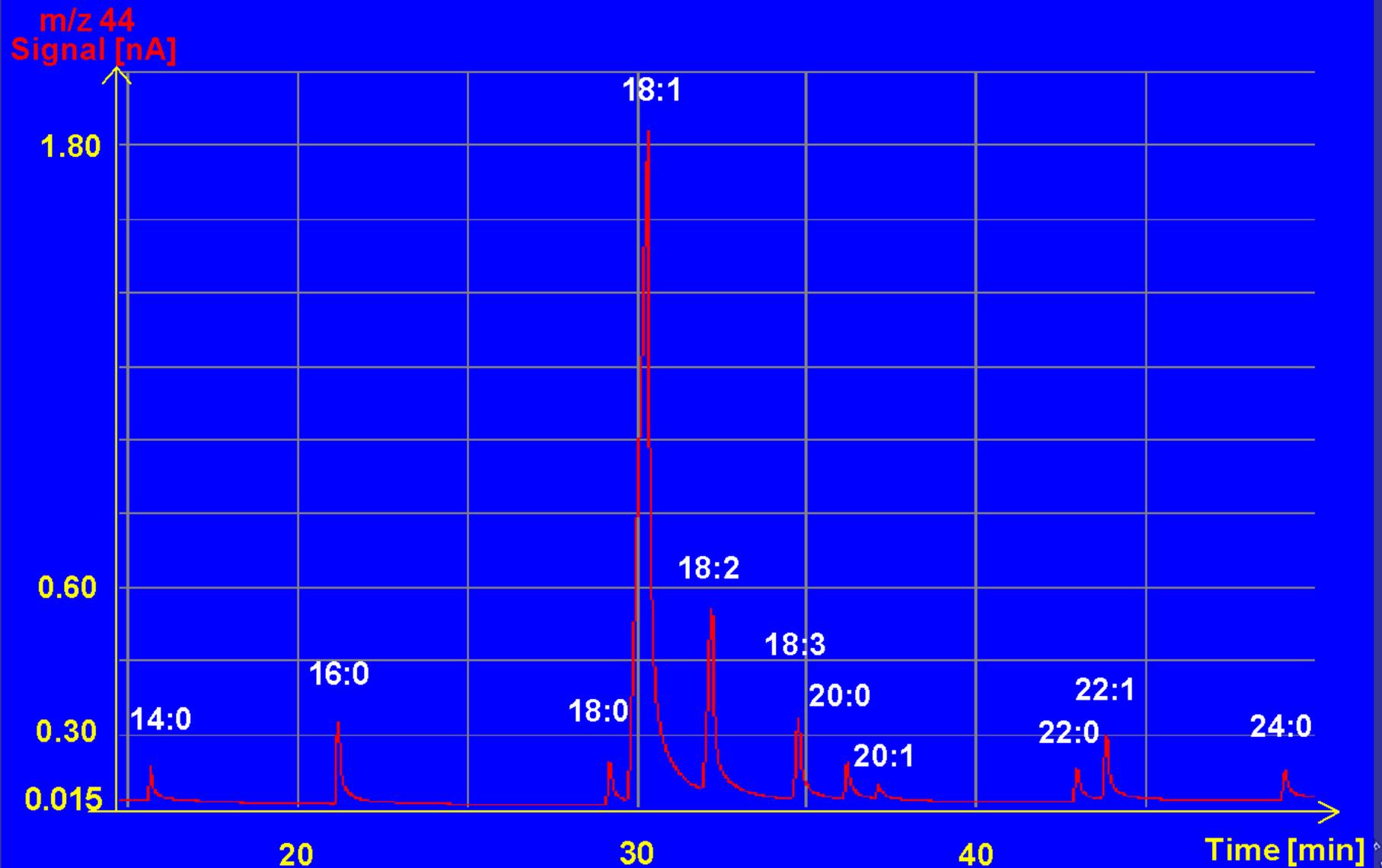
"Ambiguous" Sample Conversion



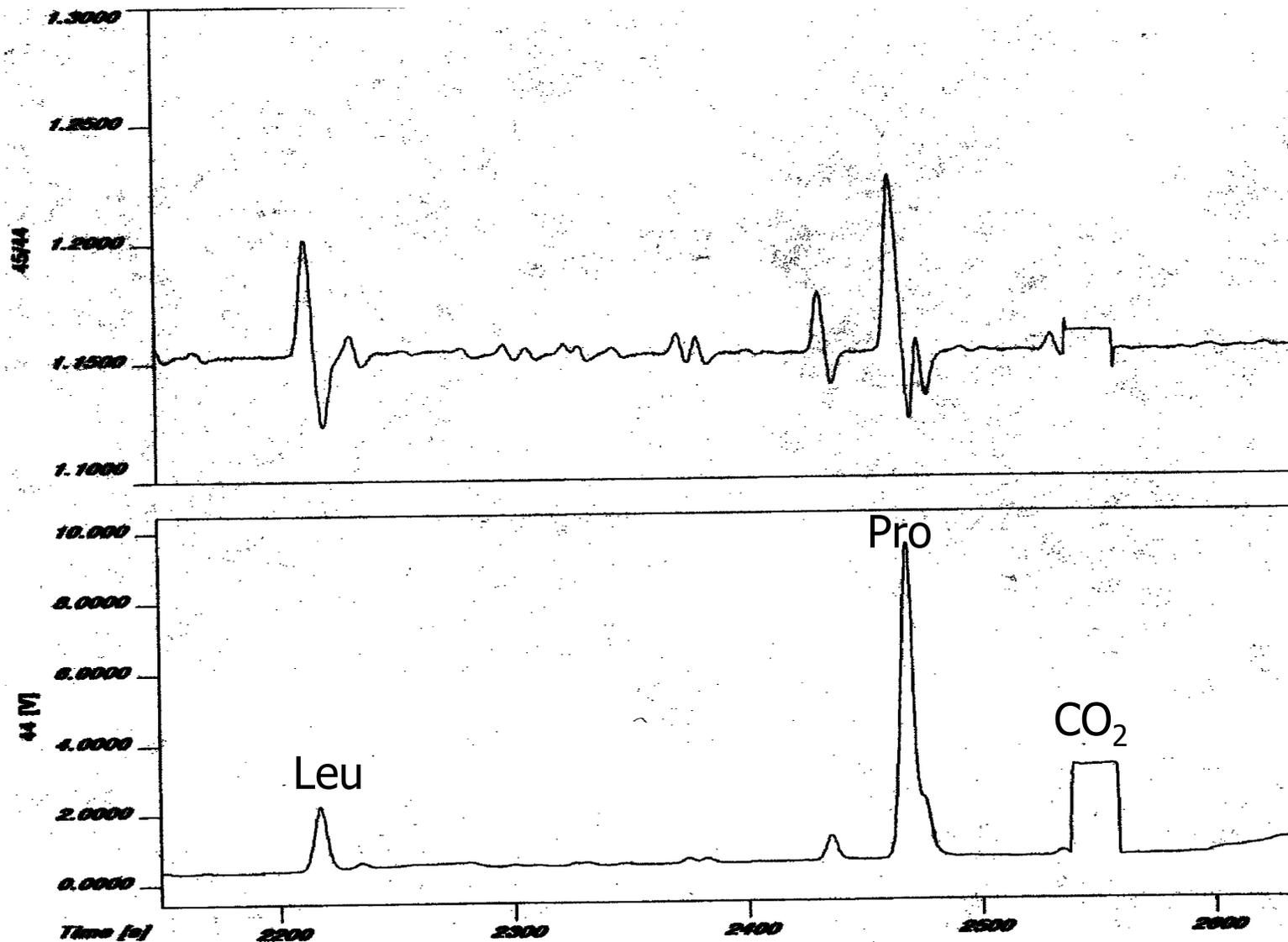
Non-Representative Isotopic Calibration



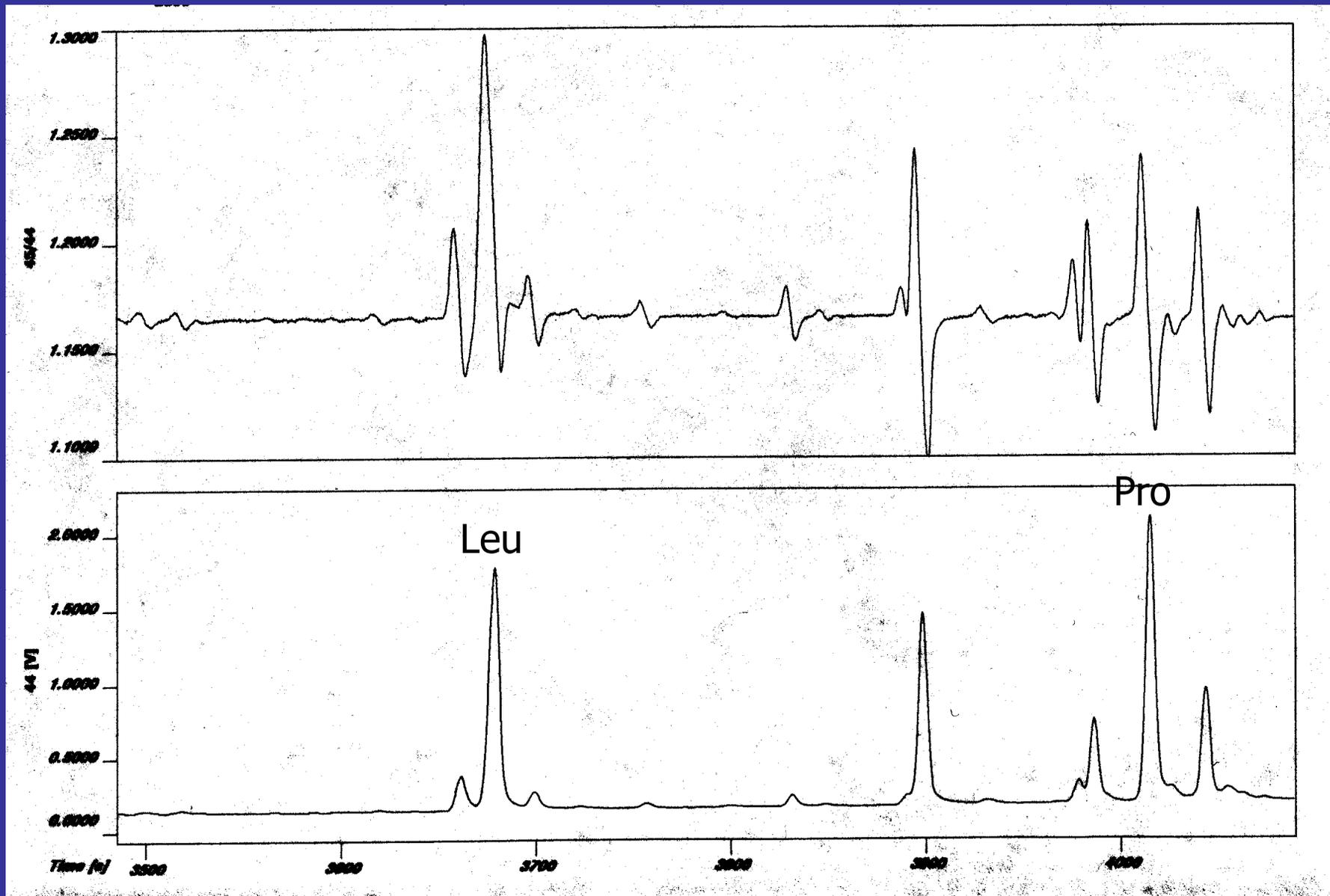
Insufficient Peak Resolution



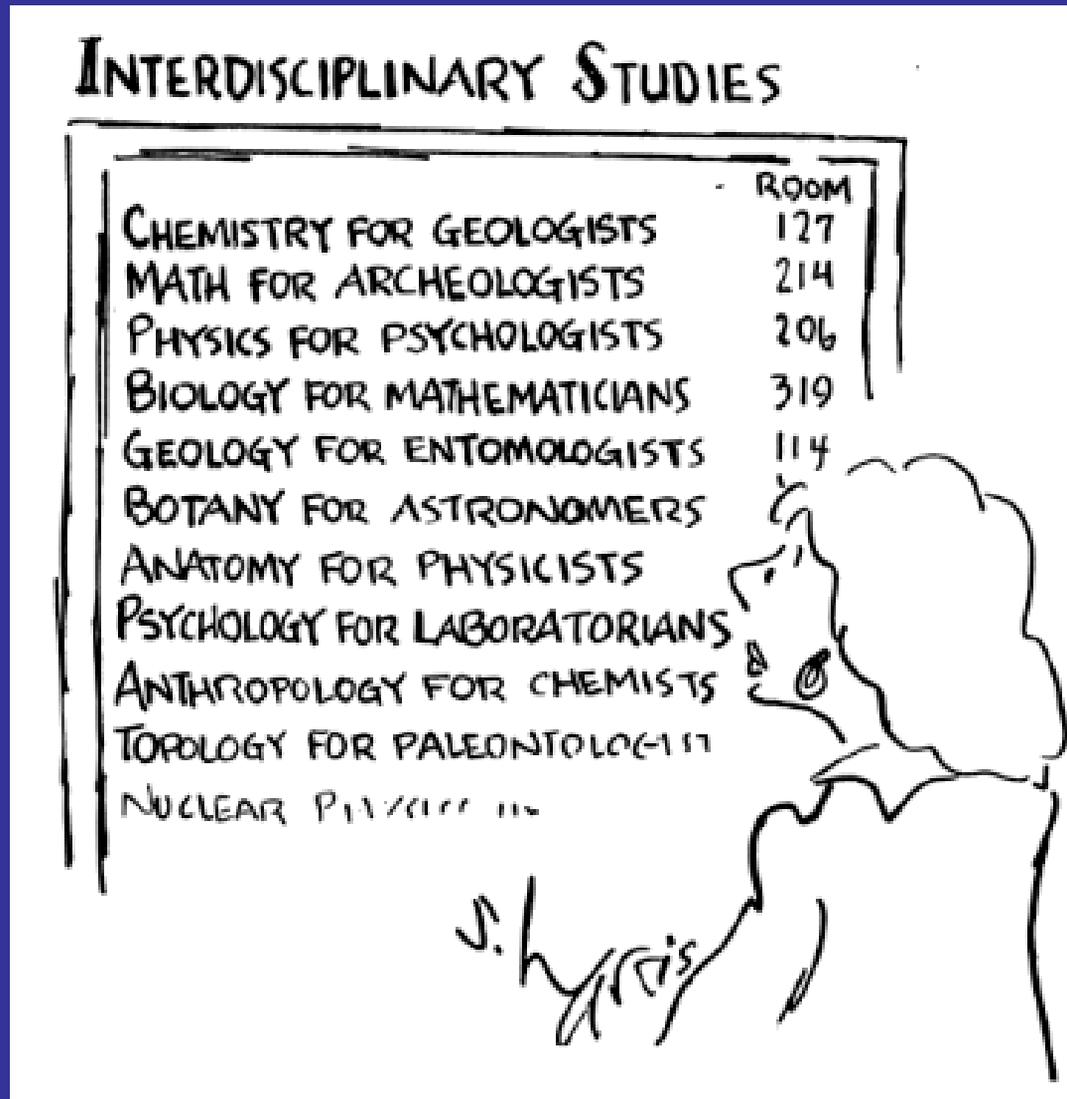
^{13}C -Analysis of Amino Acids from Bone Collagen - before -



^{13}C -Analysis of Amino Acids from Bone Collagen - after -



CSIA Requires Interdisciplinary Skills



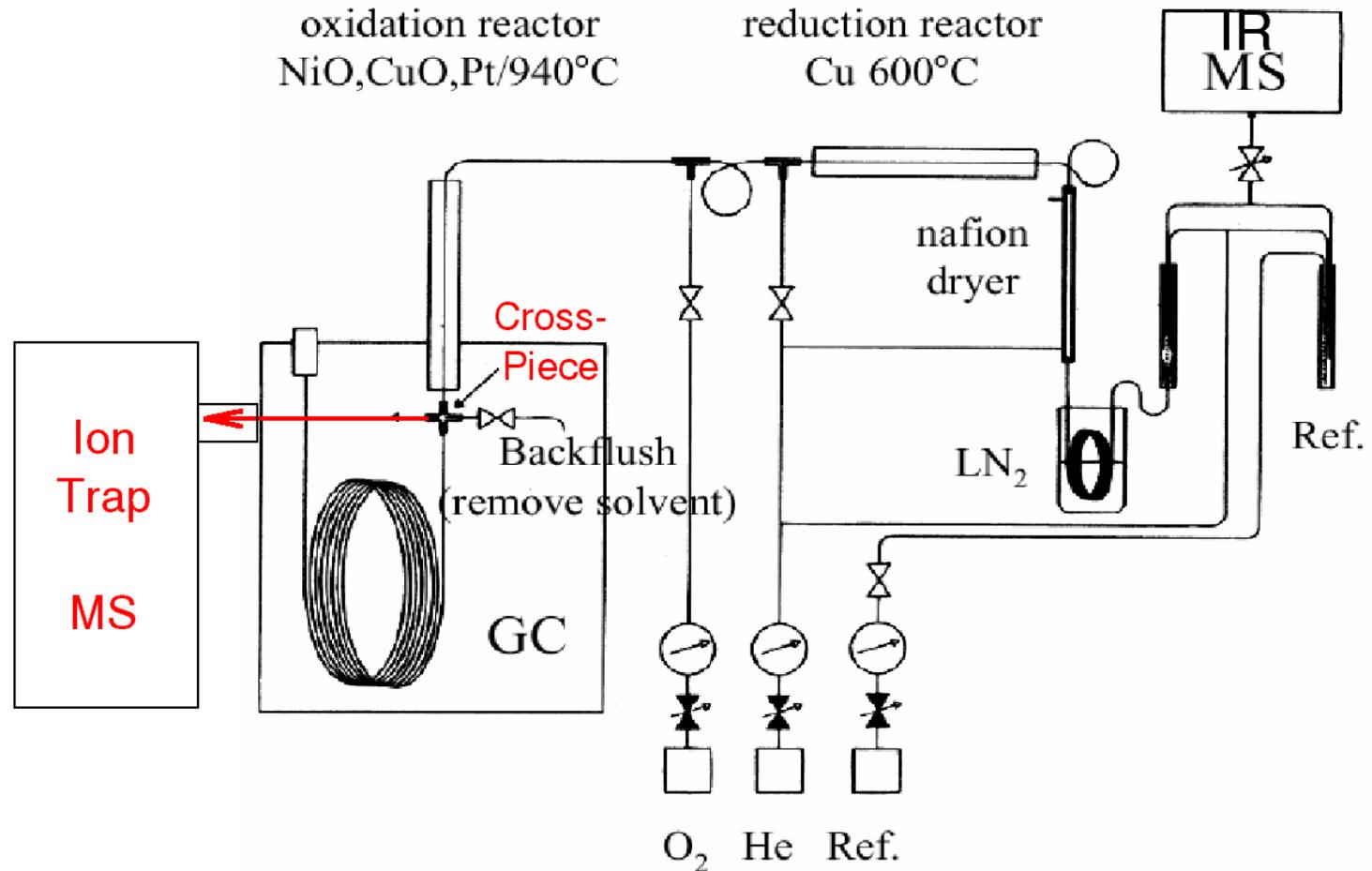
Potential of GC/C-IRMS - I

- Accurate and precise CSIA of bio-organic and man-made organic compounds to identify origin and source.
- Alcohol, sugar, organic acids, fatty acids, amino acids.
 - ✘ Food authenticity; source of ethanol; geographic origin.
- Alkaloids and derivatives.
 - ✘ Origin and source of narcotic drugs.
- Nitrogenous organic compounds.
 - ✘ Origin and source of organic explosives.

Potential of GC/C-IRMS - II

- Terpenoids.
 - ✘ Origin of flavours and perfumes.
- Steroids.
 - ✘ Doping control in athletics and sports.
- Hydrocarbons and PAHs.
 - ✘ Maturity of oil / gas; environmental control.
- Hydrocarbons, organic solvents and co-solvents.
 - ✘ Arson investigation: origin / manufacture, batch identification.

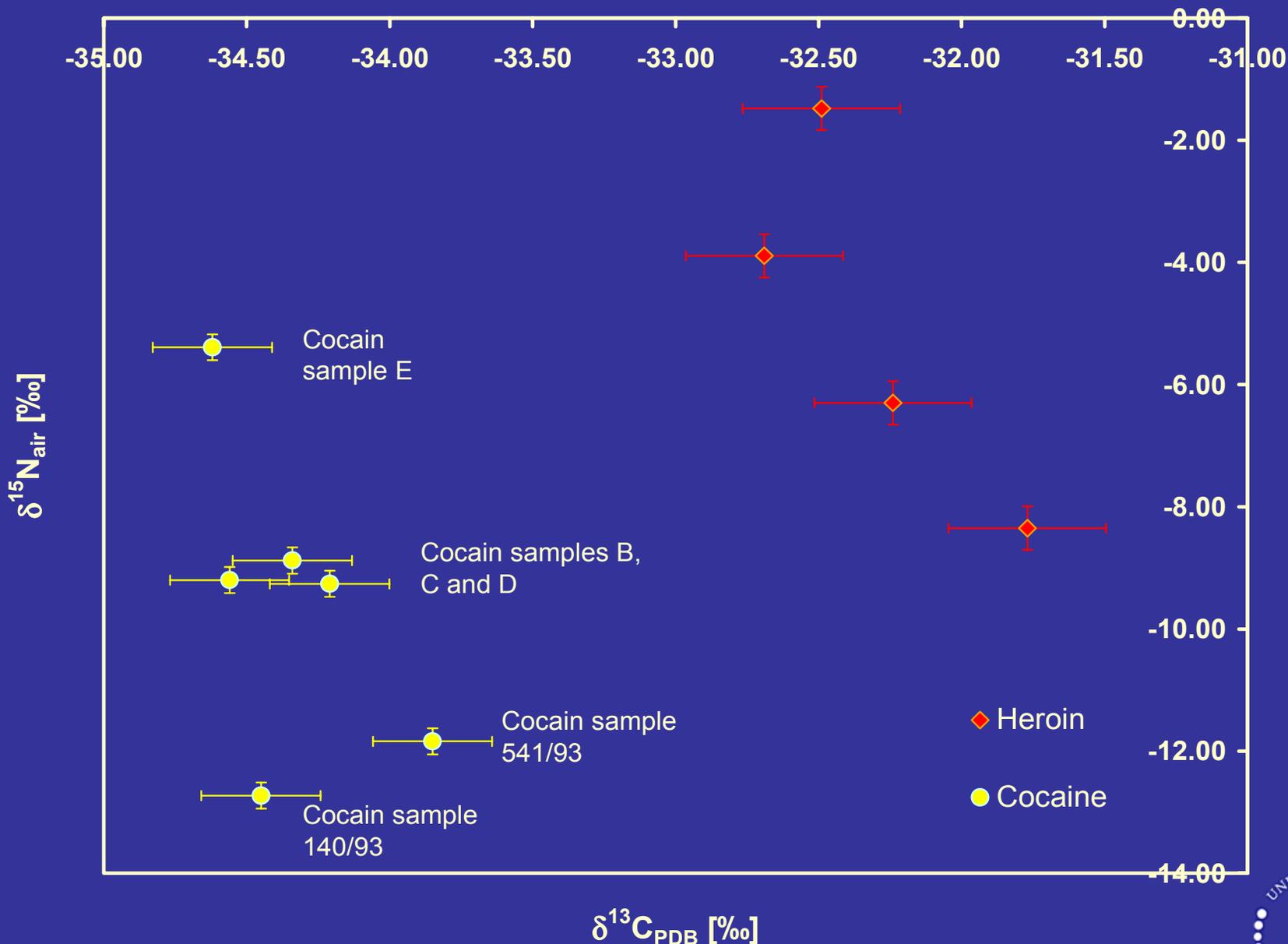
Schematic of GC[-MS]/C-IRMS Hybrid



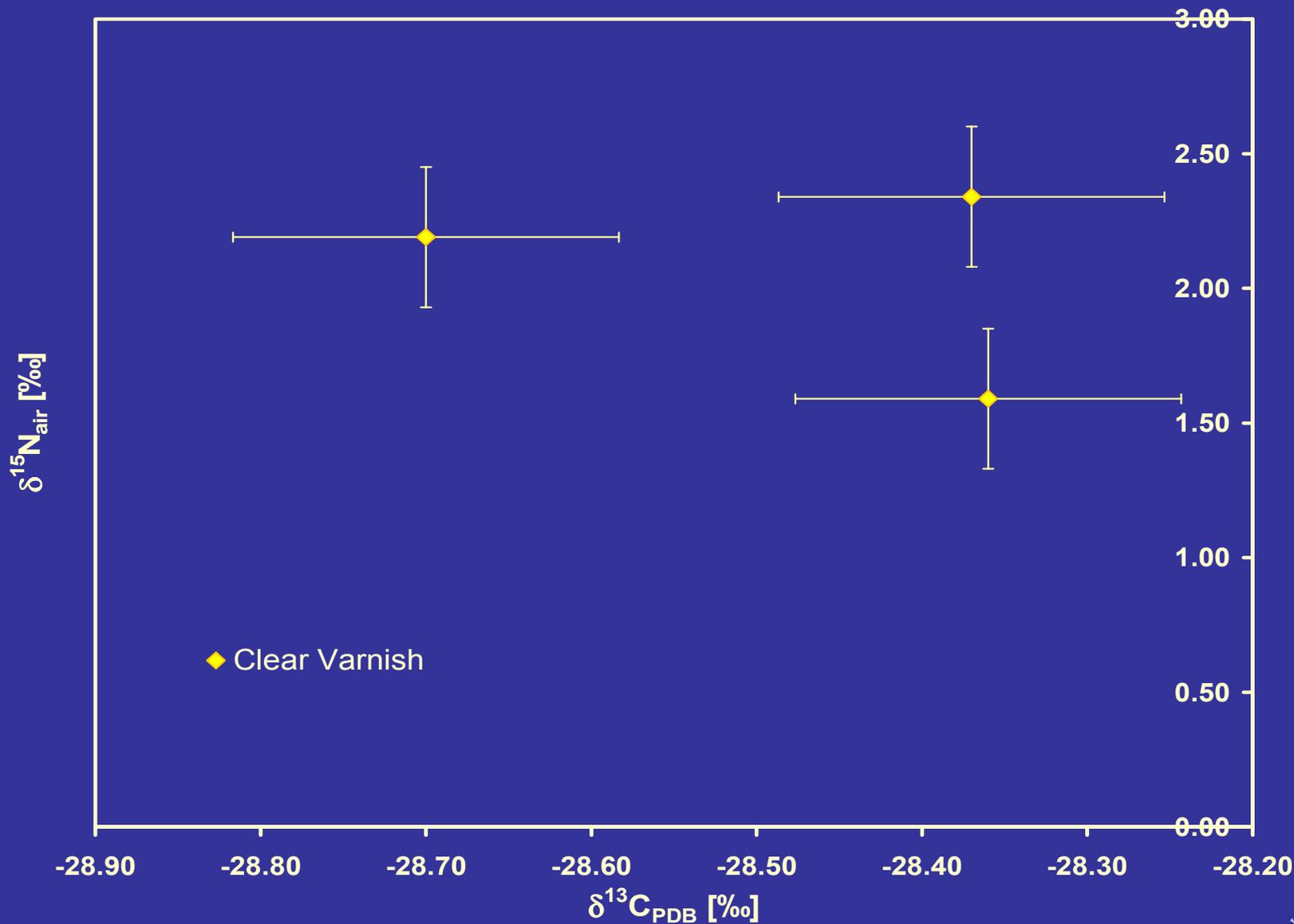
Reasons for Ion Trap/IRMS Hybrid

- Combining isotopic analysis with simultaneous identification of sample constituents thus avoiding any ambiguity in peak identity.
- High sensitivity and, hence, minute sample requirement of Ion Trap MS.
- MS/MS capability of Ion Trap MS.
- Highly cost-effective method of analysis.

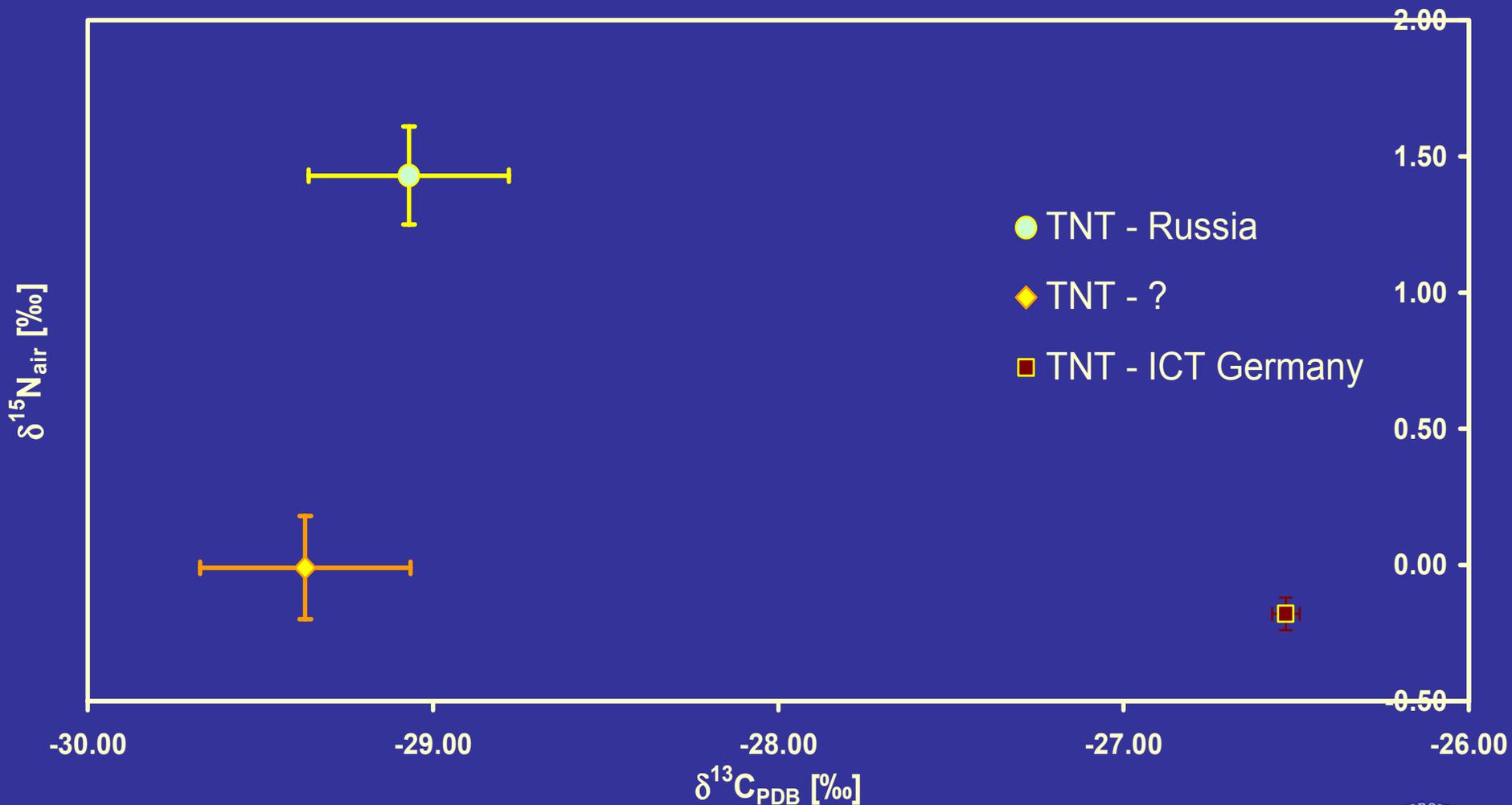
$^{13}\text{C}/^{15}\text{N}$ Fingerprinting of Drugs



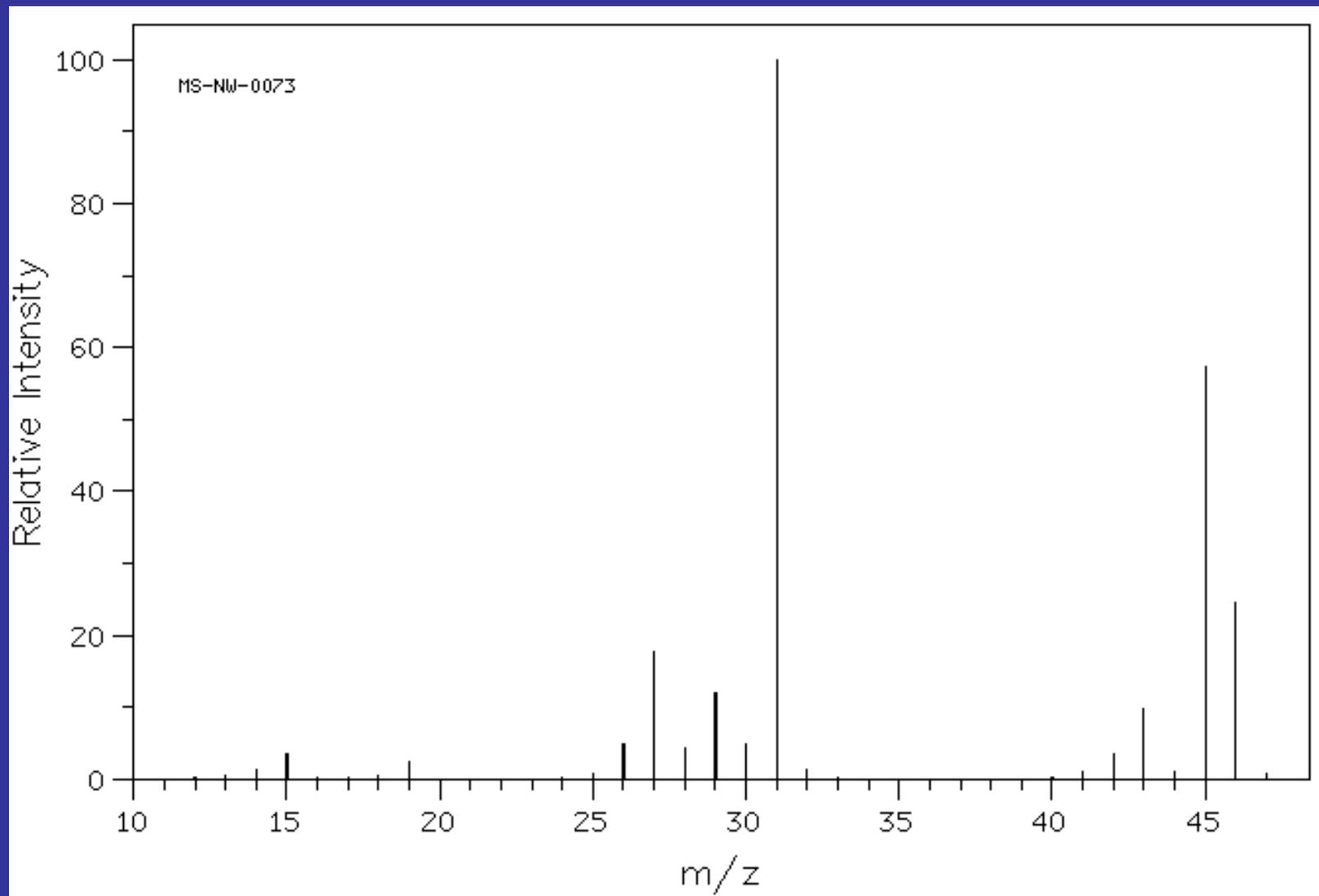
$^{13}\text{C}/^{15}\text{N}$ Fingerprinting of Potential Accelerants



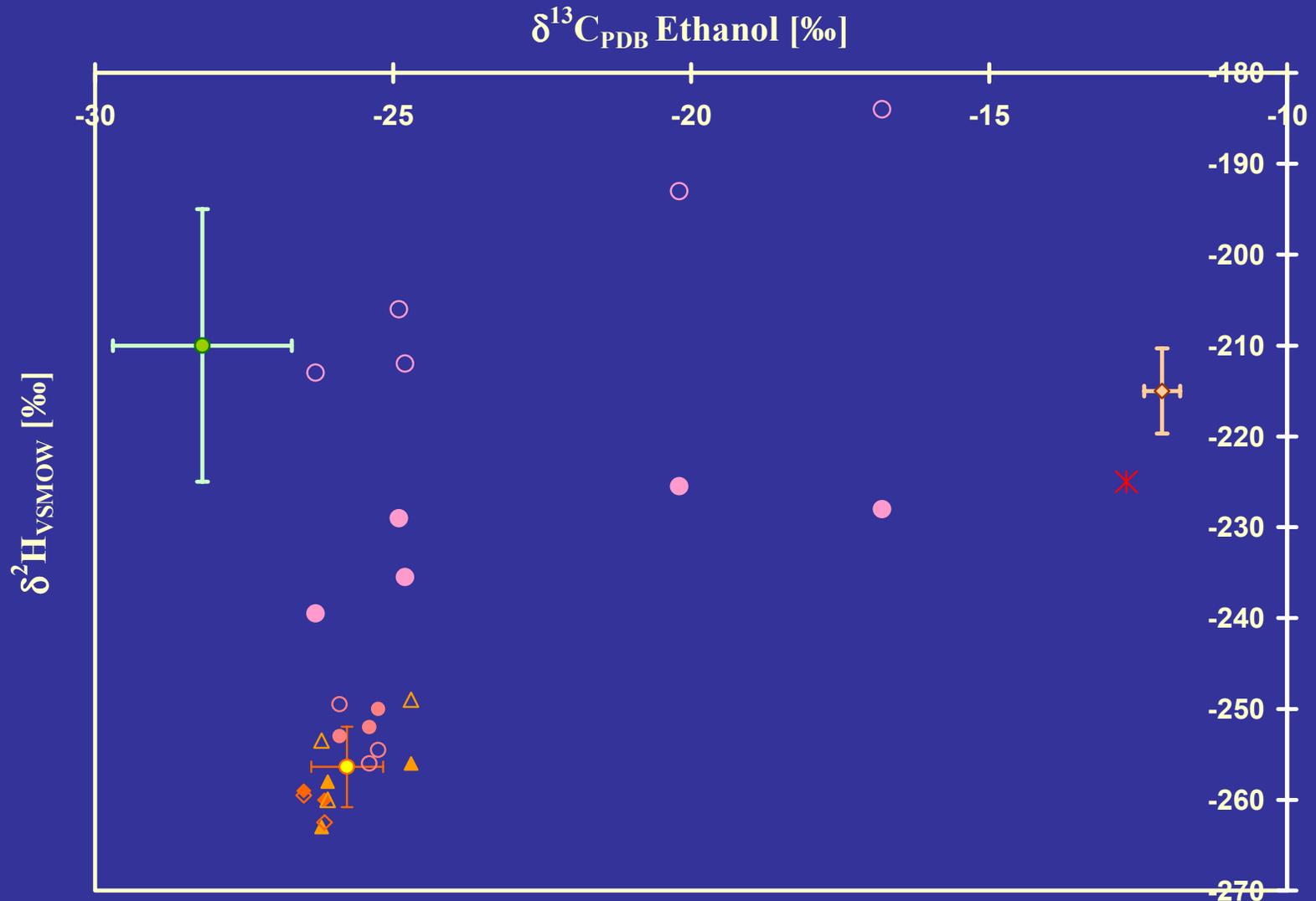
$^{13}\text{C}/^{15}\text{N}$ Fingerprinting of Explosives



EI-MS of Ethanol

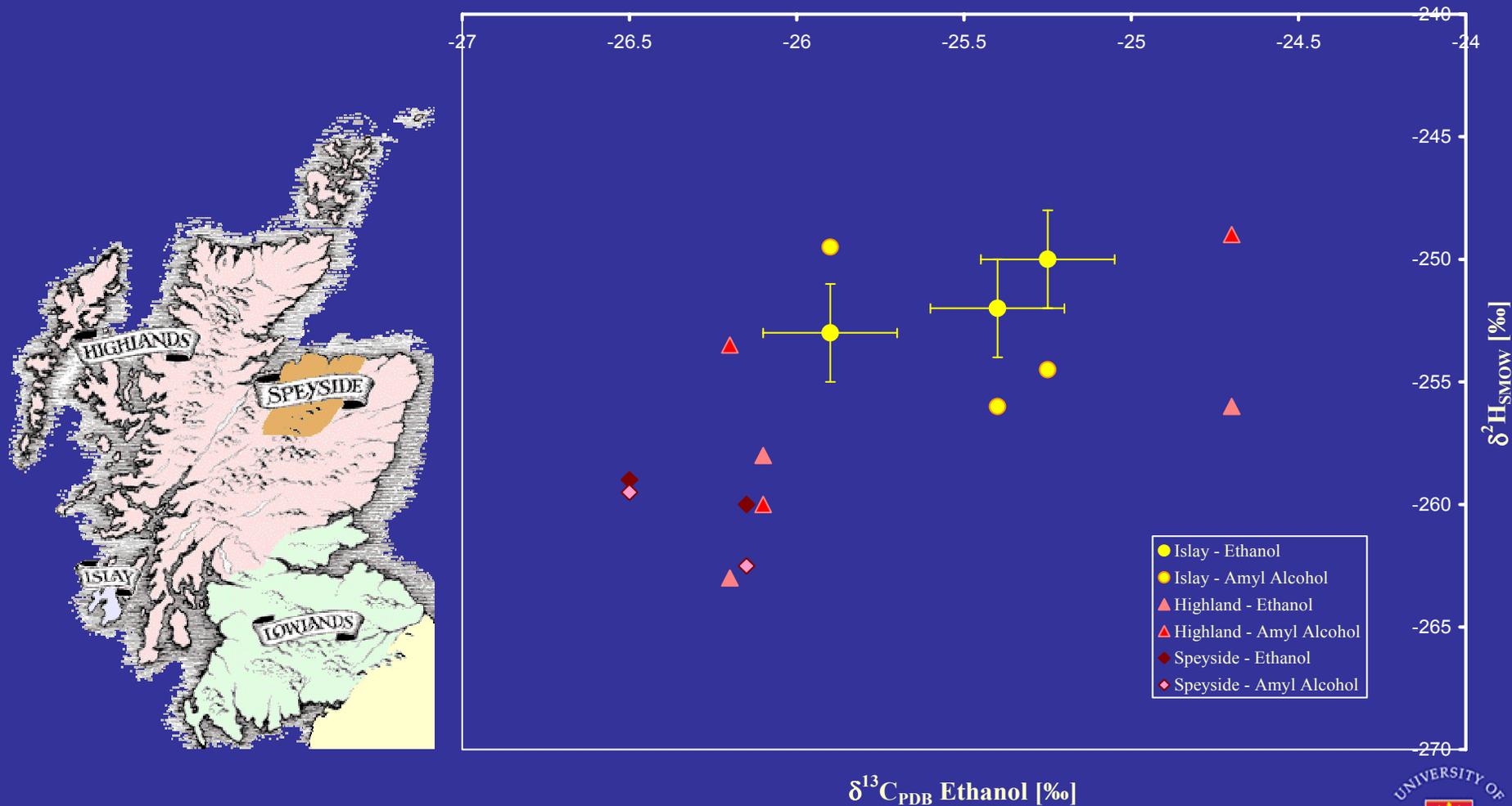


Isotopic Signatures of Alcohol from Different Sources



- ✖ Bourbon
- ▲ Highland
- Amyl alcohol - Islay -
- European Wines mean
- Blended
- ◆ Speyside
- △ Amyl alcohol - Highland -
- Single Malts mean
- Islay
- Amyl alcohol - Blended -
- ◆ Amyl alcohol - Speyside -
- ◆ Rum mean

Isotopic Signatures of Alcohol Single Malt Whisky

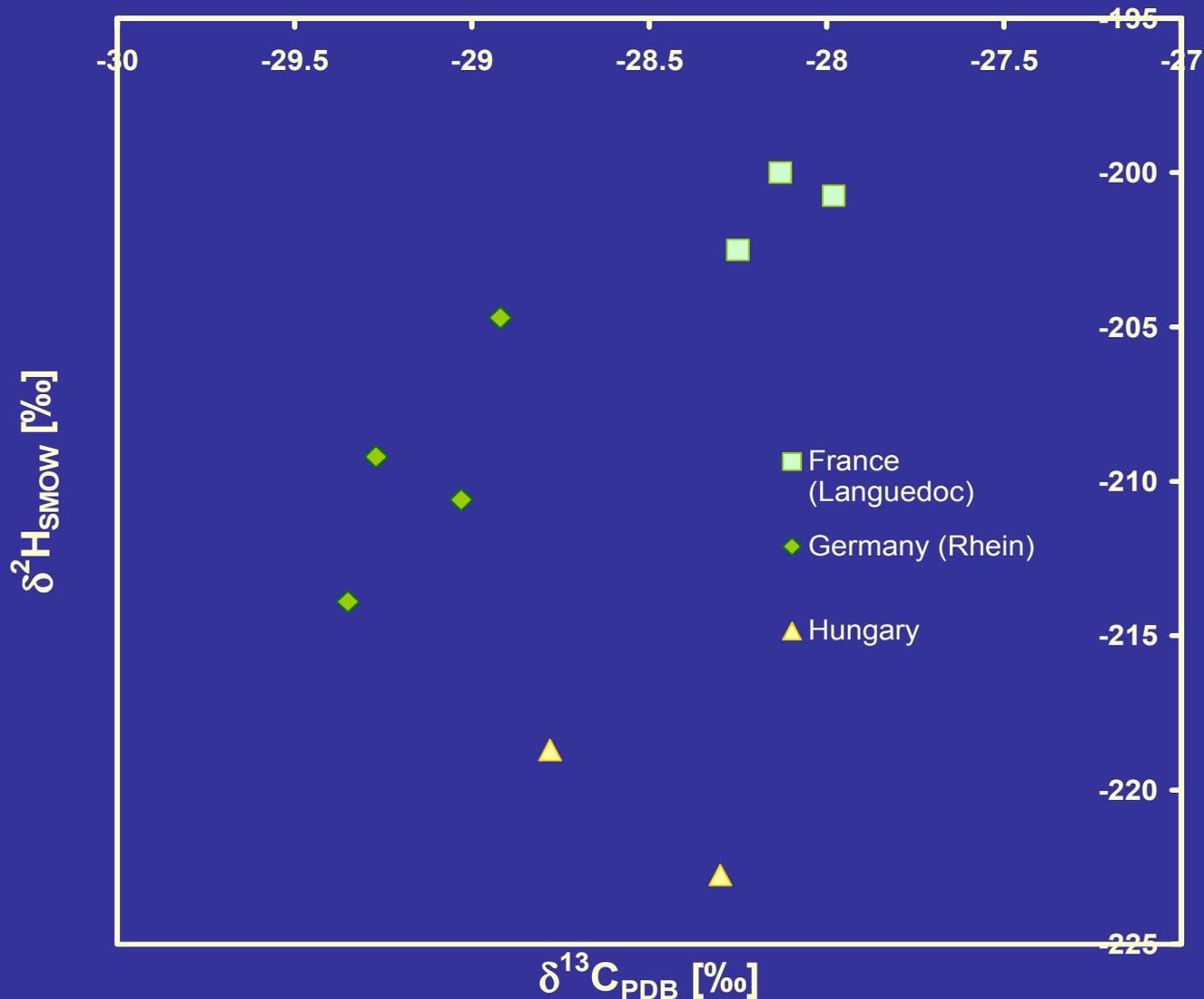


Data courtesy of Dr Ian Begley (Iso-Analytical, UK)

WMA



$^{13}\text{C} / ^2\text{H}$ Signatures of Ethanol and Geographic Origin of White Wine

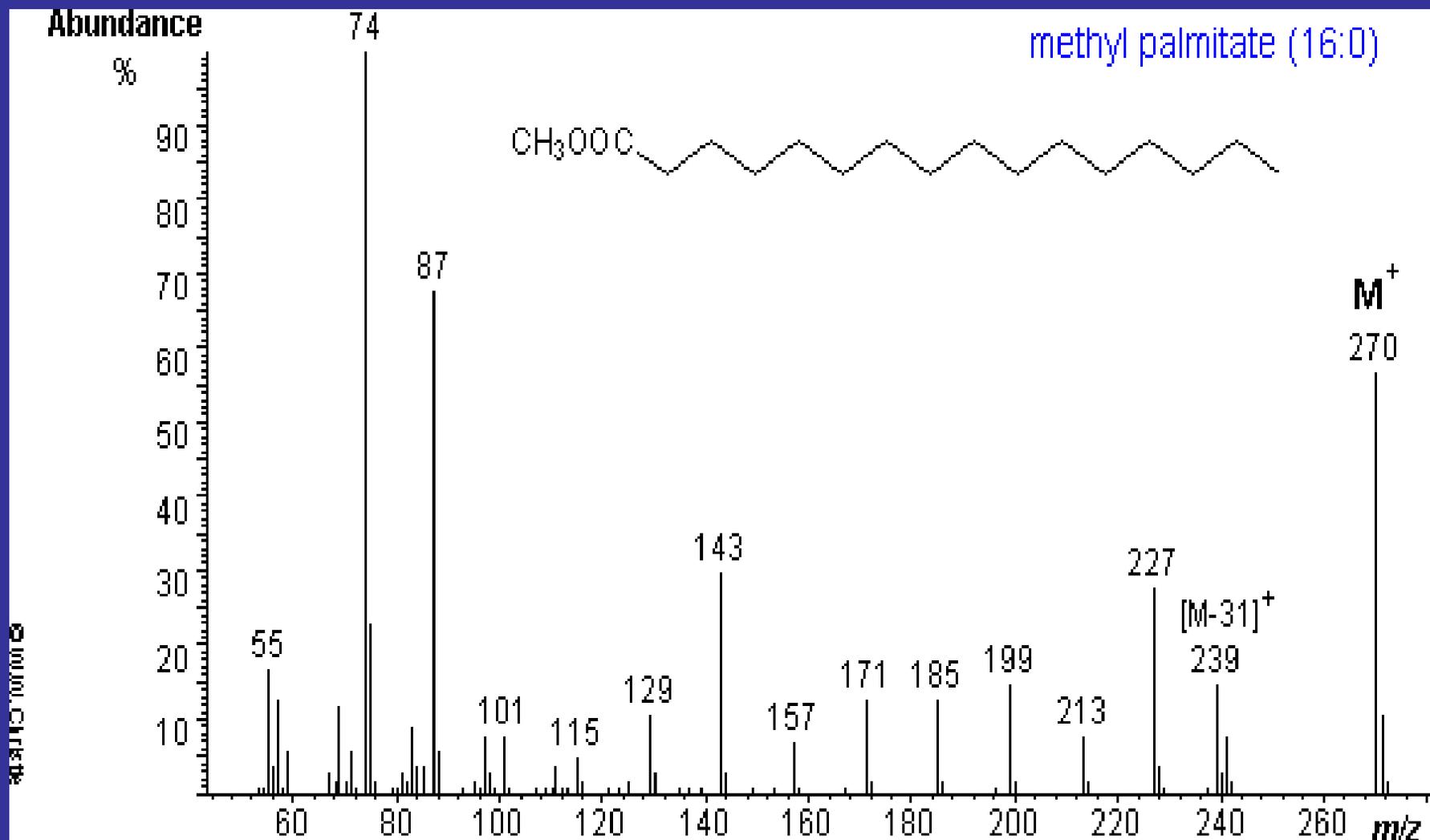


Data courtesy of Dr Ian Begley (Iso-Analytical, UK)

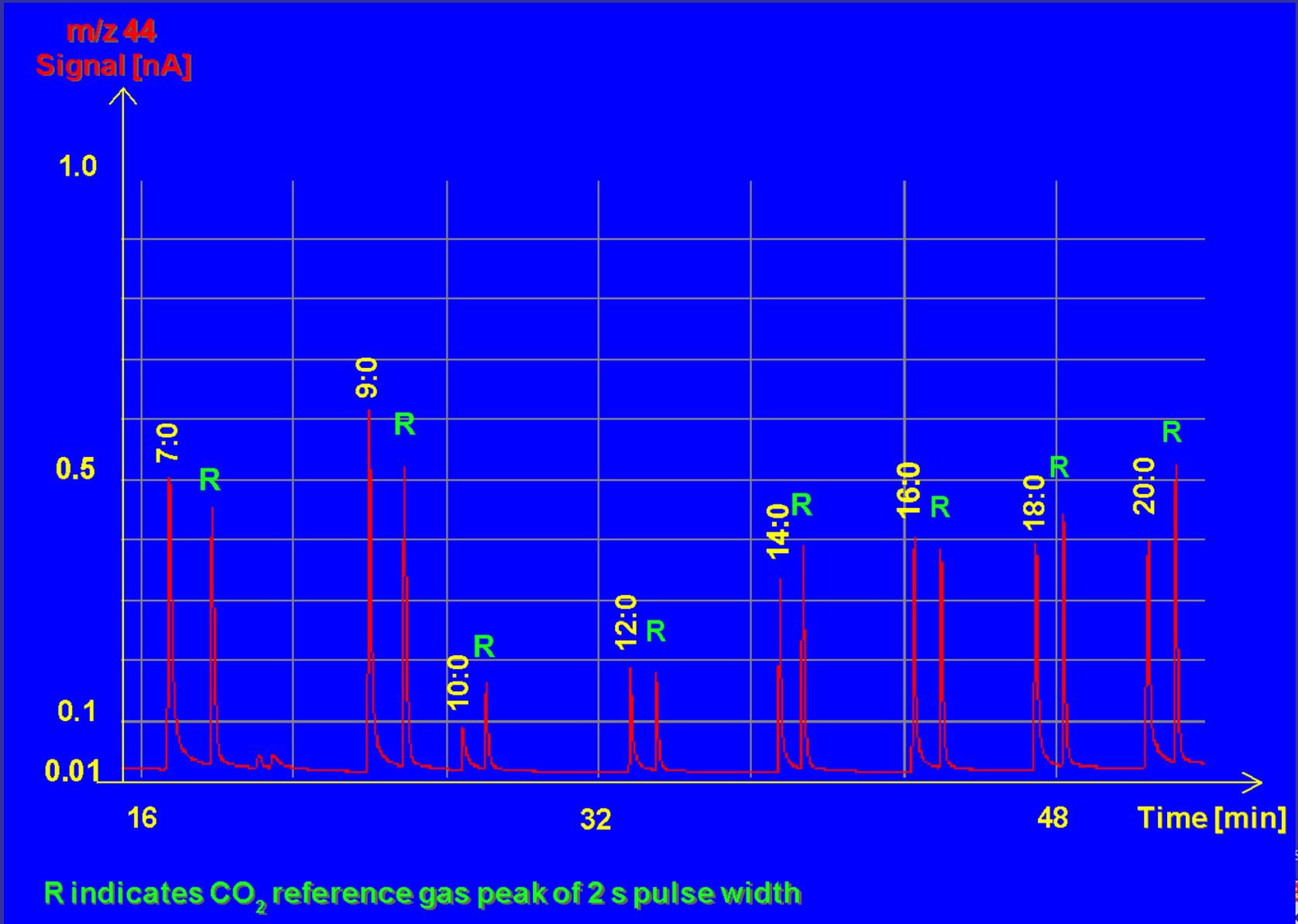
WMA



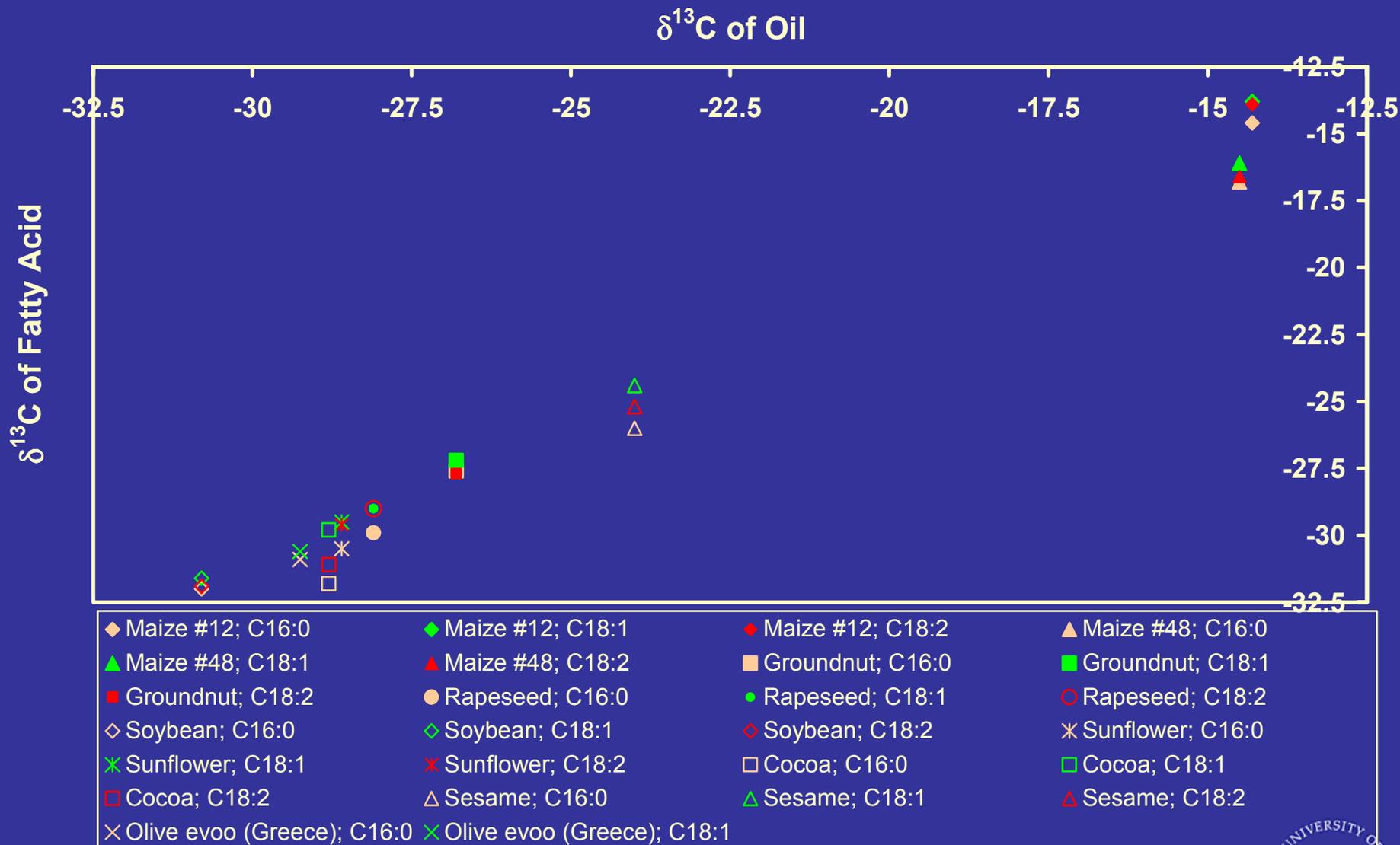
EI-MS of Methyl Palmitate



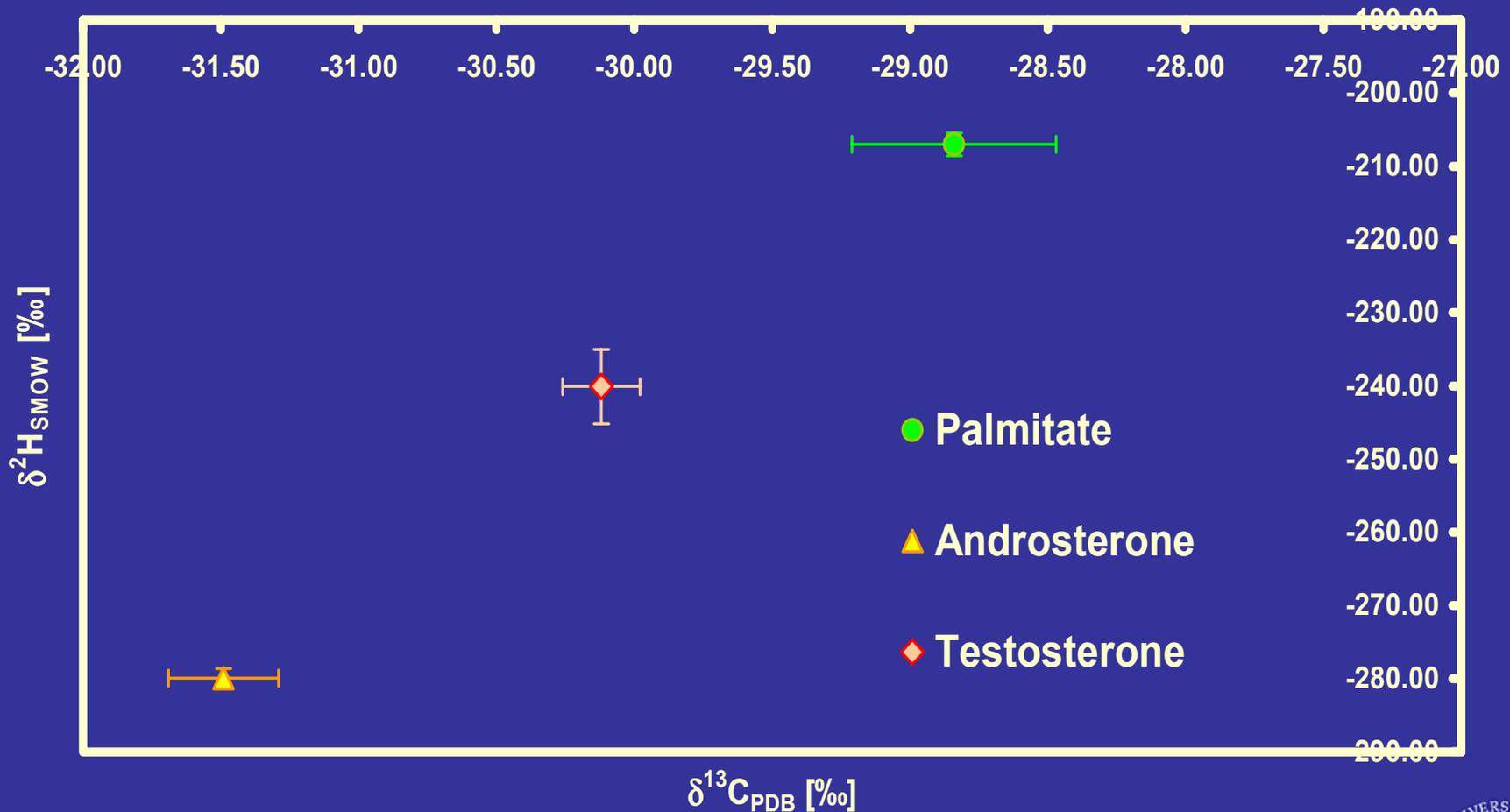
^{13}C -Analysis of Odd and Even Saturated Fatty Acids



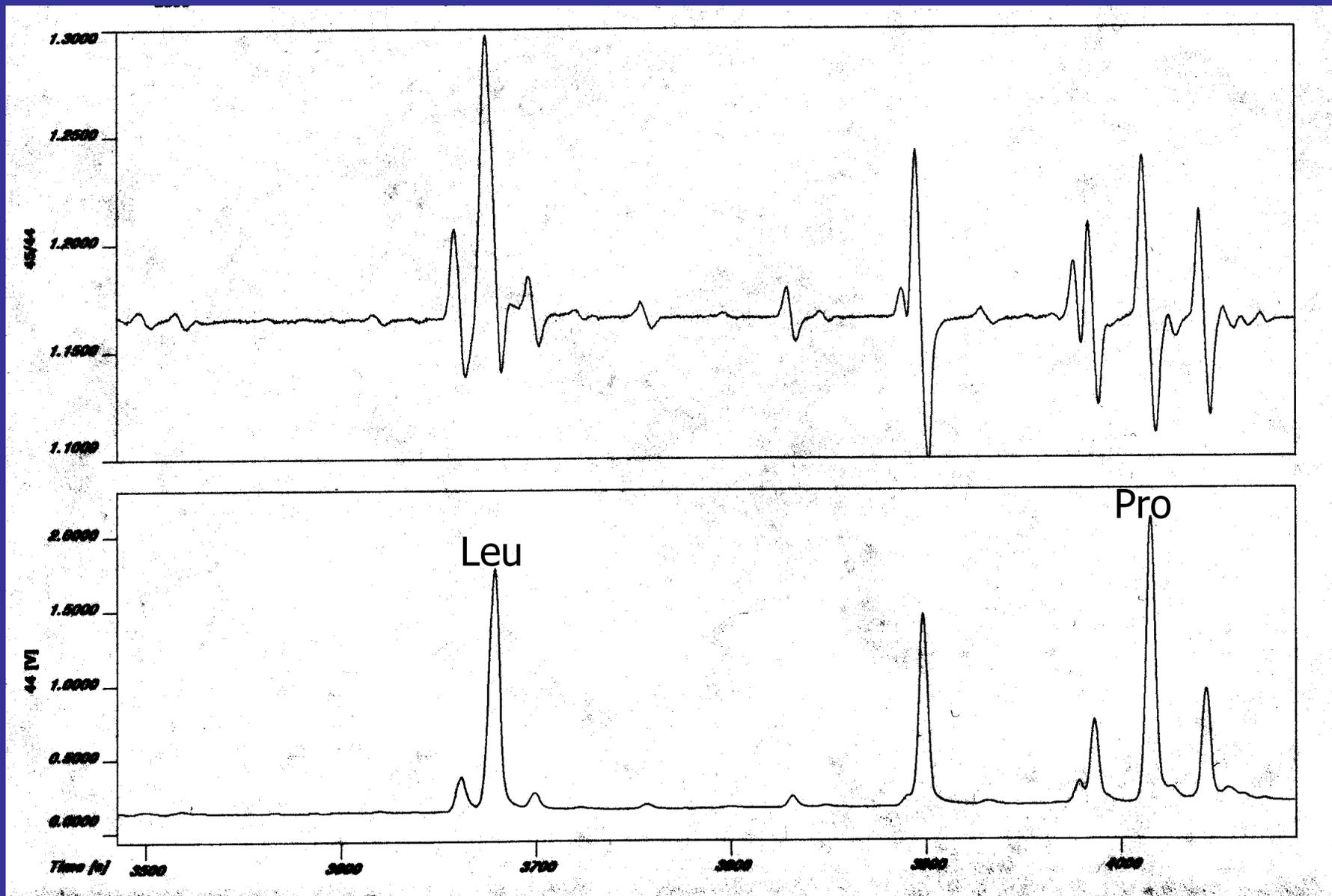
Isotopic Signatures of Plant Oils



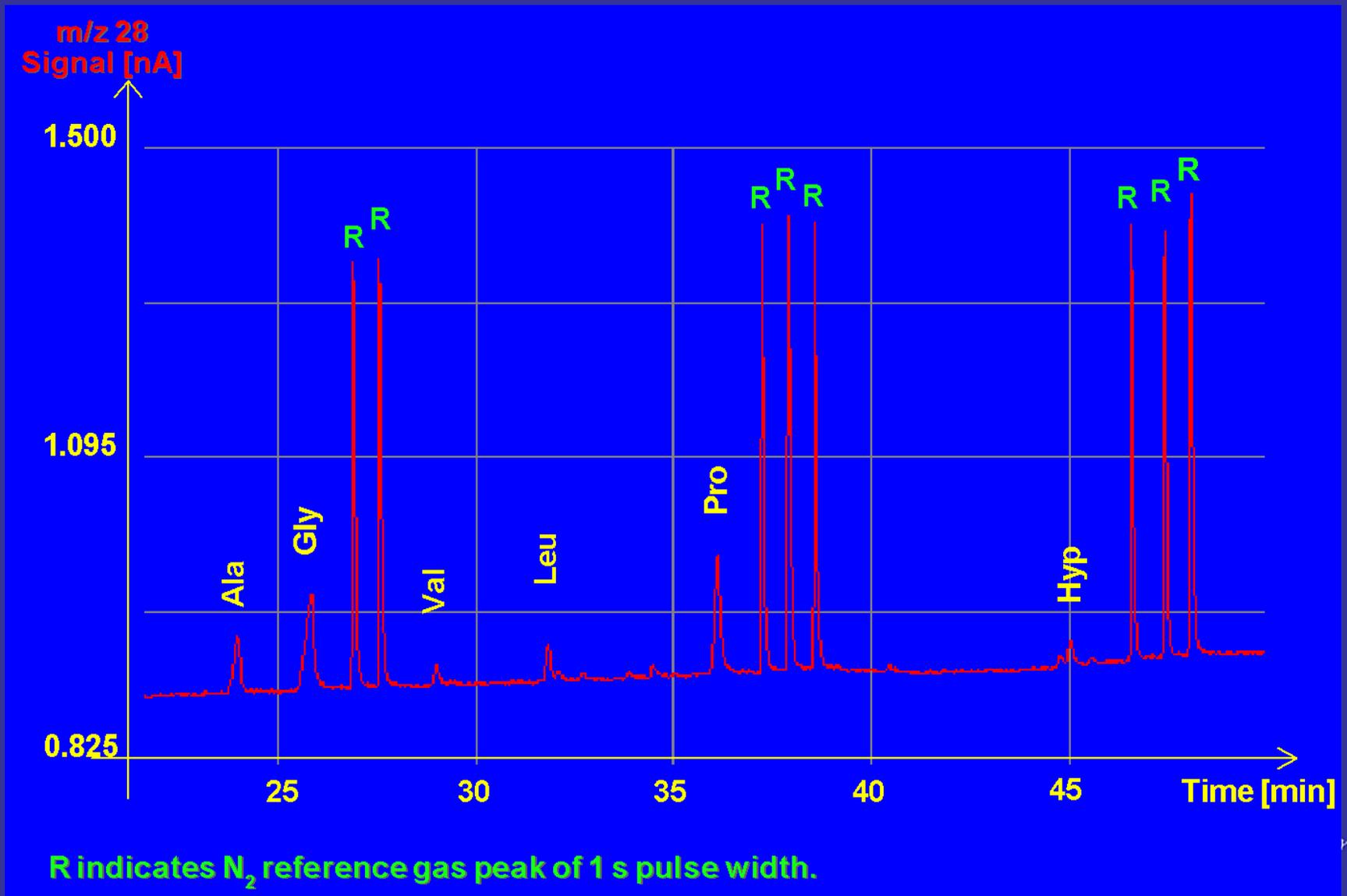
^{13}C / ^2H Signatures of Palmitate and Anabolic Steroids



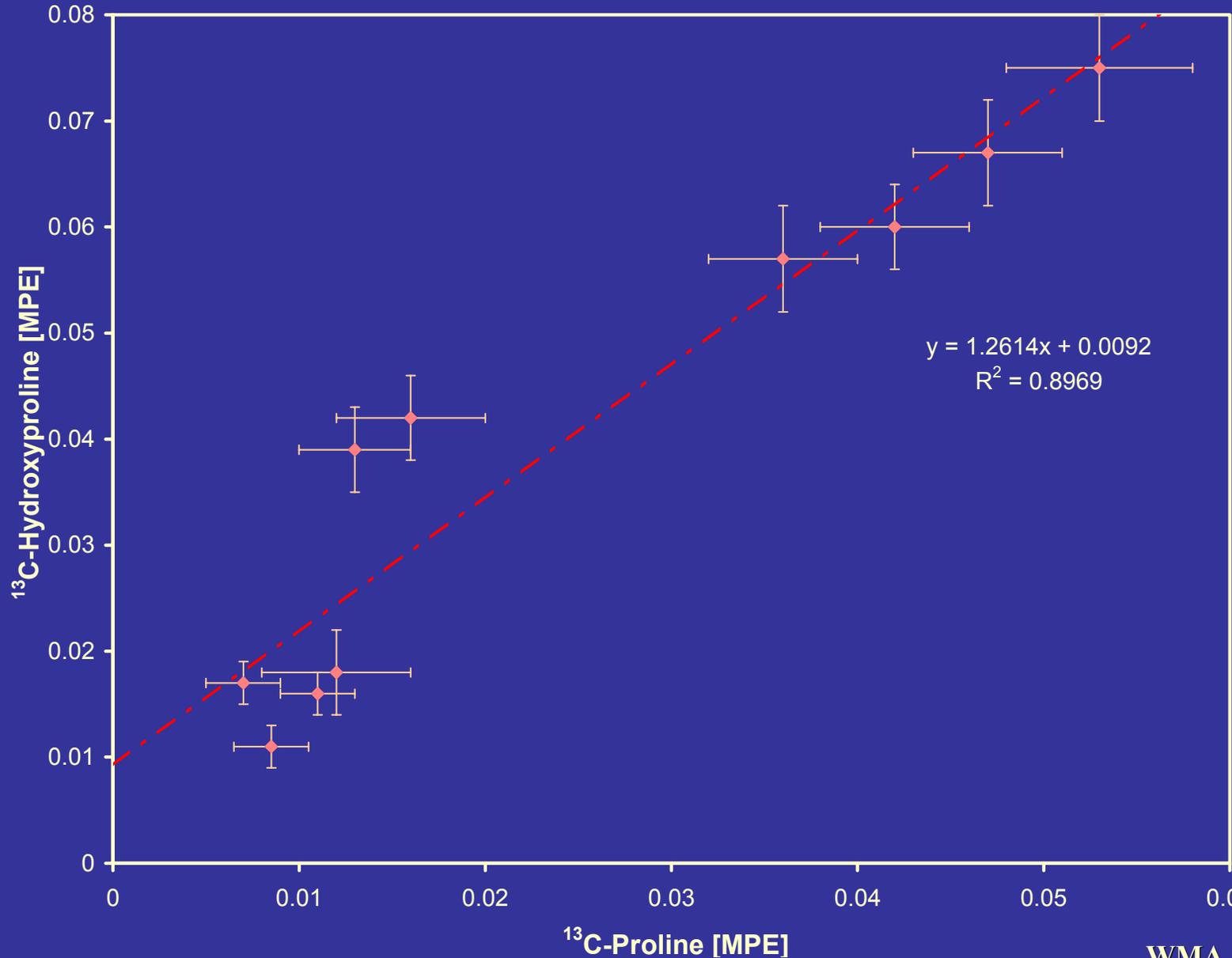
^{13}C -Analysis of Amino Acids from Bone Collagen



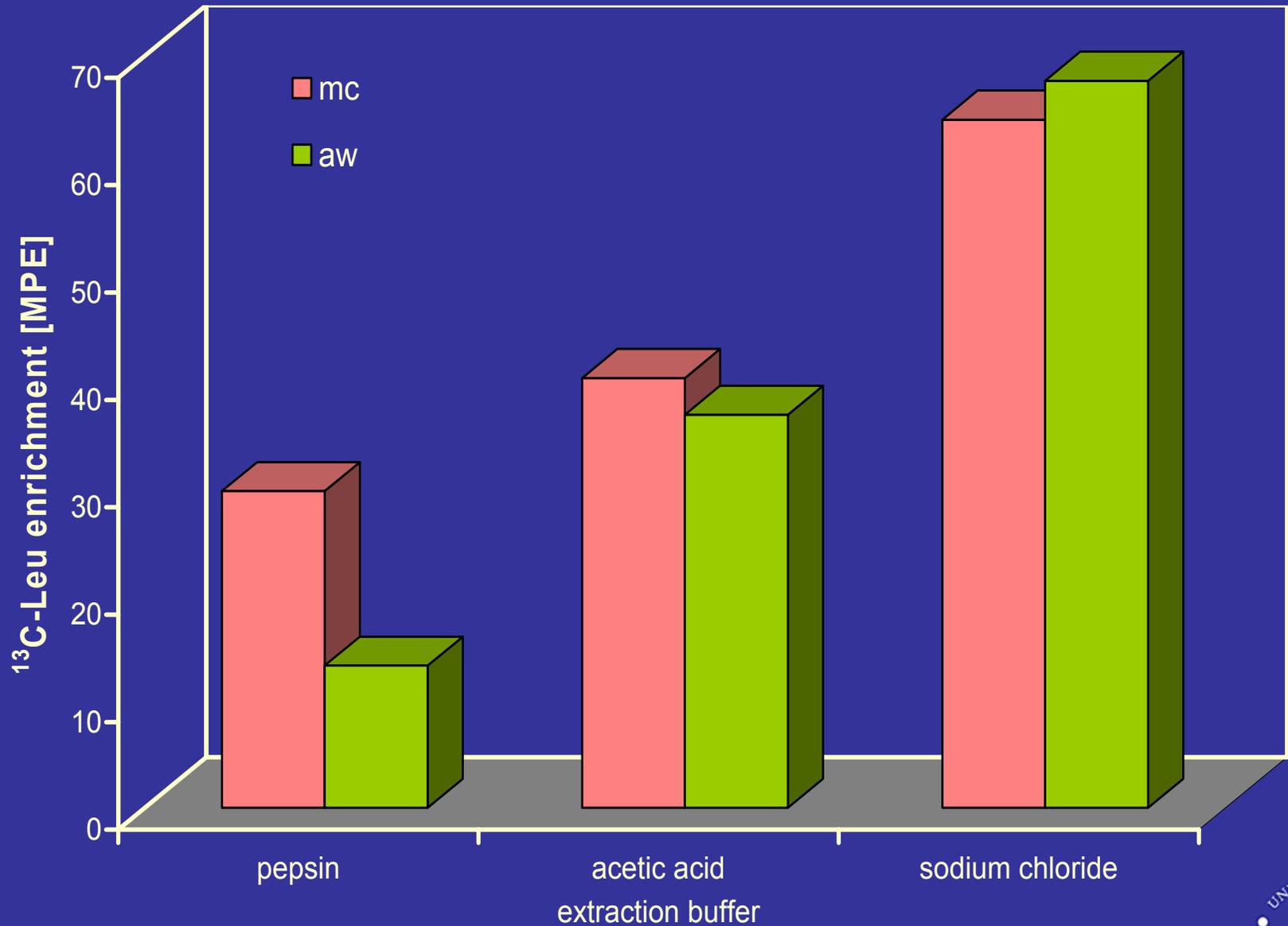
^{15}N -Analysis of Amino Acids from Collagen



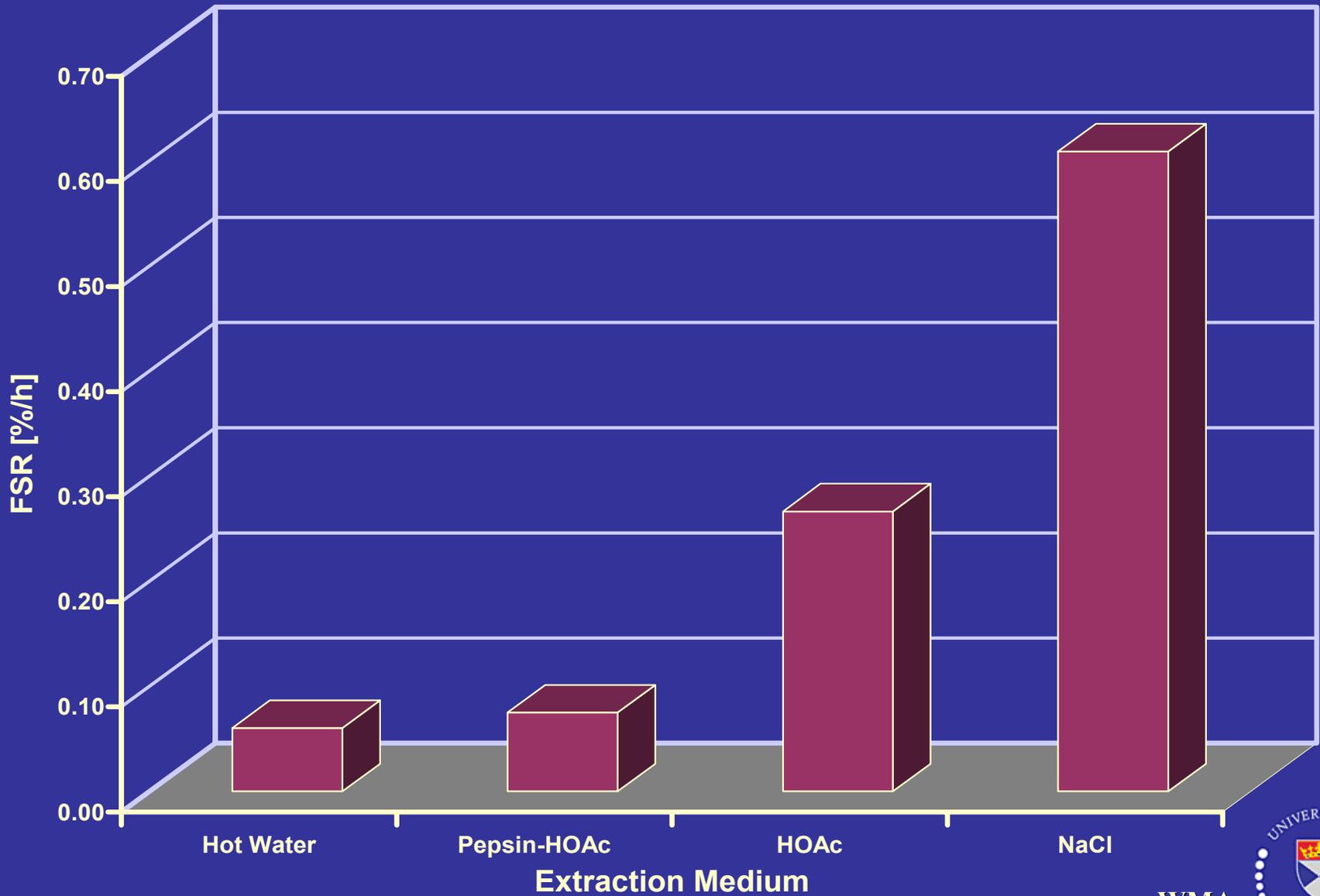
Labelling of Bone Collagen derived Proline and OH-Proline



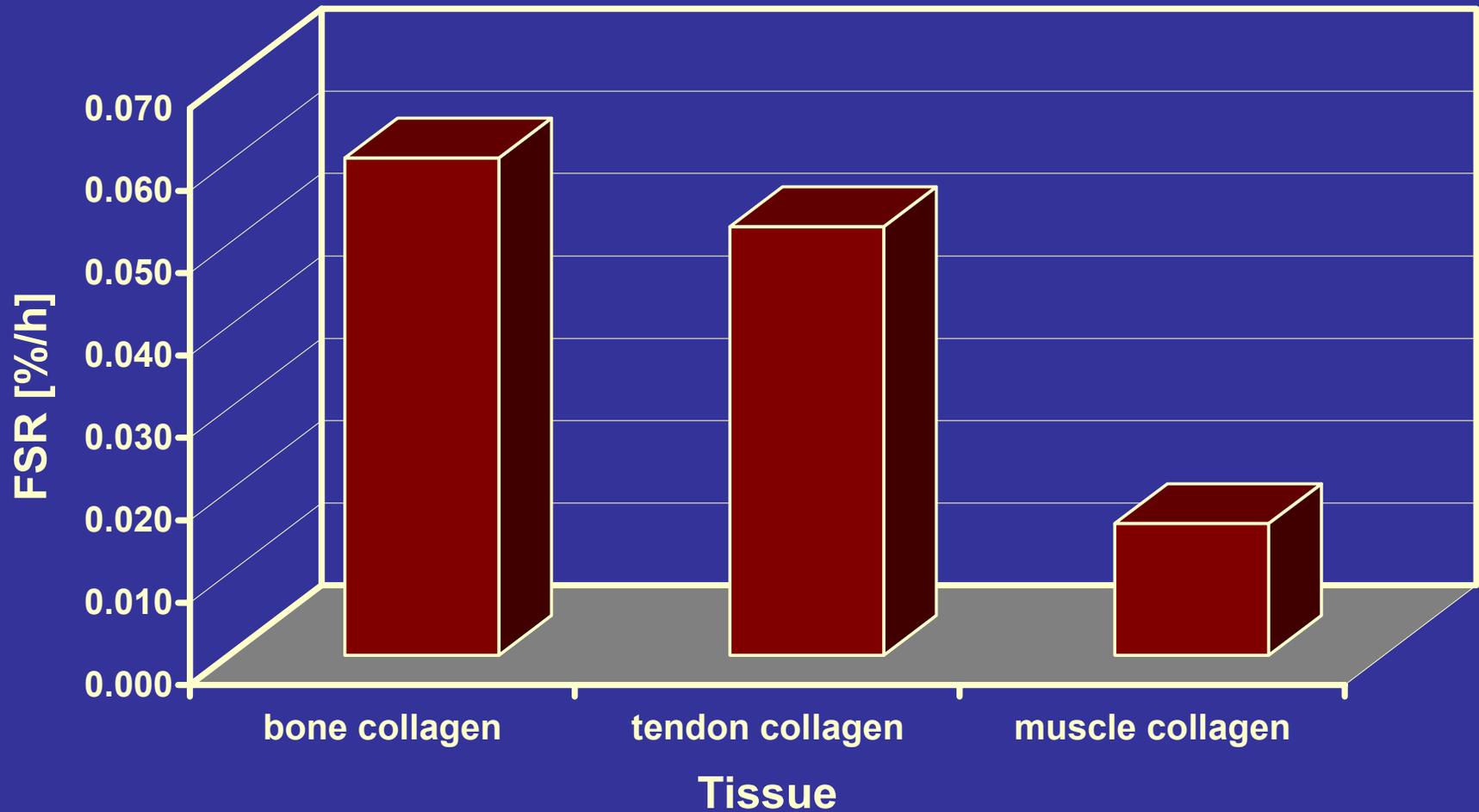
Labelling of Total Bone Collagen derived Leucine



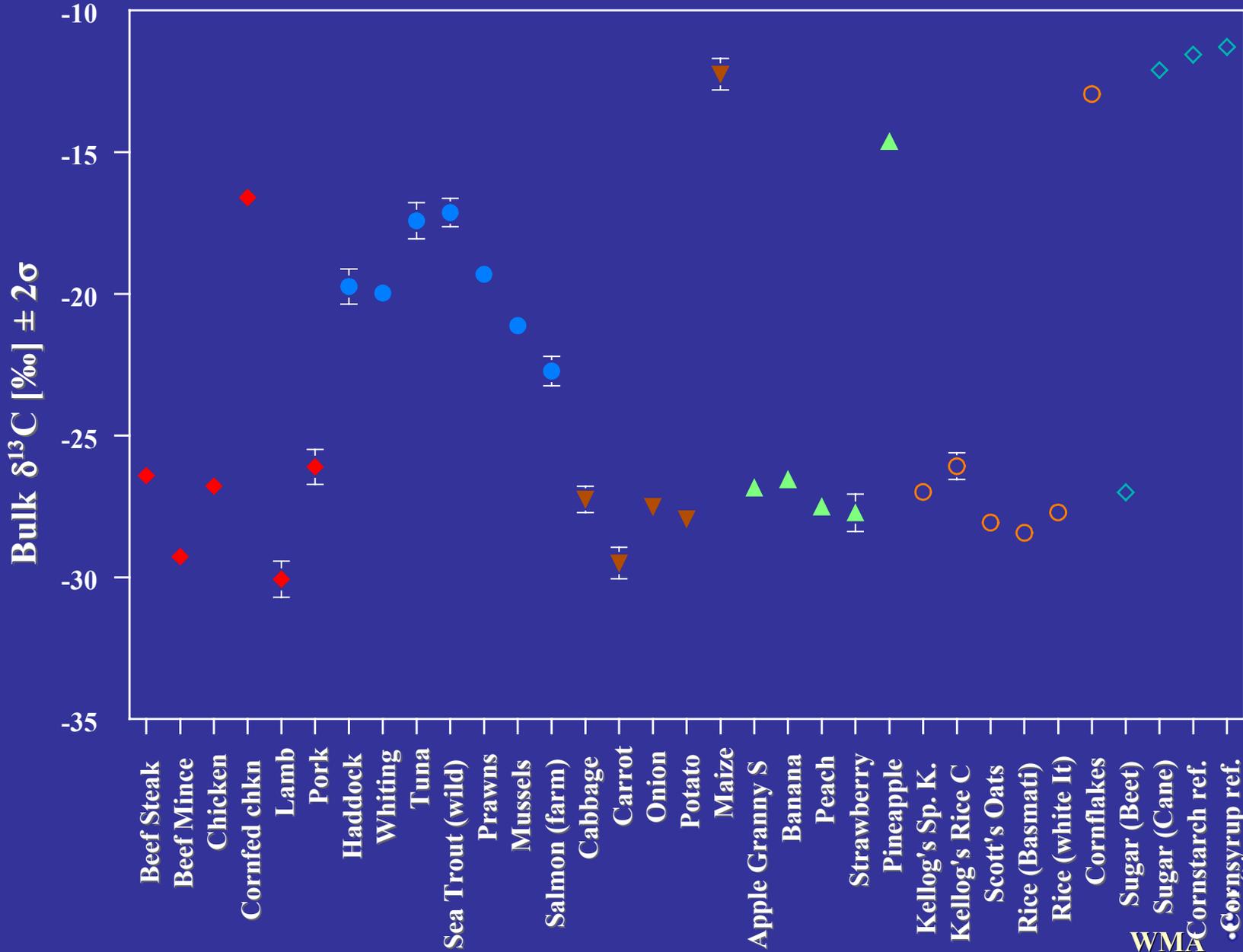
Synthesis Rates for Collagen from Different Pools



Collagen Synthesis Rates in Different Tissues

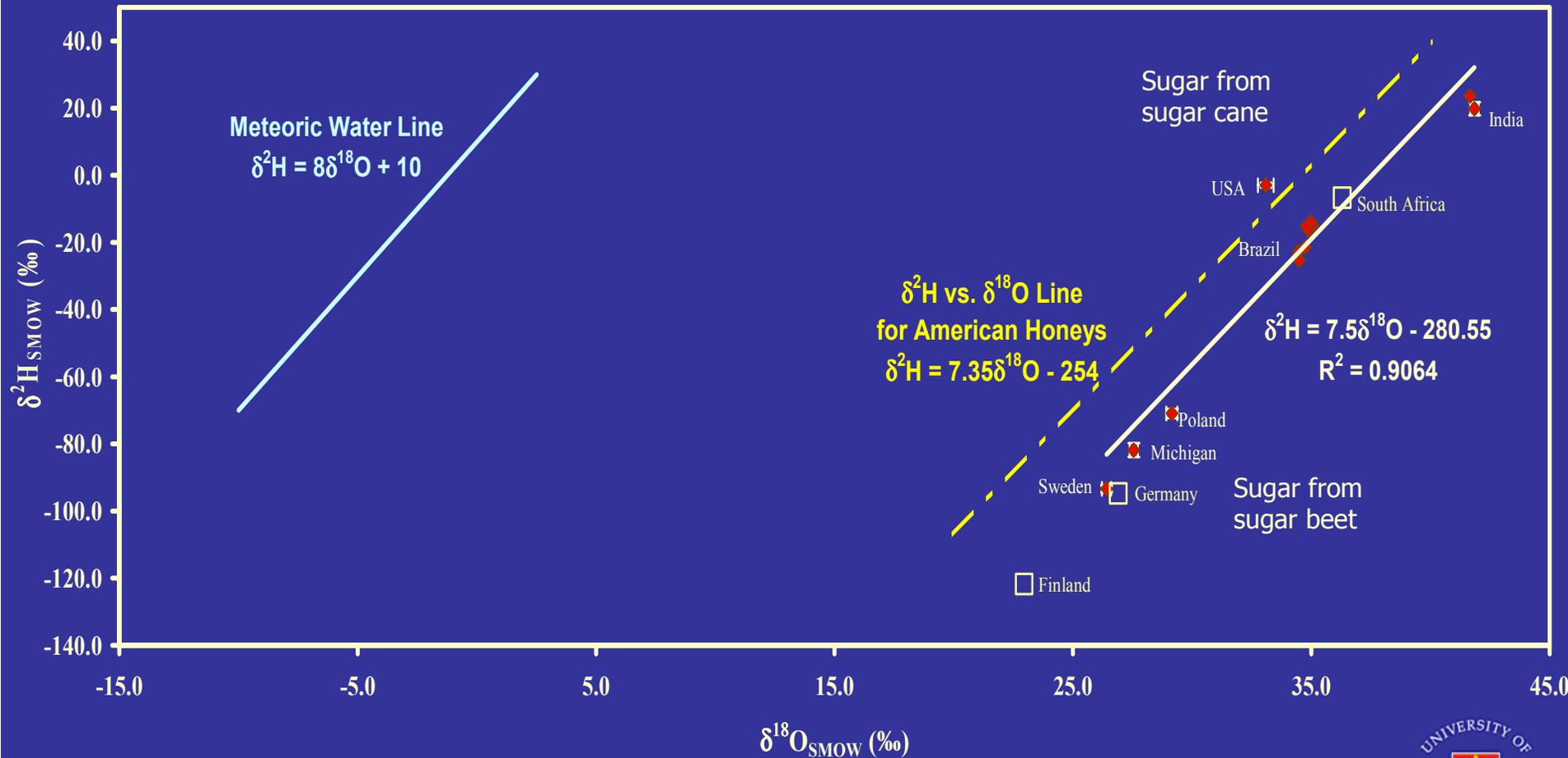


^{13}C -Abundance in Food Stuffs



Isotopic Analysis of Commercial Sugar

simultaneous analysis of $\delta^2\text{H}$ & $\delta^{18}\text{O}$ with quantitative carbon reduction by thermal conversion



Stable Isotopes in the Human Body

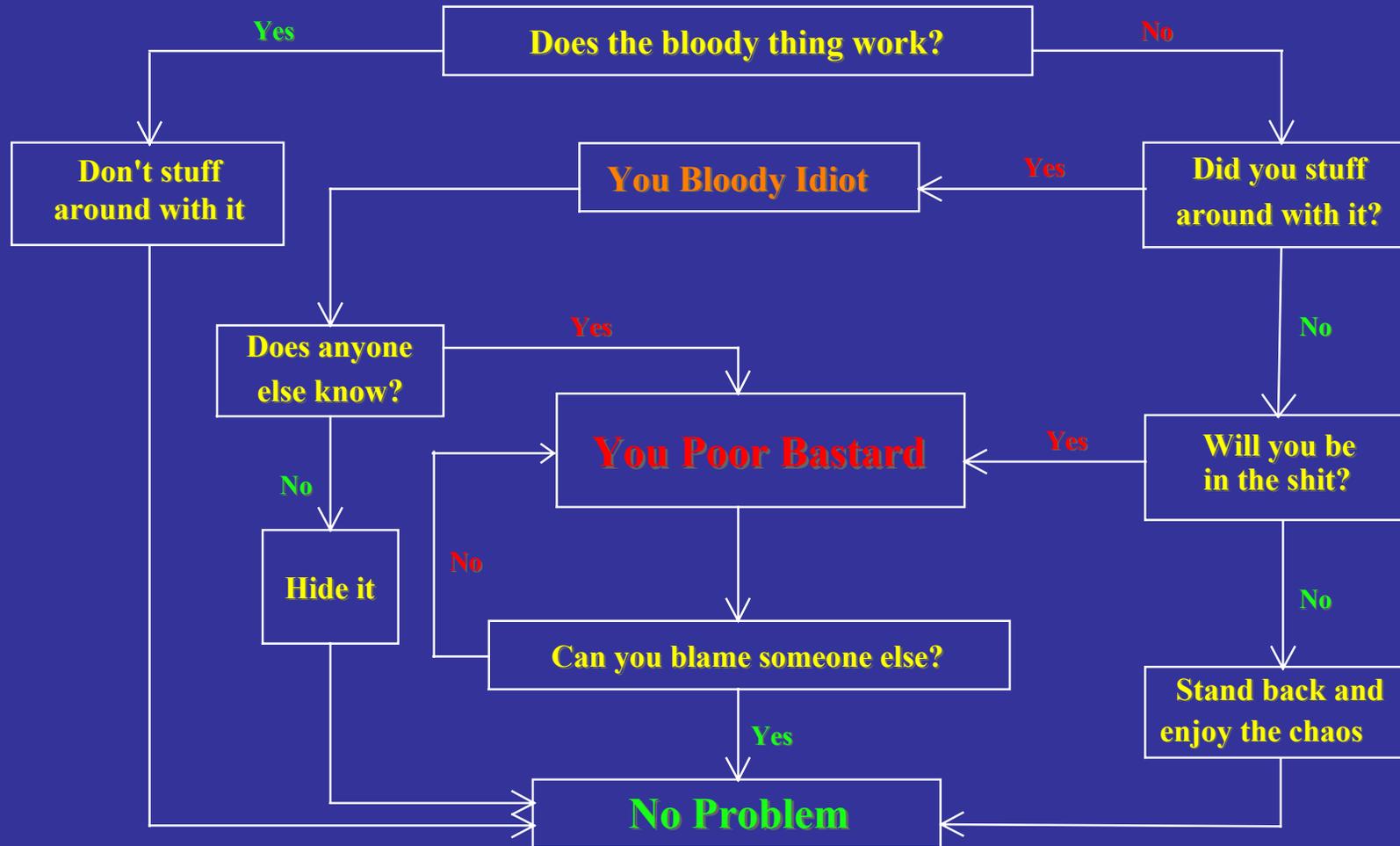


Other Applications for Forensic IRMS



Dealing with Pitfalls

PROBLEM SOLVING FLOWCHART



Acknowledgements

- All our volunteers, both controls and patients.
- Prof. Michael J Rennie, Dr Peter W Watt, Dr Helen F Kemp, Dr Kenneth Smith and John Babraj.
- Dr Ian Begley (Iso-Analytical Ltd).
- The Dietmar-Hopp-Foundation for Medical Research and Studies (Walldorf, Germany); The European Union's 3rd Framework R&D Programme; Europa Scientific Ltd (UK); Thermo-Finnigan MAT (Bremen); The Wellcome Trust.