

Addressing adulteration with stable isotopes.

March 2008

Food Authentication

- Flavours, wine, juices, honey adulteration

Environmental Science

- Agriculture, Forestry and Ecology *Plant, litter, soil, filters, respired CO₂, etc.*
- Archaeology and Anthropology
- Wildlife Tracking

Atmospheric Chemistry

- Source apportionment of greenhouse gases

Earth Science

- Deuterium tracing, oil/oil correlation, gas sourcing, carbonates
- Climatic change, oceanic-atmospheric interactions

Medical Research

- Mass balance, blood bicarbonate, breath
- Metabolism, doubly labelled water, total body water
- Gastric emptying, liver function
- Protein turnover

Forensics

- Drug doping, drug sources



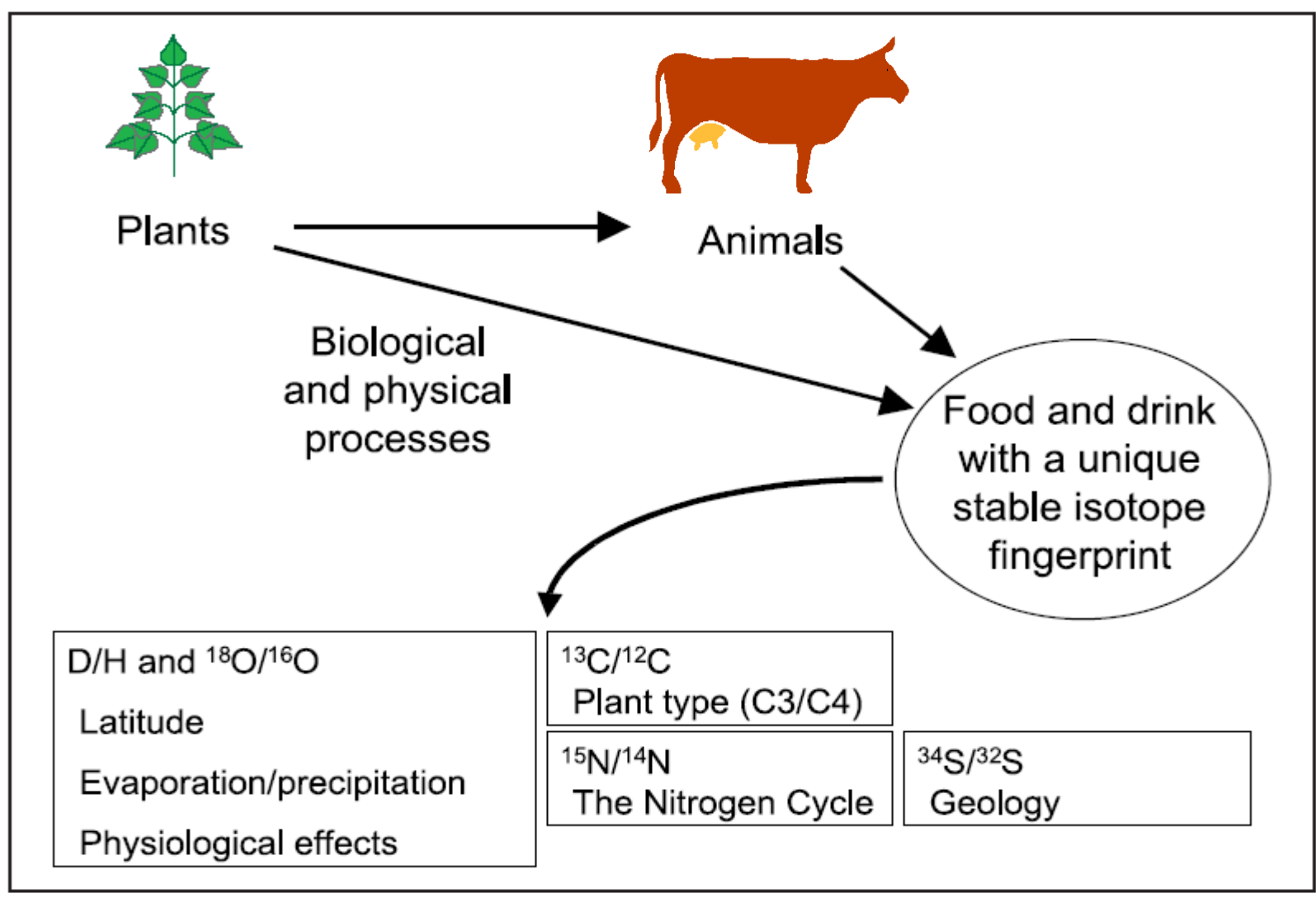
Main type of Adulteration

- The authenticity of food relates to information on name, ingredients, origin or processing.
- Frauds include undeclared addition of water or other inexpensive materials (adulteration) and false statements about sources of ingredients (*i.e.* geographic, plant or animal origin)
- Increase profit and unfair competition for honest producer.
- Cheating Consumer.

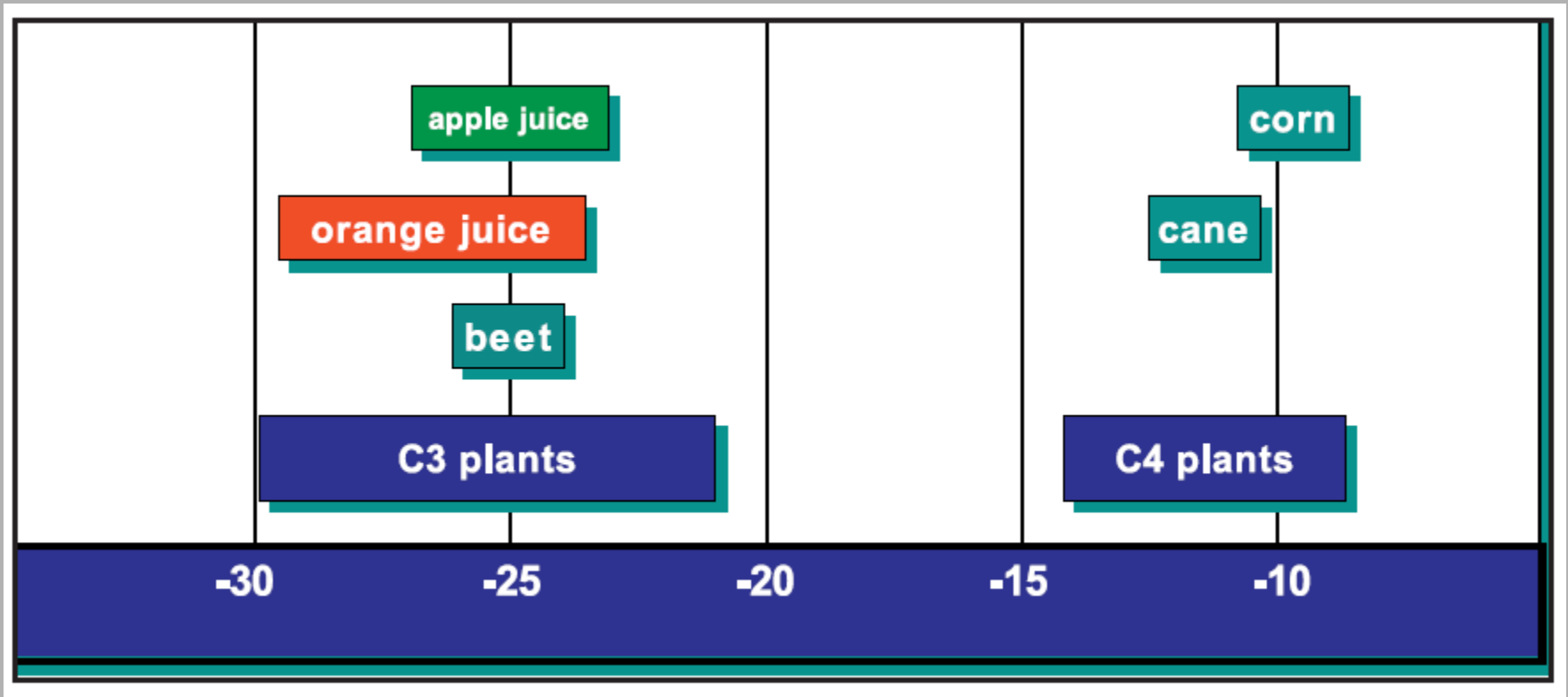
Isotopic Tools

- Adding water can be detected by ^{18}O measurements
- Adding sugar can be detected by ^{13}C , ^{18}O or ^2H measurements
- False origin (multi element isotopic approach; C, N, H, & S)
- As it is not commercially viable to circumvent isotopic detection, stable isotopes have provided a way by which these types of frauds can be detected

- IsoprimeTM – IRMS
- Inlets interface such as GC, EA or LC



Isotopic fractionation of carbon isotopes in plants



Decreasing ^{13}C content

- Fruit juice
- Vanillin



- The most common type of fraud is extension of the juice by adding sugars and water

- Water added to mask addition of concentrated juice



- Cane, corn or beet sugar can be use

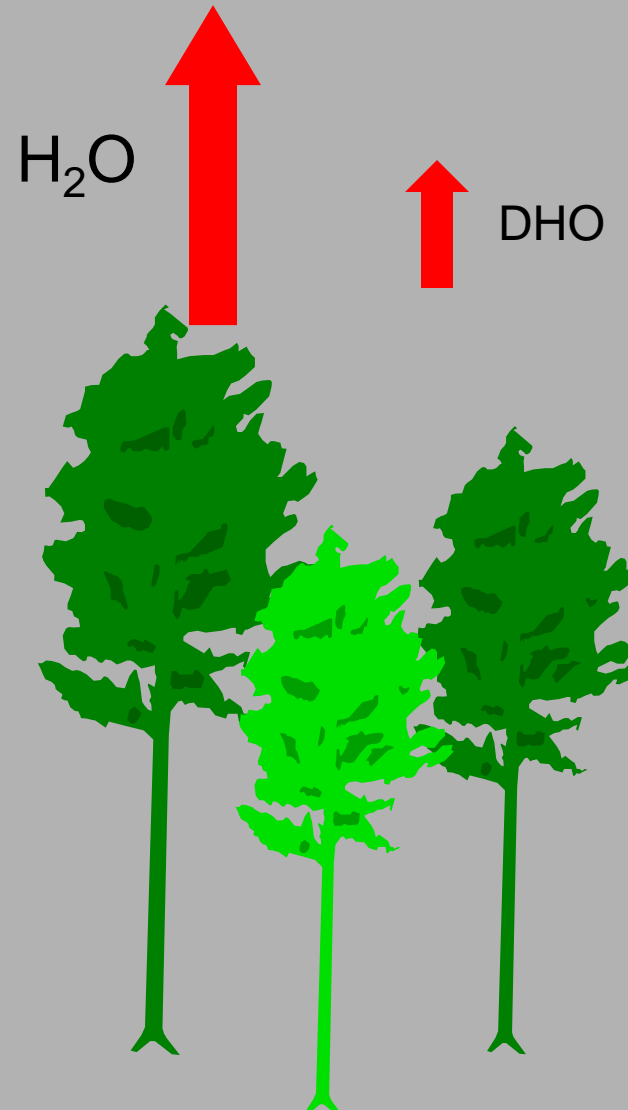
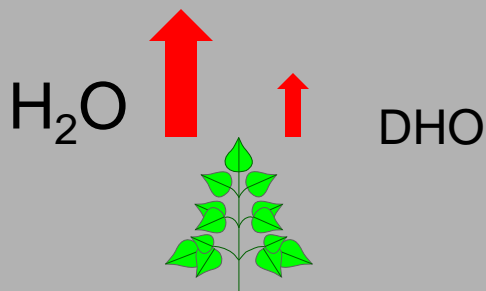
Can be used to detect the addition of **C4 sugars**
e.g. cane and corn syrups to juice

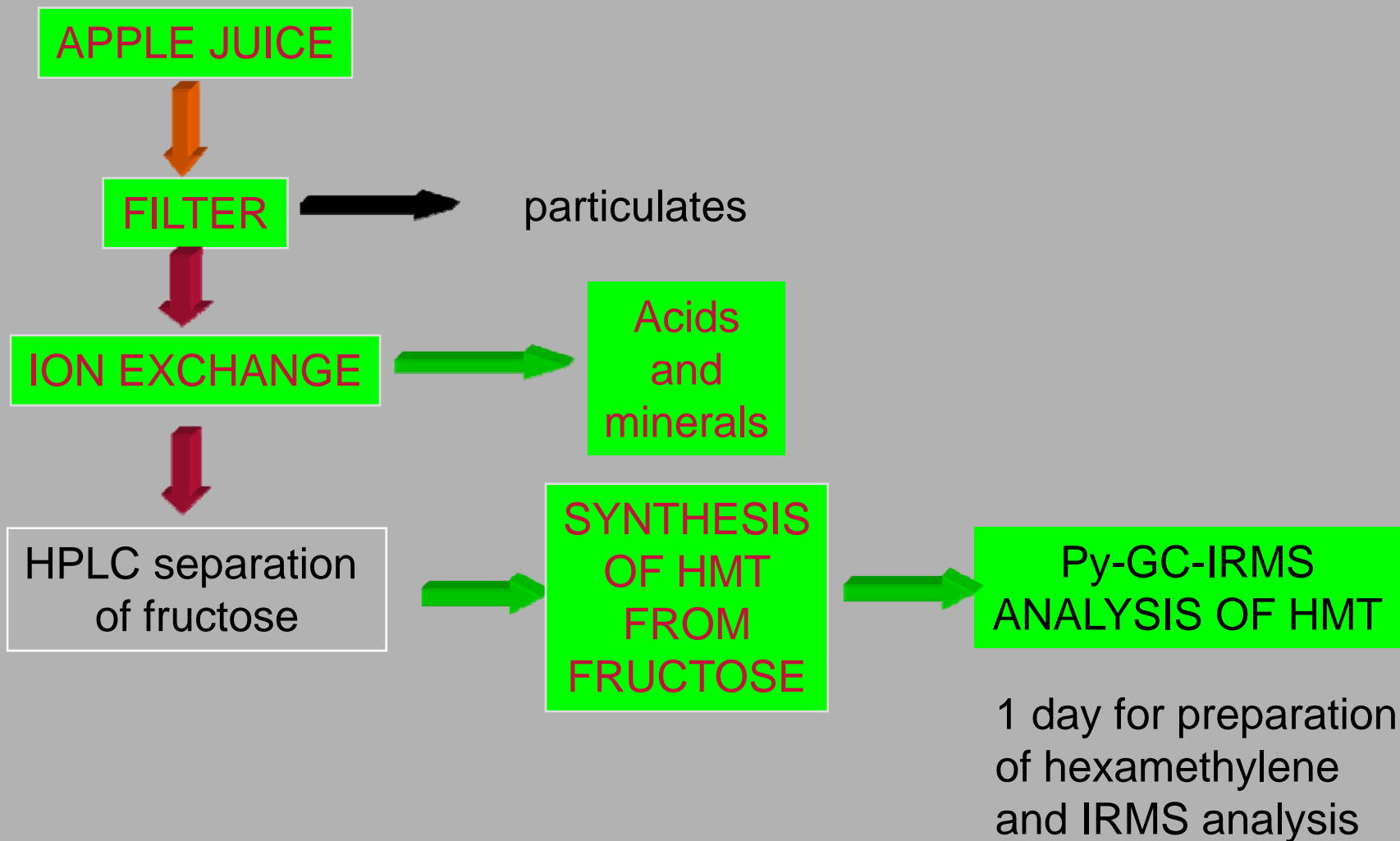
Key limitation

Not possible to distinguish between the sugars in apple
or orange juice and those from beet sucrose

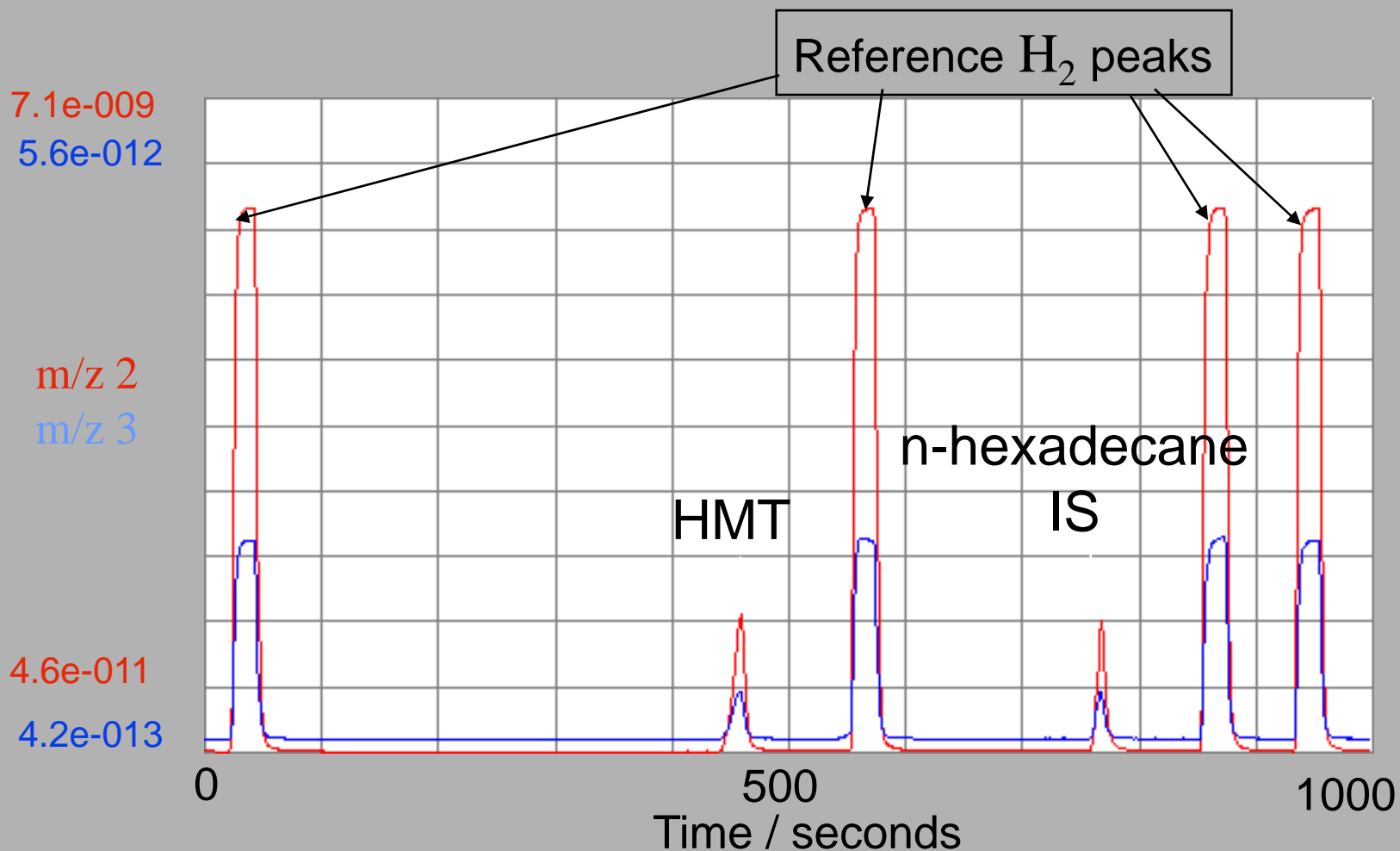
	$\delta^{13}\text{C}$ ‰ range	Reference
Apple Juice	-25.5 to -26.8	Rossmann et al (1990)
Orange Juice	-23.5 to -28.1	Bricout & Koziat (1987)
Corn Syrup	-9.5 to -10.7	Rossmann et al (1990)
Cane Sugar	-11.2 to -11.7	Bricout & Koziat (1987)
Beet Med Invert Syrup	-24.0 to -25.7	Kelly et al (1994)
Beet Sugar	-25.3 to -26.0	Kelly et al (1994)

Differing rates of evapotranspiration between ground (beet) and aerial plants (apple trees) give rise to relatively enriched apple sugars





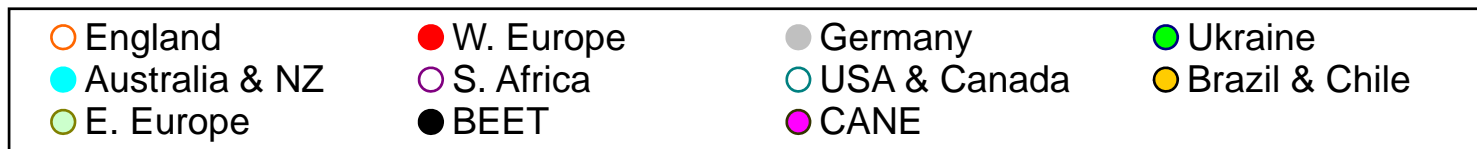
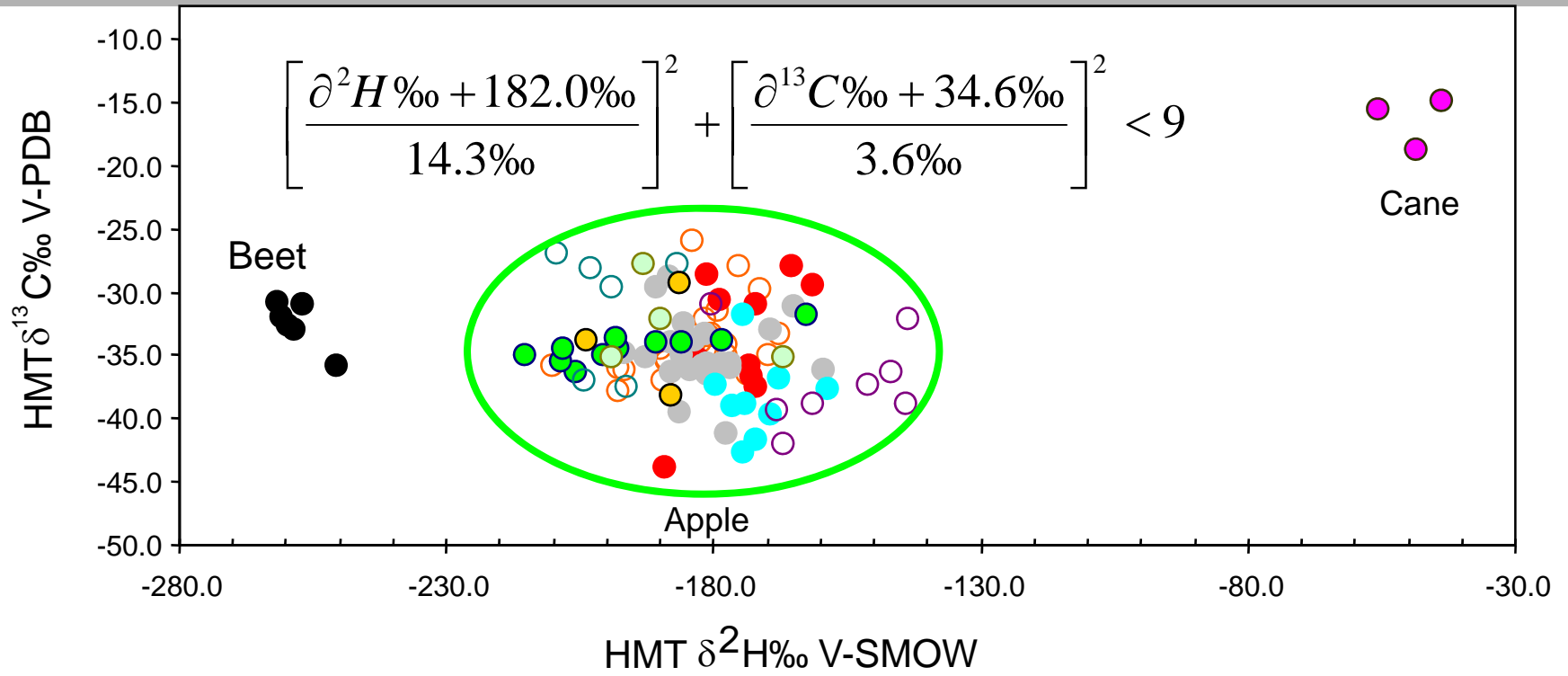
Typical Ion Chromatogram of HMT and an Internal Standard

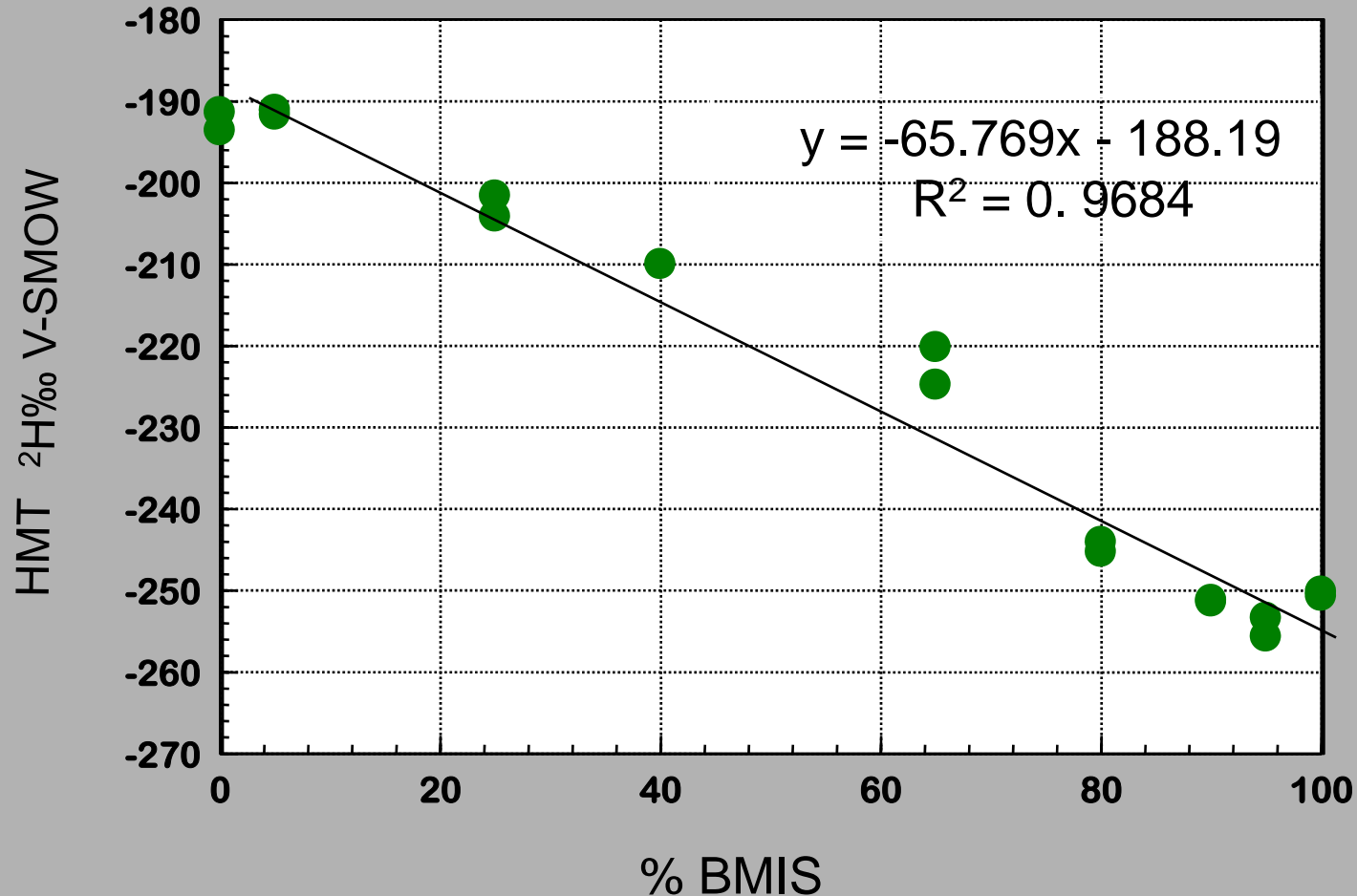


Rapid detection of added sugar in apple juice using hexamethylenetetramine

Sugar source material	PYROLYSIS			NMR		
	2H Py-CF-IRMS (ppm)	sd (ppm)	n	D-NMR D/H (ppm)	sd (ppm)	n
beet sugar	118.9	0.2	4	118.1	2.5	10
cane sugar	146.0	0.1	4	148.6	1.4	3
apple juice sugars	132.7	0.2	4	130.2	1.5	6

Comparison of D/H and $^{13}\text{C}/^{12}\text{C}$ ratios for, Beet Sugar, Cane Sugar and Apple Juices





- origin assignment and authenticity check of food,
- discrimination between conventional and organic production,
- identification of recent and prehistoric nutrition bases,
- ecological, biological and environmental investigations?

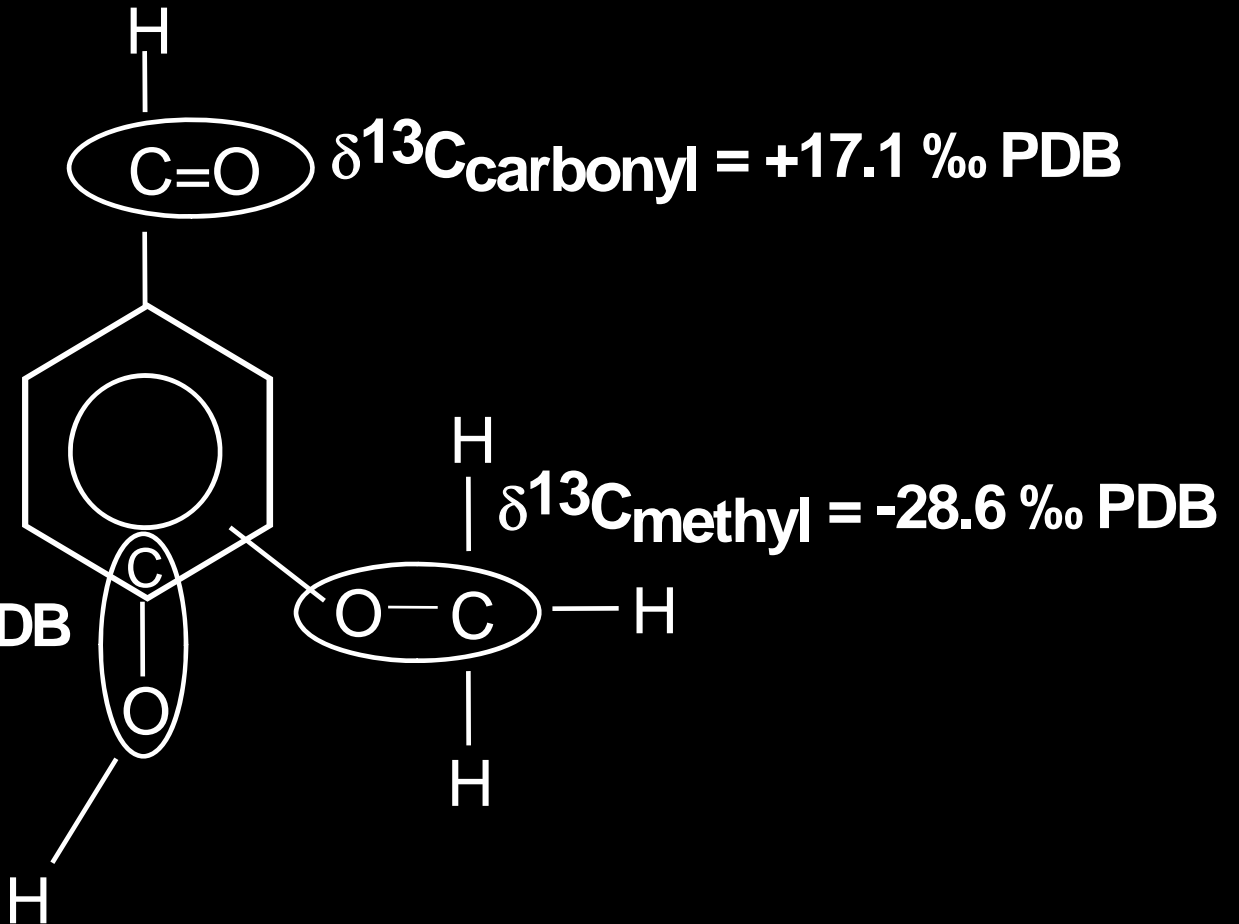
–Fruit Juice

–Vanilin

SAMPLE	COMBUSTION
	$\delta^{13}\text{C}\text{‰ PDB CO}_2$ (45/44)
VANILLIN (LIGNIN)	-27.7
VANILLIN (GUAIACOL)	-27.2
VANILLIN 'C'	-19.9
VANILLIN (NATURAL)	-20.1

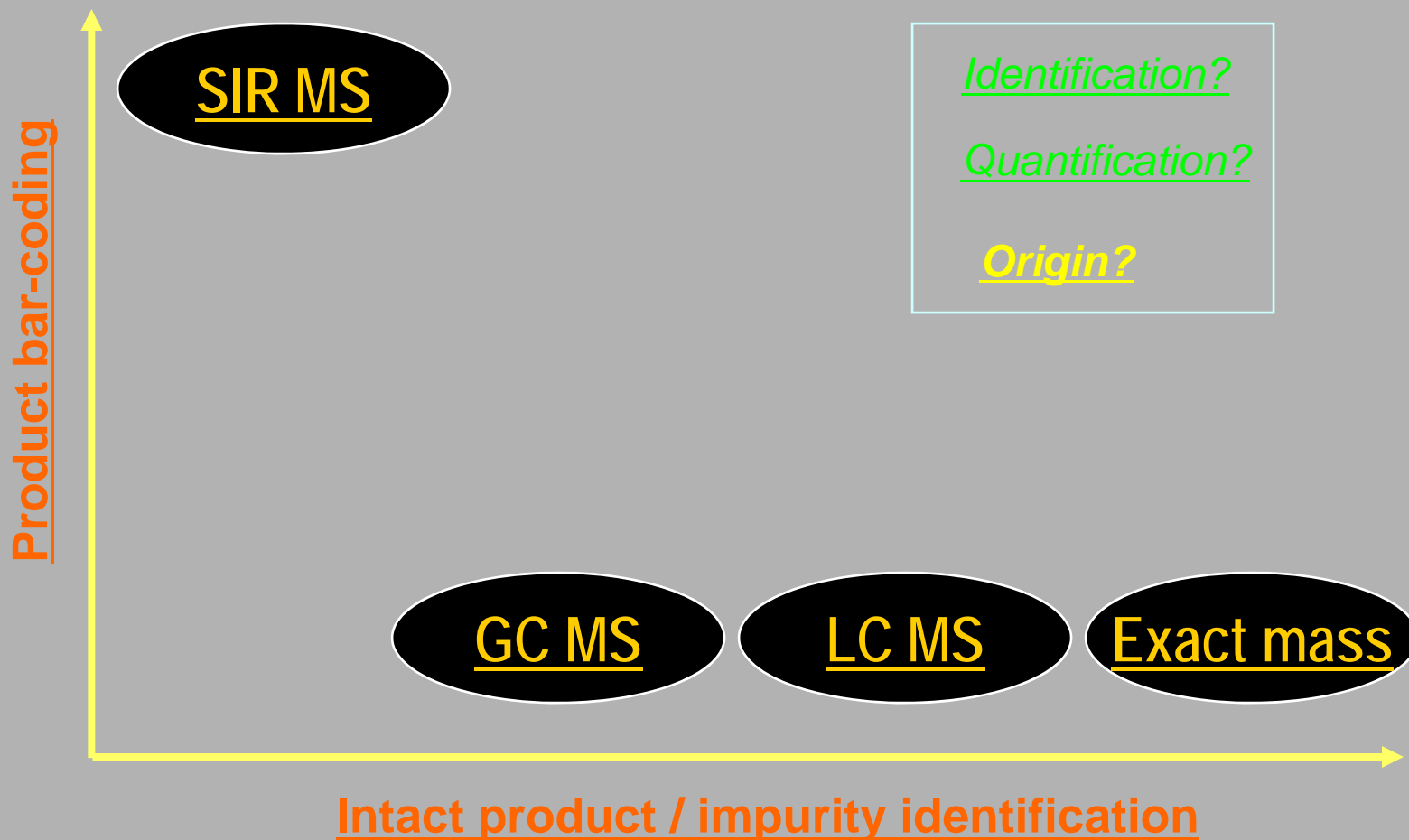
SAMPLE	COMBUSTION	PYROLYSIS
	$\delta^{13}\text{C}\text{‰ PDB CO}_2$ (45/44)	$\delta^{13}\text{C}\text{‰ PDB CO}$ (29/28)
VANILLIN (LIGNIN)	-27.7	-28.4 ± 0.1
VANILLIN (GUAIACOL)	-27.2	-31.3 ± 0.3
VANILLIN C	-19.9	-13.0 ± 0.2
VANILLIN (NATURAL)	-20.1	-20.6 ± 0.3

$\delta^{13}\text{C}_{\text{average}}$
-19.9 ‰ PDB



SAMPLE	COMBUSTION	PYROLYSIS		
	$\delta^{13}\text{C}\text{‰ PDB CO}_2$ (45/44)	$\delta^{13}\text{C}\text{‰ PDB CO}$ (29/28)	$\delta^{18}\text{O}\text{‰ VSMOW CO}$ (30/28)	$\delta^2\text{H}\text{‰ VSMOW H}_2$ (3/2)
VANILLIN (LIGNIN)	-27.7	-28.4 ± 0.1	$+12.7 \pm 0.4$	-190.7 ± 2.1
VANILLIN (GUAIACOL)	-27.2	-31.3 ± 0.3	-2.2 ± 0.6	-69.7 ± 3.1
VANILLIN C	-19.9	-13.0 ± 0.2	-2.7 ± 0.3	-65.6 ± 0.3
VANILLIN (NATURAL)	-20.1	-20.6 ± 0.3	$+14.7 \pm 0.2$	-100.7 ± 1.1

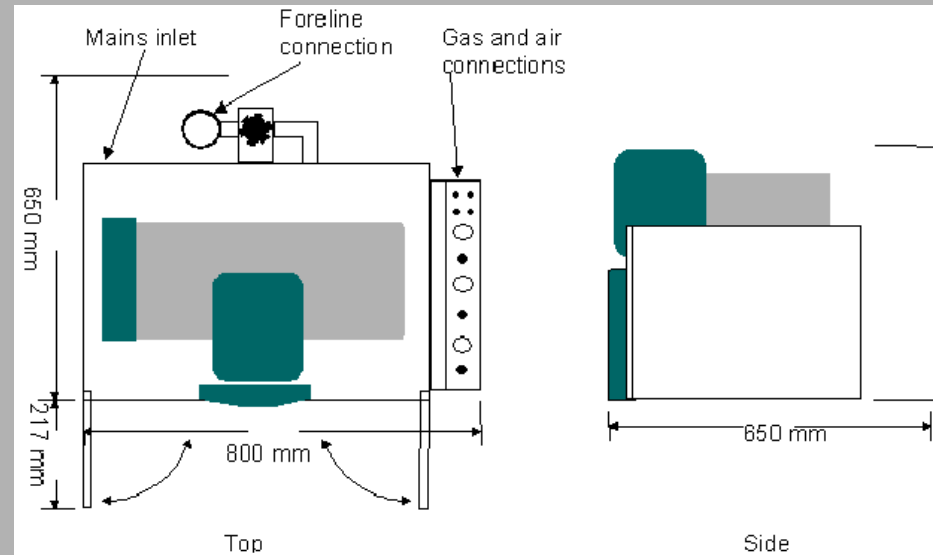
- Rapid continuous flow method
- Allows determination of ^2H abundance in organics
- $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ “substituent specific” measured simultaneously
- Rapid detection of isotopically manipulated vanillin

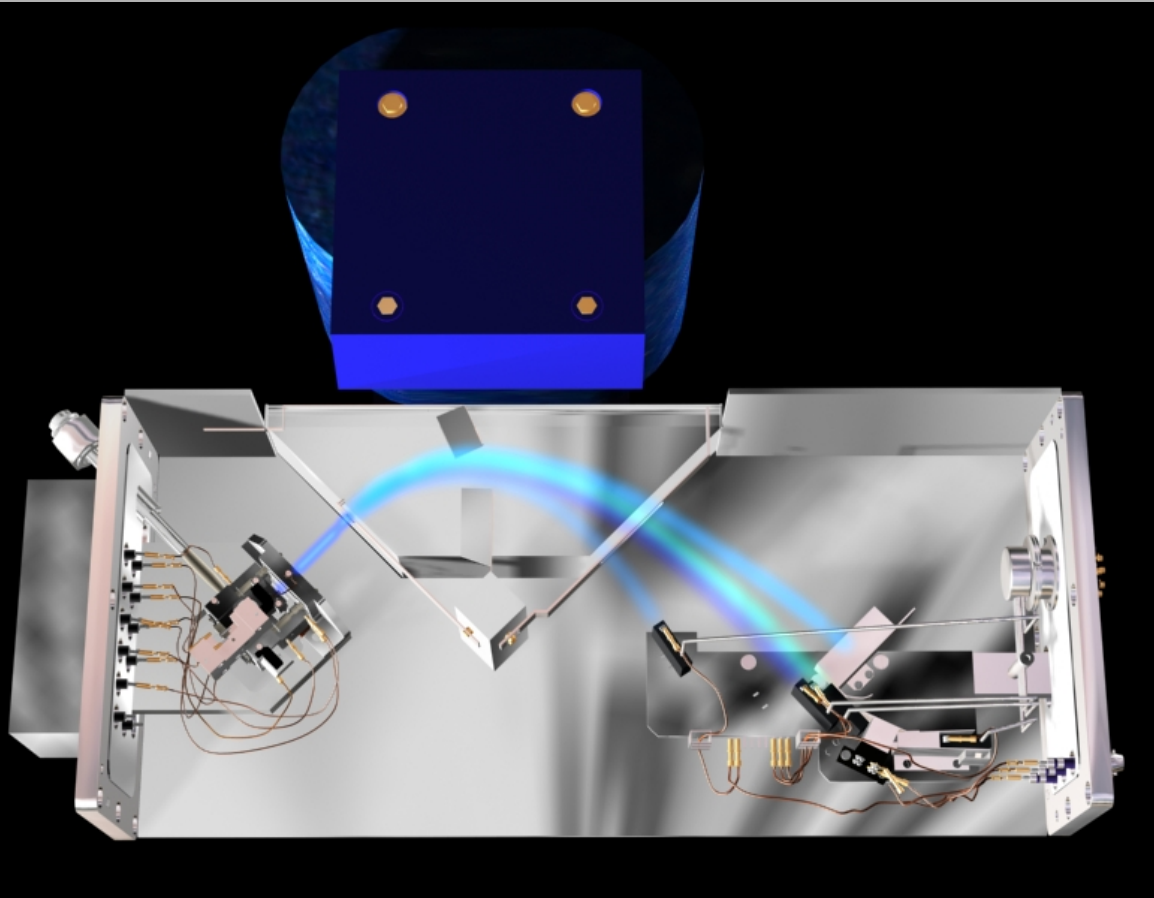


IsoPrime-Benchtop IRMS

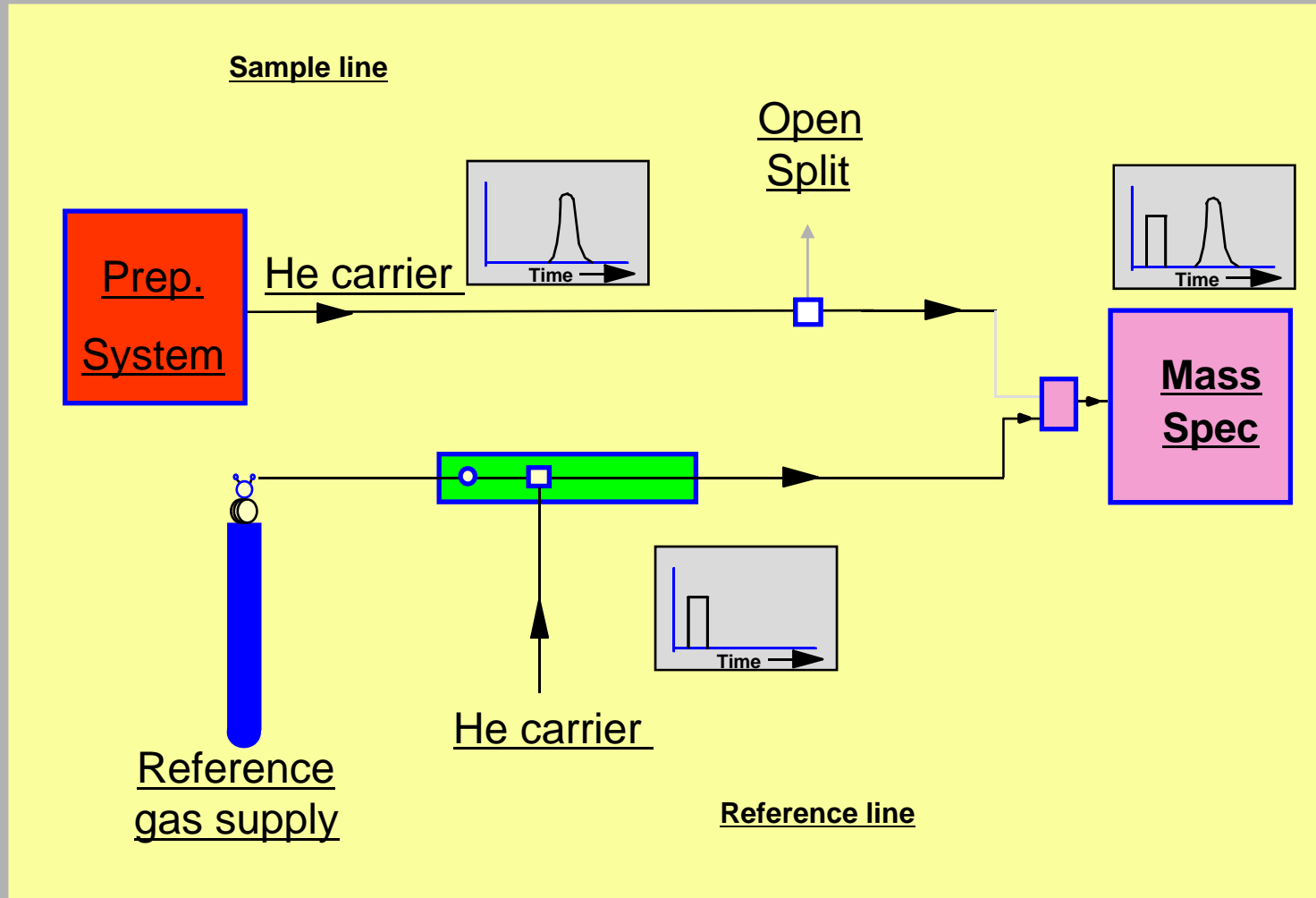


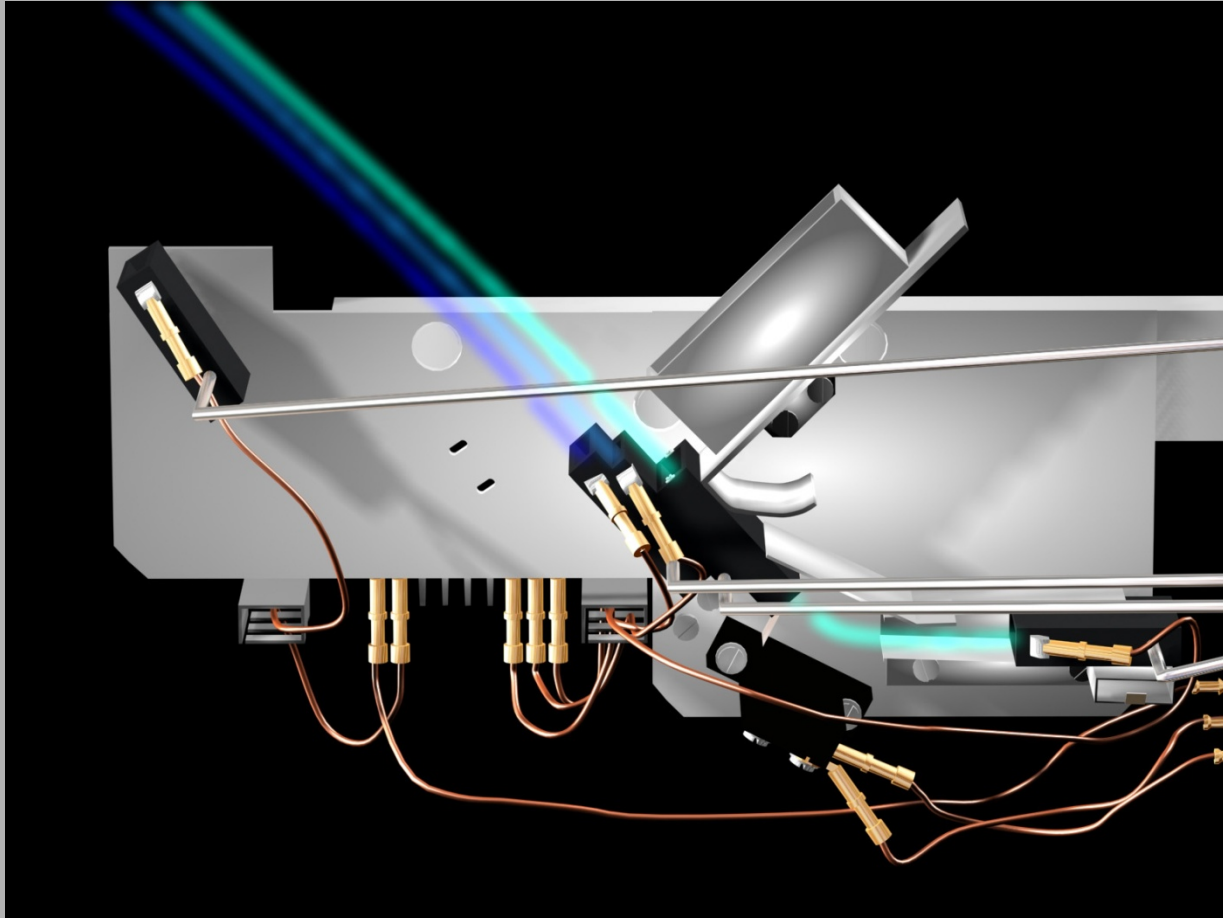
- A true benchtop stable isotope mass spectrometer
- An easy addition to any laboratory

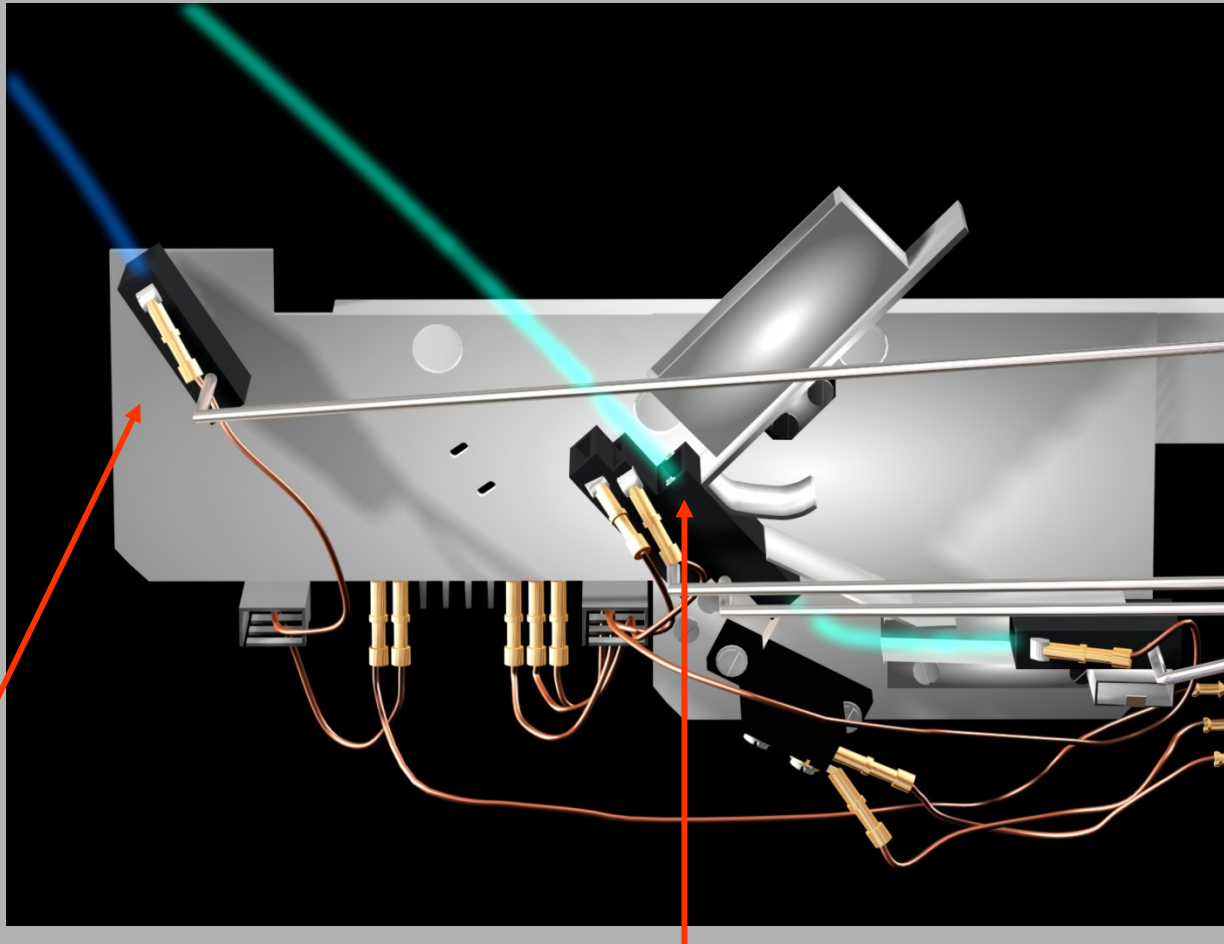




- Horizontal flight tube
- 90° asymmetric geometry
 - Effective magnetic deflection of 108mm
- Turbomolecular pump mounted under source block
- Analyser housing can be baked to 120°C (bake-out heaters fitted as standard for dual inlet systems).







Extra bucket (mass 2) is used with the wide (46) bucket

$^2\text{H}^*$, ^{18}O Waters, Urea, juice, wine



Sample Size

200 μl

Specification

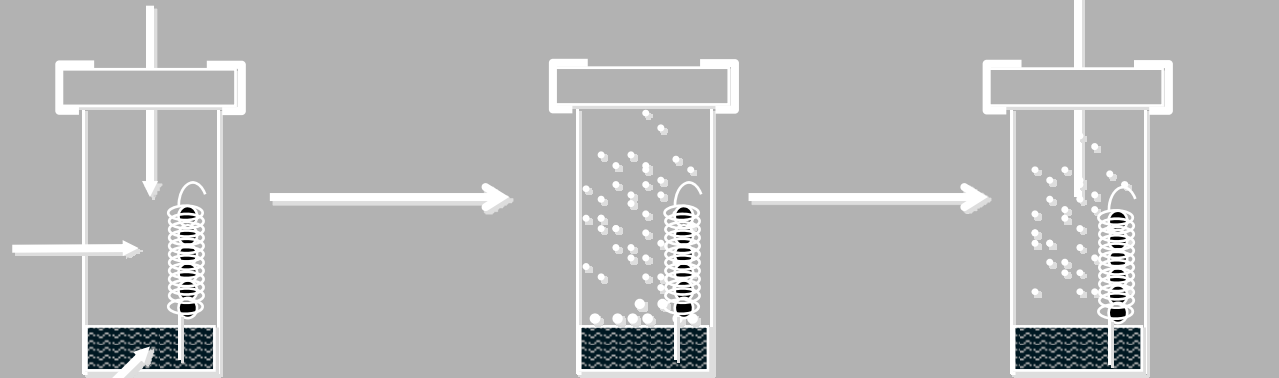
$\delta^{18}\text{O}$: $\leq 0.15\text{‰}$

$\delta^2\text{H}$: $\leq 2.0\text{‰}$

$\delta^2\text{H}$: He + 10% H_2
 $\delta^{18}\text{O}$: He + 5% CO_2

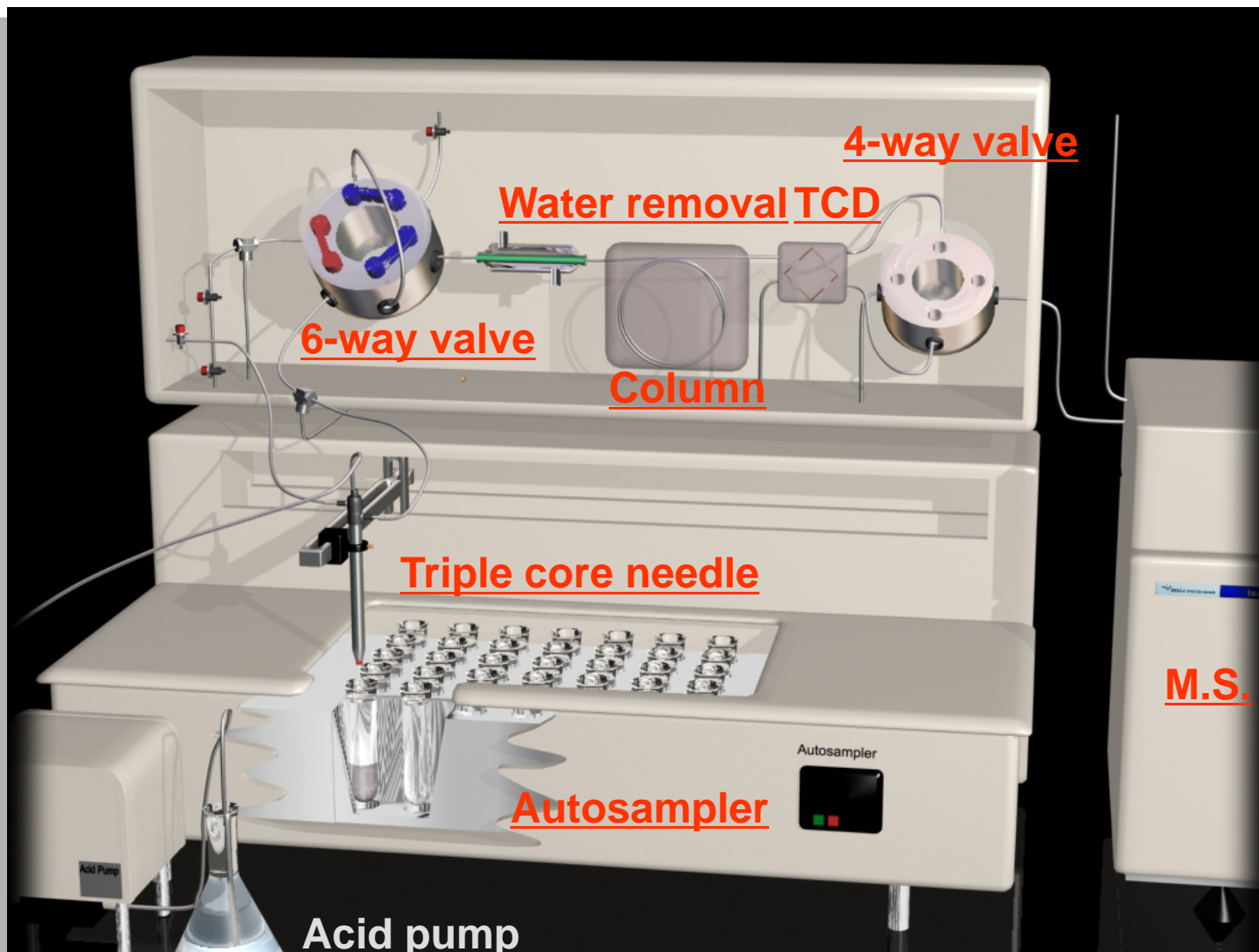
Pt catalyst
for H_2 only

200 ml of sample



IRMS

Analysis Time = 1.5 minutes/sample





Specification

$\delta^{13}\text{C}$: $\leq 0.2\text{‰}$

$\delta^2\text{H}$: $\leq 4.0\text{‰}$

☞ **COMBUSTION**

^{13}C , ^{15}N analyses from mixtures separated by GC and combusted to CO_2 and N_2

☞ **PYROLYSIS**

D/H, analyses from mixtures separated by GC and pyrolysed to H_2

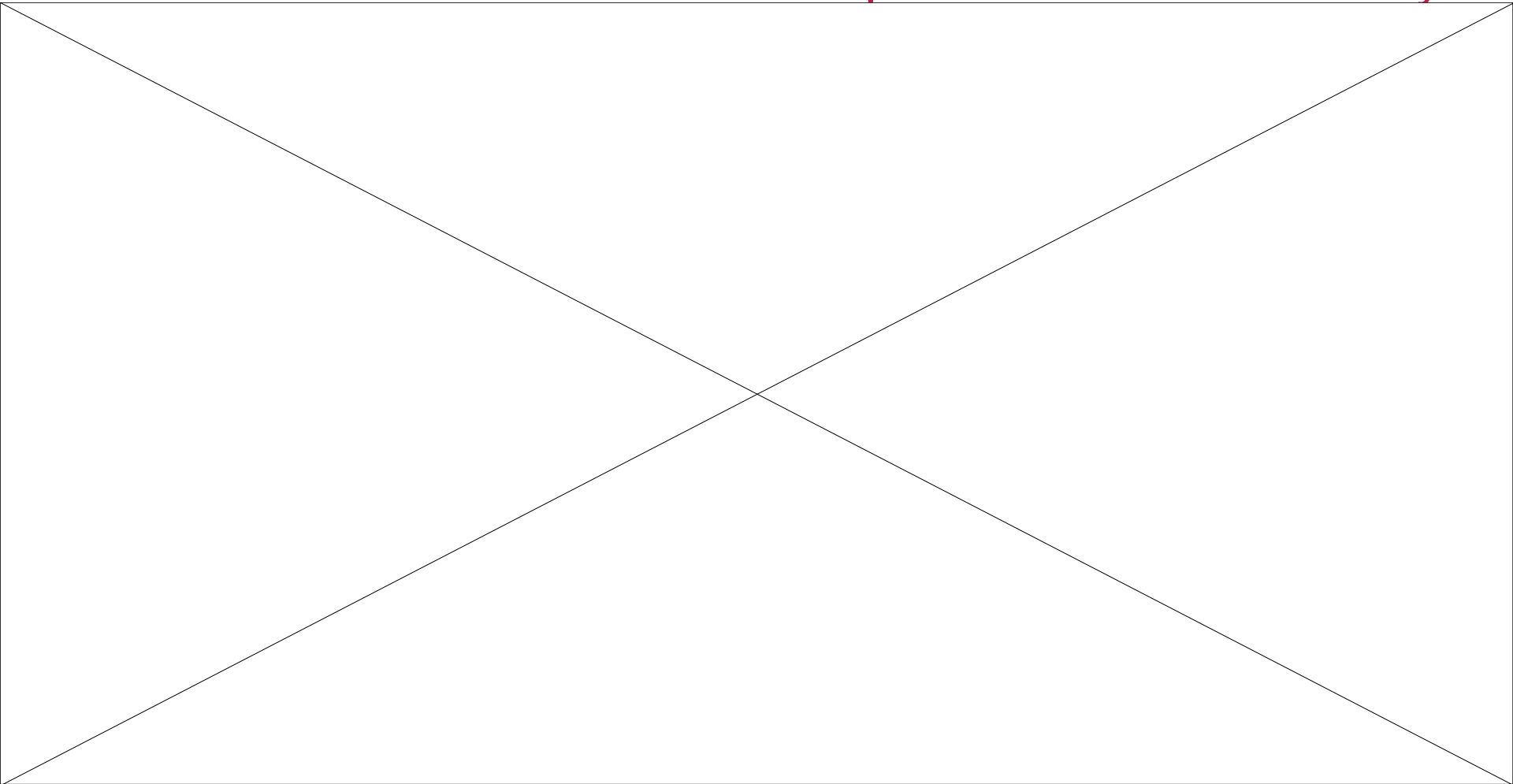
Key Features

- ‘Heart-split’ mechanism
 - combustion of all, or sections of, the GC effluent
- High efficiency Combustion Furnace
 - production of CO₂, N₂, H₂O (cf. methane)
- Chrome*HD*TM technology
- unique technology for production of H₂ for GC-pyrolysis
- Water trapping efficiency
 - membrane or cryogenic traps
- Calibration methods
 - internal reference compound (usually deuterated)
 - external reference gas (Reference Gas Injector)
- Background subtraction software

Elemental Analyser: vario MICRO cube



- Optimized for micro samples
Fully digitalized
- Simultaneous CNS (IRMS) or
CHNS (TCD)
- Low Blank auto sampler



I) Conventionally: Three samples for the IRMS of four elements

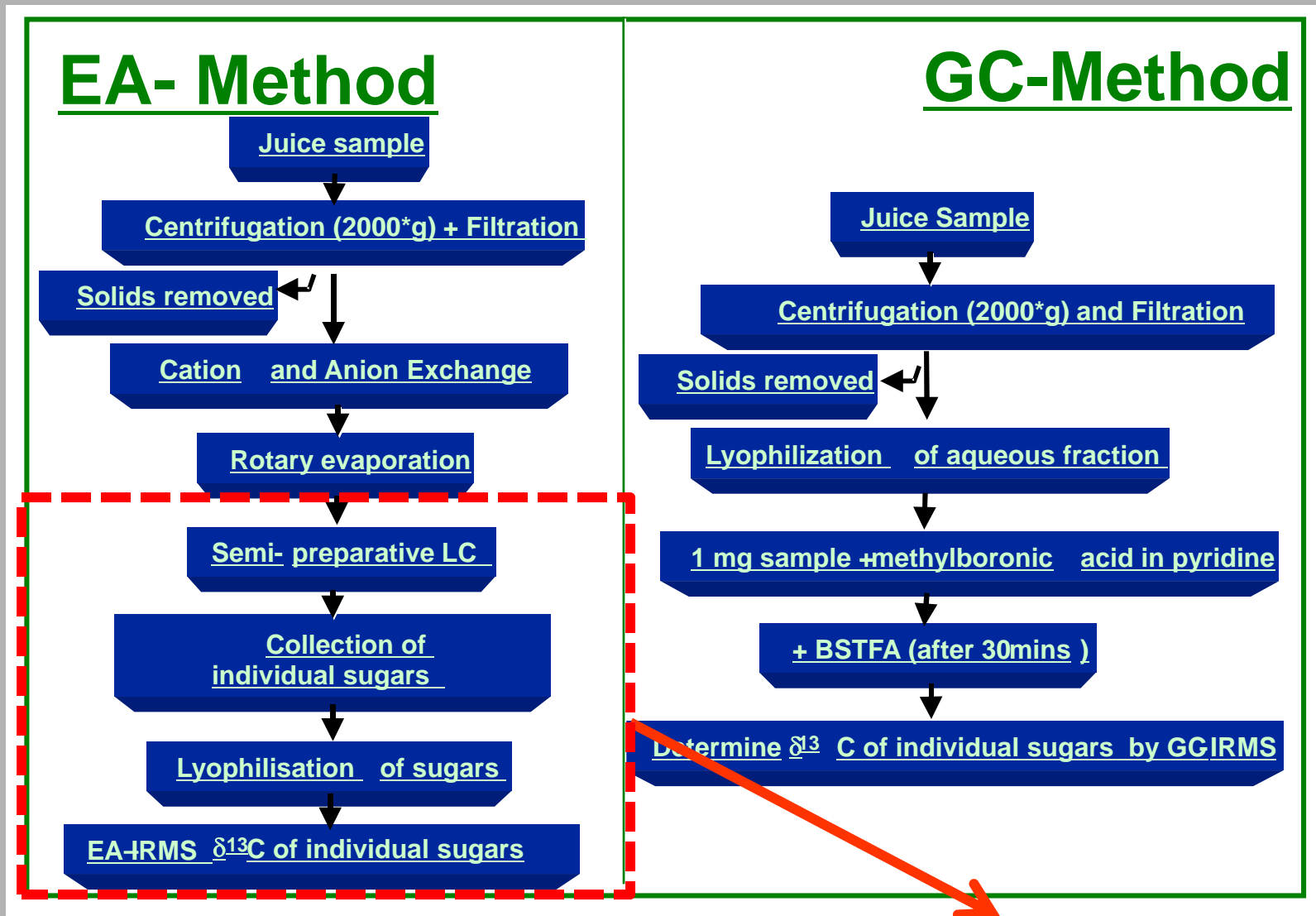
^{13}C , ^{15}N : Combustion, GC separation of N_2 and CO_2 ; IRMS

^2H , (^{18}O): Pyrolysis, GC separation of H_2 and CO (in absence of N); IRMS

^{34}S : Combustion, GC separation of SO_2 ; IRMS

II) By our system: One sample for the IRMS and EA of four elements

^{13}C , ^{15}N , ^2H , ^{34}S : Combustion, adsorptive separation of all gases; reduction of H_2O ; IRMS



LiquiFace



Dionex ICS 3000



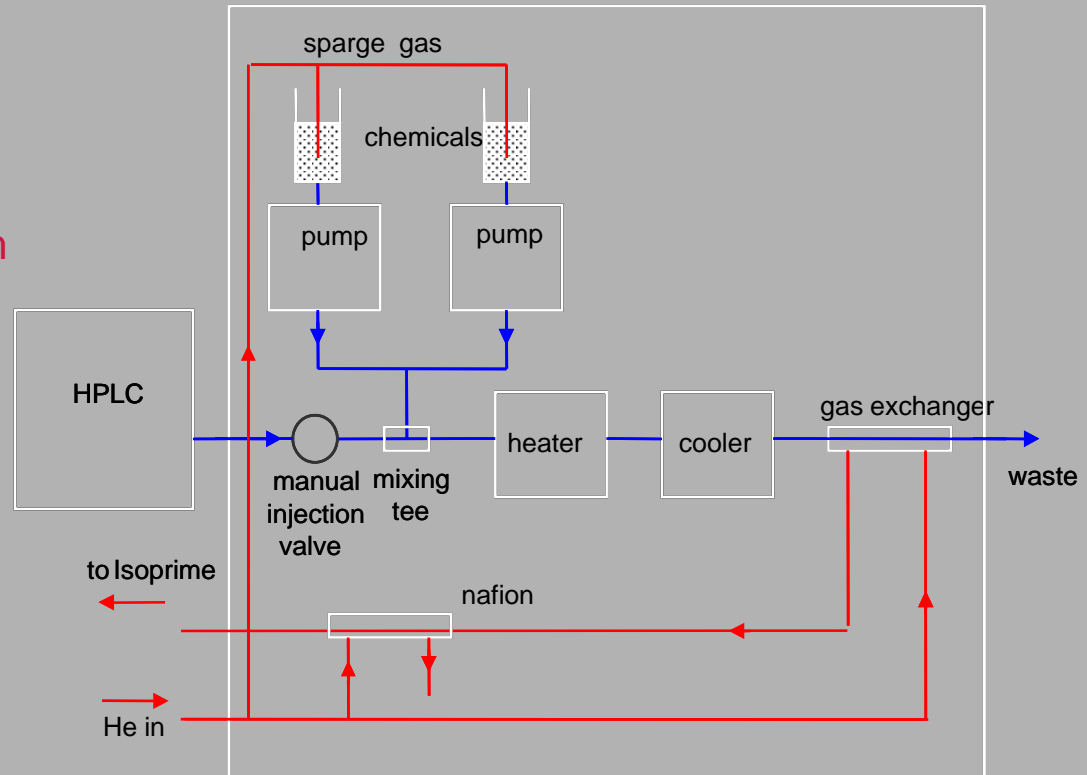
Sugars

Amino acids

Organic acids

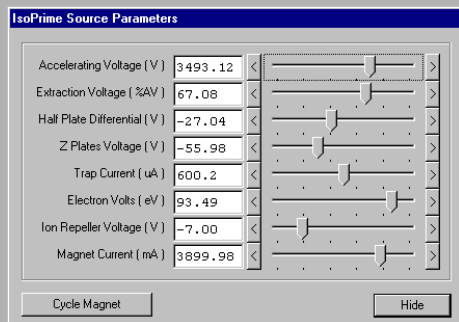
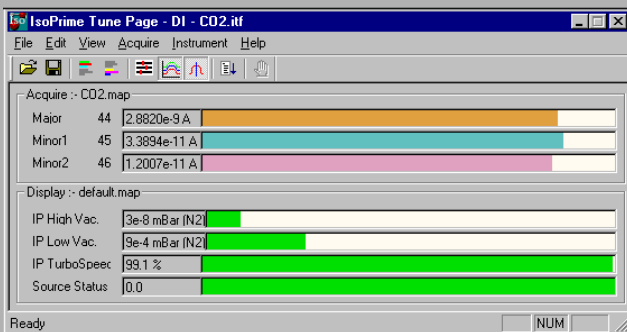
Schematic of the LC Interface

- Dissolved material converted to gaseous form by reaction with suitable oxidizing agents
- Then passed through heater at 98 °C to speed up conversion to CO₂
- The cooler returns the solution to room temperature to reduce vapor pressure of water
- Cooling the solution minimizes the passage of water vapor through membrane
- The He/CO₂ then passes through a Nafion drier and finally into MS



IsoPrime: The True XP IRMS

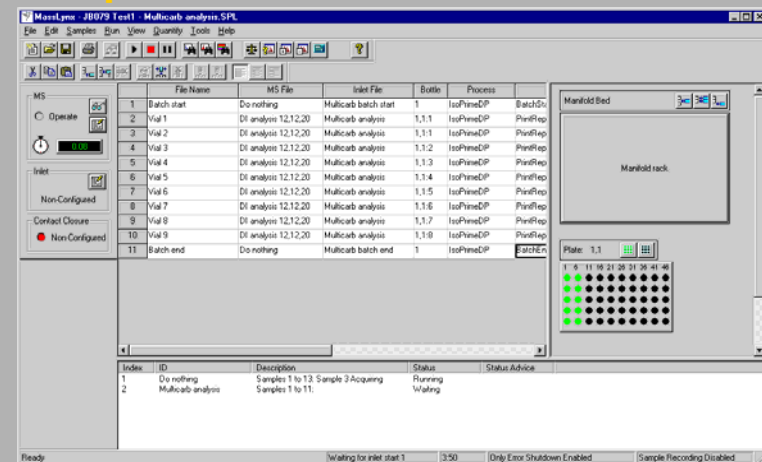
IsoPrime Instrument control



Advanced settings

A Stable Future for Stable Isotopes

Sample list



Dual Inlet control

