

# GC-IRMS: $\delta^{13}\text{C}$ Analysis of PAHs in Soil and Sediment Samples using High Resolution GC Coupled with Isotope Ratio MS

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## Key Words

GC-IRMS, PAHs, Compound Specific Isotope Analysis, Isotope Ratio MS

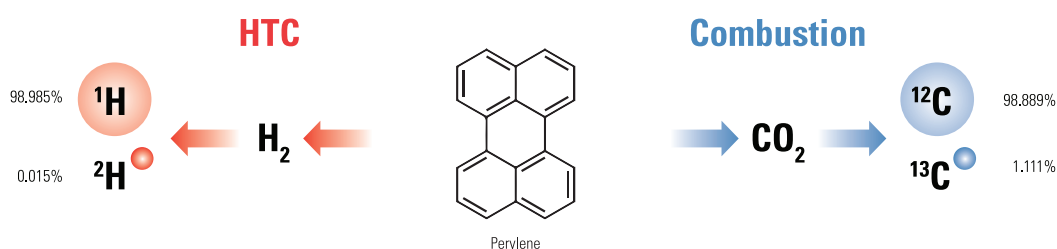


Figure 1. Basic principle of IRMS.

## Introduction

Gas chromatography coupled with Isotope Ratio MS (GC-IRMS) has entered into widespread applications like environmental studies and forensics enabling compound specific isotope analysis (CSIA). Isotopic fingerprints analyzed by GC-IRMS may still provide information where classical GC/MS methods based on compound quantitation cannot. The potential of using CSIA for source differentiation of environmental polycyclic aromatic hydrocarbons (PAHs) has already been demonstrated.

Polycyclic aromatic hydrocarbons (PAHs) are one of the most widespread organic pollutants that consist of fused aromatic rings and do not contain hetero atoms or carry substituents. Natural crude oil and coal deposits contain significant amounts of PAHs, arising from chemical conversion of natural product molecules, such as steroids, to aromatic hydrocarbons. In addition to their presence in fossil fuels they are often the by-product of petroleum combustion and arise from coal and wood burning and vehicle emissions with their isotopic compositions linked to their sources. These potent organic pollutants are persistent and ubiquitous distributed in soils, sediment and oily substances. They tend to accumulate in top soils and sediments. Due to their carcinogenic characteristics at relatively low concentrations, they are of particular environmental concern.

The toxicity of PAHs is structure-dependent. Isomers (PAHs with the same formula and number of rings) can vary from being nontoxic to extremely toxic. Seven PAHs have been classified by the US EPA as probable human carcinogens and their toxic characteristics and persistent nature place them among the most extensively monitored organic contaminants.

GC-IRMS has revolutionized Isotope Ratio Mass Spectrometry within the last 20 years. While GC/MS is applied to structural elucidation and compound quantitation, GC-IRMS reveals the history and origin of compounds by reading their isotopic signature with ultra-high precision. Small variations of the natural isotope abundances cannot be detected with GC/MS analysis of the compound.

Only the combination of a GC and an online sample preparation device which decomposes the compound into simple gases like  $\text{CO}_2$  and  $\text{N}_2$  prior to the online measurement of the isotope abundances in an isotope ratio mass spectrometer, is capable of routinely achieving the required precision.

## Methods

### System Setup

Organic compounds eluting from the GC column are converted into simple gases when traversing one of the capillary micro reactors.

A 4-port valve directs the GC flow into the combustion or the pyrolysis reactor which allows for the first time the analysis of  $^{13}\text{C}/^{12}\text{C}$ ,  $^{15}\text{N}/^{14}\text{N}$  and  $^2\text{H}/^1\text{H}$  within one batch of sequences.

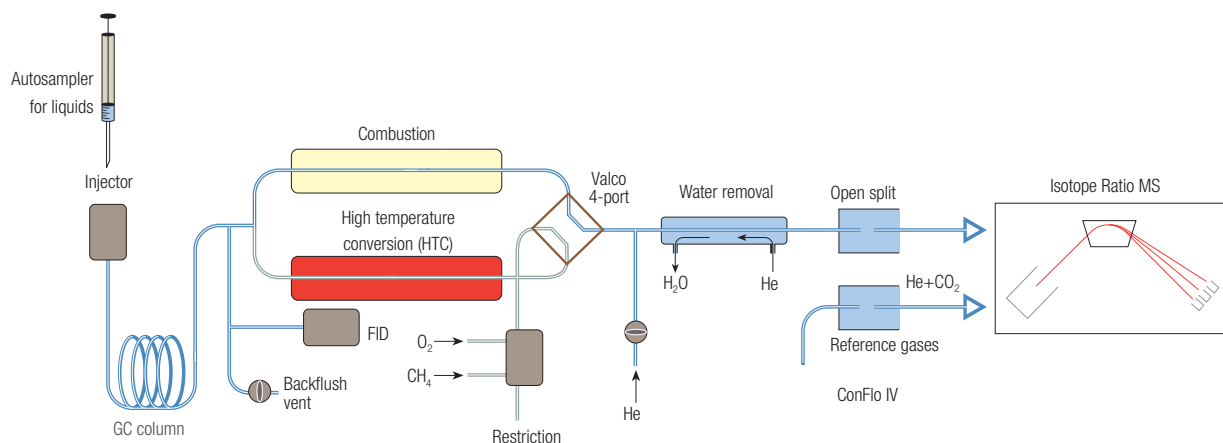


Figure 2. Schematic of the *irm*-GC/MS system with the Thermo Scientific™ GC IsoLink™.

### Combustion Reactor Design

The new interface concept incorporates an improved reactor design. Up to recently a combination of CuO/NiO/Pt wires braided into a ceramic tube has been employed. The new reactor design comprises a NiO tube in combination with NiO and CuO wires to maximize oxidation capacity. Higher temperatures can be applied, which guarantee quantitative conversion for most stable compounds such as PAHs, pesticides or methane.

The combustion reactor system is typically operated at 950 - 1100°C. Highly stable compounds such as PAHs might require high conversion temperature. Nitrogen containing compounds are quantitatively converted into  $\text{N}_2$ . Total capacity of the reactor is significantly increased up to 120  $\mu\text{g}$  of carbon before automatic reoxidation by a gentle flow of oxygen has to be performed.

### Two conversion techniques are applied:

1. Quantitative high temperature combustion for  $^{13}\text{C}/^{12}\text{C}$  and  $^{15}\text{N}/^{14}\text{N}$  determination converts compounds into  $\text{CO}_2$ ,  $\text{N}_2$ , and  $\text{H}_2\text{O}$  at up to 1100°C. The  $\text{H}_2\text{O}$  formed in the oxidation process is removed on-line by a water separator incorporating a nafion membrane.
2. Quantitative high temperature pyrolysis for  $^2\text{H}/^1\text{H}$  and  $^{18}\text{O}/^{16}\text{O}$  determination converts organic H to  $\text{H}_2$  at 1450°C and organic O to CO at 1280°C in inert and reductive capillary reactors.

### GC Parameters

Injector	Split/splitless, splitless mode
	Purge time: 1 min
	Injection volume: 1 $\mu\text{L}$
Carrier gas	Helium, 1.4 mL/min, constant flow mode
Column	TG-5MS, 30 m x 0.25 mm x 0.25 $\mu\text{m}$
Oven temp. program	50°C, 1 min
	10°C/min to 300°C (30 min)
	30°C/min to 320°C (5 min)

### IRMS Parameters

Preparation device	GC IsoLink CNH
Interface	ConFlo IV
Combustion temp.	1050°C
Carrier gas	Helium, pressure: 1.6 bar

Compound	Retention Time (s)	Expected $\delta^{13}\text{C}_{\text{PDB}}$ (‰)	Measured $\delta^{13}\text{C}_{\text{PDB}}$ (‰)	Precision (‰)	Difference (‰): Expected-Measured
C-16	839	-30.67	-31.45	0.11	0.78
C-17	905	-31.48	-30.94	0.33	-0.54
C-18	967	-31.17	-31.16	0.12	-0.01
C-19	1027	-33.25	-33.27	0.13	0.02
C-20	1084	-32.38	-32.26	0.04	-0.12
C-21	1138	-29.15	-29.37	0.31	0.22
C-22	1190	-32.91	-32.91	0.18	0.00
C-23	1241	-31.79	-31.71	0.07	-0.08
C-24	1290	-33.39	-33.33	0.12	-0.06
C-25	1336	-28.62	-28.50	0.07	-0.12
C-26	1380	-33.07	-32.75	0.22	-0.32
C-27	1424	-28.62	-28.67	0.15	0.05
C-28	1465	-32.11	-32.31	0.12	0.20
C-29	1506	-31.17	-31.18	0.06	0.01
C-30	1548	-33.16	-33.33	0.06	0.17

Table 1. Evaluation of accuracy and precision of GC-IRMS using an international accepted reference compound mixture (Schimmelmann B2).

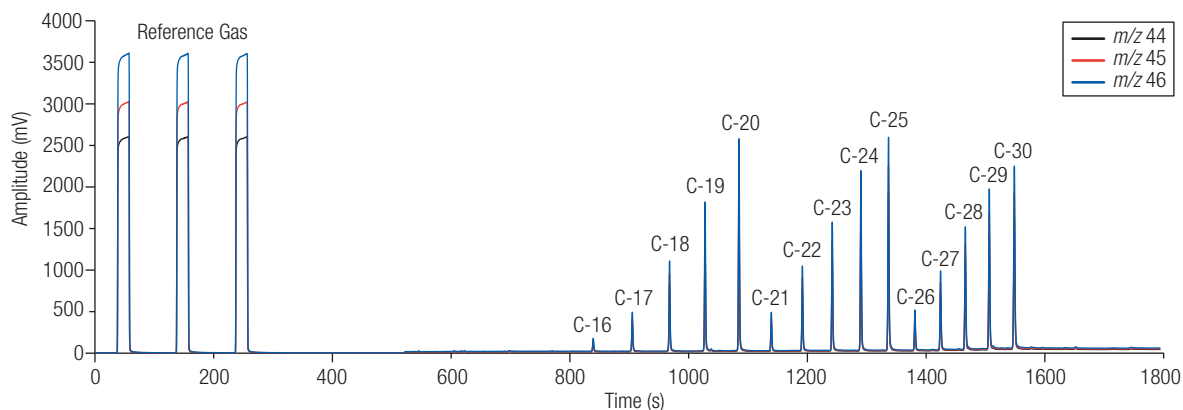


Figure 3. Chromatogram ( $m/z$  44) of the Schimmelmann mixture B2.

## Results

The new concept has been carefully evaluated by analyzing various calibrated standard mixtures. For many years the Biochemical Laboratories at Indiana University have provided stable isotope reference materials for the research community. One of the reference mixtures is the alkane mixture B2 which contains fifteen n-alkanes (C-16 to C-30) in a five-fold range of concentrations arranged in three pentads with rising concentrations. The mixture B3 is internationally accepted and widely used for instrument calibration and evaluation of accuracy and precision. Figure 3 shows the chromatogram of B2 with  $m/z$  44, 45 and 46. Table 1 reports the delta values in comparison to the expected values. The delta values of the compounds are in agreement with the expected values. Higher variation can be observed for the first two minor compounds.

Figure 4 shows a chromatogram of a sediment sample from a fresh water lake. Such complex environmental samples require an analytical system with high separation efficiency. Peak broadening and loss of resolution by the conversion process are not acceptable. As shown by the chromatogram the new interface concept maintains the integrity of the chromatographic separation.

Typical carbon isotopic values from coal conversion are in the range of -24 to -25‰. The sediment sample, exemplarily shown in Figure 4, exhibits more negative delta values for the target compounds. Isotopic values of -28 to -31‰ are observed for diesel particulates. The impact of biodegradation of organic pollutants using stable isotope ratios will be addressed by further investigations.

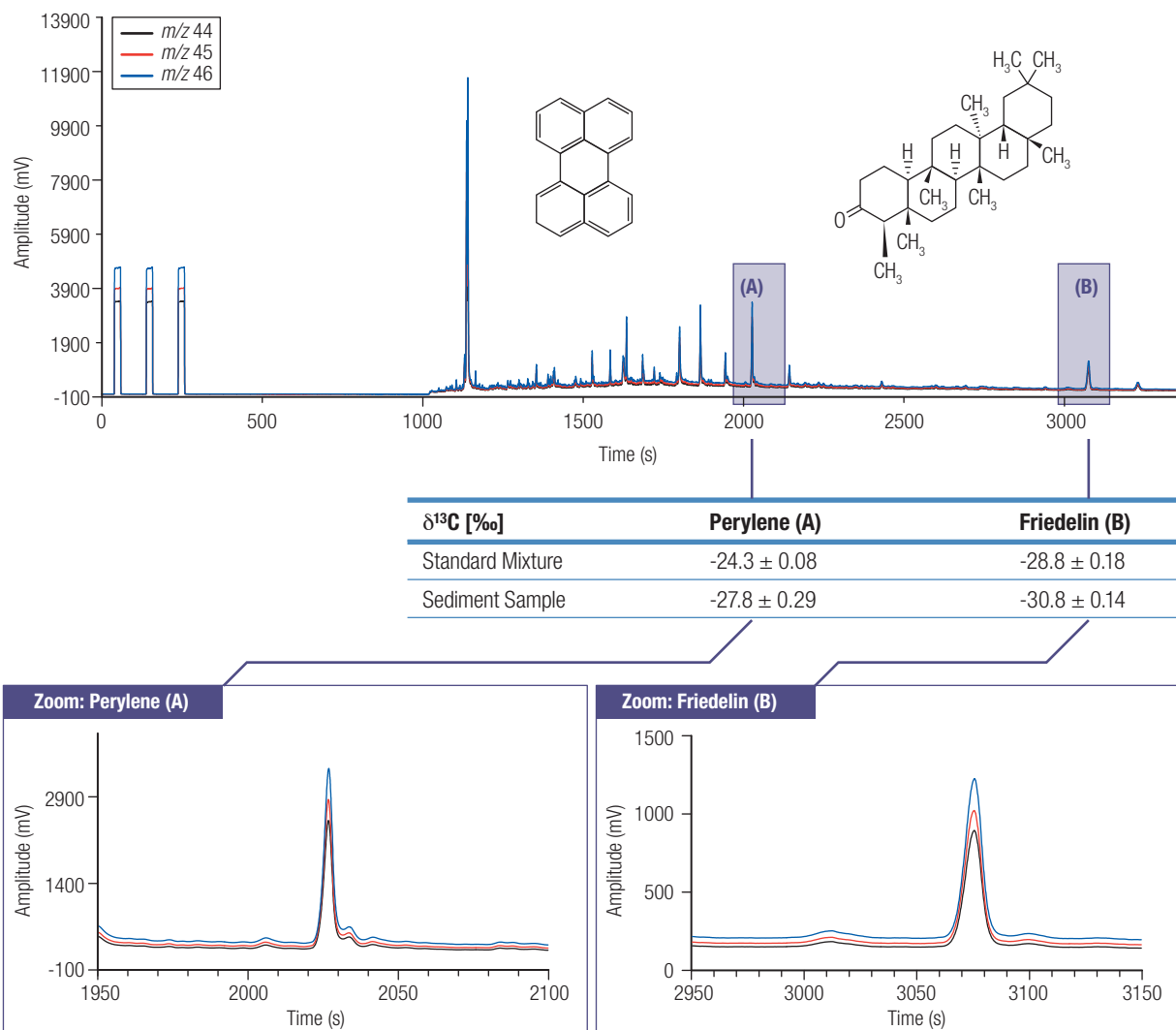


Figure 4. Chromatogram ( $m/z$  44) of a sediment samples from fresh water lake. The table lists the  $\delta^{13}\text{C}$  values and the standard deviation of the sediment sample and a standard mixture.

## Conclusion

The new concept for coupling gas chromatography with isotope ratio mass spectrometry with the GC IsoLink comprises a new combustion technology using temperatures up to 1100°C. A single combustion reactor setup can be applied for  $^{13}\text{C}/^{12}\text{C}$  and  $^{15}\text{N}/^{14}\text{N}$  isotope ratio analysis. Automatic switching from combustion to high temperature conversion reactor is accomplished for carbon, nitrogen and hydrogen isotopic analyses within one sequence.

Peak shapes are preserved due to improved transfer, fewer and shorter connections in the system. This new GC-IRMS system allows the determination of the isotope ratios from all individual compounds in a complex mixture. All fields of application using GC and GC/MS benefit from isotope ratio monitoring. Comprehensive insights can be expected from stable isotope studies in the area of environmental forensics.

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