

A photograph of an industrial refinery or chemical plant at sunset. The sky is a mix of orange, yellow, and blue. Several tall distillation columns and pipes are visible, with some emitting white steam or smoke. The foreground shows more industrial structures and a large spherical storage tank.

# GC-IRMS: Tracing pollutants in soil and sediment using carbon isotope fingerprint

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## Goal

Discriminate between pyrogenic and petrogenic PAHs using  $^{13}\text{C}$  isotope fingerprints.

## Introduction

Polycyclic aromatic hydrocarbons (PAHs) are persistent pollutants in the air, soils and sediments. Many PAHs are toxic, carcinogenic or mutagenic to organisms and humans, depending upon their structure, placing them among the extensively monitored organic contaminants. PAHs are present in the environment from natural sources including fossil fuels, such as coal, from volcanic eruptions and forest fires. In addition, PAHs derive from anthropogenic sources, as a by-product of vehicle emissions, burning of fireplace wood and fuel oils and various industrial processes.

The major sources of PAHs to the environment are pyrogenic and petrogenic processes. Pyrogenic PAHs are formed by incomplete combustion of organic material, such as during cracking process, combustion of motor fuels or wood in forest fires, while petrogenic PAHs are formed during crude oil maturation or released due to fuel transportation spills. Although the sources of PAHs are generally well-known, investigating whether PAHs originate from oil, wood or coal is important in order to reduce the health risk which they pose and for source identification. PAHs are especially inspected in relation to oil and gas explorations as their presence in the aquatic environment can be easily distributed in the food web, for example.

In this application brief, we show how carbon isotope Fingerprints ( $^{13}\text{C}$ ) can be used for source identification of PAHs on local to global scales.

## Analytical configuration

The Thermo Scientific™ GC IsoLink II™ IRMS System provides a routine methodology for carbon, hydrogen, nitrogen and oxygen stable isotope analysis. After the chromatographic separation of compounds in Thermo Scientific™ TRACE™ 1310 GC, their conversion to a simple gas is performed by combustion or pyrolysis in Thermo Scientific™ GC IsoLink II™ Conversion Interface. Subsequently, produced gasses are transferred in helium carrier gas flow to Thermo Scientific™ DELTA V™ Isotope Ratio Mass Spectrometer via Thermo Scientific™ ConFlo IV™ Universal Interface.

For carbon isotope measurement of PAHs in sediments from a fresh water lake, 1  $\mu\text{L}$  of the sample was injected splitless with 1.4 ml/min Helium carrier gas flow in constant flow mode. 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 in Figure 1, the integrity of the chromatographic separation was well preserved by the holistic capillary approach of the GC IsoLink II System. Chromatographic separation was obtained by the Thermo Scientific™ TraceGOLD™ TG-5MS GC Column.

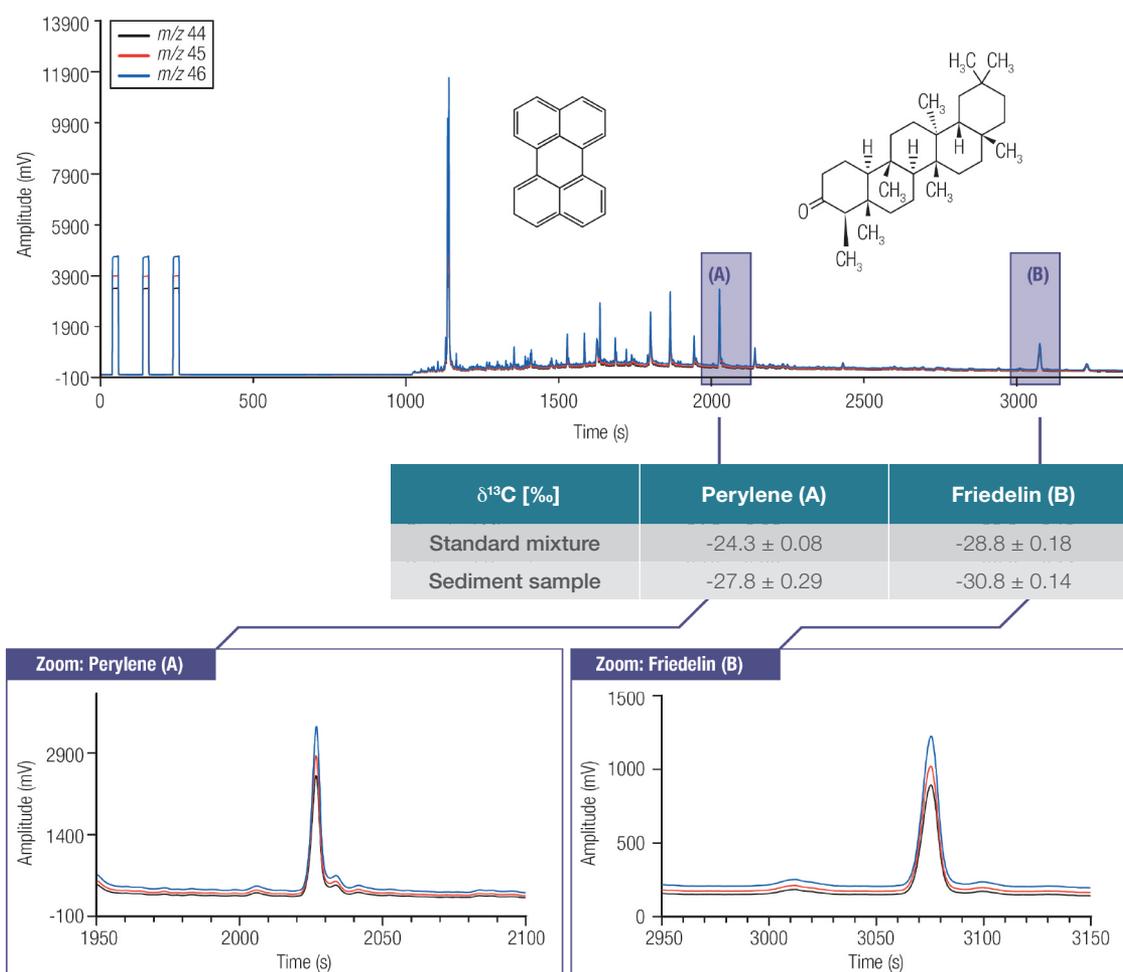


Figure 1. Chromatogram of a sediment samples from fresh water lake. The table lists the stable carbon isotope values of the sediment sample and a standard mixture.



### Carbon isotope fingerprints of PAHs

The carbon isotope fingerprints of PAHs are expected to reflect those of the original organic matter prior to combustion. Typical carbon isotopic values ( $\delta^{13}\text{C}$ ) from coal conversion are in the range of -23‰ to -25‰. The sediment sample here exhibits more negative values for the target compounds (Figure 1). Pyrogenic PAHs are typically less depleted in  $^{13}\text{C}$  than their petrogenic counterparts: this differentiation can be used for source identification (Elsner, 2012).  $\delta^{13}\text{C}$  values of -28‰ to -31‰ are observed for diesel particulates, typically, which allows the identification of the PAH's analyzed here as having a pyrogenic nature.

### Conclusion

Isotope fingerprints analyzed by GC-IRMS enable to differentiate between pyrogenic and petrogenic PAHs. With the GC IsoLink II IRMS System, laboratories gain an effective analytical solution based on fast, reliable analysis with full automation.

GC-IRMS analysis of PAHs is successfully applied in diverse studies for detailed source identification of organic pollutants, allowing users to distinguish PAHs from coal and wood burning or vehicle exhausts (Okuda, 2002; O'Malley, 1994; McRae, 1996). The US Environmental Protection Agency has identified 16 parental PAHs as priority pollutants. Variations in the isotopic fingerprint between these sources provide a basis for using compound specific IRMS analysis as a powerful tool for environmental forensics investigations of these potentially carcinogenic pollutants.

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