



## Review

# Stable carbon isotopic ratio measurement of polycyclic aromatic hydrocarbons as a tool for source identification and apportionment— A review of analytical methodologies

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## ABSTRACT

The measurement of the ratio of stable isotopes of carbon ( $^{13}\text{C}/^{12}\text{C}$  expressed as a  $\delta^{13}\text{C}$ ) in the individual components of a sample may be used as a means to identify the origin of these components. This article reviews the approaches and reports on the successes and failures of source identification and apportionment of Polycyclic Aromatic Hydrocarbons (PAHs) with the use of compound-specific isotope analysis (CSIA). One of the conditions for a precise and accurate analysis of isotope ratios with the use of GC–C–IRMS is the need for well separated peaks, with no co-elutions, and reduced unresolved complex mixture (UCM). Additionally, special care needs to be taken for an investigation of possible isotope fractionation effects introduced during the analytical treatment of samples. With the above-mentioned problems in mind, this review discusses in detail and compares current laboratory methodologies, mainly in the extraction and subsequent clean-up techniques used for environmental samples (air particulate matter, soil and sediments). Sampling strategies, the use of isotopic internal standards and the ranges for precision and accuracy are also reported and discussed.

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## Contents

1. Introduction . . . . .	436
2. Potential of CSIA for source identification and apportionment . . . . .	438
2.1. Combustion and/or pyrolysis of materials—determination of the isotopic signature of sources . . . . .	438
2.2. Application to environmental samples . . . . .	442
2.2.1. Sediments . . . . .	442
2.2.2. Soils . . . . .	444
2.2.3. Origin of perylene . . . . .	444
2.2.4. Air particulate matter . . . . .	444
3. Fractionation issues . . . . .	445
3.1. Investigation of the possibility of isotopic fractionation during the laboratory procedures . . . . .	445
3.2. Investigation of the possibility of isotopic fractionation of PAHs in the environment . . . . .	446
4. Environmental sample type . . . . .	447
5. Sample size . . . . .	447
6. Sampling of sources . . . . .	447
7. Sample treatment prior to extraction . . . . .	447
8. Extraction . . . . .	447
9. Sample clean-up and class separation . . . . .	448
10. Clean-up experiments . . . . .	448
11. Internal standard . . . . .	448
12. Analytical column . . . . .	448
13. Precision and accuracy . . . . .	449

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14. Summary and conclusions . . . . .	449
Acknowledgements . . . . .	449
References . . . . .	449

## 1. Introduction

Analysing the ratio of stable isotopes of carbon ( $^{13}\text{C}/^{12}\text{C}$  expressed as a  $\delta^{13}\text{C}$ ) in the individual components isolated from various environmental samples is one of the means to identify the origin of these components [1]. In contrast, the bulk  $\delta^{13}\text{C}$  value of a given sample represents an average of all carbon compounds present in the sample, and thus averaging of all their sources. The allocation of the contaminants to a specific source allows an appropriate method of risk reduction to be taken, or can be used to identify the parties responsible for the contamination [2].

Some of the first studies on source identification applying gas chromatography coupled to isotopic ratio mass spectrometry (GC–IRMS), were published by Matthews and Hayes [3], Freeman et al. [4] and Riely et al. [5]. In this technique the components of the sample are converted to a desired gas (e.g.  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{N}_2$ ) as they elute from a chromatographic column whilst the effluent is continuously analysed by IRMS for isotopic composition. For this reason, it is often referred to as Gas Chromatography–Combustion–Isotopic Ratio Mass Spectrometry (GC–C–IRMS). Later, following technical and software improvements, the technique became widely applied. GC–C–IRMS is described in detail elsewhere, e.g. by Ricci et al. [6] or a review by Meier-Augenstein [7].

The variations in isotopic abundances are normally very small, thus the carbon isotopic data are given as per mil (‰) difference from the reference [8]. The reference for carbon is Vienna Pee Dee Belemnite (VPDB) which  $\delta^{13}\text{C}$  defines 0‰ on the VPDB scale. The conventional  $\delta$ -notation is expressed as

$$\delta^{13}\text{C} = \frac{^{13}\text{C}/^{12}\text{C}_{\text{sample}}}{^{13}\text{C}/^{12}\text{C}_{\text{VPDB}}} - 1$$

VPDB is a hypothetical standard substitute for PBD (Pee Dee Belemnite), a cretaceous belemnite, *Belemnitella Americana*, from the Pee Dee formation of South Carolina [9] which was originally used as an international standard. The equation above originally contained a term \*1000 which denoted per mil. The convention, however, requires the user to additionally place the symbol ‰ after the numerical value [10] and thus, according to the latest IUPAC guidelines [10], to minimise the confusion the term \* 1000 should be deleted from the equation.

Polycyclic Aromatic Hydrocarbons (PAHs) are a class of compounds that contain two or more fused benzene rings. They are widely spread in the environment (e.g. atmosphere, sediments, soil) and can be classified into three general categories: petrogenic-derived from slow maturation of organic matter under geothermal gradient conditions; pyrogenic-derived from incomplete combustion of organic matter; and short-term diagenetic products derived from biogenic precursors [11]. Major sources for PAHs are: combustion of fossil fuels (coal, oil, natural gas and wood), arising from vehicle exhausts, power and heat generation plants, residential heating, incinerators, several industrial processes (e.g. coke production, aluminium smelting); fuel oil or gasoline spills, natural seeps and creosote releases. The anthropogenic emissions contribute the greater proportion of PAHs [12]. They are suspected carcinogens and the US EPA (US Environmental Protection Agency) has identified 16 parental PAHs as priority pollutants. Because of the hydrophobic and lipophilic

properties of PAHs they are adsorbed on particulate matter and eventually accumulate in sediments or soils [13].

The investigation of molecular ratios is the most common approach for source identification of PAHs [14–17]. Such an approach suffers, however, from many complications. In addition to the non-uniqueness of some source signatures [13,18,19] and the fact that molecular compositions of PAHs depend on various factors such as source material, combustion temperature, air/fuel ratio [1,20], various processes, including physical, chemical and microbial transformations may alter these molecular compositions, so that they may no longer resemble the original fingerprint of the source [1,12,13,21–24]. Thus, source investigations using molecular considerations, especially for heavily weathered samples, can often be difficult. In such cases, the use of additional information, e.g. carbon isotopic ratios, are needed to improve the studies of the origin or fate of PAHs [25]. The stable carbon isotope composition of individual PAHs is expected to reflect those of the organic matter after processes such as combustion [1] and is relatively resistant to environmental degradation. It can complement the molecular methods, providing an effective additional tracer [26]. As an example, the use of compound-specific isotope analysis (CSIA) (PAHs extracted from the sediments of Elisabeth River, VA, USA) made it possible to separate the two signatures derived from similar sources—coal and coal gasification [11]. The sole use of isomer ratios (fluoranthene/pyrene and benzo(a)anthracene/chrysene) did not allow the source contributions to be differentiated.

Compound-specific isotope analysis of carbon isotopes has been successfully applied as an alternative [12] or complementary method to molecular fingerprint investigations as a means of source identification and apportionment of PAHs pollutants [11,13,19,27–36]. One of the conditions for a reliable analysis of isotope ratios when applying GC–C–IRMS is to obtain well separated peaks, free of co-elutions and unresolved complex mixture (UCM) [26,37]. During the chromatographic separation, an isotope effect associated with the partitioning of the analyte between the mobile and stationary phase occurs. The isotopically heavier molecules elute slightly earlier, thus, the isotope ratios vary significantly across the widths of peaks. The beginning of the peak is strongly enriched in  $^{13}\text{C}$  whilst the end of the peak is depleted [6]. In the case that compounds of interest are not well resolved from each other or from the impurities present in the sample, an artificial enrichment of the preceding peak in  $^{13}\text{C}$  would occur and the depletion of the following compound during the separate integration of peak areas. If the carbon isotope ratio of a co-eluting compound, even of a minor one, is significantly different from the target component, it can have a significant effect on its isotope ratio [26]. Samples, particularly these contaminated by oil, contain UCM, which usually appears as a broad hump in the gas chromatogram and can degrade the precision and accuracy of the isotope measurement of PAHs [38].

The aim of this paper is to review the existing publications on carbon stable isotope measurements in PAHs isolated from environmental samples such as soils, sediments and air particulate matter in order to facilitate the source identification and apportionment of these toxic organic pollutants. We focus mainly on the methodologies used for extraction of PAHs from these samples and further steps performed such as sample clean-up and class separation in order to accurately measure the isotopic ratios

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