Chemosphere 89 (2012) 1407–1413

Contents lists available at SciVerse ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Compound specific carbon and hydrogen stable isotope analyses of volatile organic compounds in various emissions of combustion processes

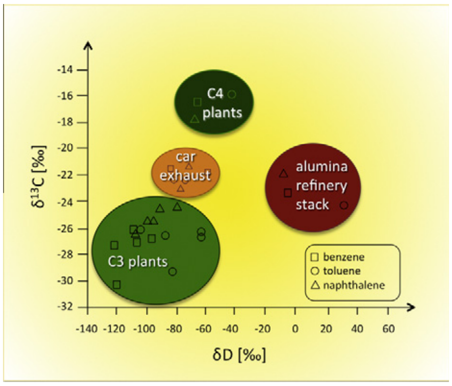
Christiane D. Vitzthum von Eckstaedt[a], Kliti Grice[a,*], Marisa Ioppolo-Armanios[b], David Kelly[c], Mark Gibberd[c]

[a] Department of Chemistry, WA-Organic and Isotope Geochemistry Centre, The Institute for Geoscience Research, John de Laeter Centre for Mass Spectrometry, Curtin University, GPO Box U1987, Perth, WA 6845, Australia
[b] Alcoa World Alumina, Technology Delivery Group, PO Box 161, Kwinana, WA 6167, Australia
[c] Department of Environment and Agriculture, Curtin University, PMB 1 Bussell Hwy., Margaret River, WA 6285, Australia

HIGHLIGHTS

- ▶ TD–GC–irMS is applicable to various emission sources to analyse δ^{13}C and δD of VOCs.
- ▶ δD of individual VOCs from C3 plant combustion are lighter than from C4 plants.
- ▶ δD values indicate that aromatic compounds may derive largely from lignin/cellulose.
- ▶ δ^{13}C and δD of car related emissions can vary significantly.
- ▶ Combined δ^{13}C and δD values allow differentiation between emission categories.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 17 September 2011
Received in revised form 5 June 2012
Accepted 11 June 2012
Available online 24 August 2012

Keywords:
Compound specific isotope analysis
Thermal desorption
Industry emission
Biomass combustion
Car exhaust emission
Source characterisation

ABSTRACT

This study presents carbon (δ^{13}C) and hydrogen (δD) isotope values of volatile organic compounds (VOCs) in various emission sources using thermal desorption–gas chromatography–isotope ratio mass spectrometry (TD–GC–irMS). The investigated VOCs ranged from C6 to C10. Samples were taken from (i) car exhaust emissions as well as from plant combustion experiments of (ii) various C3 and (iii) various C4 plants. We found significant differences in δ values of analysed VOCs between these sources, e.g. δ^{13}C of benzene ranged between (i) -21.7 ± 0.2‰, (ii) -27.6 ± 1.6‰ and (iii) -16.3 ± 2.2‰, respectively and δD of benzene ranged between (i) -73 ± 13‰, (ii) -111 ± 10‰ and (iii) -70 ± 24‰, respectively. Results of VOCs present in investigated emission sources were compared to values from the literature (aluminium refinery emission). All source groups could be clearly distinguished using the dual approach of δ^{13}C and δD analysis. The results of this study indicate that the correlation of compound specific carbon and hydrogen isotope analysis provides the potential for future research to trace the fate and to determine the origin of VOCs in the atmosphere using thermal desorption compound specific isotope analysis.

1. Introduction

Volatile organic compounds (VOCs) are hydrocarbons (and related compounds) defined by a sufficient vapour pressure to enter the atmosphere under ambient conditions. Studying VOCs is very important because they can have an impact on the environment

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* Corresponding author. Tel.: +61 (0) 8 9266 2474; fax: +61 (0) 8 9266 2300.
E-mail addresses: C.v.Eckstaedt@gmx.de (C.D. Vitzthum von Eckstaedt), K.Grice@curtin.edu.au (K. Grice).

http://dx.doi.org/10.1016/j.chemosphere.2012.06.005

and human health (WHO, 2000). Their effects, like irritation but also diseases, have been seen at very low levels of exposure in many epidemiological studies. VOCs are involved in the photochemical formation of ozone and smog in the troposphere and affect local air quality and global climate (Atkinson, 2000). VOCs can derive from various sources of non-combusted petroleum products or formed during combustion of organic material. VOCs are emitted by various anthropogenic (e.g. transportation, industry and biomass burning) and biogenic activity (e.g. microbial production and plant emissions) (Kesselmeier, 1999; Kansal, 2009). However, an anthropogenic activity does not necessarily mean a synthetic origin (chemical industry) but also can be derived from natural (e.g. oil, coal, wood) materials. Understanding the fate and tracking the source of a compound can only begin with a detailed knowledge of the source itself.

Analysing organic compounds in air samples is mostly done by using GC in combination with various detectors such as flame ionization (FID), electron capture (ECD), or mass spectrometry (MS). Sampling techniques can be categorised in passive and active methods. Passive sampling is used over longer periods of time e.g. work place monitoring whereas active sampling represents a composition and concentration at a given time. For active sampling a certain amount of volume is either drawn into a vacuumed air reservoir (e.g. canister or Teflon bag) or the air sample is pumped through a solid sorbent tube where the VOCs are trapped onto an adsorbent material. The advantages of using adsorbents are various, for instance, it is less costly and easier to transport than canisters, sample concentration can be increased and the adsorbent choice determines the range of VOCs to be collected. When sorbent sampling is used GC–MS analysis is mostly combined with thermal desorption (TD) to transfer the sample from the sorbent to the analytical instrument. Today TD–GC–MS is widely established for characterising sources of VOCs. A good overview of available VOC sampling techniques with their assets and drawbacks is given in Rudolph et al. (1990) and Czaplicka and Klejnowski (2002).

Knowing the composition of a sample is often not sufficient to distinguish different sources of VOCs (Ras-Mallorqui et al., 2007; Liu et al., 2008). Since different processes and reactions can lead to distinct isotopic signatures due to isotopic fractionations some compounds (classes) may be more susceptible and show larger differences than others. Therefore stable isotope analysis and especially compound specific isotope analysis (CSIA) were also applied in many studies for tracing a variety of organic compounds (Meier-Augenstein, 1999; Slater, 2003; Schmidt et al., 2004 and Pilgrim et al., 2010). The literature provides a range of studies investigating stable carbon isotopic composition (δ^{13}C) of VOCs in emissions (Goldstein and Shaw, 2003; Giebel et al., 2010) but only a very few results on stable hydrogen isotopes (δD) of such compounds in air have been presented to date (Rice and Quay, 2009; Vitzthum von Eckstaedt et al., 2011a, 2011b). However, previous research on tracing VOCs in air showed that δ^{13}C alone often could not clearly differentiate between sources. For example Turner et al. (2006) showed that the differences between δ^{13}C values of VOCs in an industry emission compared to those from a car exhaust were negligible. A dual isotope approach (C and H) had effectively distinguished the sources of higher molecular organic compounds like polycyclic aromatic hydrocarbons (PAHs) in a previous study and is therefore anticipated to be a promising tool for establishing sources of VOCs (Sun et al., 2003).

In this study we present δ^{13}C and δD values of VOCs ranging from C6 to C10 derived from car exhaust emissions as well as those derived from plant combustion experiments (C3 and C4 plants). For this purpose we applied the recently developed method of thermal desorption–gas chromatography–isotope ratio mass spectrometry (TD–GC–irMS) using TenaxTA as adsorbent material (Vitzthum von Eckstaedt et al., 2011b). Since GC–irMS analysis requires a relative large sample amount the TD technique is especially useful due to its ability to concentrate the sample to a sufficient level. The dual approach of δ^{13}C and δD of VOCs present in both investigated emission sources was used to compare these results to those in an aluminium refinery emission (Vitzthum von Eckstaedt et al., 2011a).

2. Materials and methods

2.1. Sampling technique

Sampling was conducted in accordance with the method optimised for TD–GC–irMS using stainless steel sampling tubes packed with TenaxTA as described in Vitzthum von Eckstaedt et al. (2011a; 2011b). In brief, the sampling device consisted of six parallel sampling tubes for replicate analyses. The sampling tubes had Silcosteel® coating on the inner wall to protect the sample from reacting with the metal surface. Two sampling tubes per device were equipped with subsequent breakthrough (BT) tubes. Sampling volumes varied according to the concentration in the emission. However, the volume flow of 200 mL min^{-1} per sampling tube was maintained consistent for all sampling events.

2.2. Emission sources

Two different types of emission sources were sampled:

(i) *Car exhaust*: samples were taken from a Ford Laser (year built 1996) running on unleaded petrol (ULP). Samples were taken directly at the exhaust pipe at a high and a low fuel tank level (at 100% and ca. 15%, respectively) from the same fuel. Sampling with a high fuel tank level (HF) was carried out 14 d prior to sampling the exhaust emission with a low fuel tank level (LF), but samples for δ^{13}C and δD analyses were taken consecutively on the same day. Prior to sampling the car was run for 20 min and was held at a constant elevated number of revolutions (ca. 3000 rpm) during sampling (steady state). The sampling volume amounted to 4.3 L per sampling tube.

(ii) *Plant combustion*: A series of plants were chosen according to a difference in their metabolic pathways for carbon fixation in photosynthesis (C3 and C4 plants) (O'Leary, 1988). In total eight different plants were chosen including five species of C3 plants and three species of C4 plants (Table 1). The collected plant material (1 kg) contained a representative mix of leaves/needles, bark, duff, twigs and branches (O'Connell and Menage, 1982; Burrows, 1994). The experimental set up included a cylindrical combustion chamber (150 L) with an air blower (to supply an efficient amount of oxygen for oxidation during combustion), a water bath (to reduce the emission temperature in the exhaust pipe) and a 25 m^3 tent (to capture the emitted combustion gases). 2.6 L and 3.0 L samples were taken per sampling tube (C and H analysis, respectively) from inside the tent where ventilators created a homogeneous composition. The combustion temperature was monitored in three zones of the chamber (T_1 = above embers, T_2 = 10 cm above T_1, T_3 = at the chamber outlet) and one at the exhaust in the tent (T_4). The maximum temperature occurred during each combustion trial is given in Table 1. Samples for δD analysis were taken five months prior to samples for δ^{13}C analysis from separate sampling events. However, the sample material for both sampling events was taken from same batches of dry, dead fully mature and established plant material. The plant material was stored in a cool and dry place. The amount of six parallel