



Measurement of the stable carbon isotope ratio of atmospheric volatile organic compounds using chromatography, combustion, and isotope ratio mass spectrometry coupled with thermal desorption



Hiroto Kawashima*, Mai Murakami

Department of Management Science and Engineering, Faculty of Systems Science & Technology, Akita Prefectural University, 84-4, Ebinokuchi, Tsuchiya, Yurihojo, Akita 015-0055, Japan

HIGHLIGHTS

- $\delta^{13}\text{C}$ values of atmospheric volatile organic compounds were measured.
- $\delta^{13}\text{C}$ values of 36 VOCs could be measured and reasonable as comparison with other researches.
- Samples collected from some sources and ambient air were analyzed and compared.

ARTICLE INFO

Article history:

Received 22 August 2013

Received in revised form

1 January 2014

Accepted 17 February 2014

Available online 18 February 2014

Keywords:

Volatile organic compounds

Stable carbon isotope ratio

Vehicle emissions

Source apportionment

Thermal desorption

TD–GC/IRMS

ABSTRACT

The isotopic analysis of atmospheric volatile organic compounds (VOCs), and in particular of their stable carbon isotope ratio ($\delta^{13}\text{C}$), could potentially be used as an effective tool for identifying the sources of VOCs. However, to date, there have been very few such analyses. In this work, we analyze the $\delta^{13}\text{C}$ values of VOCs using thermal desorption coupled with chromatography, combustion, and isotope ratio mass spectrometry (TD–GC/IRMS). The measured peak shapes were of high quality and 36 compounds in a standard gas containing 58 VOCs (C_5 – C_{11}) were detected. The measured $\delta^{13}\text{C}$ varied widely, from -49.7‰ to -22.9‰ , while the standard deviation of the $\delta^{13}\text{C}$ values varied from 0.07‰ to 0.85‰ ($n = 5$). We then measured samples from two passenger cars in hot and cold modes, three gas stations, roadside air, and ambient air. In comparison with existing studies, the analytical precision for the 36 compounds in this study was reasonable. By comparing the $\delta^{13}\text{C}$ values obtained from the cars and gas stations, we could identify some degree of the sources of VOCs in the roadside and ambient air samples.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Volatile organic compounds (VOCs) can have a serious effect on human health as they contribute to the formation of ozone and photochemical oxidants (e.g., Atkinson, 1990; Finlayson-Pitts and Pitts Jr, 2000; Seinfeld and Pandis, 1998), and some VOCs, e.g., benzene and 1,3-butadiene, are known or suspected to be carcinogens and mutagens (e.g., USEPA, 1998; USEPA, 2002). To reduce overall VOC emissions, it is necessary to elucidate and estimate their sources using a statistical receptor model (Fujita et al., 1994; Watson et al., 2001; Liu et al., 2008), but if the sources have similar profiles in the receptor model or if the atmospheric chemical processes are too complex, it is difficult to accurately estimate source apportionment.

* Corresponding author.

E-mail address: kawashima@akita-pu.ac.jp (H. Kawashima).

The stable carbon isotopic ratios ($\delta^{13}\text{C}$) of various compounds can be used to identify and/or distinguish their sources and origins in complicated matrices (e.g., Goldstein and Shaw, 2003). Such an approach has been used in various fields; for example, in environmental science, $\delta^{13}\text{C}$ values of non-methane hydrocarbons (NMHCs) have been measured using thermal desorption (Rudolph et al., 1997; Tsunogai et al., 1999; Hunkeler and Aravena, 2000; Rudolph et al., 2002; Saito et al., 2002; Love et al., 2003; Asano and Akiyama, 2005; Komatsu et al., 2005; Turner et al., 2006; Nara et al., 2006; Vitzthum von Eckstaedt et al., 2011a; Vitzthum von Eckstaedt et al., 2011b; Vitzthum von Eckstaedt et al., 2012; Kawashima and Murakami, 2014) or those of VOCs using a purge and trap method (Jochmann et al., 2006), and used to determine the sources of these compounds in the samples.

A combination of gas chromatography with on-line combustion and isotope ratio mass spectrometry (GC/IRMS) has been developed (Sano et al., 1976; Matthews and Hayes, 1978) that is capable

of measuring $\delta^{13}\text{C}$ values of VOCs. Examples of this include the $\delta^{13}\text{C}$ values of C_1 to C_5 alkanes, which were first measured by the paper (Baylis et al., 1994) with very high precision using gas-tight syringes in conjunction with GC/C/IRMS ($1\sigma = 0.07\text{--}0.21$). Rudolph et al. (1997) measured $\delta^{13}\text{C}$ values of NMHCs in ambient air by combining cryogenic pre-concentration with GC/C/IRMS, and reported that the isotopic ratios of VOCs in the atmosphere depend on the VOC source and on the isotopic fractionation of VOCs by reactions with OH radicals or ozone. Next, they investigated the stable carbon kinetic isotope effects (KIEs) associated with the reactions of several hydrocarbons with OH radicals (Rudolph et al., 2000), and subsequently determined the photochemical age (Rudolph and Czuba, 2000). Additionally, they measured the $\delta^{13}\text{C}$ values of NMHCs in ambient air and VOC sources such as tunnels, fuel stations, underground garages, and refineries using GC/C/IRMS, and found slight differences therein (Rudolph et al., 2002). Turner et al. (2006) also investigated VOC sources by measuring the $\delta^{13}\text{C}$ values of VOCs (benzene, toluene, chlorobenzene, ethylbenzene, *m*-xylene, and propylbenzene) in vehicle exhausts and industrial emissions using a thermal desorption (TD) instrument coupled with GC/C/IRMS. Asano and Akiyama (2005) reported a new GC/C/IRMS instrument comprising a multi-dimensional GC system with a cryo-focusing unit coupled to an IRMS instrument. Although they could only measure the $\delta^{13}\text{C}$ values of a few compounds, namely benzene, toluene, ethylbenzene, *m*- & *p*-xylenes, and *o*-xylene, owing to the cryo-focusing system being ahead of the IRMS, they obtained higher precision than had previously been achievable. They showed that the $\delta^{13}\text{C}$ values of the measured compounds for gasoline purchased at various locations in Japan were found to fall within a very narrow range (Asano and Akiyama, 2005).

Most recently, Vitzthum von Eckstaedt et al. (2011a) developed a method for the measurement of the stable hydrogen isotopic ratios ($\delta^2\text{H}$) and $\delta^{13}\text{C}$ values of VOCs (C_6 to C_{10}) using TD–GC/C/IRMS. In addition, the same group also measured the $\delta^2\text{H}$ and $\delta^{13}\text{C}$ values of VOCs in stack emissions from the alumina industry, and they found the average $\delta^{13}\text{C}$ values in the calcination emission to be -22‰ to -31‰ , which is similar to other natural sources and reflects their origin (bauxite organics) (Vitzthum von Eckstaedt et al., 2011b). Moreover, Vitzthum von Eckstaedt et al. (2012) investigated the $\delta^2\text{H}$ and $\delta^{13}\text{C}$ values of VOCs (C_6 to C_{10}) taken from car exhaust emissions, as well as from combustion experiments from various C_3 and C_4 plants. The results were essential to successfully differentiate between emission categories such as car exhaust emissions, biomass combustion, and industrial emissions.

However, little studies which treated the $\delta^{13}\text{C}$ of atmospheric VOCs about lot sources and ambient air were conducted. In this study, we analyze the $\delta^{13}\text{C}$ values of atmospheric VOCs from sources and ambient using TD–GC/C/IRMS. Then, we discuss the results of these measurements and compare them with previous studies, as well as evaluating the availability of $\delta^{13}\text{C}$ analyses for the identification of VOCs sources. First, we repeatedly measured the $\delta^{13}\text{C}$ values of VOC standards to confirm the analytical precision of TD–GC/C/IRMS. Next, we measured the $\delta^{13}\text{C}$ values of VOCs in vehicle emissions (hot mode and cold mode) and vaporized gasoline (gas station). Finally, we measured the $\delta^{13}\text{C}$ values of VOCs in ambient air and compared with lot of sources.

2. Experimental methods

2.1. Stable carbon isotope analysis

We measured $\delta^{13}\text{C}$ values using the same GC/TC/IRMS instrumental set-up and similar conditions as those used by Kikuchi and Kawashima (2013) for $\delta^2\text{H}$ values. In brief, gaseous samples were collected in 10-L or 50-L Tedlar bags (10 L, DEK-10, GL Sciences Inc.,

Tokyo, Japan; 50 L, As one Inc., Osaka, Japan) using a flex pump (Omi Odor-air service Co., Shiga, Japan) at a flow rate of approximately 2 L min^{-1} . Then, the gases were injected into the TD apparatus (200 mL/min) (GAS10, TOA DKK Co., Tokyo, Japan) via a Nafion[®] tube (Perma Pure Dryers, GL Sciences Inc., Tokyo, Japan). The adsorption tubes were packed with Tenax TA 60/80 mesh ($3\text{ mm} \times 3\text{ cm} \times 2\text{ tubes}$) (Supelco, Sigma–Aldrich Japan Inc., Tokyo, Japan). The adsorption time varied according to the concentration of each sample and was chosen such that a suitable peak area was acquired. The TD was coupled to the injection port of the GC (Trace GC, Thermo Fisher Scientific K.K., Bremen, Germany) interfaced with the IRMS (MAT253, Thermo Fisher Scientific K.K.) by a continuous flow system (Conflo IV, Thermo Fisher Scientific K.K.). The details of the GC/C/IRMS method are described below. The Tedlar bags were conditioned before use by heating at 100 °C for 12 h in an oven and then cleaning five times with pure N_2 (99.9995% pure, Taiyo Nissan Inc., Tokyo, Japan). After use, the bags were conditioned, heated at 80 °C for 2 h in an oven, and then cleaned three times with pure N_2 . After the conditioning of our methods, the peaks for target compounds in only pure N_2 were not detected at all during this research.

A Petrocol DH150 ($150\text{ m} \times 0.25\text{ mm i.d.}$, $1\text{ }\mu\text{m}$ film thickness, Supelco, Sigma–Aldrich Japan Inc.) capillary column was used for chromatographic separation with helium as the carrier gas. The flow rate of the carrier gas was directly controlled by a high-pressure regulator at 2.0 mL min^{-1} (30 °C). The temperature program was as follows: an initial temperature of 30 °C was held for 26 min, then heated to 75 °C at 1.2 °C min^{-1} , held at 75 °C for 0 min, then heated to 95 °C at 5 °C min^{-1} and held for 15 min, then heated to 110 °C at 2 °C min^{-1} and held for 6 min, then heated to 140 °C at 5 °C min^{-1} and held for 2 min, and finally heated to 280 °C at 40 °C min^{-1} and held for 10 min. Following the GC, the gas entered the combustion interface, which was maintained at 850 °C .

$\delta^{13}\text{C}$ values were measured by IRMS using the ISODAT NT 2.0 software (Thermo Fisher Scientific K.K.) supplied with the instrument. The stable carbon isotope composition, expressed in delta (δ) notation of per mil (‰) units, was calculated as follows:

$$\delta^{13}\text{C}(\text{‰}) = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000 \quad (1)$$

$\delta^{13}\text{C}$ values are reported in δ -notation (per mil) relative to the Vienna Pee Dee Belemnite standard (VPDB) with known isotopic composition. At the beginning and end of every measurement, a CO_2 reference gas (ultra-high purity, $>99.9999\%$) was automatically injected through a separate open split. The CO_2 reference gas was calibrated to NBS-19 (RM8544, National Institute of Standards and Technology, Gaithersburg, Maryland, USA; $+1.95\text{‰}$) by means of an elemental analyzer (Flash EA 1112, Thermo Fisher Scientific K.K.) coupled with the same IRMS (MAT253). The CO_2 reference gas ($>99.9999\%$) was calibrated every month owing to the probability of isotope fractionation in the high-pressure steel bottle.

2.2. Precision of analysis

We analyzed a standard gas containing 58 VOCs (PAMS 58 standard gas, 1 ppm, Takachiho Chemical Industrial Co., Tokyo, Japan) collected in a Tedlar bag. The adsorption time was 2 min (200 mL/min).

2.3. Source sampling

Vehicle emissions and vaporized gasoline samples were collected in Tedlar bags by described above method. Sample volumes of vehicle emissions and vaporized gasoline were

Download English Version:

<https://daneshyari.com/en/article/6340149>

Download Persian Version:

<https://daneshyari.com/article/6340149>

[Daneshyari.com](https://daneshyari.com)