Journal of Aerosol Science 66 (2013) 72–82

Contents lists available at ScienceDirect

Journal of Aerosol Science

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

Technical note

A thermal desorption system for measuring $\delta^{13}C$ ratios on organic aerosol

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ARTICLE INFO

Article history:
Received 13 May 2013
Received in revised form
9 August 2013
Accepted 12 August 2013
Available online 27 August 2013

Keywords:
Organic aerosol
Stable carbon isotopes
13C
Thermal desorption method
Isotope ratio mass spectrometry
Aerosol filter samples

ABSTRACT

We developed a system that links a thermal desorption oven for aerosol filter samples to an isotope ratio mass spectrometer (IRMS) via a combustion interface. Organic compounds are desorbed from the filter sample in He at 7 temperature steps between 100 and 400 °C and subsequently oxidized to CO_2, which is analyzed for $\delta^{13}C$. We tested the system for isotopic fractionation, reproducibility and linearity using organic test compounds and aerosol filter samples. An oxalic acid standard with known $\delta^{13}C$ value shows no isotopic fractionation when it is desorbed at temperatures well above its melting point. When organic acids are heated at a temperature close to their melting point only a fraction of the compound (10–80%) evaporates which shows depleted $\delta^{13}C$ values at this temperature step. At the next higher temperature step, when the rest of the compound is desorbed, $\delta^{13}C$ values are enriched. This effect is stronger for compounds with a lower molecular weight than for compounds with a higher molecular weight. In ambient samples this should only have a moderate effect on the overall $\delta^{13}C$ value, since hundreds of different compounds are desorbed at each temperature step. Choosing different values for temperature steps does not strongly change the $\delta^{13}C$ values for ambient aerosol filter samples. For typical ambient samples the reproducibility lies below $\pm 0.3‰$ for oven temperatures below 200 °C and below $\pm 0.5‰$ for oven temperatures above 200 °C. Tests with oxalic acid and ambient filter samples show that the IRMS is linear for peak areas in the operational range of 1–20 V s.

1. Introduction

Stable carbon isotopes have been used for several decades to investigate sources of organic aerosol and its chemical processing (e.g., Cachier et al., 1985; Ballentine et al., 1996; Simoneit, 1997; Turekian et al., 1998; Norman et al., 1999; Conte & Weber, 2002; Widory et al., 2004; Irei et al., 2006; Narukawa et al., 2008; Fisseha et al., 2009a, b; Kirillova et al., 2010; Pavuluri et al., 2011; Kawashima & Haneishi, 2012). Many studies have measured $\delta^{13}C$ values for the total aerosol carbon (TC), which has proven useful to distinguish marine and terrestrial sources of the aerosol (e.g., Cachier et al., 1985; Ceburnis et al., 2011; Narukawa et al., 2008). This distinction is possible because $\delta^{13}C$ values of marine carbon are enriched ($-20‰$ to $-22‰$;

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http://dx.doi.org/10.1016/j.jaerosci.2013.08.005

Turekian et al., 2003 and references therein) compared to aerosol carbon emitted by most terrestrial sources such as biomass burning, biogenic emissions or fossil fuel emissions. The terrestrial sources arise largely from C3 plants, whose metabolism strongly discriminates against $^{13}CO_2$, resulting in $\delta^{13}C$ values around −25‰ to −30‰ (e.g., Smith and Epstein, 1971), with a few exceptions, such as natural gas (e.g. Widory, 2006). Therefore, it is difficult to distinguish fossil, biogenic and biomass burning emissions by measuring $\delta^{13}C$ of total carbon alone. For example, aerosol carbon emitted from burning different fossil fuels (such as coal, gas, or gasoline) has similar $\delta^{13}C$ values, even though some of the fuels themselves can differ in $\delta^{13}C$ (Widory, 2006). However, measurements of $\delta^{13}C$ in total carbon have still proven useful in aerosol sources apportionment, when combined with extensive chemical (e.g. Fu et al., 2012) or other isotope measurements (e.g. Ceburnis et al., 2011).

Therefore there are many efforts to refine stable isotope analysis on organic carbon. Measurements on carbon subfractions such as organic, elemental or water soluble carbon are common in radiocarbon analysis (e.g., Szidat et al., 2004; Bernardoni et al., 2013; Kirillova et al., 2010; Dusek et al., 2013). They are also sometimes used for ^{13}C analysis and show some interesting seasonal or spatial differences in ^{13}C isotopic composition (e.g., Huang et al., 2006; Ho et al., 2006; Kawashima & Haneishi, 2012). However, these differences are usually difficult to interpret in terms of sources and atmospheric processing of the aerosol. Water-soluble organic carbon (WSOC) is often enriched in ^{13}C compared to total carbon (Fisseha et al., 2009a). Enrichment of WSOC seems related to long range transport (Kirillova et al., 2013) or influence from marine sources (Miyazaki et al., 2012), but possible causes are still speculative.

Measurements of $\delta^{13}C$ on individual organic compounds show more clear isotopic signatures, because $\delta^{13}C$ ratios of individual compounds can differ strongly from the bulk organic carbon (e.g., Fisseha et al., 2009b) or from each other (e.g., Wang et al., 2012; Pavuluri et al., 2011). This has been exploited for improved source apportionment for individual compounds such as polycyclic aromatic hydrocarbons from fossil sources (e.g., Okuda et al., 2002) or biomass burning (Guillon et al., 2013) or such as alkanes from plant emissions (e.g., Bendle et al., 2006). Compound specific isotope analysis can also help to identify isotopic signatures of chemical processes that act on individual compounds (e.g., Gensch et al., 2011; Rudolph & Czuba, 2000). For example, the low $\delta^{13}C$ values of oxalic acid consistently encountered in ambient samples (e.g., Pavuluri et al., 2011; Wang & Kawamura, 2006; Wang et al., 2012) can likely be explained by catalyzed photolysis in aqueous phase (Pavuluri & Kawamura, 2012). The disadvantages of isotope analysis on individual compounds are that it is often very time consuming and that the studied compounds comprise only a small fraction of the total organic aerosol.

The main purpose of the setup presented in this paper is to refine $\delta^{13}C$ analysis on bulk organic carbon by measuring $\delta^{13}C$ of organic compounds at different desorption temperatures. Compound classes are desorbed from aerosol filter samples at different temperatures and the $\delta^{13}C$ value of all compounds desorbed at a particular temperature step is measured. The dependence of carbon amount and $\delta^{13}C$ values on desorption temperature is termed 'thermogram'. This method is more detailed than isotope analysis on bulk carbon, and at the same time more comprehensive than isotope analysis on individual compounds. However, it is necessary to test that possible trends in $\delta^{13}C$ with desorption temperature are not caused by measurement artifacts. This study describes the evaluation of the $\delta^{13}C$-thermogram method with simple test compounds and atmospheric samples.

2. Methods

2.1. System description

Figure 1 shows the setup of the thermal-desorption IRMS system. The thermal desorption part consists of a quartz glass tube, the second half of which is surrounded by two home-made tube ovens. For analysis, an aerosol filter sample is moved from the cold section into oven 1 using a movable filter holder made from quartz glass. The temperature of oven 1 can be varied stepwise from 20 to 400 °C. A Labview code is used to control the magnitude and duration of the temperature steps at which organic compounds are desorbed from the filter. Oven 2 is filled with a Pt catalyst at a constant temperature of 550 °C, which fully oxidizes the organic compounds to CO_2. The ovens can be either flushed with He, which is used for the desorption of organic compounds from the filter or with O_2, which is used to replenish the catalyst with oxygen between measurements. The flow rate through the ovens can be varied but is usually set to 62 ml/min by a mass flow controller. A six port valve connects the ovens to two liquid nitrogen traps, followed by a gas chromatography column (Varian CP7351, at room temperature) to separate the CO_2 from possible contamination with N_2O. A Nafion dryer removes water vapor

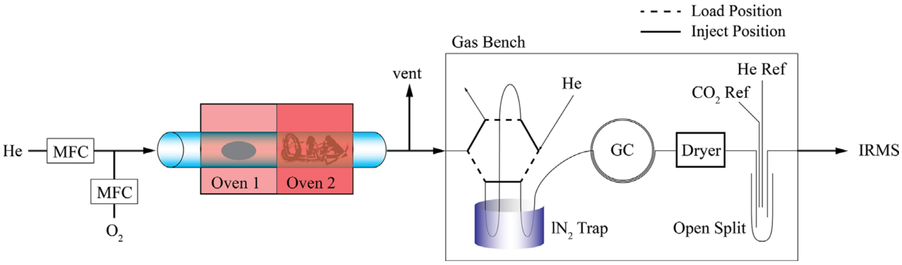

Fig. 1. The setup of the $\delta^{13}C$-thermogram system.