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RESEARCH PAPER

Thermal Desorption-Gas Chromatography or Gas Chromatography-Mass Spectrometry for Analysis of Semi-Volatile Compounds on Atmospheric Particulate Matters

MENG Hu[1,2], ZHAO Jing-Hong[1], DUAN Chun-Feng[1], HAO Liang[1,2], GUAN Ya-Feng[1,*]

[1] Key Laboratory of Separation Science for Analytical Chemistry, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China
[2] University of Chinese Academy of Sciences, Beijing 100039, China

Abstract: A thermal desorption (TD) device was developed and coupled to gas chromatograph (GC) or gas chromatograph-mass spectrometer (GC-MS) for the qualitative and quantitative analysis of semi-volatile organic compounds on atmospheric particulate matters (PM). The TD was operated by direct heating and placed on the top of GC injector, leading to high heating rate and easy transfer of analytes to GC without re-focusing of analytes by cold trap. The materials used for supporting PM samples, desorption temperature and time, and types of sample injection were investigated for the detection of sixteen polycyclic aromatic hydrocarbons (PAHs) and nine *n*-alkanes. The limits of detection of the proposed TD-GC method were in the range of 0.014–0.094 ng for PAHs, and 0.016–0.026 ng for *n*-alkanes, with coefficients of correlation above 0.9975. The TD-GC method was applied to the determination of trace PAHs and *n*-alkanes on PM10 samples from three cities. The recoveries were in the range of 95%–135% (PAHs) and 95%–115% (*n*-alkanes). Finally, the TD was coupled to GC-MS for comparison of the contents of PAHs and *n*-alkanes on PMx with different particulate size (x = 10, 5, 2, 1, 0.5, 0.25, 0.1).

Key Words: Atmospheric particulate matters; Semi-volatile organic compound; Thermal desorption; Particulate matter 2.5

1 Introduction

Atmospheric particulate matter, also known as particulate matter (PM) or atmospheric aerosol, are tiny pieces of solid or liquid matter suspended in the atmosphere. Subtypes of atmospheric particulate matter are defined by the size of the particle, such as respirable suspended particles (diameter of 10 μm or less; PM10) and fine particles (diameter of 2.5 μm or less; PM2.5). Although the content of atmospheric particulate matter in the Earth's atmosphere is very low, they have adversely impacts on air quality, visibility and human health. Small particulates can cause greater danger than large ones.

Among the complex components of respirable suspended particles, various organic compounds are identified including alkanes, alkenes, heterocycles, alkanoic acids, polycyclic aromatic hydrocarbons (PAHs), ketones, esters and so on[1–3]. The concentration of each organic component is extremely low, usually in the range of 0.1–100 ng m^{-3} [1]. For trace analysis of organic components associated with PM, continuous air sampling for one day by large-volume sampler is required, followed by solvent extraction of filters, concentration by nitrogen blowing and detection by chromatography-mass spectrometry[3–6]. In recent years, ultrasonic extraction[3–5], microwave assisted extraction[7,8] and accelerated solvent extraction[9–11] have been used to extract organic compounds in PM2.5, which shortened time for sample preparation, decreased solvent consumption and improved extraction efficiency.

Compared with solvent extraction, thermal desorption (TD) is more advantageous because organic solvent is undesired,

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* Corresponding author. Email: guanyafeng@dicp.ac.cn

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avoiding the contamination of sample by impurities in solvent. TD is facilitated to be on-line coupled with modified gas chromatography (GC) injector[12,13], leading to direct sample injection and extremely low sample loss approximate zero. However, this method usually suffers from sample residual and system pollution. Ho *et al*[14] developed an in-injection port TD method by directly inserting the sample filters into the injector liner tube of GC for desorption. The cross sample pollution could be avoided by changing the liner tube. However, the raise of the injector port temperature to 275 °C required 11 min and the heating rate could not be controlled precisely. Other methods[15,16] were developed for the analysis of organic compounds such as PAHs and alkanes in PM2.5 by using commercial TD device combined with GC-MS. However, due to the requirement of focusing by cold trap after TD, it increases the complexity and cost of the analytical method.

In this work, a TD device operated by direct heating with high heating rate was constructed. With the design of carrier gas purging, the extra-column dead volume was decreased and the sample residual was avoided. The TD device could be placed on the top of a GC injector directly and coupled to GC or GC-MS for qualitative and quantitative analysis of trace semi-volatile organic compounds on atmospheric PM with different sizes.

2 Experimental

2.1 Apparatus and reagents

Sixteen standard solutions of PAHs and some other standard solutions of *n*-alkanes (C13–C19, C23, C26, C32) were purchased from AccuStandard (America). Methanol and *n*-hexane were of pesticide analysis grade and obtained from Tedia (America). Naphthalene, acenaphthene, phenanthrene, anthracene and pyrene were purchased from Beijing Chemical Factory (China).

The atmospheric PM samples were provided by School of Environment, Tsinghua University and collected from Beijing in winter, Ningbo in autumn and Chongqing in summer, respectively. Sampling apparatus were self-made by School of Environment, Tsinghua University, which simultaneously collected seven-level PM_x (x = 10, 5, 2, 1, 0.5, 0.25, 0.1). PM samples were supported on aluminum films with sampling volume of 24 m^3 per piece. Then, the aluminum films were equally divided into four portions by clean scissors for qualitative, quantitative and recovery analysis, respectively.

2.2 Thermal desorption method

A quartz liner with a convergent at outlet end was used as TD tube. Quartz wool was plugged the convergent end of the TD tube. Before analysis, the liner was purged by nitrogen under 330 °C for 2 h to pre-clean the system. A quarter of an aluminum film was cut into thin strips and put into the TD tube. After thermal desorption at 310 °C for 10 min, the organic compounds desorbed were purged into the liner of the GC injector or directly into large-bore capillary column by carrier gas for separation and analysis.

2.3 Chromatographic separation condition

Quantitative analysis was carried on Varian CP-3800 GC equipped with a split/splitless injector and a flame ionization detector (FID). Nitrogen was used as carrier gas and auxiliary gas. Splitless injection mode and a constant flow of carrier gas (5 mL min^{-1}) were adopted. The temperatures of injector and detector were kept at 250 and 300 °C, respectively. An SE-54 silica capillary column (30 m × 0.53 mm × 0.6 μm, Dalian Scien-Tech Instrument Inc., China) was used for GC separation. The GC oven temperature was programmed as follows: initial oven temperature 40 °C, held for 10 min, raised to 120 °C at 20 °C min^{-1}, then programmed at 6 °C min^{-1} to 280 °C and held for 10 min.

A Polaris Q GC/MS (Thermal Co., USA) system was used for qualitative analysis. The injection was operated in splitless mode and started to purge after 10 min of injection. The temperatures of the injector, detector and transfer line were kept at 280, 290 and 260 °C, respectively. An SE-54 silica capillary column (30 m × 0.25 mm × 0.25 μm, Dalian Scien-Tech Instrument Inc., China) was used for separation. The column temperature was programmed as follows: initial temperature 40 °C, held for 10 min; programmed at 20 °C min^{-1} to 120 °C, programmed at 6 °C min^{-1} to 260 °C, and then held for 20 min. Helium was used as carrier gas and auxiliary gas. The flow rate of carrier gas was programmed as follows: initial flow rate 0.1 mL min^{-1}, held for 10 min, then raised to 0.8 mL min^{-1} at 10 mL min^{-1}. The full scan range of m/z 50–500 at a scan rate of 2 times per second. The excitation voltage was 70 eV. Solvent delay time was set as 10 min. The NIST standard database was used for qualitative retrieval.

3 Results and discussion

3.1 Design of TD device

The TD device was constituted of desorption unit, heater unit, gas flow system and transfer capillary (Fig.1). The TD device was operated by direct heating with two heater rods (100 W) embedded in an aluminum block to yield uniform temperature distribution. The high heating rate controlled by an artificial intelligence regulator was 100–150 °C min^{-1}, by which the time that the temperature increased from 20 °C to 320 °C was less than 2 min. A thermocouple was used to measure the temperature of the desorption unit. A fan was located in one side of the desorption unit, which was activated after desorption for cooling.