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Filtration efficiency validation of glass wool during thermal desorption–gas chromatography–mass spectrometer analysis of fine atmospheric particles

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ABSTRACT

Thermal desorption–gas chromatography–mass spectrometer (TD–GC–MS) technique has been widely used for analysis of semi-violate organic compounds on atmospheric aerosol. To prevent GC column from being damaged by fine solid particles during thermal desorption process, glass wool as filter mat is indispensible. However, the filtration efficiency has never been validated. In this paper, the most penetrating particle size and the minimum packing thickness of glass wool were calculated based on classical filtration theory. According to the calculation results, packing parameters of glass wool were optimized experimentally using silica particles. It is demonstrated that glass wool with a packing thickness of 30 mm, solidity of 0.039 can effectively block these fine solid particles from penetrating at normal thermal desorption conditions (T = 300 °C, u = 0.4–4 cm/s). Finally, the filtration efficiency of glass wool was further confirmed with real PM2.5 samples. Under the validated filtration condition, TD–GC–MS was applied for the analysis of non-polar organic compounds on real PM2.5 samples, and very good results were obtained.

1. Introduction

Fine atmospheric particles [1] (PM2.5; fine aerosols; particles with aerodynamic diameters equivalent to or less than 2.5 μm) have received special attention due to their effects on human health [2,3], air visibility and climate change [4]. To understand these effects and find out reliable pollution source tracers [5–7], organic matter (OM) composition of PM2.5 have sparked increasing interest. In many aerosol studies [8–10], the OM composition of atmospheric particulate has been characterized through solvent extraction (SE) followed by GC–MS analyses. Despite some documented advantages of SE–GC–MS methods (e.g., selectivity, feasibility), it is generally labor and time intensive, and consumes large amount of sample and organic solvents.

TD–GC–MS technique [11–13] has been applied to analysis of OM on atmospheric particulates. Its advancements and applications had been summarized by Hays [14] and Chow [15] respectively. Compared with SE methods, TD requires only sub-milligram sample material, and more accurate results could be obtained [16–19].

During TD process, filter samples were directly inserted into a liner of GC injector. With rapid heating, desorbed OM was swept from the liner to the GC column by the carrier gas flow. However, some particles were also blown away from the filter, which could cause serious problems as they got into the GC–MS system. They could deposit on the GC injection port, enter GC column, or even get into MS system. As the particles accumulated, the delicate GC–MS will soon get malfunctioned. In addition to hardware damage, analyte loss, background signal elevation, and peak broadening and overlap maybe happened also. Thus, these floating fine solid particles must be filtered as completely as possible before being introduced into GC system. In order to deal with this problem, glass wool had been suggested and packed in the liner as filter media to block these free fine particles and to allow gaseous compounds to flow through the filter [16,20,21].

Fibrous filter has been proven to be an effective filtration material at common filtration conditions [22,23]. However, to the best of our knowledge, there is no such report on filtration efficiency study of glass wool during TD. In addition, as usually <1 mg of sample was used during TD–GC–MS analysis of PM samples,

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the negative effect caused by penetrated particles can hardly be observed in a few analysis. Sometimes, the gradual deterioration of GC–MS performance has also not been attributed rightly to the particle penetration. Therefore, it is necessary to systematically study the filtration efficiency of glass wool during TD.

In this work, the filtration theory [24–26] was used to study the filtration efficiency and packing parameter of glass wool. It was proposed that the penetrated particles were first collected in liquid solution, and then quantified with an evaporative light scattering detector (ELSD). Thus, the filtration efficiency of glass wool can be validated reliably. Under the optimized conditions, TD–GC–MS method was finally applied to analyze non-polar organic compounds on the real PM2.5 samples.

2. Experimental

2.1. Chemicals and materials

The monodisperse silica microspheres with the particle size of 0.5 μm were purchased from Baseline Chromtech Research Center (Tianjin, China). It was originally dispersed in a mixture of water and ethanol (1:1, v/v). Before use, it was centrifuged and re-suspended in methanol of chromatography grade. Deactivated glass wool (deactivated with dimethyldichlorosilane) with an average fiber diameter of 5 μm were supplied by Shimadzu Corporation of Japan.

Alkanes (n-C12–n-C26, n-C28) were purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China). Six polycyclic aromatic hydrocarbons (PAHs) including naphthalene, acenaphthene, phenanthrene, anthracene, fluoranthene and pyrene were purchased from Shanghai Chemical Reagent Co. (Shanghai, China). Standard mixtures of n-alkanes were prepared in n-hexane, and PAHs were prepared in methanol.

2.2. Instrumentation and analytical conditions

A Varian 380-LC series ELSD (Agilent Technologies, USA) was used to quantify the amount of fine particle suspended in the solution. Throughout this study, the ELSD parameters were set as follows: nebulization temperatures 50 °C, evaporation temperatures 90 °C, and gas flow-rate 1.6 L/min (SLM).

A GC-MS-QP2010SE System (Shimadzu, Japan) fitted with a SE-54 column (50 m × 0.32 mm i.d. × 0.40 μm) was used for organic compounds analysis. The instrumental operation conditions were as follows: the injector temperature 300 °C; the carrier gas was helium at a constant flow rate of 1 mL/min. The oven temperature was 40 °C for 1 min, then 60 °C/min up to 200 °C, hold for 7 min, and finally 10 °C/min up to 280 °C and maintain for 30 min. The injection was operated in split mode at a split rate of 8. The MS system was operated with transfer line temperature of 280 °C and ion sours temperature of 220 °C.

A home-made thermal desorption unit (TDU) was used for both filtration efficiency validation and TD–GC–MS analysis of organic compounds on PM2.5 samples. Its construction has been reported in previous works [27]. For coupling with GC–MS, it was directly mounted on the injector of a GC, the transfer line of 0.1 mm i.d. capillary was inserted through the injector septum into the GC injector about 3 cm deep. In the TDU, a quartz tube of 78 mm × 4 mm i.d. and 6 mm o.d. was used as liner. Typically, glass wool of 30 mg was loosely packed inside the liner for 30 mm. A glass fiber filter with PM 2.5 collected were rolled and inserted into the liner. The liner was then placed into the TDU. The desorption temperature was set at 300 °C, programmed from room temperature to 300 °C within 3 min, then hold for 7 min for complete desorption. Helium gas with a flow rate of 3 mL/min was kept constant throughout desorption and analytical process. After desorption, the GC separation program was initiated.

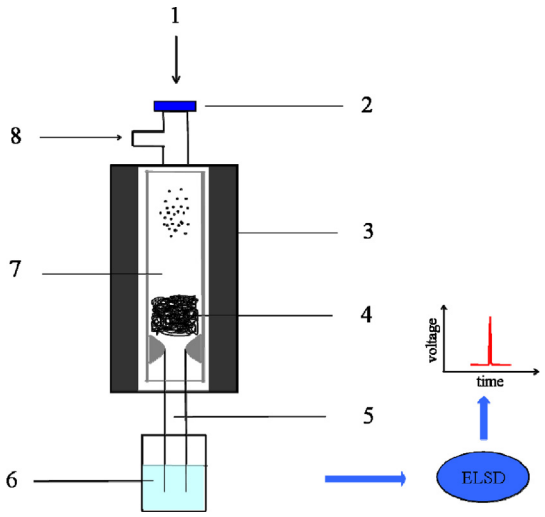

Fig. 1. Schematic drawing of filtration efficiency test of packed glass wool during TD. 1, monodisperse silica microspheres; 2, septum injector nut; 3, thermal desorption unit; 4, glass wool; 5, 0.53 mm i.d. capillary tube; 6, water; 7, TD liner; 8, carrier gas.

A PM2.5 sampler (ZR-3930 PM2.5 sampler, Qingdao Junray Intelligent Instrument Co., Ltd., China) was used for collecting fine atmospheric particles onto glass fiber filter (Φ = 47 mm). PM2.5 collection was carried out at a flow rate of 16.7 L/min for 24 h. Glass fiber filters were pre-baked for 4 h at 500 °C to remove any potential organic residues. The sampling site was on the rooftop of a 15 m height building adjacent to the Xinghai Park in the southeast of Dalian (38°53′ N, 121°37′ E). Immediately after sampling, samples were transported to the laboratory and cut into four equal portions. The pieces of cut filters were wrapped in cleaned aluminum foil and stored in glass jars at −4 °C until analysis.

2.3. Method of filtration efficiency test

For the filtration efficiency test, TDU was modified with a syringe injection port on top, as shown schematically in Fig. 1. Mono-disperse silica microsphere methanol suspension was used as testing samples. Methanol was used as blank solution. The test process was listed as follows.

First, the liner packed with filtration material was inserted into TDU and conditioned 3 times for each cycle of 10 min at 300 °C with carrier gas. Second, each 2 μL of sample or blank solution was injected into the liner with a GC syringe as shown in Fig. 1. The particles generated [28] would fly through the packed filtering material by carrier gas. The outlet gas flow was directed into a small glass bottle filled with 300 μL of water by a piece of capillary tube. Particles those can penetrate through the glass wool bed will be collected in water. In order to avoid the carryover of particulates, blank solution were always injected and tested before each sampling of silica microsphere methanol suspension, and the capillary tube was cleaned with ultrasonic between each sampling. The amount of the particle collected in water was quantified by ELSD.

To validate the filtration efficiency of glass wool during TD, real PM2.5 samples were desorbed in a TDU. The TD gas flow was directed into a centrifugal tube filled with 500 μL of methanol by a piece of capillary tube. After TD, the centrifugation tube with methanol solution was centrifuged at 12,000 rpm for 5 min. Then, the upper part of methanol solution were discarded and residuary particles were further cleaned in a vacuum oven at 200 °C for 2 h to remove organic matter. The cleaned particles were re-suspended into 100 μL pure water and quantified by ELSD.