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Short communication

Fullerenes-extracted soot: a new adsorbent for collecting volatile organic compounds in ambient air

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Abstract

Fullerenes-extracted soot (FES) is the by-product of fullerenes production. Retention characteristics at different temperatures for 17 volatile organic compounds (VOCs) on FES are measured. The adsorption and desorption efficiencies for VOCs on FES adsorbent tubes range from 40.8 to 117%, most of them being $100 \pm 20\%$. The values are compared with Tenax GR, an adsorbent commonly used in environmental analysis. FES can be used as an adsorbent of low cost to collect VOCs in environmental samples. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Fullerenes-extracted soot; Adsorbents; Volatile organic compounds

1. Introduction

Volatile organic compounds (VOCs) comprise an important group of pollutants commonly present in indoor and outdoor air. VOCs give rise to concern on both local and global scale because of their important roles in photochemical reactions [1] and their toxic or mutagenic impact on human life and organisms [2].

VOCs are found in trace concentration in ambient air so that a preconcentration step is required for instrumental determination [3]. Methods commonly used for concentration are adsorption in a suitable solution, cold trapping, and adsorption on solid adsorbents at ambient temperature [4]. At present,

adsorption on solid adsorbents is one of the most widely used methods. Many porous materials, including carbon molecular sieves (CMSs), graphitized carbon black, styrene and acrylate polymers and Tenax, have been evaluated and used for VOC sampling in ambient air [5–14].

Fullerenes-extracted soot (FES) results from fullerenes extraction generated by graphitized carbon evaporating under arc discharging [15]. Chen et al. [16] reported the surface area and pore size distribution of FES. They showed that the specific areas of soot before and after extracting are $270 \text{ m}^2/\text{g}$ and $254 \text{ m}^2/\text{g}$, respectively. Unlike graphite with regular slice and graphitized carbon produced from carbon blacks, FES is complex multicomponent mixture with abundantly porous and large specific area. No report has been found on the application of this by-product of fullerenes production as adsorbent to

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collect VOCs in air. With its adsorbing capability and low cost, FES has potential to be used as adsorbent. In this paper, the retention characteristics of selected VOCs on FES have been studied, and the practice of applying this new adsorbent for sampling airborne VOCs is also presented.

2. Experimental

2.1. Reagents

All reagents were analytical-reagent grade. A cocktail of heptane, benzene, toluene, styrene, methylene chloride, chloroform, tetrachloromethane, trichloroethylene, tetrachloroethylene, 1,2-dichloroethane, chlorobenzene, *m*-dichlorobenzene and xylene (mixture) was prepared in methanol. The concentrations of these compounds were about 50 mg/ml. A 50- μ l volume of the solution was flushed with nitrogen through a stainless steel line heated at 180°C into an 8.2-l gas cylinder. The cylinder was then pressurized to 130 atm (1 atm=101 325 Pa). We used this gaseous mixture as the experimental gas. Before use, the concentrations of tested compounds in the gaseous mixture were calibrated by Supelco TO-14 gas blends (Supelco, USA), gas calibration blends for US Environmental Protection Agency (EPA) Method TO-14.

The solution was also diluted to concentrations ranging from 1.221 to 3.101 ng/ μ l as experimental standard solution.

FES purchased from Wuhan University (Wuhan, China) was Soxhlet extracted in toluene and dried before use.

2.2. Procedure

2.2.1. Measurement of retention characteristics of VOCs on FES

A brass column, rinsed with acetone and dried before use, was filled with 0.4 g of FES, both ends of the tube were plugged with silanized glass wool. The filled column was connected to a gas chromatography (GC) system (Hewlett-Packard 5890) and used as chromatographic column, flame ionization detection (FID) was the detection method used.

Retention parameters were determined by injecting

20–40 μ l of the vapor of each target compound saturated at 20°C, i.e., in the range 10^{-7} to 10^{-6} g per injection into the column at different temperatures ranging from 80 to 220°C [7]. Carrier gas (nitrogen) flow-rate is 30 ml/min.

2.2.2. Adsorption and desorption efficiency measurement

A thermal-desorption unit of Tekmar 2016/6032/3000 purge&trap concentrator combined with a Hewlett-Packard 5890GC/5972 mass-selective detection system was used.

A 0.4-g amount of adsorbent was filled in a brass tube. A 40-ml volume of experimental gaseous mixtures was flushed into the tube. After adsorbing the VOC vapors, the column was connected to a Tekmar 6032 unit to purge and trap. VOCs enriched in the trap in Tekmar 3000 were thermal desorbed and analyzed by GC–mass spectrometry (MS). Standard solutions containing the same mass of VOCs were directly injected into the GC system. The efficiencies were calculated by comparing the chromatographic peak areas of the same compounds.

A capillary column, HP-VOC (30 m \times 0.2 mm, 0.5 μ m) was used under the following conditions: injector temperature, 280°C; no splitting; initial temperature, 35°C for 2 min, then increased at 6°C/min to 200°C for 2 min; flow-rate of the carrier gas (helium), 1 ml/min.

3. Results and discussion

3.1. Retention characteristics and safe sampling volumes (SSVs) of VOCs on FES

In this study, retention characteristics of 17 VOCs on FES at different temperatures were measured. There is a correlation between the specific retention volume (V_g) and temperature (T):

$$\lg V_g = A/T + B \quad (1)$$

where A and B are empirical parameters, T is column temperature. With this equation, specific retention volumes for adsorbents at near or sub-ambient temperatures can be estimated by extrapolat-

ing linear fits of $\lg V_g$ versus $1/T$ from data obtained at elevated temperatures to the lower temperatures of interest [6].

Plots of $\lg V_g$ versus reciprocal absolute temperature are presented in Fig. 1. V_g^{20} were obtained by extrapolating these plots to 20°C (usual sampling temperature). The breakthrough volume (V_B) at 20°C (V_B^{20}) was derived with following equation:

$$V_B = V_g(1 - \sqrt{4/n}) \quad (2)$$

where n is the number of theoretical plates under the experimental conditions at which V_g is measured. All data are presented in Table 1. In this table, we can find that adsorption capability varies from compound to compound. Generally, benzene family and unsaturated halocarbons, including benzene, toluene, xylene, styrene, trichloroethylene and tetrachloroethylene, have the largest specific retention volumes and breakthrough volumes. Saturated alkanes and halohydrocarbons with low polarity are smaller. Alcohols and halohydrocarbons with high polarity have the smallest values.

The breakthrough volumes of VOCs on Tenax

GR, an adsorbent frequently used for enriching trace organics in environment are presented in Table 2 [7]. Compared with FES, the breakthrough volumes of VOCs on FES are larger because FES has a larger specific area than Tenax GR. Large breakthrough volumes can avoid breakthrough of the compounds effectively, so that FES can be used to collect organics in the environment in wider ranges of concentration and sampling volume.

In order to account for the effect of various parameters on the breakthrough volume, its value is appropriately reduced. The resulting value is termed the “safe sampling volume” [11]. The lowest breakthrough volume of tested compounds was exhibited by dichloromethane, 15.6 l/g, which is at least twice that of usual sampling volumes (one to several liters). So we can reduce V_B by half and get the SSVs which can be used as the maximum sampling volumes in the field.

There is a good linear correlation between $\lg V_g^{20}$ and the boiling points of the investigated compounds (Fig. 2). With this correlation, specific retention volumes of other organic compounds can be estimated according to their boiling points.

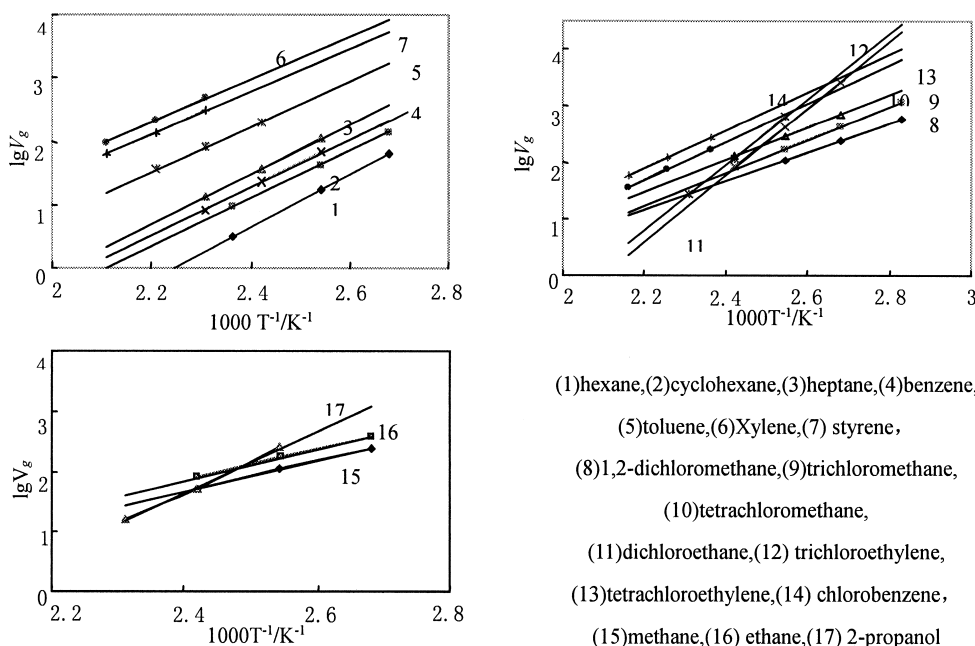


Fig. 1. Plot of $\lg V_g$ versus reciprocal absolute temperature.

- (1)hexane,(2)cyclohexane,(3)heptane,(4)benzene,
 (5)toluene,(6)Xylene,(7) styrene,
 (8)1,2-dichloromethane,(9)trichloromethane,
 (10)tetrachloromethane,
 (11)dichloroethane,(12) trichloroethylene,
 (13)tetrachloroethylene,(14) chlorobenzene,
 (15)methane,(16) ethane,(17) 2-propanol

Table 1

Extrapolated specific retention volumes (V_g) and breakthrough volumes (V_B) for organic vapors sampled on fullerenes-extracted soot adsorbent tubes^a

Compound	Boiling point (°C)	A	B	V_g^{20} (l/g)	n	V_B^{20} (l/g)
Hexane	68.4	4172	-9.38	72.3	146	60.3
Cyclohexane	81.0	3806	-8.04	89.2	203	75.7
Heptane	98.3	3914	-7.92	274.8	216	237.4
Benzene	80.5	3738	-7.80	90.6	278	79.7
Toluene	110.8	3569	-6.34	693.0	264	638.6
Xylene(s)	138~144	3397	-5.18	2598.7	237	2261.1
Styrene	142	3352	-5.02	2634.6	251	2302.1
Dichloromethane	40.7	2540	-4.43	17.4	358	15.6
Trichloromethane	61.5	2874	-5.08	53.8	306	47.7
Tetrachloromethane	76.7	2858	-4.82	86.2	142	71.7
1,2-Dichloroethane	84.1	2994	-5.01	162.8	328	144.8
Trichloroethylene	86.9	3173	-5.63	158.2	404	142.4
Tetrachloroethylene	121.0	3374	-5.74	596.3	523	544.2
Chlorobenzene	131.7	3388	-5.58	967.1	312	857.7
Methanol	64.7	2588	-4.56	18.8	547	17.2
Ethanol	78.5	2816	-4.98	42.9	483	39.0
2-Propanol	82.5	2969	-5.30	68.1	465	61.8

^a A, B: Empirical parameters of Eq. (1). n: Number of theoretical plates.

Table 2

Maximum sample volumes for organic vapors sampled on Tenax GR adsorbent tubes

Compound	V_B^{20} (l/g)	Compound	V_B^{20} (l/g)	Compound	V_B^{20} (l/g)
Dichloromethane	1.9	Chlorobenzene	360.3	Toluene	222.6
Trichloromethane	7.0	Hexane	25.1	Xylene(s)	1290.7
Tetrachloromethane	15.6	Heptane	83.6	Ethanol	1.0
1,2-Dichloroethane	44.6	Benzene	34.7	2-Propanol	5.9
Trichloroethylene	44.5				
Tetrachloroethylene	267.3				

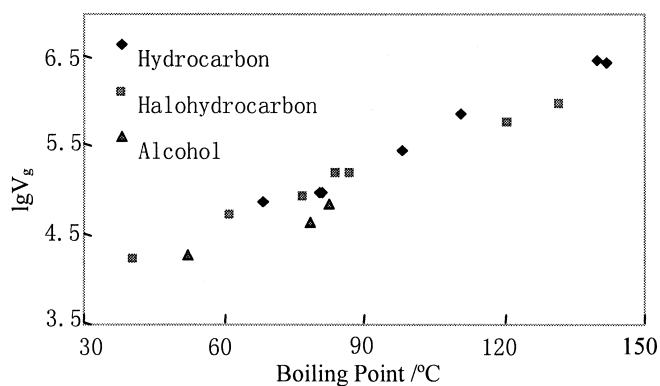


Fig. 2. $\lg V_g^{20}$ for fullerenes-extracted soot as a function of boiling point.

3.2. Adsorption and desorption efficiency

We have measured the adsorption and desorption efficiencies for VOCs on FES and Tenax GR. The data are presented in Table 3.

For most compounds in Table 3, the values for FES are almost equal to those for Tenax GR, an adsorbent that has been successfully applied to collect VOCs in ambient air. The efficiencies for *O*-dichlorobenzene on all adsorbents are less than 50% because its boiling point is 180°C so that it cannot be desorbed completely at 220°C. Its efficiencies will be higher at higher desorption temperatures.

3.3. Implication of FES in air sampling

The retention characteristics of VOCs on FES and the adsorption and desorption efficiencies imply that FES is a potentially good adsorbent for collecting airborne VOCs. Nowadays, no single adsorbent can meet all the conditions of the ideal adsorbent [10]. Commercial adsorbent tube is usually filled with several kinds of adsorbent to collect different compounds. We have used FES individually and as a component of adsorbent blends in air sampling and obtained satisfactory results, which will be reported later.

Table 3
Recoveries and standard deviations of adsorption and desorption for VOCs on fullerenes-extracted soot and Tenax GR

Compound	Recovery \pm SD (%)	
	Fullerene soots	Tenax GR
Benzene	92.6 \pm 4.6	97.0 \pm 5.0
Heptane	88.4 \pm 5.8	89.5 \pm 7.6
Toluene	81.0 \pm 4.5	91.2 \pm 4.2
Xylene(s)	78.6 \pm 7.3	104.7 \pm 6.6
Styrene	73.1 \pm 5.9	93.8 \pm 4.7
1,2-Dichloroethane	87.5 \pm 6.3	87.0 \pm 7.8
Tetrachloromethane	64.4 \pm 5.0	57.2 \pm 6.9
Trichloroethylene	86.6 \pm 4.6	93.6 \pm 6.3
Tetrachloroethylene	89.1 \pm 7.9	83.4 \pm 4.4
Chlorobenzene	83.8 \pm 6.3	94.0 \pm 4.0
<i>O</i> -dichlorobenzene	44.3 \pm 8.8	43.6 \pm 7.3

4. Conclusions

FES is the by-product of producing fullerenes. Compared with Tenax GR, which is considered to be one of the adsorbents showing the overall best properties for sampling complex mixtures of volatiles [10], FES has almost the same adsorption and desorption efficiency for compounds adsorbed on it. The breakthrough volumes of VOCs on FES are greater than those values on Tenax GR.

Acknowledgements

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