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Evaluation of natural crab shell as an adsorbent for preconcentrating airborne volatile organic compounds collected in a canister

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Abstract

A method has been developed for preconcentrating the volatile organic compounds (VOCs) in ambient air using a trap filled with natural crab shell powder without the need for extensive cryotrapping with liquid cryogens. Air samples collected in the canister were concentrated on the crab shell adsorbent trap without cryotrapping and then analysed using thermal desorption followed by capillary column (DB-5) gas chromatography with simultaneous ion trap mass detection. These analytical data on ambient air have been compared with those obtained by cryotrapping volatile compounds in glass beads followed by thermal desorption. The characteristics of natural crab shell as an adsorbent have been presented and its capacity for preconcentrating airborne VOCs has been tested by measuring breakthrough volume (l/g), detection limit (ppb, v/v) and reproducibility. The application of natural crab shell adsorbent trap for the analysis of ambient air samples collected in the canister has been proved to be useful.

Keywords: Adsorbents; Air analysis; Environmental analysis; Sample handling; Volatile organic compounds

1. Introduction

Methods for the analysis of atmospheric organic compounds include a preconcentration step due to low-level pollutants [1]. Samples collected in a canister are cryotrapped using liquid cryogens [2–6] with a post desorption–cryofocusing step. Most of the time, no adsorbents are used in cryotraps, which allows desorption at moderate temperatures (40~70°C), thus avoiding interferences arising from thermal degradation of solutes. Addition of a second cryotrap, just at the entry of the chromatographic column, is necessary to obtain narrow chromatographic bands, compatible with a capillary analytical column. The reported cryogenic traps are U-shaped borosilicate glass tubes with quartz wool and U-shaped stainless steel tubes packed with 180~250 μm untreated beads, in which glass-wool was placed at both ends of the tube to keep the glass beads in place. Liquid argon or nitrogen as cryogen was used to cool the trap. This cryotrappng has led to various problems like tube plugging, transfer of water to the GC column by high water content in air. Therefore, an additional drying tube has to be inserted to remove water in the samples. Furthermore, there are difficulties in supplying liquid cryogen to the remote locations on a routine basis, and the cost can be high

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[7]. An alternative approach employs microtraps filled with a suitable adsorbent which allows direct thermal desorption into a capillary column thereby by-passing the cryofocusing step [8–10]. Conventional methods use adsorbent beds consisting of activated charcoals [11], porous polymers (e.g., Tenax TA [12]) or combinations of sorbents (e.g., charcoal–polyurethane foam [13], graphitised carbon black-carbon molecular sieve [14], Carboxen 1000/1003 [15] and Tenax–Carbotrap [16]).

Crab shell is widespread in nature and has been recently utilized for the treatment of wastewater, such as removal of heavy metals or phenols [17,18]. The fact that the crab shell has adsorption properties [18,19] gives rise to an idea that it could be utilized as an adsorbent for trapping and preconcentrating volatile organic compounds (VOCs) in air samples.

In this report, we present the characteristics of the natural intact crab shell powder as an adsorbent material for preconcentrating airborne VOCs. The analytical results using crab shell powder as an adsorbent without liquid cryogen will be compared with those performed using a cryogenic preconcentration method at AtmAA (Calabasas, CA, USA) [20] thus demonstrating that the application of natural crab shell adsorbent trap for the analysis of ambient air samples collected in a canister is useful.

2. Experimental

2.1. Reagents and materials

Certified calibration gas mixture of standards was purchased from Supelco (Scott Specialty Gases, Plumsdteadville, PA, USA) whose concentration was 100 ppb (v/v) (ppbv) and were quantitatively diluted with N_2 (99.999%) to concentrations from 1 ppbv to 10 ppbv by dynamic diluter (Entech, Model 4560SL, USA) into the Summa Passivated Canister (Scientific Instrumentation Specialists, Moscow, ID, USA).

The trap was made of a stainless steel tube (Tekmar, Cincinnati, OH, USA) of 12 in.×1/8 in. O.D., and filled with 180~250 μm crab shell powder (0.75 g) (1 in.=2.54 cm). Quartz-wool was placed at both ends of the tube to keep the crab shell powder in place. The tube was maintained at ambient temperature during adsorption. The trap was heated for desorption by applying 60 V a.c. from a variable transformer to an external heating wire wrapped around the trap, this raised the temperature to approximately 50°C in 10 s. The adsorbent tube was prepared freshly by conditioning for an hour at 200°C. The crab shell changed from a red to a yellow color at 250°C, which indicated that the crab shell material would be unstable at temperatures higher than 250°C, therefore, the temperature of trap was kept below 250°C. The tube was then analysed to confirm the absence of contaminants.

2.2. Surface analysis

The physical properties such as adsorption surface area, total pore volume and pore diameter of crab shell adsorbent were measured with ASAP 2000 (Micromeritics, GA, USA) and the image of the intact crab shell surface was obtained by TEM(transmission electron microscopy, Phillips, CM-30, Netherlands) [21].

2.3. Sampling

Air sampling was carried out with a 6-l stainless steel canister (SIS, Summa air sampling container) in an urban area (Ulsan, South Korea) nearby a petroleum industrial park. The canister was cleaned and tested using gas chromatography (GC), and was confirmed to be free of any contaminants before sample collection. In preparation for subatmospheric collection, the canister was evacuated to 0.1~10.1 Pa. The sample was collected in a canister using a pump to achieve a $10.34 \cdot 10^4$ Pa final canister pressure with 10~15 ml/min flow-rate for 2 h.

2.4. Preconcentration and calibration

The canister containing standard gas or sample was attached to the sorbent tube and then flow was controlled by using a mass flow meter (Sierra Instruments, Monterey, CA, USA) in order to obtain precise flow-rates. The adsorption flow was adjusted to 40 ml/min. In order to determine adsorption volume, 10 ppbv standard gas was trapped at a series of volumes from 200 through 800 ml, and finally 800 (or 500) ml was selected as the preconcentration volume at room temperature. 1~10 ppbv standard

gases were adsorbed into the trap for calibration at the 800 (or 500) ml volume.

2.5. Thermal desorption

A purge-and-trap concentrator (Tekmar, LSC 2000, USA) was used for thermal desorption. Dry purge time for the residual water purge was 0.5 min, desorption time was 2 min at 180°C and adsorbent bake time was 5 min at 200°C for eliminating the contaminants. Helium was the carrier gas which flowed at the rate of 40 ml/min and was split to 1 ml/min in the split–splitless GC injector without cryofocusing.

2.6. GC–MS conditions

Analysis was carried out by GC–MS (Finnigan Magnum, San Jose, CA, USA). Separation of 12 compounds (chloroform, 1,1,1-trichloroethane, benzene, carbon tetrachloride, trichloroethene, toluene, tetrachloroethene, ethylbenzene, *m*-, *p*-xylene, styrene, *o*-xylene) was performed with a DB-5 fused-silica capillary column (30 m×0.25 mm I.D., 0.25 μm film thickness), and then they were detected by ion trap mass spectrometry (MS). GC conditions used in the experiments are as follows, carrier gas, Ultrapure 99.999% helium; GC flow-rate, 1 ml/min; initial oven temperature, 34°C (10 min); ramp rate, 5°C/min; final oven temperature, 135°C (2 min); transfer line temperature, 110°C; MS conditions are as follows, scan range, 30~350 u; scan rate, 1 s; threshold, 1 count; mass defect, −50; ionization mode, electron impact (EI); auto gain control, on; manifold temperature, 200°C.

3. Results and discussion

3.1. Tube conditioning

The Adsorption tube and adsorbents require a clean-up process before use, and this clean-up process was carried out by tube conditioning at 200°C. Air and acetone are identified for 5 and 25 min conditioning but for an hour conditioning they are not observed in the gas chromatogram during the tube conditioning process (not shown). Air and acetone appear to be traces remaining when the tube is cleaned with acetone before it is packed with crab shell adsorbent. This indicates that crab shell adsorbent material does not generate any VOCs (or hydrocarbons) after 200°C baking and it is safe to desorb at 200°C.

3.2. Breakthrough volume, adsorption and desorption

The breakthrough volume of the adsorbent is determined as the volume of gas passed through the tube until 5% of the applied chemical appears in the outlet stream when a known concentration is passed through the adsorbent bed and is expressed in liters per gram of adsorbent. Breakthrough volumes of the adsorbent trap for the preconcentration of VOCs were estimated by connecting two tubes in series and measuring the peak of each compound from the second tube at the specified volume. Table 1 summarizes the breakthrough volumes for each compound in which the quantity of sorbent was 0.75 g and the tested concentration was 5 ppbv for each compound. This crab shell sorbent has breakthrough volumes greater than 0.5 l for nine organic compounds and less than 0.5 l for three organic compounds as shown in Table 1.

Since the breakthrough volumes for three organic compounds (1,1,1-trichloroethane, benzene, carbon tetrachloride) were lower than the sampled volume (0.8 l), the analytical work for these three organic compounds has been performed using 0.5 l of the sampled volume and analytical results for 12 organic compounds have been shown to be linear.

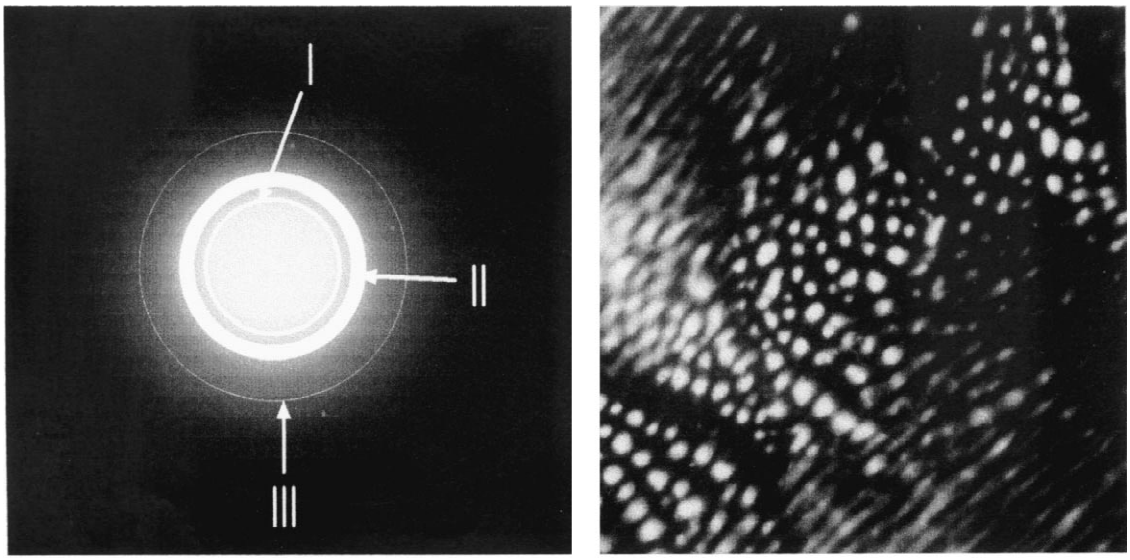
The adsorption surface area of crab shell adsorbent measured by the BET sorptometer was 14.52 m^2/g, and total pore volume and pore diameter were 0.0767 ml/g and 211.24 Å, respectively. Surface area is smaller than that of graphitized carbon blacks (e.g., Carbotrap C, Carbopack C and Carbopack F) which can be used for C_1–C_{10} compounds including alcohols, free acids, amines, ketones, phenols and aliphatic hydrocarbons. As shown in the physical properties of crab shell, the material of crab shell is composed of relatively large pore size and the small number of pores per unit area in comparison to porous polymers available commercially, which indicates that crab shell adsorbent reflects good adsor-

Table 1
Breakthrough volume, detection limits and R.S.D. for 12 compounds using crab shell adsorbent in GC–MS for the analysis of ambient air sampled by canister

	Breakthrough volume (l/g)[a]	Detection limit (ppbv), $n=6$	R.S.D. (%), $n=7$
Choroform	>0.67	0.48	10.7
1,1,1-Trichloroethane	≤0.67	0.74	12.0
Benzene	≤0.67	0.21	10.3
Carbon tetrachloride	≤0.67	0.65	12.9
Trichloroethylene	>0.67	0.10	8.5
Toluene	>1.60	0.44	10.1
Tetrachloroethylene	>0.67	0.05	6.4
Ethylbenzene	>1.60	0.50	5.9
m-, *p*-Xylene	>1.60	0.47	5.8
Styrene	>2.93	0.57	7.3
o-Xylene	>2.93	0.58	5.7

[a] When 5% of the applied chemicals appeared in the outlet stream after a known concentration (5 ppbv) is passed through the adsorbent tube.

ptivity for the large airborne compounds. In order to understand the micro-structure of crab shell material in detail, we have investigated it using TEM. Fig. 1A shows the SAD (selected area diffraction) ring pattern of the crab shell. Distances between diffraction planes, d can be calculated as, $d=L\lambda/r$, where r is the distance from focus to diffraction point, L is the camera length (300) and λ is the wavelength (0.0251 Å) and calculated distances are 3.01, 1.93, 1.12. This reveals that the major component of the crab shell, calcium carbonate is the calcite and its structure is rhombohedral which has the diffraction planes to the directions of (1 0 4), (2 0 2), (1 2 11). Fig. 1B displays the 10^4-fold magnified dark field



(A) (B)

Fig. 1. (A) Selected area diffraction ring pattern [I(1 0 4), II(2 0 2), III(1 2 11)] (it was reconstructed for clear identifcation). (B) The 10^4-fold magnified dark field image of crab shell surface taken by TEM.

image of crab shell interior measured by TEM. As shown in this image, a lot of white colored and pipe shaped pores were observed, these pores serve as the adsorption site for airborne VOCs.

In order to determine the most adequate desorption temperature, the temperature of the trap was varied from 120 to 200°C. As demonstrated in Fig. 2, most of tested compounds showed the maximum peak area at 180°C, the optimum desorption temperature.

3.3. GC–MS analysis

Desorbed compounds at 180°C were separated with a DB-5 (30 m×0.25 mm, 0.25 μm) capillary column and then detected by ion trap MS. Quantitation was carried out using the area of mass chromatogram for the selected ions. Mass chromatograms for the selected ions showed better selectivity than the total ion chromatogram (TIC) by lowering the background even when the peaks overlapped.

3.4. Calibration

Calibration curves for the 12 compounds were obtained at the concentration levels of 1~10 ppbv. The results are listed in Table 2. All compounds showed fairly good linearity with correlation coefficients (r) higher than 0.99, which are quantitatively useful calibration results, and these correlation coefficients demonstrate that the crab shell powder works well as an adsorbent for trapping and preconcentrating airborne VOCs.

3.5. Detection limits and reproducibility

Detection limits were determined with the analyte concentration that produces a chromatographic peak having a height equal to three-times the standard deviation of the baseline noise from the six measurements for each compound [22]. They ranged from 0.05 to 0.74 ppbv (Table 1). In addition, reproducibility was estimated from the R.S.D. (relative standard deviation) for seven measurements. R.S.D.s (Table 2) were 5.8~12.9% which are relatively precise and these results would be an acceptable values on the basis of the EPA (US Environmental Protection Agency) TO-15 criteria which prescribes detection limit and precision criteria as 0.5 ppbv and 25%, respectively.

3.6. Air sample analysis

In order to apply this method to real sample analysis, concentrations analyzed from the cryogenic trapping method at AtmAA and crab shell adsorbent method in this laboratory using GC–MS were compared with each other (Table 3). They have shown good agreement with correlation coefficients of 0.90~0.99. Therefore, it is clear that this method

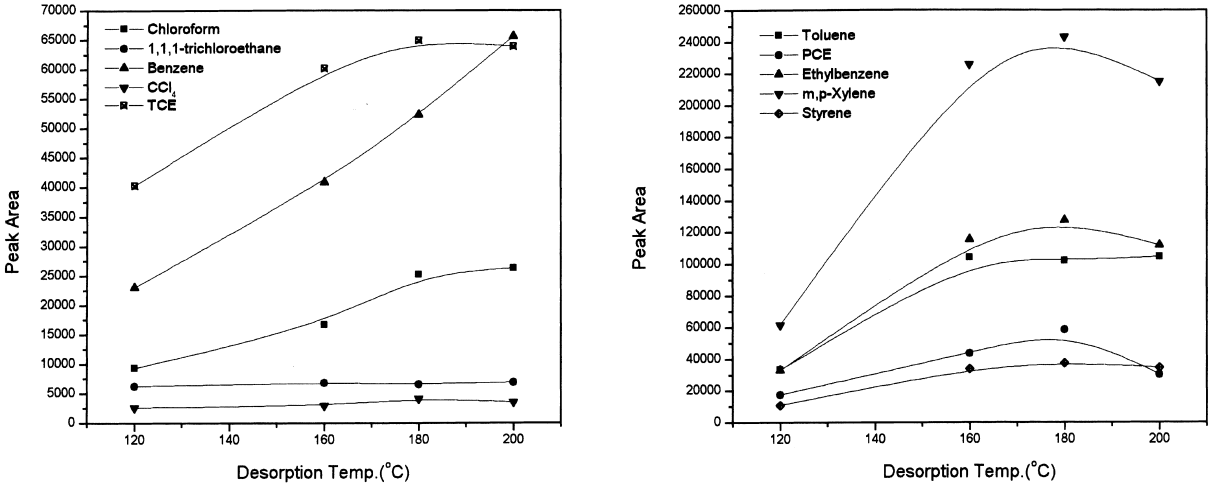


Fig. 2. The variation of peak areas as a function of the desorption temperature of adsorbent trap.

Table 2
Calibration results for the 12 compounds using crab shell powder as the preconcentrating adsorbent

Compound	$y=a+bx$		Correlation coefficient (r)
	a	b (±S.D.)[a]	
Choroform	80.7	1143.3(±88.7)	0.997
1,1,1-Trichloroethane	−21.7	505.3(±29.7)	0.998
Benzene	1112.2	1545.5(±68.2)	0.999
Carbon tetrachloride	17.3	245.5(±35.6)	0.989
Trichloroethylene	1985.1	10857.1(±306.6)	0.999
Toluene	340.3	2083.2(±102.7)	0.998
Tetrachloroethylene	766.6	1345.6(±101.9)	0.997
Ethylbenzene	−266.1	3001.6(±125.2)	0.999
m-, *p*-Xylene	−95.3	5735.6(±160.3)	0.999
Styrene	−328.9	1137.6(±99.5)	0.996
o-Xylene	−430.9	2794.1(±133.3)	0.998

[a] S.D.: Standard deviation.

would be applicable to analyze the VOCs in air by GC–MS with a reliable accuracy.

4. Conclusions

It has been shown that the VOCs can be quantitatively trapped and desorbed from a crab shell adsorbent trap without the use of liquid cryogens. The adsorption mechanism was not studied, but the results indicated that it would be possible to trap and preconcentrate the VOCs from a 800 ml air sample at the room temperature using crab shell adsorbent. There was no need for special purification of crab shell adsorbent before use. We used crude crab shell powder as an adsorbent after conditioning at 200°C for an hour.

This method of recycling the waste crab shell into an adsorbent could be the basis of a new efficient and cost effective method for the preconcentration of ambient air. Furthermore, crab shell adsorbent could be a good alternative for an active sampling tube if

Table 3
Real sample concentrations analyzed by AtmAA[a] and this laboratory

Compound	Sample														Correlation coefficient (r)
	1		2		3		4		5		6		7		
	A	B	A	B	A	B	A	B	A	B	A	B	A	B	
Chloroform	0.37	ND[b]	ND	ND	0.20	ND	0.20	ND	0.10	ND	0.37	0.71	0.14	ND	–
1,1,1-Trichloroethylene	0.12	ND	ND	ND	0.21	ND	0.24	ND	ND	ND	0.46	ND	0.18	ND	–
Benzene	2.6	2.76	3.80	2.57	1.06	0.72	0.40	ND	1.34	1.93	5.07	6.07	0.25	ND	0.90
Carbon tetrachloride	0.21	0.94	ND	0.69	0.17	0.77	0.15	ND	0.11	ND	0.34	ND	0.15	ND	–
Trichloroethylene	0.39	0.45	0.36	ND	0.35	ND	0.13	0.27	0.10	0.21	0.25	0.36	0.10	ND	0.99
Toluene	5.37	6.84	5.37	6.05	3.83	4.07	3.68	4.21	0.76	133	8.22	10.23	2.62	4.49	0.97
Tetrachloroethylene	ND	ND	ND	ND	ND	ND	0.13	ND	ND	ND	0.10	0.06	ND	ND	–
Ethylbenzene	1.14	1.69	1.19	1.31	0.78	0.88	0.53	0.58	0.13	ND	1.47	2.02	0.22	ND	0.96
m-, *p*-Xylene	8.82	6.04	1.53	2.11	1.86	1.22	1.69	1.82	0.50	0.90	3.98	5.29	0.66	0.84	0.91
Stylene	1.38	2.20	0.47	0.93	0.33	0.73	0.34	ND	0.07	ND	0.96	1.51	0.04	ND	0.99
o-Xylene	1.48	1.74	1.21	1.27	0.71	0.86	0.58	0.59	0.18	ND	1.35	1.75	0.23	ND	0.98

[a] AtmAA: Crygenic trapping method was used.
[b] ND: Not detected.
When the sampling was performed, the humidity and the temperature were about 80% and 18°C, respectively.
A: Analyzed by AtmAA, B: analyzed by this experiment.

breakthrough volume, flow-rate and the temperature for safety sampling are determined.

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