

Measurement of Benzene in Air by Iranian Single-Wall Carbon Nanotubes

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ABSTRACT

Background: Nanotechnology is a new approach that has been lionized in recent years. One of its applications is its consumption as an absorbent. In this study, the single-wall carbon nanotubes (SWCNTs) were used as an absorbent for sampling benzene in the air.

Materials and Methods: For this study, SWCNTs manufactured by Iran and SKC's activated charcoal were used for sampling benzene vapors. Preparation and analysis of the samples were done by carbon disulfide and GC-FID (gas chromatography-flame ionization detector), respectively

Results: The results indicated that the performance of SWCNTs is less than conventional activated charcoal for sampling benzene vapors in the air

Conclusion: The findings of this study showed that the performance of SWCNTs in the sampling of benzene vapors in the air is very poor and, therefore, cannot be a good alternative to SKC's activated charcoal.

Keywords: Activated Charcoal, Air Pollution, Benzene, Carbon Nanotubes, GC-FID.

INTRODUCTION

Today, air pollution is one of the fundamental problems of human societies that has caused many disorders. Most air pollutants are made of industrial materials among them volatile organic compounds can be noted due to their chemical properties which are used in broad industries. Among the volatile organic compounds, benzene is particularly important since it is widely used in many industries and it has been introduced as a definitive carcinogenic in humans by many prestigious organizations, such as Environmental Protection Agency (EPA), National Institute of Occupational Safety and Health (NIOSH), American Conference of Governmental Industrial Hygienists (ACGIH), and International Agency for Research on Cancer (IARC).

At room temperature benzene is a colorless liquid with a sweet odor which is highly flammable (1). It evaporates into the air very quickly and causes chromosome aberration in laboratory animals (2) and people are exposed to benzene through respiration (3-5). The results of correlate literature reviews in

this context have shown that exposure to benzene causes leukemia, bone marrow cancer, and lung, kidney, and liver damages (4, 6-8).

Therefore, noticing the extensive use of benzene in different industrial sectors, such as plastic, pesticide, and pharmaceutical industries (9) and its toxicology, identification, and control are necessary. For this purpose, different sampling methods for benzene exist (1501 NIOSH, 2549 NIOSH, 3700 NIOSH, 12 Occupational Safety and Health Administration (OSHA), 1005 OSHA)(10,11). However, access to new methods is important since in addition to saving time and money, higher efficiencies achieved. One of the solutions to this problem is using technologies, such as nanotechnology that has been lionized in recent years. Nanotechnology is related to the preparation of materials at nanoscale, such as nanofiber, nanoparticles, nanowires, or nanotubes (12).

Carbon nanotubes are a major type of nano-structured materials that have lately been used (13-17) because of their chemical and thermal stability, high surfaces area, large affinity to the non-polar compounds (18), low-cost, and lightweight(12). Hence in this study,

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the application of Iran manufactured Single Wall Carbon Nanotubes (SWCNTs) for adsorption of benzene vapors was investigated.

MATERIALS AND METHODS

Materials

Benzene (99.5%), carbon disulphide (99.5%), and nitric acid (66.4%) were obtained from Merck (Germany). Aitec syringe pump (model Sep-10S) was used for standard atmosphere generation and the low flow sample pump 222 series workhorse for sorbent tubes was purchased from SKC (SKC, USA). Charcoal tubes (150 mg) were purchased from

SKC. The SWCNTs with internal diameter (ID) and outer diameter (OD) of respectively 0.9 and 1.5 nano meter were purchased from Iran Research Institute of Petroleum Industry (Figure 1).

Before using the SWCNTs, they were treated with conc. HNO_3 at 80 °C temperature for 24 hours until elimination of amorphous and impurities. Then the excess nitric acid was removed by centrifuging and the deposit SWCNTs were washed by deionized water until 6 pH. At the end of this process, SWCNTs were dried at room temperature (19, 20).

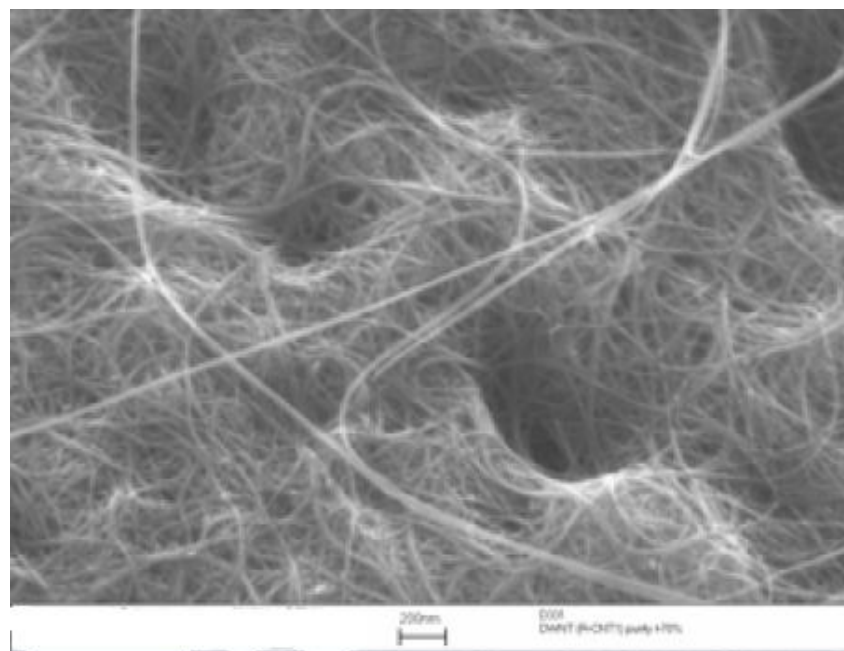


Figure 1. SEM micrograph of SWCNTs (L = 10 μm , Brunauer, Emmett, and Teller (BET) surface area = 700 (m^2/gr))

Preparation of the sampling tubes

In order to use SWCNTs, charcoal tubes were used as glass tubes (10 cm \times 4 mm internal diameter (ID) and 2 mm wall thickness). The sampling tubes of SWCNTs were assembled according to an original NIOSH specification that was applied to charcoal tubes. Also small amounts of deactivated glass wool were used in front of sampling tubes to eliminate humidity and reach a uniform pressure drop. Finally, all tubes were

plugged by plastic caps and stored at room temperature.

Instruments and procedure

All analyses were performed by Varian GC CP 3800 with a flame ionization detector (FID). The GC was fitted with a packed column (10% PEG. C.W 100-120). The column, injection, and detector temperatures were respectively kept at 50, 200, and 200 °C for 8 minutes. The carrier gas was nitrogen 99.99% (Roham Gas Co. Tehran, Iran). Under

these conditions, the benzene peak was extracted at about 4.12 minutes.

Generating the standard atmosphere

In order to prepare the specified concentrations of benzene within the desirable range, a dynamic atmosphere generation system was built in laboratory (Figure 2). In this chamber, air was heated to 25°C by an electrical coil that was actuated by a temperature sensor located in the chamber and thermocouple system (SAMWON ENG, Model SU-105). Humidity was generated by heating water up to a 40% output which was detected by a hygrometer (Model Testo 601, Germany).

The stable concentration of benzene in this sampling chamber was generated by syringe pump (AITECS syringe pumps SEP-

10S Plus). The injection rate was set proportional to the desired concentration that was calculated according to the following equation at 25 °C.

$$Q = \frac{\rho \times 24.45 \times IR \times 10^6}{MW \times C \times 60}$$

Where, ρ is the density of analyte that will be injected in g/ml, IR is injection rate (ml/hr), MW is molecular weight of analyte, C is the desirable concentration in chamber in part per million (ppm), and Q is gas flow rate liters per minute (LPM). The gas flow rate in this system was checked continuously by a dry gas meter calibrated according to the primary standard device. Air was drawn through the chamber for 30 minutes to reach a steady state every day.

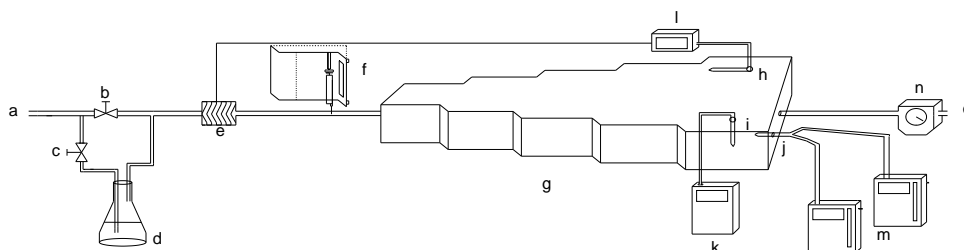


Figure 2. Schematic diagram of the test atmosphere of the generation system

- | | |
|-------------------------------|--------------------------|
| a: Air inlet | i: Humidity sensor |
| b: Bypass valve | j: Active sampling port |
| c: Valve to humidity system | k: Hygrometer |
| d: Humidity generation system | l: Thermocouple |
| e: Electrical coil | m: Personal sampler pump |
| f: Syringe pump | n: Dry gas meter |
| g: Sampling chamber | o: Outlet (to hood) |

(Created by: AutoCAD 2007)

Method of sampling

Sampling of benzene in the standard chamber was carried out according to NIOSH-1501 and OSHA-1005 standard methods.

Proportional to this standard, the flow rate of the sampling pump was kept at 100 ml/min in the whole sampling time. At the end of sampling process, the front and back sections of the charcoal and SWCNTs tubes were

placed in separate vials. Then 1 ml carbon disulphide (CS₂) was added to each vial and allowed to stand for 30 minutes with gentle agitation by a shaker (Fater Rizpardaz Model FR602). Finally, 5 µl of the sample was directly injected onto the GC-FID injector with medium sensitivity.

RESULTS

Adsorption efficiencies of benzene vapor on SWCNTs and activated charcoal

In this study, the adsorption efficiencies of benzene vapor were compared between SWCNTs and activated charcoal at 3 concentrations. The mean of the sampling results are demonstrated in Table 1. Sampling conditions for both absorbers were the same.

The results showed that the adsorption efficiency of activated charcoal to be higher than SWCNTs.

Table 1: The comparison between adsorption efficiencies for SWCNTs and activated charcoal

The type of absorber	Concentration in standard chamber (mg/m ³)	Concentration in the absorber (mg/m ³)
SWCNTs	17	7
	7	4.88
	3	2.9
Activated charcoal	17	16.65
	7	6.54
	3	2.98

Estimation of adsorption capacity

Adsorption capacity plays a key role in selecting the absorber. Therefore, this study dealt with the breakthrough values in SWCNTs and activated charcoal. The word "breakthrough" in this paper refers to a condition in which the concentration of benzene in the back section of absorber is

more than 1% of the front section. The breakthrough values of benzene for the concentration in different times in 2 types of absorber are listed in Table 2.

The results showed that the breakthrough value in SWCNTs is higher than activated charcoal.

Table 2. Benzene adsorption capacities of the SWCNTs and activated charcoal

Benzene concentration in standard chamber (mg/m ³)	Time (min)	Benzene concentration of SWCNTs (mg/m ³)		Benzene concentration of activated carbon (mg/m ³)	
		Front section	Back section	Front section	Back section
6	540	1.96	0.65	5.48	0
	240	1.82	0.62	5.41	0
	120	1.78	0.416	4.47	0
	60	1.64	0.08	5.12	0

Assessment of storage stability

For storage stability assessment, 3 samples with the same sampling condition by activated charcoal and SWCNTs were taken.

One sample of any absorber was analyzed immediately. Other samples were accurately plugged by plastic caps and kept at refrigerator temperature (4±1°C) and then analyzed after 15 and 30 days. Table 3 shows the results of

mass recovery under different storage times for benzene vapors.

The results showed that storage stability in activated charcoal at the end of the 30-day

period is very good but these results are not exactly observed in SWCNTs.

Table 3. Storage stability of Benzene in SWCNTs and activated charcoal

Benzene concentration in standard chamber (mg/m ³)	Storage time (day)	Benzene concentration of SWCNTs (mg/m ³)		Benzene concentration of activated carbon (mg/m ³)	
		Front section	Back section	Front section	Back section
4	0	3.1	0.1	3.95	0
	15	2.7	0.5	3.9	0.023
	30	2.4	0.9	3.85	0.056

CONCLUSION

The findings of this study suggest that SWCNTs are not good absorbers for detecting benzene in the air since they have low absorption capacity and maintenance ability. The comparison between activated charcoal and SWCNTs expressed the poor activity of SWCNTs in absorption process. Rao and colleagues in their study (1999) stated that the SWCNTs are good absorbers for sampling benzene (21).

Bystrzejewski and Pyrzynska (2010) showed that CNTs granolas have a higher efficiency in capturing metal ions than activated carbon (22). Also, in Li *et al.*'s study, SWCNTs had lower breakthrough than charcoal for sampling Volatile Organic Compounds (23); however, the findings of our study showed that Iranian SWCNTs cannot be excellent alternatives for activated charcoal. In addition, the cost of SWCNTs is more than SKC's activated charcoal and this item is another problem in this regard.

REFERENCES:

- Bingham E, Cohrssen B, Powell C. Patty's toxicology. Vol. 6. New York: John Wiley and Sons; 2001.
- National Toxicology Program (NTP). Carcinogenesis Studies of Benzene (CAS No. 71-43-2) in F344/N Rats and B6C3F 1 Mice (Gavage Studies). National Toxicology Program Bethesda, MD: NTP. 1986.
- International Agency for Research on Cancer. Environmental Carcinogens MoAaEM, Benzene and Alkylated Benzenes. IARC, Lyon, 1988;10:3-18
- Dean BJ. Recent findings on the genetic toxicology of benzene, toluene, xylenes and phenols. Mutation research. 1985;154(3):153-81.
- Raw GJ, Coward SKD, Brown VM, Crump DR. Exposure to air pollutants in English homes. Journal of Exposure Science and Environmental Epidemiology. 2004;14:S85-S94.
- Subrahmanyam V, Doane-Setzer P, Steinmetz K, Ross D, Smith M. Phenol-induced stimulation of hydroquinone bioactivation in mouse bone marrow in vivo: possible implications in benzene myelotoxicity. Toxicology. 1990;62(1):107-16.
- Bois FY, Smith MT, Spear RC. Mechanisms of benzene carcinogenesis: application of a physiological model of benzene pharmacokinetics and metabolism. Toxicology letters. 1991;56(3):283-98.
- National Institute for Occupational Safety and Health HHERH, National Centers for Environmental Health, Albany, New York. Cincinnati, OH:U.S. Department of Health and Human Services, Public Health Services; 1993, Report no. 93-0884-2344.
- Wolf MA, Rowe VK, Mccolloster DD, Hollingsworth RL, Oyen F. Toxicological studies of certain alkylated benzenes and benzene; experiments on laboratory animals. AMA Arch Ind Health. 1956;14(4):387-98.
- Osha.gov. [homepage on the Internet]. Sampling and Analytical Methods. U.S. Department of Labor. [cited 2010]. Available from:

- <http://www.osha.gov/dts/sltc/methods/index.html>.
11. Cdc.gov[homepage on the Internet].NIOSH Manual of Analytical Methods. [cited 2003]. Available from: <http://www.cdc.gov/niosh/docs/2003-154/method-b.html>.
 12. Iijima S. Helical microtubules of graphitic carbon. *nature*. 1991;354(6348):56-8.
 13. Diaz E, Ordonez S, Vega A. Adsorption of volatile organic compounds onto carbon nanotubes, carbon nanofibers, and high-surface-area graphites. *Journal of colloid and interface science*. 2007;305(1):7-16.
 14. Penza M, Tagliente M, Aversa P, Cassano G. Organic-vapor detection using carbon-nanotubes nanocomposite microacoustic sensors. *Chemical physics letters*. 2005;409(4-6):349-54.
 15. Balasubramanian K, Burghard M. Biosensors based on carbon nanotubes. *Analytical and bioanalytical chemistry*. 2006;385(3):452-68.
 16. Pham-Huu C, Ledoux MJ. Carbon nanomaterials with controlled macroscopic shapes as new catalytic materials. *Topics in catalysis*. 2006;40(1):49-63.
 17. Lu C, Liu C, Rao GP. Comparisons of sorbent cost for the removal of Ni²⁺ from aqueous solution by carbon nanotubes and granular activated carbon. *Journal of hazardous materials*. 2008;151(1):239-46.
 18. Hussain CM, Saridara C, Mitra S. Modifying the sorption properties of multi-walled carbon nanotubes via covalent functionalization. *Analyst*. 2009;134(9):1928-33.
 19. Yang J, Hu J, Wang C, Qin Y, Guo Z. Fabrication and Characterization of Soluble Multi-Walled Carbon Nanotubes Reinforced P (MMA-co-EMA) Composites. *Macromolecular Materials and Engineering*. 2004;289(9):828-32.
 20. Leu CM, Reddy GM, Wei KH, Shu CF. Synthesis and dielectric properties of polyimide-chain-end tethered polyhedral oligomeric silsesquioxane nanocomposites. *Chemistry of materials*. 2003;15(11):2261-5
 21. Eswaramoorthy M, Sen R, Rao C. A study of micropores in single-walled carbon nanotubes by the adsorption of gases and vapors. *Chemical physics letters*. 1999;304(3-4):207-10.
 22. Pyrzyńska K, Bystrzejewski M. Comparative study of heavy metal ions sorption onto activated carbon, carbon nanotubes, and carbon-encapsulated magnetic nanoparticles. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2010;362(1):102-9.
 23. Liu JM, Li L, Fan HL, Ning ZW, Zhao P. Evaluation of Single-walled Carbon Nanotubes as Novel Adsorbent for Volatile Organic Compounds. *Chinese Journal of Analytical Chemistry*. 2007;35(6):830-4.