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Comparison of nutshell granular activated carbons to commercial adsorbents for the purge-and-trap gas chromatographic analysis of volatile organic compounds

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Abstract

Granular activated carbons (GACs) made from agricultural by-products were investigated as adsorbents for short path thermal desorption gas chromatographic analysis of selected polar and nonpolar organic compounds. GACs made from macadamia nut, black walnut and hazelnut shells were compared to four commercially available adsorbents, namely, Tenax TA, Carboxen 569, Carbosieve SIII and coconut charcoal for their properties in purge-and-trap analysis. Adsorption values and breakthrough volumes were calculated for compounds from C_3 and C_6–C_{10}. GACs derived from macadamia nut shells were found to adsorb and desorb between 80% (benzene) and 277% (ethylbenzene) more acetone (C_3), benzene (C_6), toluene (C_7), ethyl- (C_8), *n*-propyl- (C_9), or *sec*.-butylbenzenes (C_{10}) purged from water at the 100 ppb level than the commercial adsorbents tested. © 2000 Published by Elsevier Science B.V.

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1. Introduction

The standard method for monitoring wastewater samples for volatile organic compounds involves the purging of volatile compounds from the wastewater using a continuous flow of inert gas through the sample [1]. The analytes are trapped or adsorbed onto an adsorbent and desorbed onto a gas chromatographic column. There are numerous different types of adsorbents for air monitoring and purge-and-trap sold commercially, including graphitized carbons, carbon molecular sieves, porous polymers, and a catch-all category which includes granular activated carbons (GACs) [2,3]. Each type has its own unique ability to adsorb organic compounds. The best adsorbents for purge-and-trap analysis are those that can adsorb and desorb a wide range of compounds with wide ranging molecular masses and polarities. The mesoporosity and microporosity of these sorbents are very important determinants of the compounds that activated carbons and other porous sorbents can adsorb. These physical properties are dependent upon three characteristics described by Matisova and Skrabakova: (1) type of starting ma-

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terial; (2) procedure chosen for preparation of the product; (3) conditions under which it is used [2]. Because these characteristics can produce very different properties, adsorbents are frequently combined to adsorb a wide range of compounds [4]. However, it is advantageous to use one adsorbent rather than to use a combination resulting in cost savings and convenience for the analyst.

This research project involves creating new commercial uses for agricultural wastes [5]. In this study, GACs made from macadamia, black walnut and hazelnut nutshells were compared to commercially available adsorbents, namely, Tenax TA (porous polymer), Carboxen 569, Carbosieve SIII (carbon molecular sieves); coconut shell (GAC) for their ability to adsorb selected polar and nonpolar organics in purge-and-trap analysis. Activated carbons made from the harder, denser, nutshells were chosen because they demonstrated superior adsorptive capabilities with organic compounds in water [5].

Breakthrough volumes were determined for each adsorbent in order to follow the migration of the analytes through the adsorbents at a specific flow-rate and temperature. Breakthrough studies have been used to determine the interactions of adsorbents with a certain range of analytes [6].

Our objective was to test the effectiveness of nutshell carbons as purge-and-trap adsorbents and compare them to commercial adsorbents under typical laboratory conditions. GACs made from nutshells could possibly be a low-cost alternative to commercially available adsorbents. They also offer a value-added product for the grower and sheller.

2. Materials and methods

2.1. Materials

Macadamia nut shells, hazelnut shells and black walnut shells were obtained from the Hawaiian Macadamia Co, Inc. (Keaau, HI, USA), Hazelnut Growers of Oregon (Cornelius, OR, USA), and the Hammons Products Co. (Stockton, MO, USA), respectively.

A granular activated carbon from macadamia nutshells (Ms13) and hazelnut shells (Hs2) was produced by grinding 1 kg of shells for about 15 min in a Retsch Model SK 100 mill (Glen Mills, Clifton, NJ, USA) equipped with a 4-mm screen and then sieved to a size range of 0.85 to 2.0 mm using a Ro-tap sieve shaker (W.S. Tyler, Mentor, OH, USA). The shells were pyrolyzed under nitrogen at 700°C for 1 h, then activated under a mixture of 70% N_2 and 30% CO_2 at 800°C for 6 h in a Lindberg box furnace with retort (Lindberg/Blue M, Watertown, WI, USA). A mass yield of 21% yield for Ms13 and Hs2 was obtained. Black walnut shells were milled to a size range of 0.85–2.0 mm as above, pyrolyzed at 750°C, then steam activated at 850°C for 3.5 h at a water injection rate of 111 cm^3/h to create Bws4 (at a mass yield of 24%). When the same pyrolysis and activation conditions were applied to two different samples of the same nutshell, the mass yields, surface areas and micropore and mesopore volumes were within ±5% of each other, therefore, good reproducibility was achieved. Commercial adsorbents, Tenax TA (0.18–0.25 mm granules), Carboxen 569 (0.355–0.850 mm granules), coconut charcoal (0.425–0.850 mm granules) and Carbosieve SIII (0.18–0.25 mm granules) were purchased from Supelco (Bellefonte, PA, USA). Acetone (C_3), benzene (C_6), toluene (C_7) were UV grade (J.T. Baker, Phillipsburg, NJ, USA). Ethyl- (C_8), *n*-propyl- (C_9) and *sec*.-butylbenzenes (C_{10}) were custom mixed at 100 ppm in acetone and purchased from Supelco.

2.2. Purge-and-trap

One hundred ppb solutions of acetone, benzene, toluene, and ethyl-, *n*-propyl- and *sec*.-butylbenzenes were made up in deionized, distilled water. They were purged in an S.I.S. Model TD-2 purge-and-trap system (Scientific Instrument Services, Ringoes, NJ, USA). Five-cm^3 samples were purged with dry helium at a rate of 3 cm^3/min for 11 min onto a stainless steel thermal desorption tube (11 cm×3 mm I.D.) packed with adsorbent (0.2–0.45 g) and packed at both ends with glass wool.

2.3. Thermal desorption

The analytes were desorbed at 190°C on an S.I.S. TD-2 desorption unit (Scientific Instrument Services) for 5 min with a helium flow-rate of 10 cm^3/min. C_7–C_{10} analytes were desorbed into the injection

port of the gas chromatograph at 220°C for 5 min. After desorption, the tubes were conditioned for 10 min at the desorbing temperature.

2.4. Gas chromatography

Samples were analyzed with a Hewlett-Packard Model 5890 gas chromatograph (Hewlett-Packard, Avondale, PA, USA). The inlet and detector temperatures were set at 220°C. The system was splitless (5 p.s.i. head pressure, 5 cm^3/min, helium carrier gas; 1 p.s.i.=6894.76 Pa) using a DB-624 (J&W Scientific, Folsom, CA, USA) 75 m megabore column with a 0.53 mm I.D and 3 μm film thickness. After a 6 min total time at 30°C, (to account for needle injection and desorption at 4 cm^3/min), the oven was ramped at 5°C/min to a final temperature of 150°C for 2 min for a total run time of 32 min for the C_3 or C_6 analytes. For the C_7–C_{10} analytes, the oven was ramped from 40°C at 5°C/min to a final temperature of 150°C for 4 min for a total run time of 36 min. Retention times for analytes were as follows: acetone 16.8 min, benzene 24.6 min, toluene 30.1 min, ethylbenzene 23.3 min, propylbenzene 26.7 min, and *sec*.-butylbenzene 29.1 min.

Samples and standards were run in triplicate. Peak areas were calculated by Chemstation software (Hewlett-Packard). Peak areas obtained by thermal desorption were compared to direct injection of 1 mm^3 each of 100 ppm standards which were analyzed with the same method used in the thermal desorption analyses. Adsorption was calculated on a ng analyte adsorbed per gram of adsorbent basis.

2.5. Recovery study for Ms13

A recovery study was conducted on the best performing experimental adsorbent in the purge-and-trap analyses, namely, Ms13. Standards were prepared in acetone at 1 mm^3/cm^3 except for acetone which was prepared in water. A 1-mm^3 sample was injected onto the end of a desorption cartridge filled with 0.235 g of Ms13 and plugged on each end with glass wool. The cartridge was purged with He at a rate of 3 cm^3/min for 11 min. The cartridge was analyzed with the same method described above for comparison purposes. Recoveries were based on peak areas obtained from a 1 mm^3 direct injection.

2.6. Surface area analysis

Surface areas were measured by nitrogen adsorption at 350°C using a Micromeritics Gemini 2375 surface area analyzer (Micromeritics, Norcross, GA, USA) using a 15-point BET [7]. Micropore, mesopore and macropore volumes were calculated by the BJH method [8,9]. Macropore volumes were generally less than 2% of the total pore volume and not significant for this work.

2.7. Calculation of breakthrough volumes

Adsorbent samples of 50 mg each were packed into 9 cm×4 mm I.D. glass tubing and packed on both ends with glass wool plugs. The glass tubing was adapted (with 1/4 in. to 1/16 in. SS Swagelock compact adapters; 1 in.=2.54 cm) to 0.53 mm I.D. non-polar fused-silica tubing and attached to the inlet and detector of the gas chromatograph [3].. The inlet and detector temperatures were set at 220°C. The flow-rate was set at 40 cm^3/min. Analytes were injected onto this system by sampling 50 mm^3 of headspace volume above 10 cm^3 of pure analyte in a 20-cm^3 vial.

Headspace volume was chosen so as not to saturate the adsorbent. After breakthrough, the adsorbents were conditioned at 220°C until the baseline was stable. Samples were run in triplicate. The method of Betz and Lambiase [10] was used to set up the study. The methods of Billedeau et al. [11] and Kashihira et al. [12], were used to quantify the breakthrough times. Breakthrough was determined to be the rise in baseline after injection of the analyte.

2.8. Statistical analyses

Data were analyzed by analysis of variance using Tukey's multiple comparison test to compare mean analyte adsorption and breakthrough volumes of various adsorbents while maintaining an overall type I error of 0.05 [13].

3. Results and discussion

3.1. Thermal desorption study

The analytes were evaluated in groups according to their carbon number. The supplier of the commercial adsorbents recommends that the carbon molecular sieves (Carboxen 569 and Carbosieve SIII) can only adsorb C_2–C_5. Tenax TA is recommended for C_5–C_{26} analytes. Coconut shell carbon was tested against all of the analytes as were the experimental carbons because it is also a GAC from a specific nutshell. Ms13 adsorbed more acetone, benzene, toluene, ethylbenzene, *n*-propylbenzene and *sec*.-butylbenzene than all other adsorbents evaluated (Table 1). Adsorption by Ms13 was statistically different from other adsorbents tested at $P=0.05$ by the Tukey's HSD means separation test although there were no statistical differences noted for acetone adsorption between adsorbents.

Ms13 adsorbed small as well as large molecules. Recoveries for the analytes desorbed from Ms13 were 35, 75.7, 23.7, 11, 7.9 and 7.6% for acetone, benzene, toluene, ethylbenzene, *n*-propylbenzene, and *sec*.-butylbenzene, respectively. These recoveries reflect the analysis conditions used for the adsorbent. Recoveries could increase based on purge time, and desorption temperature. Bws4 adsorbed almost the same concentration of acetone as Ms13, but is surpassed by Ms13 for the other analytes tested (Table 1).

Table 2
Surface area analysis for adsorbents in this study

Adsorbent	BET surface area (m^2/g)[a]	Mesopore volume (cm^3/g)	Micropore volume (cm^3/g)
Ms13	583	0.047	0.26
Hs2	572	0.057	0.25
Bws4	829	0.105	0.30
Coconut shell	949	0.035	0.45
Carbosieve SIII	1078	0.028	0.37
Carboxen 569	317	0.057	0.14
Tenax TA	22	0.018	0.01

[a] BET surface area was measured by nitrogen adsorption at 350°C. Mesopore and micropore volumes were calculated by the BJH method [8,9].

Micropore (2 nm or less in width) volume was reported to be the most important parameter affecting adsorption of aliphatic and aromatic compounds [14,15]. Mesopores vary between 2 and 50 nm in width [15]. Macropores are greater than 50 nm and are generally considered too large to adsorb the organic compounds used in this study [15]. Instead, they act as conduits to transport organic compounds to the interior of the granule where adsorption occurs in the micro- and mesopores [15].. According to the data in Tables 1 and 2, the adsorbents with the highest adsorptive capabilities do not have the highest micropore volumes. The adsorbent tested with the largest volume of micropores (coconut shell

Table 1
Adsorption of organic compounds by each adsorbent from the gas phase

Adsorbent	Adsorption (ng/g)					
	Acetone	Benzene	Toluene	EthBe[1]	ProBe[1]	BuBe[1]
Ms13	55.8^{a2}	409^{a}	370^{a}	437^{a}	364^{a}	325^{a}
Hs2	18.0^{a}	73.9^{c}	69.7^{c}	184^{ab}	164^{b}	160^{b}
Bws4	54.4^{a}	74.7^{c}	104^{bc}	82.0^{bc}	87.4^{bc}	83.8^{bc}
Coconut	24.7^{a}	227^{b}	198^{b}	116^{bc}	132^{bc}	120^{bc}
Carboxen 569	30.4^{a}	143^{bc}	103^{bc}	N/A	N/A	N/A
CarbosieveSIII	14.1^{a}	13.3^{c}	7.91^{c}	N/A	N/A	N/A
Tenax TA	N/A	N/A	N/A	15.3^{c}	11.3^{c}	12.1^{c}

[1] EthBe=Ethylbenzene, ProBe=*n*-propylbenzene, BuBe=*sec*.-butylbenzene.

[2] Means followed by the same letters are not significantly different at the 5% level as determined by Tukey's HSD test. Means are from triplicate determinations where the standard error was less than 5%.

N/A=Not applicable for these analytes.

carbon) at 0.45 cm^3/g was clearly not the best adsorbent.

It should be noted that coconut shell carbons are traditionally produced by steam activation. The black walnut shell carbon (Bws4) was also steam activated as mentioned previously. Macadamia nut shell carbon (Ms13), and hazelnut shell carbon (Hs2) were produced by CO_2 activation as mentioned previously. Ms13 has better adsorptive qualities than Hs2 even though the activation methods producing them were identical. Table 2 shows that their surface areas and micro-/mesopore volumes are similar. All of the precursor materials are hard, dense nutshells, yet they all have different adsorptive qualities as activated carbons. There is a strong possibility the precursor material could have an effect on the adsorptive properties of the adsorbent.

Macadamia nut shell GACs appear to be an excellent adsorbent for the polar (C_3) and nonpolar compounds (C_6–C_{10}) tested. These GACs have mesopore and micropore volumes which are conducive to adsorption of a wide range of compounds.

3.2. Breakthrough volume study

Breakthrough volume in this study is representative of a migration volume and not a breakthrough at saturation [6]. Acetone and benzene were chosen to represent the movement of polar and nonpolar compounds through the adsorbents. The breakthrough volume data in Table 3 show Carbosieve SIII to have the greatest retention of benzene, although its retention of acetone is not significantly different from the other adsorbents tested. Carbosieve SIII has a very high surface area and a very high microporosity (Table 2). The migration of the analytes was slower through Carbosieve SIII than the other adsorbents tested, indicating that an 11 min purge time was most likely not long enough for adsorption of benzene onto the micropores. The coconut shell carbon is also very microporous, but has a larger mesh size than CarbosieveSIII and does not retain the analytes as long. Of the three experimental nutshell carbons, Ms13 and Bws4 have similar breakthrough volumes for the analytes tested and retain the analytes longer than coconut shell, Tenax TA, or Carboxen 569. Tenax and Carboxen 569 showed very rapid migration of the analytes through the adsorbent at less than 1 dm^3 of helium needed to cause breakthrough of the analyte (headspace volume) through 1 g of adsorbent. These two adsorbents are relatively lower in microporosity and do not retain compounds as well as those with a higher micropore volume. Figs. 1 and 2 show an inverse relationship between mesopore (Fig. 1) and micropore (Fig. 2) volumes as they relate to breakthrough of both acetone and benzene.

These evaluations are not meant to be exhaustive characterizations of the adsorbents, but rather a comparison within a single set of conditions. The adsorbents have different particle sizes and are from different starting materials. The commercial adsorbents were used as provided by the manufacturer. Betz and Lambiase described an increase in ef-

Table 3
Breakthrough volumes for acetone and benzene for the adsorbents in this study[1]

Adsorbent	Acetone (dm^3/g at 100°C)	Benzene (dm^3/g at 160°C)
Ms13	$7.29^{a\,2}$	8.51^{b}
Hs2	3.68^{b}	1.76^{bc}
Bws4	8.99^{a}	7.92^{b}
Coconut shell	9.38^{a}	3.36^{bc}
Carbosieve SIII	9.73^{a}	22.2^{a}
Carboxen 569	$<1^{c}$	$<1^{c}$
Tenax TA	$<1^{c}$	$<1^{c}$

[1] The values in the table are expressed in dm^3 of helium needed to cause breakthrough of the analyte (headspace volume) through 1 g of adsorbent at the specified gas chromatograph oven temperature.

[2] Means followed by the same letters are not significantly different at the 5% level as determined by Tukey's HSD test. Means are from triplicate determinations where the standard error was less than 5%.

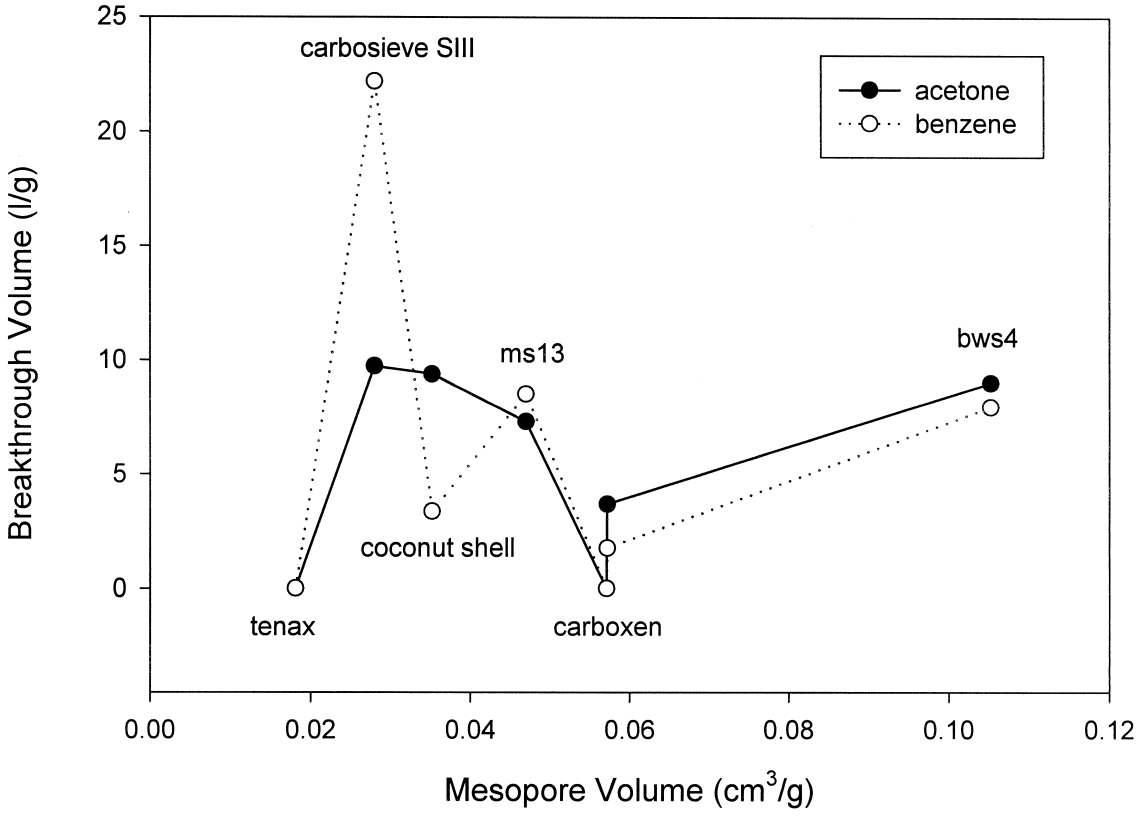

Fig. 1. Mesopore volume vs. breakthrough volume of analytes tested for each adsorbent.

ficiency of adsorbents with decreasing particle size [10]. This would indicate that the experimental nutshell carbons adsorptivity would increase with decreasing particle size.

4. Conclusion

A gas chromatographic analysis revealed that macadamia nut shell GACs seem to be an excellent adsorbent for polar and nonpolar compounds from C_3 and C_6–C_{10} tested. The evaluation of these adsorbents was conducted as a comparative study under one set of conditions. They have a mesopore and micropore volume that is conducive to adsorption of low- and high-molecular-mass compounds. Breakthrough volumes were shown to be a general indicator of analyte migration, however, they were not conclusive in determining the effectiveness of an adsorbent in adsorbing or desorbing a specific analyte. The full range of compounds and concentrations that can be absorbed quantitatively by nutshell granular activated carbons needs further investigation. Additional research is also necessary to determine if these adsorptive properties are truly due to pore volumes, to method of activation or to the precursor material.

5. Disclaimer

Mention of names of companies or commercial products is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the US Department of Agriculture over others not mentioned.

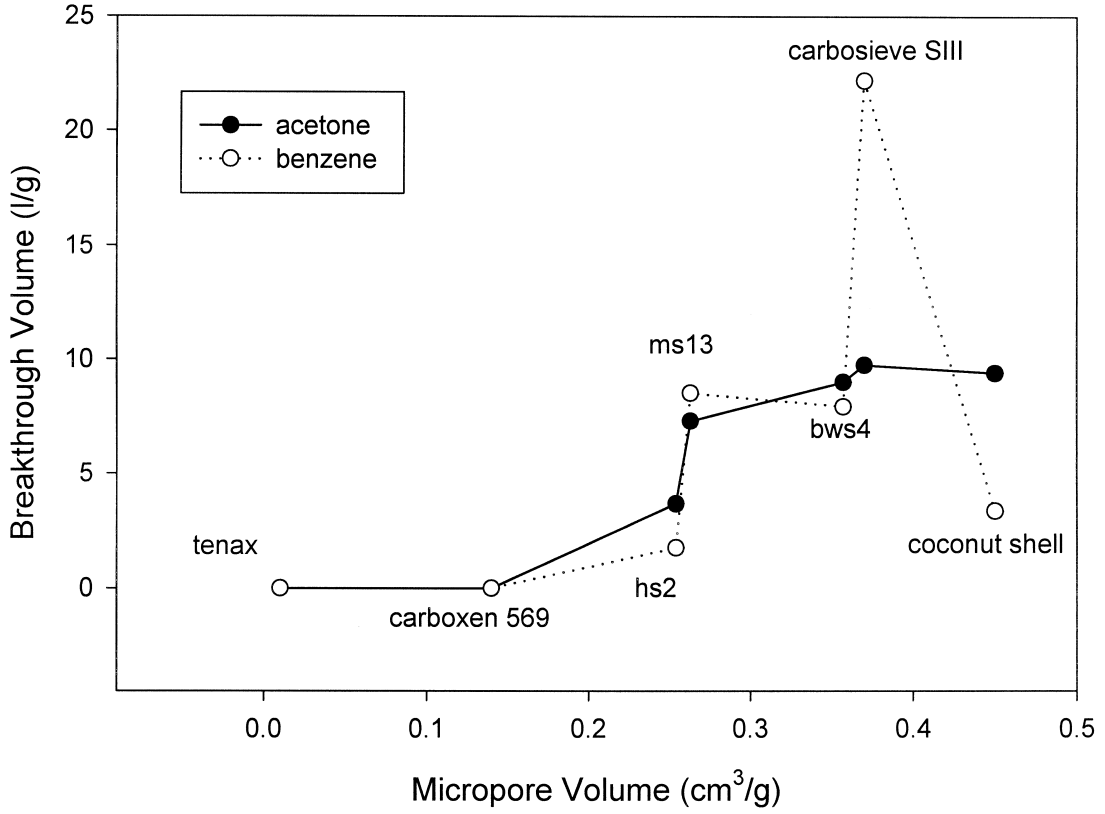

Fig. 2. Micropore volume vs. breakthrough volume of analytes tested for each adsorbent.

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