

EXAMINATION OF CRUMB RUBBER PRODUCED FROM RECYCLED TIRES

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Introduction

In June 2007 the Department of Analytical Chemistry at the Connecticut Agricultural Experiment Station (CAES) was contacted by Environment and Human Health Inc. (EHHI), a non-profit organization headquartered in the greater New Haven area, to ascertain if our laboratory would be willing to examine crumb rubber produced from used tires. The product in question has been gaining widespread use as an enhancement on athletic fields constructed from artificial turf; other applications, such as on play areas for children, are also common. Private citizens questioned EHHI as to the human health and environmental neutrality of the product. The data to answer the inquiries were not available (Anderson et al., 2006).

Figure 1 shows the crumb rubber infill on a synthetic turf field. The photo is of an actual field installed in Connecticut and was provided to us by EHHI.



Figure 1.

Given time and personnel limitations, the Department of Analytical Chemistry at the CAES agreed to conduct a very modest study of the material. Funding in the amount of \$2000 was received from EHHI to offset the cost of items such as analytical and instrumental supplies and chemical standards. This fact sheet contains scientific information, described in detail below, derived from the preliminary study. The experiments were conducted by Dr. Mehmet Isleyen, with contributions from Dr. Saim Ozdemir, both visiting scientists from Sakarya University, Engineering Faculty, Environmental Engineering Department, Sakarya, Turkey, and with

substantial input from William Berger of the Department of Analytical Chemistry. Dr. MaryJane Incorvia Mattina, the head of the Department of Analytical Chemistry, supervised the work.

Approach

It was deemed that answers to the following questions could be obtained within the time limitation imposed:

1. Are compounds volatilizing or out-gassing from the tire crumbs?
2. What is the identity of the volatilized compounds derived from the tire crumbs?
3. Can organic or elemental components be leached from the tire crumbs by water?

Experimental Details and Data

The crumb rubber examined is shown in Figure 2 and was provided to our laboratory by EHHI; the scale at the top of the photo is in centimeters (2.54cm/inch). Most of the crumbs were black, irregularly shaped particles <3mm in any dimension, although smaller particles may be seen in the photo. The material also contained lesser amounts of white crumbs similar in physical appearance to the black particles and presumed to be tire-derived rubber. The product was examined as received without any previous exposure to field conditions.



Figure 2.

Because of the substantial interest in this project, considerably more experimental details are provided in this fact sheet than is typical for such a publication. Experiments were conducted in the laboratory under conditions which approximated field conditions for parameters such as temperature and leaching solvent. The method relied on solid phase micro-extraction (SPME), a well-known and reliable analytical technique (Zeng and Noblet and references therein). The SPME fiber used was coated with 100 μ m thick polydimethylsiloxane (Supelco number 57342-U).

1. Are compounds volatilizing or out-gassing from the tire crumbs?

To obtain the data to answer this question 0.25g of tire crumbs were transferred to a glass, 2mL automated liquid sampling (ALS) vial. The vial was capped and the septum pierced with the SPME needle. The SPME fiber was exposed for 42 minutes to the headspace over the tire crumbs while the vial was warmed in a heating block to 60 °C. At the end of this period the

SPME fiber was removed from the vial and desorbed in the inlet of a gas chromatograph (GC, Hewlett Packard model 6890) at 260 °C. A 30m X 0.25mm DB-5MS+DG column (J&W Scientific) was interfaced to the mass spectrometer (MS, Hewlett Packard model 5973) detector. The GC oven was programmed as follows: initial temperature 40 °C for 5 min, ramped at 2 °C/min to 50 °C, ramped at 5 °C/min to 160 °C, ramped at 10 °C/min to 300 °C and held for 10 min. Figure 3 shows a portion of the total ion chromatographic (TIC) trace typically obtained from several replicates of this experiment. Peaks were identified using high probability matching of the actual mass spectrum with that in the NIST library supplied with the software.

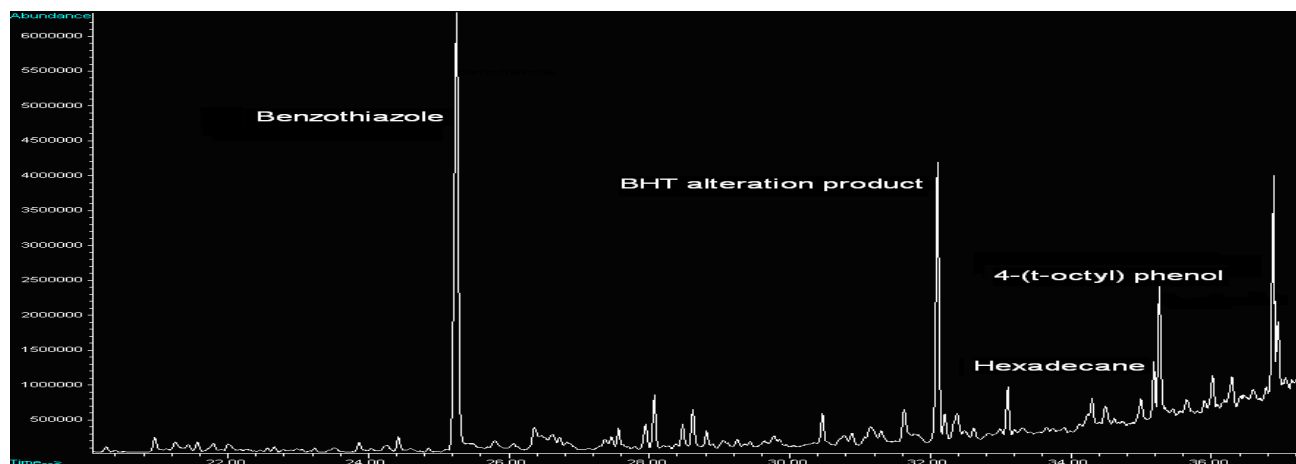


Figure 3.

Using this approach of spectral matching several compounds were identified, some of which are summarized in Table 1:

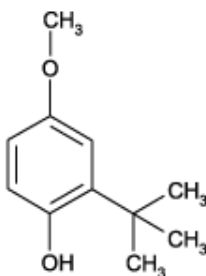
Table 1. Organic Compounds Volatilizing from Tire Crumbs

NAME	CAS NUMBER	RETENTION TIME (min)	STRUCTURE
Benzothiazole	95-16-9	25.2	
Butylated hydroxyanisole	25013-16-5	32.7	
n-hexadecane	544-76-3	35.2	
4-(t-octyl) phenol	140-66-9	35.3	

2. What is the identity of the volatilized compounds derived from the tire crumbs?

In order to confirm positively the four compounds cited in Table 1 which have good match between the archived NIST spectrum and the spectrum recorded in this experiment, authentic standards were purchased from Sigma Aldrich. Solutions of the compounds were prepared in methanol and used to spike approximately 0.6 grams clean glass beads in 2 mL ALS vials. The same SPME procedure described above to collect volatile compounds from the tire crumbs was used to collect volatile compounds from the headspace over the spiked glass beads. The GC/MS analytical settings were also the same. The identity of the four compounds was confirmed with retention time (RT) match as well as mass spectral match. In order to assure that the compounds were not artifacts from laboratory background nor from any of the supplies used in the method, the following experiments were performed: (i) several consecutive desorptions of the SPME fiber in the GC inlet; (ii) SPME analysis of the headspace over clean glass beads in an ALS vial; (iii) SPME analysis of the headspace over glass beads in an ALS vial spiked only with methanol. None of the four compounds listed above was detected in any one of these three trials.

A comment must be made regarding butylated hydroxyanisole. Analysis of the purchased standard (Sigma catalogue number B1253-5G) resulted in detection of three peaks: RT=32.1, RT=32.5, RT=32.7 (major component). It should be noted that the structure matching this CAS number does not indicate a specific position of attachment of the t-butyl group relative to the hydroxyl group as shown above in Table 1. However, CAS 121-00-6 does correspond to 3-t-butyl-4-hydroxyanisole having the structure



Based on the mass spectral library match, we conclude that the compounds at RT 32.5 and 32.7 correspond to the two diastereomers of butylated hydroxyanisole. A search of the literature strongly suggests that the compound at RT 32.1, which has ions at m/z 236, 221, 205, 180, 165, 137, is 2,6-di-t-butyl-4-hydroxy-4-methyl-2,5-cyclohexadien-1-one (Brumley et al., 1989) designated as an alteration product of 2,6-t-butyl-4-methylphenol (BHT). Peaks at the three RTs for analysis of the standard were found as well in the analysis of the tire crumbs.

Experiments were conducted to determine approximate gas phase concentrations of the organic compounds which volatilized or out-gassed from the crumb rubber. In this trial standards at different concentrations were spiked onto glass beads in ALS vials and the SPME procedure conducted. Calibration curves were constructed using the spiked standards from which gas phase concentrations of the compounds of interest in the vapor phase over the tire crumbs were determined. We make the assumption that due to the non-porous nature of the glass beads, the entire amount of the organic compound spiked onto the glass beads volatilized into the gas phase in the ALS vial. From the original amount spiked and the volume in the vial remaining after the volume of the beads is subtracted, we can calculate the amount of the compound in the

headspace over the tire crumbs. These data in Table 2 should be considered a first approximation.

Table 2. Vapor phase concentrations of compounds out-gassed from crumb rubber

Compound	ng/mL air	ng/(mL air) normalized per gram of tire
Benzothiazole	225.87	866.72
Hexadecane	1.58	6.04
4-(tert-Octyl)-phenol	5.64	21.63
Butylated hydroxyanisole or BHT alteration product	13.89	53.32

3. Can organic and elemental components be leached from the tire crumbs by water?

To determine if materials of interest are extractable from the crumbs, portions of the crumb rubber were soaked over time in distilled, deionized water at ambient laboratory temperature in capped high density polyethylene (HDPE) jars. Approximately 17g of crumbs were soaked statically in 50mL water for seven weeks. After this period the leachate was filtered and 1.5mL transferred to ALS vials. The same SPME procedure was carried out as described above. A typical TIC trace for the headspace analysis is shown in Figure 4.

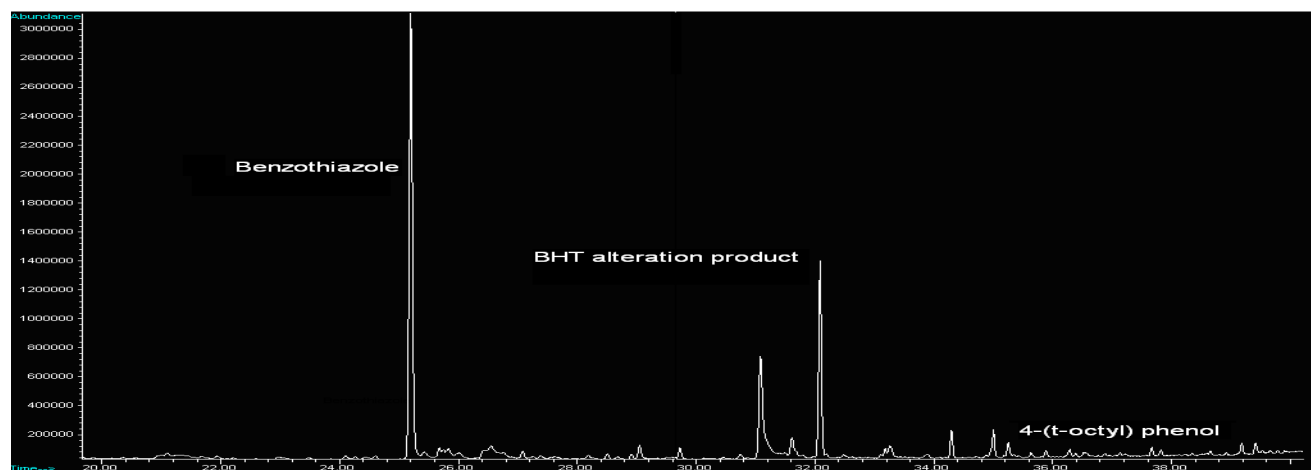


Figure 4.

Figure 4 should be compared with Figure 3. Although relative amounts of the compounds of interest differ under the two experimental conditions, the same compounds are noted in both Figures. If the SPME fiber is immersed directly into the leachate rather than exposed to the headspace over the leachate and then desorbed in the GC inlet, the same set of compounds as shown in Figure 4 was detected.

We now provide the experimental procedures used to determine if elements are leachable into aqueous solution from the crumbs. In this case 2.0 grams of crumbs were transferred into 40mL of water in 50mL centrifuge tubes. The tubes were sealed and agitated on a wrist action shaker at ambient temperature for 18 hours. Following this agitation the tubes were centrifuged for 10 minutes at 3000rpm and the leachate was analyzed using inductively coupled plasma mass spectrometry (ICP/MS, Agilent model 7500ce). In a second regime the leaching water was acidified to pH 4.2 prior to the 18 hour agitation. This procedure is based on conditions

recommended in EPA SW-846 Method 1312. Pertinent data, averages of four replicates for each trial, are presented in Table 3.

Table 3. Elements leached into water from crumb rubber

Element	Amount in water ($\mu\text{g}/\text{kg}$ tire)	Amount in acidified water ($\mu\text{g}/\text{kg}$ tire)
Zinc	20957	55010
Selenium	246	260
Lead	1.85	3.26
Cadmium	0.07	0.26

Conclusions

The laboratory data presented here support the conclusion that under relatively mild conditions of temperature and leaching solvent, components of crumb rubber produced from tires (i) volatilize into the vapor phase and (ii) are leached into water in contact with the crumbs. We note with interest that when we placed the black crumbs in direct sunlight at an exterior air temperature of 88 °F, a thermometer inserted directly into the crumbs registered 55 °C (=131 °F). Selection of 60 °C, therefore, is not beyond a reasonable temperature range accessible under field conditions.

Based on these data further studies of crumb rubber produced from tires are warranted under both laboratory, but most especially field conditions. In particular examination of compounds volatilizing from the crumbs under exterior conditions and collected at varying heights and seasonal conditions at installed fields should be compared with background levels. It is also logical to determine airborne particulate matter deriving from the product under the same conditions.

References

- M. E. Anderson, K. H. Kirkland, T. L. Guidotti, and C. Rose. A Case Study of Tire Crumb Use on Playgrounds: Risk Analysis and Communication When Major Clinical Knowledge Gaps Exist. *Environ. Health Persp.* **114**: 1-3 (2006).
- W. C. Brumley, C. R. Warner, D. H. Daniels, S. Varner, J. A. Sphon. Electron Impact Mass Spectrometry of BHT and its Alteration Products. *Biomed. Environ. Mass Spectrom.* 18:207-217 (1989).
- Y. Chien, S. Ton, M. Lee, T. Chia, H. Shu, Y. Wu. Assessment of Occupational Health Hazards in Scrap-tire Shredding Facilities. *Sci. Total Environ.* 309: 35-46 (2003).
- E. Y. Zeng and J. A. Noblet. Theoretical Consideration on the Use of Solid-Phase Microextraction with Complex Environmental Samples. *Environ. Sci. Technol.* 36: 3385-3392 (2002).