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Discovering Volatile Chemicals from Window Weatherstripping through Solid-Phase Microextraction/Gas Chromatography–Mass Spectrometry

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Supporting Information

ABSTRACT: Volatile compounds from polymeric materials such as weatherstripping were identified by solid-phase microextraction (SPME), a solvent-free analytical method, coupled to gas chromatography–mass spectrometry (GC–MS). These compounds, originating from additives and fillers used in weatherstripping processing, were mostly polycyclic aromatic hydrocarbons (PAHs). The goal of this laboratory experiment was to demonstrate that a reliable connection can be established between the ability of our everyday olfactory sense to detect noxious odors and modern analytical instrumentation. The approach discussed here will guide students to develop critical thinking by interchanging between polymer and analytical instrumentation knowledge. The conceptual simplicity of SPME makes its inclusion in the undergraduate and high school curriculum appropriate and requires 2–3 h of laboratory time to complete.

KEYWORDS: High School/Introductory Chemistry, First-Year Undergraduate/General, Second-Year Undergraduate, Analytical Chemistry, Hands-On Learning/Manipulatives, Testing/Assessment, Gas Chromatography, Mass Spectrometry, Polymer Chemistry

INTRODUCTION

As chemical educators, we often tell students that chemistry is everywhere. This may be followed by an example of something that contributes to a sense of delight or pleasure, such as the pigments in a Renoir painting, the rosin on a violin bow, or the various esters in fine perfume or a bowl of fruit. Students routinely sense the ugly side of chemistry too, and these observations are the more frequent if one leaves the relatively safe confines of modern American society.¹ The present article is motivated by observations made during travel to an emerging nation for the dual purposes of scientific collaboration and gaining an international outlook. The hotel rooms provided were comfortable, but they smelled of a railway track or a tire shop. The powerful source was eventually identified as a thin band of weatherstripping along the windows. This material contains rubber polymers prepared by polymerization of petroleum-based monomers.² While the pure polymers may not emanate an unpleasant odor, their processing includes the

addition of additives and fillers to design specific material properties such as tensile strength, abrasion resistance, and elongation.³ Many times these compounds give strong odors.

As a practical solution, the weatherstripping was taped over and trimmed using a pocket knife and regular tape and the odor all but disappeared. At the end of the weeklong trip, the “chemistry is everywhere” concept was brought home for characterization in the form of small bits of the offending weatherstripping adhered to the tape that had covered it.

Before involving analytical tools, we hypothesized that the source of the smell contained creosote, which is used to treat railroad ties and has polycyclic aromatic hydrocarbons (PAHs) as major constituents. This exercise illustrates that the nose has

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Figure 1. Schematic of the SPME/GC–MS instrument equipped with an ion-trap mass analyzer.

the qualitative ability to help the brain formulate a hypothesis and the quantitative ability to determine when more or less of a compound is present. Caution must be taken when assessing the odor of the sample to prevent olfactory fatigue. This is an important lesson for students, but instrumental analysis can take us beyond “smells like railroad ties” and “can be diminished by applying tape.”

Students also learn about the toxic nature of the omnipresent and persistent PAHs that may have a carcinogenic effect⁴ on living bodies according to the Department of Health and Human Services (DHHS).⁵ Humans pick up PAH sources by breathing air contaminated by wild and controlled fires, by eating grilled food, and by applying cosmetic products on skin. Once they have been ingested, the body machinery tries to process them, but sometimes the modified PAHs are more dangerous than the original ones. The safe limit set by the Occupational Safety and Health Administration (OSHA) is 0.2 mg of PAHs per cubic meter of air.⁶ Revealing to students the effects produced by these chemicals^{7,8} is an important lesson that helps to raise awareness regarding remediation of environmental damage⁹ and climate challenges.¹⁰

Coming back to weatherstripping, its composition was investigated by solid-phase microextraction (SPME) coupled to gas chromatography–mass spectrometry (GC–MS). SPME, pioneered by Pawliszyn¹¹ and co-workers in the 1990s has several advantages, such as short extraction time, complete elimination of solvents during thermal desorption, and reduced number of blank runs. The principle of SPME/GC–MS operation is simple: a fused-silica fiber is inserted in the sample vial heated to the desired temperature, and the resulting volatile analytes are adsorbed directly onto the fiber until equilibrium is reached. Afterward the fiber is inserted into the heated injection port of a GC–MS instrument to desorb the impregnated volatiles (Figure 1). The volatile compounds are desorbed from the SPME fiber and injected into the gas chromatograph, and with the help of the carrier gas (often helium), the analyte components interact with the stationary phase (column) on the basis of their affinities. Control over temperature, the helium

(mobile phase) flow, and column (stationary phase) dimensions ensures efficient compound separation. Low-molecular-mass species elute first, while high-molecular-mass homologues elute last. Because the separation of the compounds still occurs in a GC column by adsorption/desorption, SPME is largely a sampling method rather than a separation method.

SPME has been successfully integrated into the undergraduate curriculum, where students learn to determine the contents of certain chemicals, except polymeric materials. Determinations of the amounts of caffeine in various beverages,¹² bisphenol A leached from household plastics,¹³ fragrances from perfumes,¹⁴ and volatiles from plants^{15,16} are several examples of activities performed to spark students interest in science. Educators have also used SPME to raise awareness among students regarding the impact of day-by-day habits on their health by determining safely the amount of nicotine in urine samples.¹⁷ In regard to polymeric products, the majority contain high-molecular-weight polymers, which are nonvolatile species. Therefore, SPME is suitable to detect the nature of the volatile additives used during processing to enhance polymer properties.

These activities assist students to develop cognitive processes that enable their critical-thinking and problem-solving skills. Specifically, this laboratory experiment guides students in formulating and testing scientific hypotheses using the olfactory sense and SPME/GC–MS as natural and scientific tools, respectively. As the content develops, it becomes apparent that an opportunity exists to teach students the difference between the impressive detection capabilities of the olfactory system and molecular identification and quantitation.

■ EXPERIMENTAL MATERIALS AND APPARATUS

A Supelco SPME holder for manual injection was used. The holder is equipped with a fused-silica fiber coated with a stationary phase consisting of a nonbonded polydimethylsiloxane (PDMS) film (100 μm thick), a plunger, and an adjustable depth gauge with needle guide and a stainless steel retaining

nut. The fiber is jacketed by a 24 gauge needle and can be made to protrude from that needle during sampling or withdrawn for protection while loading onto the GC column or to guard against evaporation. A picture of the SPME fiber is presented in Figure 2.

Figure 2. Components of an SPME fused-silica fiber coated with a nonbonded 100 μm PDMS film for manual injection.

Clear 3M packaging tape was used to collect the weatherstripping samples for analysis.

GC–MS was performed using a Varian CP-3800 gas chromatograph with a Saturn-2200 ion-trap mass spectrometer (Agilent) as the detector. The column used in the analysis was a J&W DB-5MS capillary, 30 m $\times$ 0.25 mm, with a 0.25 μm thick film of a phenylarylene polymer equivalent to a (5% phenyl methylpolysiloxane (Agilent)).

EXPERIMENTAL PROCEDURES

A. Sample Preparation

Three sets of measurements were involved. For the first set, about 60 mg of the tape containing weatherstripping was placed inside a vial and sealed with a septum cap. The vial was placed in a preheated sand bath on a hot plate for 60 min at 45 $^{\circ}\text{C}$. The blank tape and the control runs were prepared under the same conditions. Figure 3 depicts the setup used to prepare the samples.

B. Fiber Conditioning

Before the fiber can be used at all, it must be activated by conditioning, which means the thermal removal of polymer coatings or other materials that might have been adsorbed during manufacture, packaging, or storage. The holder is placed inside the injection port and heated for 30–45 min at 250 $^{\circ}\text{C}$. A blank run or “bakeout” follows the conditioning to confirm that no analytes are present to interfere with the sample of interest, as shown in Figure 4.

C. SPME/GC–MS Measurements

The GC–MS analysis was controlled by the VarianWS real-time analysis software. The chromatographic conditions were as follows: the initial oven temperature of 40 $^{\circ}\text{C}$ was held for 15 min, followed by a temperature gradient of 5 $^{\circ}\text{C}\cdot\text{min}^{-1}$ up to 200 $^{\circ}\text{C}$ for 5 or 10 min. A constant flow of the carrier gas (helium) at 1.5 $\text{mL}\cdot\text{min}^{-1}$ was used in splitless mode. The

Figure 3. Setup used to prepare the samples using a SPME fiber.

Figure 4. Chromatograms obtained before (blue) and after (black) fiber conditioning. The blue trace has been offset by 2.5×10^5 counts for better clarity.

injection port purge was turned off, and its temperature was set to 250 $^{\circ}\text{C}$. Then the fiber carrying the volatiles was inserted into the port and heated to 250 $^{\circ}\text{C}$ for 2–3 min. The mass spectrometer was scanned from m/z 40 to 650 at 3 scans $\cdot\text{s}^{-1}$ after a 1 min delay. The spectral signals were matched to those derived from the NIST/EPA/NIH Mass Spectral Database.

HAZARDS

The experiments described here are hardly dangerous. The bicycle rubber repair kit (Supporting Information) has an unpleasant odor when the seal is freshly broken. Students should not assess the odor of the patch for a prolonged time. If they will be allowed to run their own experiments, special care

must be taken to insert the SPME fiber into the GC inlet, set at high temperature (250 °C), to prevent skin burns. In addition, students must be instructed on safely handling hot plates.

RESULTS AND DISCUSSION

To test the hypothesis that creosote derivatives were the main source of the unpleasant odor, the measurements started with the tape containing small bits of weatherstripping. Even months after this sample was collected, it still had a perceptible odor, and the SPME/GC–MS instrument produced ample signals. The profile for the volatile chemicals in the vapor phase appears in Figure 5A. The identified compounds are listed in Table 1.

The measurements confirmed the presence of the creosote derivatives in the rubber weatherstripping, especially polycyclic aromatic hydrocarbons: phenanthrene (labeled as P9, m/z 178), fluoranthene (labeled as P19, m/z 202), and pyrene

(labeled as P20, m/z 202). The highest peaks detected were attributed to phthalate esters, common compounds used as plasticizers. In order to discern between the pyrene and fluoranthrene peaks, a pyrene standard was run to determine its retention time centered at 50.2 min (Figure 5B). It is known that components of creosote, especially PAHs, degrade with time when exposed to heat, oxygen, sunlight, and micro-organisms.¹⁸ Several PAH degradation products were detected, such as 9,12,15-octadecatrienoic acid (labeled as P3, m/z 436), decahydro-2,6-dimethyl-3-octylnaphthalene, (labeled as P7, m/z 278.5), perhydrophenanthrene (labeled as P8, m/z 192), and 2',3,3,4',5'-pentamethyl-3-[2-quinonyl]propionaldehyde (labeled as P16, m/z 234). Discrimination between the analytes assigned to P15 and P17 was not possible using the available standard samples. The SPME/GC–MS results showed that creosote derivatives were the most abundant volatiles in weatherstripping and confirmed the hypothesis formulated prior to analytical investigations.

Blank Measurements and Controls

The detected volatiles resulted not only from the weatherstripping but also from the tape itself. Thus, control experiments on the pristine tape were necessary to identify its volatile compounds. Figure 5C presents the ion chromatogram of the blank tape. The most abundant volatile was identified as being a mixture of phthalates. Consequently, the peaks listed in Table 1 were predominantly from weatherstripping. To guard against the possibility that trace compounds remained on the column, bakeouts were conducted before and after each analyte run. To demonstrate such interferences from residual compounds, the ion chromatogram for the blank tape was collected without running bakeouts after collection of the pyrene standard ion chromatogram. A close inspection of the chromatogram in Figure 5C reveals a peak centered to 50.2 min corresponding to remnant pyrene.

TEACHING OPPORTUNITIES

We have demonstrated how students can rely on their olfactory system to make predictions and investigate the accuracy of their hypothesis. We designed this work in such a way as to be a useful guide for teachers to develop fun and attractive projects involving undergraduate students at any level. Our own hypothesis that weatherstripping contained creosote derivatives proved true. Because the smelly weatherstripping described here may be difficult to find, the Supporting Information provides an example that uses readily available materials to confirm the hypotheses formulated in the main text. Many other samples can be collected by students from their own environments, and hypotheses can easily be formulated and tested. At the college or university level, chemistry and biochemistry students are generally made familiar with the GC–MS and HPLC techniques, which are important parts of analytical curricula. Thus, the inclusion of SPME should be easy because this technique is often coupled with the former two.

If the SPME/GC–MS instruments are not available, as will sometimes be the case in small colleges and high schools, the samples can be taken to an academic or industrial lab as a field exercise or even mailed to such a facility. Many universities offer free support for these activities through their outreach programs. The downside to the experiments is the relatively long times needed to acquire the data; however, this can be used to correct a misconception often seen in crime lab television shows—chemistry gets faster all the time, but it does

Figure 5. Total ion chromatograms of volatile organic compounds for impregnated tape (A), pyrene standard (B), and blank tape (C). The highest values for several peaks were cut in order to access the less abundant ones. No bakeout was run before the blank tape (C).

Table 1. Sample Codes, Names, Chemical Formulas, Gas Chromatographic Retention Times, and Molecular Weights of the Compounds Detected in the Weatherstripping Vapor Phase

Code	Name	Chemical Formula	Retention Time (min)	Molecular Weight (g·mol ⁻¹)
P1	Diethyl phthalate ^a	C ₁₂ H ₁₄ O ₄	39.20	222
P2	(Z)-8-Methyl-9-tetradecenoic acid	C ₁₅ H ₂₈ O ₂	41.32	240
P3	9,12,15-Octadecatrienoic acid ^b	C ₁₈ H ₃₀ O ₂	42.06	278
P4	Methyl 9,12-hexadecadienoate	C ₁₇ H ₃₀ O ₂	42.41	266
P5	2-(3,4-Dihydroxyphenyl)morpholine	C ₁₀ H ₁₃ NO ₃	42.52	195
P6	<i>p</i> -Menth-1-en-3-one ^b	C ₁₀ H ₁₆ O	42.73	152
P7	Decahydro-2,6-dimethyl-3-octylnaphthalene ^c	C ₂₀ H ₃₈	42.91	278
P8	Perhydrophenanthrene ^b	C ₁₄ H ₂₄	43.00	192
P9	Phenanthrene ^d	C ₁₄ H ₁₀	43.16	178
P10	Methyl octadeca-9-ynoate	C ₁₉ H ₃₄ O ₂	43.32	294
P11	Methyl hexadecanoate	C ₁₇ H ₃₄ O ₂	43.42	270
P12	1-Hexacosene	C ₂₆ H ₅₂	43.76	364
P13	Methyl 11,14-eicosadienoate	C ₂₁ H ₃₈ O ₂	44.10	322
P14	1,2,3,6,7,8-hexahdropyrene	C ₁₆ H ₁₆	44.76	208
P15	Butyl phthalyl butyl glycolate ^e	C ₁₈ H ₂₄ O ₆	44.97	336
P16	2',3,3',5'-Pentamethyl-3-[2-quinonyl]propionaldehyde ^c	C ₁₄ H ₁₈ O ₃	46.00	234
P17	Butyl phthalyl butyl glycolate ^e	C ₁₈ H ₂₄ O ₆	46.84	336
P18	Fluoranthene ^c	C ₁₆ H ₁₀	48.91	202
P19	Pyrene ^c	C ₁₆ H ₁₀	50.21	202

^aPlasticizer. ^bPAH degradation derivative. ^cPAH derivative. ^dPAH. ^eThe library assigned the compound butyl phthalyl butyl glycolate for both peaks. As a result of different affinities to the column, two compounds can elute at the same time. In such cases, additional control experiments are required and involve standard compounds (see Figure 5 for pyrene as an example).

not often operate at the pace envisioned by crime drama writers. Culinary television shows suggest an answer to this: prepare and inject the sample, so that students may see the instrument in action, but display data collected from an earlier run of a similar sample.

CONCLUSION

Volatile compounds from creosote were identified in the vapor phase of the weatherstripping bands used for sealing windows. Polycyclic aromatic hydrocarbons and their degradation products were the most abundant detected compounds. Plasticizers such as diethyl phthalate were identified in both weatherstripping and blank tape, the latter of which was used as a barrier for the noxious odor. Pyrene was used as a standard to distinguish itself from the fluoranthene homologue. Ordinary packaging tape can be used as a barrier to obstruct the noxious odors, just as the nose test suggests. The SPME/GC–MS measurements proved that the human nose is a good detector. Given packaging tape, students can reduce the odors, thereby exploring molecular transport. Collaborations with a chemistry department or industrial laboratory can demonstrate the molecular complexity of everyday odors.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.6b00791.

Details of the experiments with readily available tire repair rubber patches (PDF, DOCX)
 Student and instructor notes (PDF, DOCX)
 Laboratory worksheet (PDF, DOCX)

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Notes

The authors declare no competing financial interest.

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