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Laboratory Experiment

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Headspace GC−MS Analysis of Halogenated Volatile Organic Compounds in Aqueous Samples: An Experiment for General Chemistry Laboratory

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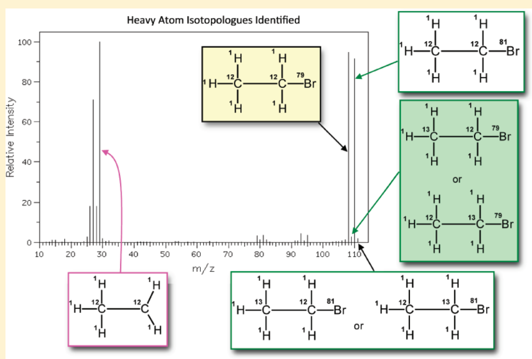
Supporting Information

ABSTRACT: Analysis of halogenated volatile organic compounds (HVOCs) by GC−MS demonstrates the use of instrumentation in the environmental analysis of pollutant molecules and enhances student understanding of stable isotopes in nature. In this experiment, students separated and identified several HVOCs that have been implicated as industrial groundwater contaminants and deduced the isotopic content by analyzing the molecular ion region of the mass spectra. The HVOCs were analyzed by direct sampling of the headspace vapor over a dilute aqueous solution, which is designed to simulate a contaminated groundwater sample. The rapid headspace sampling and analysis allowed completion of the experiment by many lab classes per week. The impact of the lab was assessed using online surveys before and after the lab that queried student perceptions of their understanding, skills, and attitudes toward science and chemistry. The surveys showed noticeable gains in understanding and skills; however, few changes in attitudes were seen among students, the majority of whom already seemed committed to science and engineering careers and majors.



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A laboratory experiment was developed and implemented for the first-semester general chemistry laboratory that introduces students to gas chromatography−mass spectrometry (GC−MS) analysis of environmentally relevant halogenated volatile organic compounds (HVOCs) and addresses the issue of stable isotope occurrence in molecules. HVOCs are industrial solvents that occur as contaminants in surface and groundwater near industrial spillage sites.[1−3] They are also produced during chlorination of public water supplies and in small-scale use of household bleach[4] and are the products of natural biosynthetic processes in marine algae.[5] According the National Energy Technology Laboratory, "HVOCs are the most significant organic contaminants in groundwater associated with disposal sites in the United States."[6] The frequent appearance of these compounds as environmental pollutants should spark the interest of chemistry, biology, and civil and environmental engineering students. Additionally, HVOCs are attractive as an experimental subject because they can be rapidly separated by GC and contain an interesting mixture of isotopes that are easy to observe and quantify with a low-resolution mass spectrometer.[1,7]

The main learning goal of the HVOC−GC−MS experiment is to help students understand the nature of isotopes and the practical consequences of atoms occurring in nature as different stable isotopes. In this lab, students explore the halogen isotope content of the HVOCs by obtaining experimental evidence for multiple Cl or Br isotopes using GC−MS with headspace sampling. The subject of isotopes and the use of GC−MS in the study of isotopes have been described for other general chemistry experiments,[7−10] and several studies have described other kinds of GC−MS experiments for the general chemistry lab.[11,12] The novel components of this study are (i) the rapid sampling method that makes the experiment practical for large general chemistry classes and (ii) a large-scale investigation of the impact of the experiment on the students' perceived learning gains in terms of content understanding, skills, and attitudes. An online student assessment of the learning gains (SALG) instrument[13] was used to compare the students' perceptions of skills, understanding, and attitudes toward laboratory science before and after performing the experiment.[14]

EXPERIMENT

Chemicals and Sample Preparation

Dilute aqueous solutions of benzene, toluene, chloroform, 1,1-dichloroethane, carbon tetrachloride, tetrachloroethylene,

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chlorobenzene, or bromobenzene were prepared by adding a small volume of a methanol stock solution to deionized water. The stock solutions and aqueous samples were prepared prior to the lab period. Methanol exits the column before appearance of the first analyte peak, $CHCl_3$. To observe approximately equal peak heights, the final concentrations were adjusted to 3–8 mg/L. These concentrations are well below the water solubility of the least soluble compound used here (tetrachloroethylene, 150 mg/L). Student unknown samples included one VOC and one HVOC. Detailed recipes for stock and sample solutions are provided in the Supporting Information.

Instrumentation

The experiment was carried out with an Agilent model 5975C GC–MS equipped with a standard 15 m nonpolar GC column, and a CTC Analytics CombiPal sampler with a headspace sampling module. A 5 mL gastight syringe thermostated at 37 °C was used to remove headspace vapor (0.25 mL) from the 20 mL sample vial containing an aqueous HVOC solution. The method included a 30 s shake of the sample vial in the headspace incubator oven at 37 °C prior to headspace vapor removal.

Procedure

Working in pairs, students transferred a 1.0 mL sample containing one VOC and one HVOC into an Agilent 20 mL headspace screw-top vial using an automated pipet in the fume hood. The labeled vials were placed in the GC–MS sample tray, and an analysis sequence that included a 3 min temperature programmed GC method was entered in the Agilent ChemStation software. After the sequence finished, data files were transferred via the local network to computers in the student lab running a standalone version of the Agilent MSD ChemStation. The visit to the GC–MS instrument provided an opportunity for the teaching assistant to explain the basic parts and operation of the instrument to the class.

Analysis of the molecular ion region of the mass spectra, and identification of the unknown compounds, was facilitated by use of the "Isotope Peaks of Ionic Fragments in Mass Spectrometry" Web site that contains a Java applet for calculating and illustrating the molecular ion pattern for any given molecular formula.[15] Student pairs identified the compounds in their sample and were given data from two additional samples to identify the compounds. The teaching assistant highlighted the rules-of-thumb that can help make sense of the molecular ion patterns. For example, for hydrocarbons, the mass of the lightest isotopologue is always even numbered and usually only one reasonable formula will fit a given mass. In addition, the molecular ion regions of monochloro, dichloro, monobromo, dibromo, and other small HVOC's show typical patterns that allow one to guess easily the halogen content of the molecule. For example, for dibromobenzene, the lightest peak in the molecular ion region is at m/z 234 and the symmetric triplet of peaks indicates the presence of two Br's. The rest of the molecule has a mass of $234 - (2 \times 79) = 76$ amu, which fits a formula of C_6H_4.

■ HAZARDS

In high concentrations, all the analytes are toxic or carcinogenic. However, the aqueous solutions used in this experiment can be safely handled in the fume hood using nitrile gloves, because the solutions are very dilute and the only student procedure is a single pipetting into a screw-cap vial that is subsequently sealed.

■ STUDENT ASSESSMENT OF LEARNING GAINS (SALG)

Students were asked to complete online surveys[13] aimed at documenting possible impacts that may have resulted from participating in the HVOC–GC–MS laboratory. The surveys were given once before lab and again the week after lab. The survey instruments contained 17 questions concerning the students' perceptions about their understanding of the material, current skills, attitudes toward experimental science, and academic major and future plans, plus several demographic questions (in the pre-lab questionnaire only). Of 210 students who finished the course, 147 completed both pre- and post-lab surveys. Students logging on to the Web site were assigned a code by the Web site server so that before-and-after responses of individuals could be compared. The anonymity encouraged student participation and maximized the honesty of responses. The complete questionnaires and numerical results are available in the Supporting Information.

■ RESULTS AND DISCUSSION

Experiment

The eight compounds were well separated in less than 3 min by the GC method (Figure 1), and each displayed an interpretable

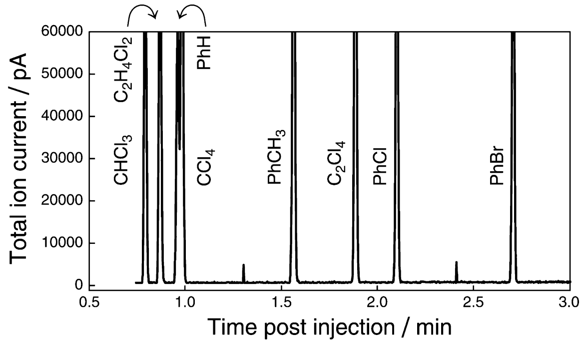

Figure 1. GC separation of 8 HVOCs and VOCs as aqueous headspace vapor. The 1 mL water sample contained chloroform (4.0 mg/L), 1,2-dichloroethane (7.7 mg/L), benzene (2.7 mg/L), carbon tetrachloride (3.0 mg/L), toluene (4.0 mg/L), tetrachloroethylene (3.6 mg/L), chlorobenzene (3.0 mg/L), bromobenzene (6.3 mg/L), and methanol (1.9 g/L). GC conditions: Agilent DB-1-MS column (15 m, 0.25 mm, 0.25 μm); He flow rate 1.2 mL/min; 50:1 split ratio; temperature program 40 °C, 1 min, then 40–95 °C linear ramp in 2.1 min. The mass spectrometer was run in full scan mode starting at 0.65 min.

molecular ion region, or large halogen-containing fragment, in the electron impact mass spectrum. Ten data files can be generated in less than 1 h. While waiting for their results, students started the MSD ChemStation program on the lab computers and reviewed the mass spectrum of bromoethane. This compound was introduced in the student handout, and students filled in entries in a table that identifies the major isotopic components of each peak visible in the molecular ion region. During the last hour of the lab, the chromatograms and mass spectra of unknown compounds were analyzed in a similar fashion, and the data and answers were entered into the experiment report.

A benefit of headspace sampling is the clean GC trace that shows solute peaks only, with no solvent peak. Headspace sampling also increases the lifetime of syringe, injector ports, chromatography column, and the ion source of the mass

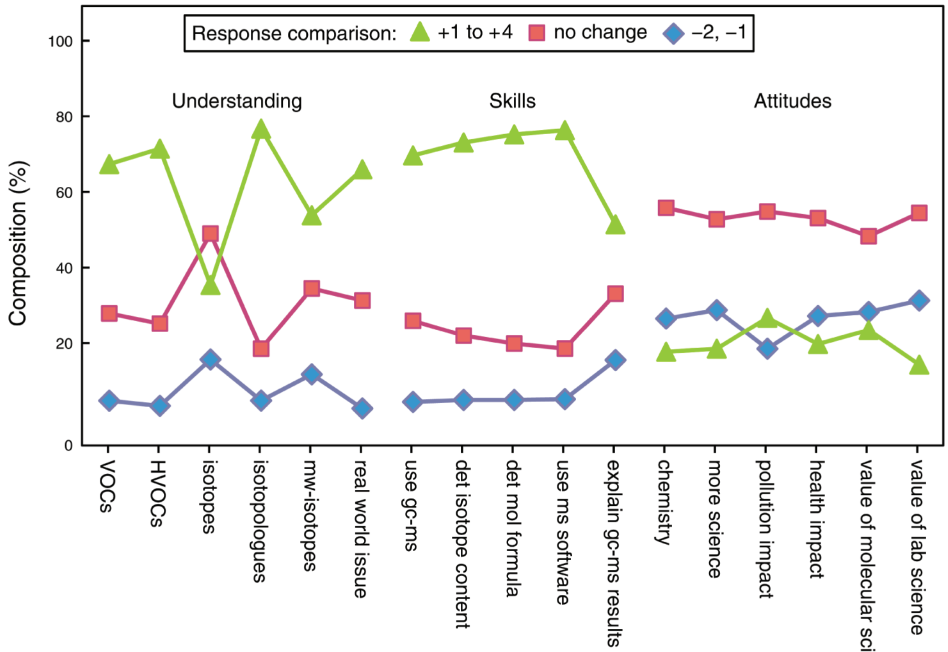

Figure 2. SALG survey. Changes in individual student responses before and after the experiment ($N = 147$): "+1 to +4", percent of responses that were more positive after the experiment on a five-level scale; "no change", percent of responses that were unchanged; "−2 to −1", percent of responses that were more negative after the experiment.

spectrometer, which is an important consideration when many samples from a large class must be analyzed.

Student Assessment of Their Learning Gains (SALG)

SALG survey results relating to understanding, skills, and attitudes are summarized in Figure 2. The answer blocks in these sections of the questionnaire contained five possible response levels ranging from negative to strongly positive (plus "not applicable").[16] The relative responses recorded before versus after the lab are compared in Figure 2. Some student responses became more negative after the lab (change of −1 or −2), some were unchanged, and others became more positive (change of +1 to +4). Under "understanding" and "skills", there was an increase in positive responses after the lab, where students acknowledged definite improvement in these areas. There was a somewhat less positive change observed for "understanding what isotopes are", because many students claimed to already understand this concept before the lab. In the "attitudes" section, much less change was observed. A few students showed increased interest in chemistry and laboratory sciences after the lab, but this was counter-balanced by a decrease in interest by others. Significantly, absolute responses in the "attitudes" section were mostly "a lot" or "a great deal", which suggests that students already had strong interests in science and engineering, and these attitudes were not much affected by the lab.

■ CONCLUSIONS

The combination of instrumentation, software, low molecular weight HVOC/VOC analytes, and the headspace sampling used in this experiment allows for rapid throughput of samples appropriate for large number of students. Working in pairs, a 20-student lab can complete the whole experiment including data entry and analysis within 3 h. Online self-assessment surveys showed that after completing the lab, students identified a definite improvement in their knowledge and skills related to mass spectroscopy and isotope chemistry. Self-assessment of attitudes revealed no large shift of interest in pursuing a chemistry or molecular science after completing the HVOC−GC−MS lab. It was probably unrealistic to expect that one 3-h chemistry laboratory class would significantly change student career attitudes, at least within the two- to three-week period when the surveys were taken.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

SALG pre- and post-questionnaires, numerical data, demographic and future plans data, mass spectra for HVOCs, CAS numbers, the procedure for preparing GC−MS samples, information for adapting the experiment locally, and student handouts including background information, pre-lab exercise, and report form. This material is available via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Safarova, V. I.; Sapelnikova, S. V.; Djazhenko, E. V.; Teplova, G. I.; Shajdulina, G. F.; Kudasheva, F. K. *J. Chromatogr., B* **2004**, *800*, 325−330, DOI: 10.1016/j.jchromb.2003.10.070.

(2) Zogorski, J. S.; Carter, J. M.; Ivahnenko, T.; Lapham, W. W.; Moran, M. J.; Rowe, B. L.; Squillace, P. J.; Toccalino, P. L. *Volatile Organic Compounds in the Nation's Ground Water and Drinking-Water Supply Wells*, U.S. Department of the Interior, U.S. Geological Survey: Denver, CO, 2006.
(3) Dobrzynska, E.; Posniak, M.; Szewczynska, M.; Buszewski, B. *Crit. Rev. Anal. Chem.* **2010**, *40*, 41−57, DOI: 10.1080/10408340903547054.
(4) Odabasi, M. *Environ. Sci. Technol.* **2008**, *42*, 1445−1451, DOI: 10.1021/es702355u.
(5) Lovelock, J. E. *Nature* **1975**, *256*, 193−194, DOI: 10.1038/256193a0.
(6) Romanosky, R. R.; Lewis, R. E.; Schabron, J. F.; DOE National Energy Technology Lab, 2008. http://www.netl.doe.gov/technologies/coalpower/advresearch/pubs/ARSS-001_4P.pdf (accessed Feb 2012).
(7) Pfennig, B. W.; Schaefer, A. K. *J. Chem. Educ.* **2011**, *88*, 970−974, DOI: 10.1021/ed900010q.
(8) Reeves, P. C.; Pamplin, K. L. *J. Chem. Educ.* **2001**, *78*, 368−370, DOI: 10.1021/ed078p368.
(9) Pamplin, K. L.; Reeves, P. C. *Chem. Educator* **2001**, *6*, 112−113, DOI: 10.1007/s00897010452a.
(10) Solow, M. *J. Chem. Educ.* **2004**, *81*, 1172−1173, DOI: 10.1021/ed081p1172.
(11) Quach, D. T.; Ciszkowski, N. A.; Finlayson-Pitts, B. J. *J. Chem. Educ.* **1998**, *75*, 1595−1598, DOI: 10.1021/ed075p1595.
(12) Larsen, R. K.; Boyd, A. M. In *Book of Abstract*, 230th ACS National Meeting, Washington, DC, Aug 28−Sept 1, 2005; American Chemical Society: Washington, DC, 2005; p CHED-159.
(13) SALG Home Page. http://www.salgsite.org/(accessed Feb 2012).
(14) Seymour, E.; Daffinrud, S. M.; Wiese, D. J.; Hunter, A.-B. G. *Book of Abstracts*, 219th ACS National Meeting, San Francisco, CA, March 26−30, 2000; American Chemical Society: Washington, DC, 2000; CHED-480.
(15) Efstathiou, C. E. Isotope Peaks of Ionic Fragments in Mass Spectrometry. http://www.chem.uoa.gr/applets/AppletMS/Appl_Ms2.html (accessed Feb 2012).
(16) The responses in the questionnaire were (1) not applicable, (2) not at all, (3) just a little, (4) somewhat, (5) a lot, and (6) a great deal.