Understanding Our Energy Footprint: Undergraduate Chemistry Laboratory Investigation of Environmental Impacts of Solid Fossil Fuel Wastes

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Supporting Information

ABSTRACT: Engaging undergraduates in the environmental consequences of fossil fuel usage primes them to consider their own anthropogenic impact, and the benefits and trade-offs of converting to renewable fuel strategies. This laboratory activity explores the potential contaminants (both inorganic and organic) present in the raw fuel and solid waste remaining after thermal conversion. Using portable X-ray fluorescence, students analyze the heavy metals present in these solid samples following Environmental Protection Agency (EPA) method 6200. Sample extracts were analyzed via gas chromatography—mass spectrometry to measure polycyclic aromatic hydrocarbons, byproducts of incomplete combustion, in the samples using a semiquantitative internal standard approach. Across a series of raw, semicarbonaceous char and ash samples from oil shale and coal, students found levels of arsenic and naphthalene exceeding EPA



regional screening levels for industrial soils. This exercise teaches students about X-ray safety, EPA measurement protocol, solid– liquid extraction techniques, gas chromatograph–mass spectrometry, and semiquantitative analysis techniques, and more broadly about the environmental externalities of solid fuel use. The experimental results provide a basis for a discussion about the risks posed by disposal of energy processing waste on the environment, impediments to potential byproduct utilization, and the sustainability of alternative energy sources.

KEYWORDS: Second-Year Undergraduate, Analytical Chemistry, Environmental Chemistry, Mass Spectrometry, Quantitative Analysis, Gas Chromatography, Laboratory Instruction, Hands-On Learning/Manipulatives, Aromatic Compounds, Instrumental Methods

■ INTRODUCTION

The energy landscape is evolving to meet increasing electricity demands in an age of resource uncertainty and growing environmental consciousness. While political pundits campaign on the need for renewable fuel policies, and scientists warn of possible irreversible climate change from our fossil fuel dependence, the fact remains that over 25% of the United States' and almost 40% of the world's electricity generation is from coal, a conventional fossil fuel.^{1,2} In Estonia, almost 70% of that country's energy needs are met by oil shale, an alternative fossil fuel.³ To prepare students to shape the global transition to renewable fuels, they must understand the environmental ramifications of fossil fuel usage beyond climate change rhetoric; students need hands-on experience evaluating consequences of fossil fuel usage, such as the postprocessing of solid waste. This undergraduate laboratory investigation was performed over the course of several years in the Chemistry Department at Simmons College, and can be incorporated into an environmental chemistry or, with additional calibrations, a

quantitative analysis course. Initially designed to investigate fossil fuel (coal and oil shale) waste, this experiment could include byproducts of a range of solid fuels, from biomasses, to charcoal from a cook-out, to spent embers from a home fireplace.

Coal is often cited as a primary contributor to global warming.⁴ To produce electricity, it is pulverized and fed into boilers to generate steam to feed turbines. The byproducts of this process are bottom (what drops through the boiler grates) and fly (what leaves through the flue gas) ashes. There are 600–800 million tons of ash generated annually; while some finds its way into building materials and as flue gas desulfurization adsorbents, the majority is disposed of dry or in slurry form into lakes, the ocean, or landfills.⁵ Coal ash contains heavy metals, which leach under acidic conditions and

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contaminate surface and groundwater,⁶ as well as polycyclic aromatic hydrocarbons (PAHs), carcinogens that form from the incomplete combustion of carbonaceous sources.⁷ In addition to combustion, it is possible to extract gaseous and liquid fuels, as well as platform chemicals, hydrogen, and ammonia, by heating coal in limited or no oxygen conditions (pyrolysis, liquefaction, or gasification).⁸ In these scenarios, the primary byproduct is a semicarbonaceous char system comprising inorganic matter and residual carbon not devolatilized during processing. While some of these solids are used as byproducts, many form slag and ash.⁹

Given the recent instability in the price per barrel of crude oil, oil shale is increasingly being considered as a commercial energy source. There are upward of 2.8 trillion barrels of recoverable oil from shale rock in the world, a substantial quantity of which is estimated to be in the Green River formation.¹⁰ There are two utilization pathways for oil shale. One is direct combustion for electricity generation that yields a silica-based ash.¹¹ The second involves extraction of the oil contained within the rock via pyrolysis between 500 and 900 °C. Current oil extraction processes produce vast quantities of a semicarbonaceous waste known as "semicoke". Less than 10% of semicoke is incorporated into construction materials; the majority is disposed of in open landfills.¹² Semicoke's relatively high carbon content and surface areas have led some to propose its use as a commercial sorbent.^{13,14} However, with a plethora of entrained heavy metals and PAHs,¹⁵ the in situ positioning of semicoke as a sorbent may prove problematic. A second potential use for semicoke is as a cofired fuel. While PAHs present in the semicoke are likely oxidized during cofiring, elements such as sulfur present in the semicoke may lead to troublesome emissions, and ash still remains.

To integrate ecotoxicological concerns of energy production into the chemistry laboratory, students were charged with determining the extent of PAH and heavy metal contamination present in ash and semicoke of both coal and oil shale. Several activities recently published in this Journal concern the production, properties, and evaluation of laboratory fabricated and commercially available biofuels (e.g., refs 16-21). The undergraduate chemistry laboratory experiment presented here complements such experiences by *first* engaging students in the environmental ramifications of fossil fuel from a waste generation standpoint.²² This laboratory is accompanied by a discussion or lecture (outline provided in the Supporting Information) introducing the processing of fossil fuels to extract liquid/gaseous fuels versus combustion, and associated environmental ramifications of these processes. In terms of expected learning outcomes, through this laboratory exercise students will gain an understanding of:

- Application of an EPA method to quantitatively analyze metal content of solid samples
- Extraction and semiquantitative analysis of semivolatile components via gas chromatography-mass spectrometry
- Data analysis/interpretation in the context of contaminant screening levels to make recommendations on potential hazards of solid waste disposal
- Environmental consequences of fossil fuel usage

The goal of the experiment is to determine the levels of heavy metals and polycyclic aromatic compounds present in various solid fuel, semicoke, and ash samples that pose risks to human health and the environment through exposure to the solid waste.

EXPERIMENTAL SECTION

Before the laboratory session, instructors prepared "ash" and "semicoke" samples from a series of previously characterized oil shales (U.S. Green River, Chinese, Estonian^{13,23}) and coals (high volatile bituminous Pennsylvanian, Illinois No. 6, and Venezuelan^{24–27}). Coal can be purchased online (e.g., Amazon.com) and at local hardware stores (Tractor Supply Co., Aubuchon, Lehman's) and coal dealers (Blaschak Coal Corp, Centaur Forge, Center Coal Co.) if no local utilities' coal is available. The authors are happy to supply samples of oil shale, and as noted previously, this investigation can be duplicated with other char systems.

Samples were ground and sieved to a particle size less than 300 μ m. Samples were placed in porcelain boats in a 2 in. MTI tube furnace and either pyrolyzed under N₂ at 750 °C ("semicoke") or oxidized at 900 °C under air ("ash") for 2 h. Other solid samples that could be used in this investigation include charcoal or biomass combusted in a bomb calorimeter to create "ash" (and measure heating content) or burned in a home fireplace or barbeque grill. With samples prepared, students in teams of 3 or 4 can complete both portions of this exercise in approximately 3 h with one sample per team (using an autosampler on the GC–MS).

Determination of Heavy Metals

Approximately 3 g of dry sample was loaded into analysis "cups" (PREMIER Lab Supply, Inc.) and analyzed by X-ray fluorescence using a Thermo Fisher Scientific Niton XL3t portable analyzer that employs a 50 kV miniaturized X-ray tube. Factory calibrated, the instrument reports results for multiple elements simultaneously in parts per million (ppm). While it is possible to achieve quantitative results with XRF using standard addition calibration methods to obtain greater precision, the goal for this initial investigation was a semiquantitative survey of contaminants to introduce students to this indispensable field instrument, where the precision is estimated as $\pm 10\%$.

The XRF was programmed for EPA method 6200 for field portable soil and sediment analysis.²⁸ Each XRF run takes 90 s, making this portion of the experiment suitable for larger groups of students. For each sample, the instrument tabulates the average concentration of each metal along with the instrument's standard deviation. In their laboratory write-ups, students presented XRF measured value and ± 2 standard deviations, representative of a 95% confidence interval.

Analysis of PAH Contaminants

After the samples were (nondestructively) analyzed with XRF, 200-300 mg of the semicoke/ash was extracted with 10 mL of 50:50 (vol %) mixture of pesticide grade hexane and dichloromethane for 15 min for analysis using a gas chromatograph-mass spectrometer (PerkinElmer Clarus 500). During the extraction step, the solvent was spiked with internal PAH standards (Supelco CRM 46955) to estimate the concentration of the extracted PAH analytes. Because the extraction and sample preparation for the PAH analysis using GC-MS introduces the students to several new laboratory techniques, we used the internal standard method for students in an environmental science class or an introductory analytical chemistry course. This calibration approach is used to improve precision and accuracy of analysis when volume errors are potentially problematic. Errors that can be minimized by using an internal standard include evaporation of solvents and multistep sample preparation involving transfers, extractions, and dilutions. This present approach is semiquantitative since it

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assumes that the response factor of the PAH analytes is equal to that of the internal standards with elution times nearest the analyte of interest; however, this was not verified for every analyte. If desired (especially for an advanced quantitative analysis course), an external PAH calibration could be performed before the laboratory session. In addition, multiple extractions of the samples can be done with other solvents; this was beyond the scope of the course. The extracted samples were also spiked with a surrogate solution (Supelco 48925) to characterize potential analyte recovery issues inherent in the analytical method. Recoveries were typically 40–150%. Once the analyte identity and concentration in the extract solution is determined via GC–MS, the students determined PAH concentration in the original sample, assuming all of the analyte was extracted from the sample.

GC–MS analysis conditions were optimized for PAH and semivolatile compound detection using a Restek Rxi-5Sil MS column (30 m × 0.25 mm i.d., 0.25 μ m stationary phase) under an oven program initially at 40 °C, held 1 min, 12 °C min⁻¹ to 250 °C, 20 °C min⁻¹ to 330 °C, held 7.5 min; He carrier gas flow 1.5 mL min⁻¹. Chromatographic analysis required ~45 min per sample, including oven cooling and re-equilibration. The MS used electron impact ionization with a single quadrapole mass analyzer, scanning from m/z 40 to 450 at 5 scans per second. Quantitative data were obtained from the mass chromatograms corresponding to each analyte's base peak mass. Additional experimental details are provided in the Supporting Information.

HAZARDS

Protective clothing, gloves, and eyewear should be used at all times. All procedures should be done in a fume hood away from open flames. The processed samples are fine powders and should not be inhaled. Hexane is flammable, and harmful or fatal if swallowed, and causes irritation to skin, eyes, and the respiratory tract. Dichloromethane is harmful if swallowed or inhaled and is readily absorbed through skin; the EPA has determined that it is a probable cancer-causing agent. The XRF generates X-rays and must be operated according to the manufacturer's instructions.

RESULTS AND DISCUSSION

This experiment was performed over several years; we present here the average annual results for each sample (multiple entries indicate a sample run over several years). The heavy metals present in the solid samples are presented in Table 1.

The Pennsylvania coal samples were determined using XRF to contain 1.4-1.7 wt % sulfur, in good agreement with the 1.73 wt % sulfur content reported by the local utility company who provided the sample. In contradistinction, the Pennsylvania coal ash sulfur levels are significantly lower (~0.3%), consistent with the loss of sulfur through combustion. The evolution of gaseous sulfur during coal combustion can initiate a conversation about a number of environmental issues such as acid rain, air pollution, and air quality regulations.

The heavy metal content of the oil shale semicokes from China and the United States are in line with those previously reported, ranging from 15 ± 4 to 41 ± 5 ppm for Pb and 14 ± 5 to 69 ± 5 for As.¹⁵ Prior work demonstrated that as pyrolysis temperature increases, and thus more volatile carbon is removed from the solid matrix, that overall heavy metal concentration tends to increase, as it represents a larger fraction Table 1. Lead, Arsenic, and Sulfur in Semicoke, Ash, and Coal Samples Determined via XRF

		Elemental Composition, ppm				
Type of Sample	Source	Pb	As	s ^a		
	Oil Shale Samples					
Semicoke	China Maoming Mine A	28	49	7,000		
Semicoke	China Huadian Mine A	14	18	9,700		
Semicoke	China Huadian Mine C	32	50	7,700		
Semicoke	Green River Colorado 19 GPT	26	31	2,000		
Semicoke	Green River Colorado 19 GPT	30	40	2,100		
Semicoke	Green River Colorado 19 GPT	35	40	2,300		
Semicoke	Green River Colorado 50 GPT	34	66	7,000		
Semicoke	Estonia	12	15	6,800		
Ash	Estonia	62	17	8,600		
Coal Samples						
Coal	Pennsylvania	9	14	17,500		
Coal	Pennsylvania	11	17	14,600		
Ash	Pennsylvania	103	149	3,390		
^a Limit of detection (LOD) for sulfur is 90 ppm. Replicate samples						

were analyzed by different students.

of the total residual mass, with the 100% burnoff ("ash") sample having the highest concentrations.¹⁵ The variability is to be expected; oil shale is a heterogeneous rock with varied composition. Each year we used a small portion of a larger rock sample.

The U.S. EPA's regional screening level (RSL; regions 3, 6, and 9, compiled²⁹) for As in industrial soil is 3.0 ppm. For lead, the RSL in industrial soil is between 270 and 800 ppm depending on the form, which is up to 1 order of magnitude higher than any sample measured here. These results, where one potential contaminant is present in higher quantities and another significantly lower than acceptable risk models, open the discussion to students about the need to investigate multiple potential contaminants in the same sample, and not to make assumptions regarding the "safety" of a given waste material based only on one compound. As a result of this portion of the investigation, students were charged with investigating potential health effects of arsenic exposure and reading about leachability of metals from solid wastes.

The GC–MS analysis of extracts from semicoke showed naphthalene at high concentrations. The EPA RSL for naphthalene in industrial soil is 17 ppm (other PAHs range from 1.8 ppm for benzo[*j*]fluoranthene to 2.3×10^5 ppm for anthracene).²⁹ Other than the Green River Colorado 19 GPT semicoke, naphthalene was detected in concentrations several orders of magnitude higher than the RSL for all the oil shale semicoke samples, as shown in Table 2. Naphthalene is classified as a possible carcinogen; according to the National Institute of Health,³⁰ exposure may destroy red blood cells. Federal Drinking Water guidelines suggest a maximum concentration of 100 μ L/L.

The GC-MS analysis of extracts from coal ash did not detect PAHs. However, analysis of extracts from raw coal revealed a number of PAH compounds. Using the NIST mass spectra library software, we were able to tentatively identify a number of PAH compounds (see Table 2, note a) as 3,6-dimethylphenanthrene, phenanthrene, 2-methyl naphthalene, and 2-*t*-butyl-naphthalene. A number of other hydrocarbons were also tentatively identified, trimethylbenzenes, 1-ethyl-

Table 2. PAHs Detected in Semicoke and Coal Samples Determined via GC-MS

Type of Sample	Source	PAH Detected	Concentration in Solid, ppm		
Oil Shale Samples					
Semicoke	China Maoming Mine A	Naphthalene	8,700		
Semicoke	China Huadian Mine C	Naphthalene	12,000		
Semicoke	Green River Colorado 19 GPT	Not detected	Not detected		
Semicoke	Green River Colorado 50 GPT	Naphthalene	4,700		
Semicoke	Estonia	Naphthalene	4,500		
Coal Samples					
Coal	Pennsylvania	3,6- Dimethylphenanthrene ^{<i>a</i>}	152		
Coal	Pennsylvania	Naphthalene	54		
Coal	Illinois	Pyrene	6		
Coal	Illinois	2-Methyl naphthalene ^a	211		
Coal	Venezuela	2- <i>t</i> -Butyl-naphthalene ^{<i>a</i>}	34		
^a Tentative identification using the NIST mass spectra library software.					

benzene, and saturated hydrocarbons, but were not quantified. Calibration standards were only available for the 16 PAHs on the EPA Priority list,³¹ which enabled PAH confirmation using retention times for naphthalene and pyrene. Sample calculations are available in the Supporting Information.

From the analysis of the PAHs present in the semicoke, students were asked to consider the consequences of organic pollutants in soil systems. As Wise et al. show, the concentration of PAH in ambient air in the U.S. has decreased over the past 25 years; primary sources are traffic and nontraffic fuel combustions.³² Students were engaged in discussion concerning the anthropogenic inputs of pollutants such as PAHs into the atmosphere, and the need to consider volatilization as a potential pathway of PAHs to the atmosphere from open disposal of solid wastes.

ASSESSMENT, IMPLICATIONS, AND LIMITATIONS

Student achievement of learning outcomes was assessed via a formal laboratory report, in classroom discussions, and through anonymous free-response surveys. Lab reports demonstrated that all students in the classes were able to interpret and analyze the XRF results in the context of EPA RSLs; students recognized that the semicoke and ash samples contained some metals above and some below their respective RSL. Students were able to infer that the potential open disposal of the materials could present a hazard to human health through multiple pathways, including particulate transport through air, and leaching due to rainwater intrusion. The rubric used to assess student reports is provided in in the Supporting Information.

The GC-MS analysis proved "more advanced and complex" than many students thought (verbatim survey response). This was the students' first exposure to the analysis of complex mixtures via GC-MS, and they were initially overwhelmed by the myriad peaks on the chromatograms. In future years, we recommend an in-class activity prior to the lab exercise that has students analyze such complex mixture data by comparing retention times and ionization spectra, similar to ways in which

we teach NMR,^{33–35} or as Pacot et al. recently suggested, through first analyzing a set of data from a standard mixture.³⁶

Classroom discussions and free-response surveys demonstrated that students gained an appreciation for the inherently complex nature of pollutant mixtures, and the potential risks posed at what students first think are "small" (ppm) concentrations. Said one student: "Even small concentrations of many of the PAHs found in this experiment have health risks... detection and regulation of even small amounts through quantitative analysis is important to ensure the health and safety of our water sources, crops, and the environment..."

Finally, this exercise could be split into two stand-alone exercises, one analyzing metals and the other organics. For the purposes of our course and an engaging in-class discussion, we run it as a combined exercise so students can evaluate potential risk posed by organic and inorganic contaminants in the same sample. The XRF component, especially, is suitable to nonscience majors as it is a facile instrument requiring minimal training to use, while bringing to light important environmental impacts of solid fuels.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.7b00104.

Lecture and instructor notes, student hand-outs, and additional suggested references (PDF, DOCX)

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Notes

The authors declare no competing financial interest.

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