

Organic Combustion Fingerprints of Three Common Home Heating Fuels

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The chemical structures of three common home heating fuels are discussed: wood, coal and No. 2 fuel oil. GC and GC/MS data are then presented which demonstrate how the thermal destruction of each of these fuels results in the production of a characteristic group of organic compounds. In the case of wood, where the chief structural element is the lignin polymer, these are the methoxy phenols, the methoxy benzenes, and the alkyl benzenes. In the case of coal, where the polymer contains more fused-ring structures, the chief products are fused-ring aromatics with structures of 3-rings or more, the benzothiophenes, and to a lesser extent the methyl-substituted phenols. In the case of oil, the chief by-products are shown to be unburned droplets of the oil itself. The paper concludes with a brief discussion of how these "fingerprints" might be used as apportionment guides in complex airsheds.

Organic pollutants in complex urban-suburban airsheds can have a variety of sources, and sorting them out for purposes of apportionment can be a daunting task. Some researchers¹ have had success in using elemental tracers such as potassium and carbon-14. Potassium is a good tracer for vegetable matter, and C_{12}/C_{14} ratioing can often be used to discriminate between woodfire and fossil fuel effluents. However, these two techniques also have their drawbacks. Wind currents can stir up local soils and badly skew potassium findings, and C_{12}/C_{14} ratioing can be upset by local and distant sources of radioactive isotopes, such as nuclear power plants or weapons testing, including underground tests, when inadvertent venting occurs. Therefore, it would be useful to have some other tool with which to verify apportionment results. The purpose of this paper is to suggest such a tool, at least where home heating devices are concerned. The paper will show the relationship

between the chemical structures of three common home heating fuels and their combustion products and then demonstrate through the use of gas chromatograph mass spectrometer (GC/MS) data how this relationship produces a recognizable fingerprint for each. For purposes of concision, only a few samples will be examined in detail. However, they are representative of hundreds analyzed by the author. In one study,² for example, effluents from 10 separate household woodstoves and fireplaces were studied over the course of a winter heating season; and in another related study³ a similar number of household oil furnaces was examined.

Wood Chemistry and Woodfire Effluents

Unprocessed tree wood is a complex substance consisting of lignin and various celluloses, waxes, resins, tannins and

terpenes. For purposes of fingerprinting, lignin is the most important.

Lignin constitutes up to 30 percent of all woods⁴ and may be described as an almost infinite network of branch-chain polymer molecules. Other constituents, such as the celluloses and the hemicelluloses combine with lignin to give wood its rigidity in a structure that resembles reinforced concrete (the lignin forming the core and the celluloses the supporting mesh). While the precise structure of the lignin polymer has not been fully determined, it can be said to consist chiefly of two structural units. These are a guaiacyl nucleus in a guaiacylpropane skeleton and a syringyl nucleus in a syringylpropane skeleton.⁴ (Figure 1)

As has been demonstrated by Genuit et al.⁵ and latterly by Hawthorne and Barkley⁶

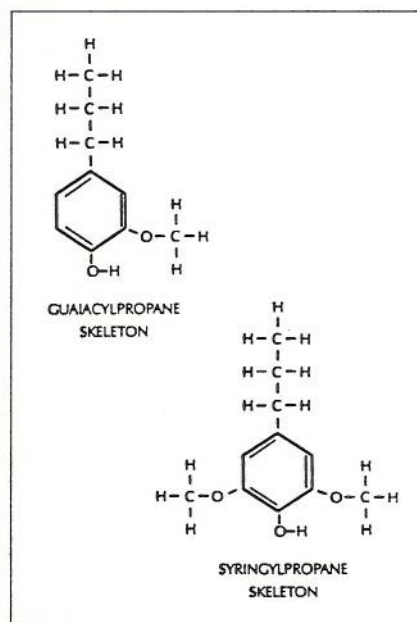


Figure 1. Lignin structural units.

Implications

This paper presents data on the organic fingerprints produced by the combustion of three common home heating fuels. These fingerprints could be useful in source apportionment work and therefore have implications in the design and implementation of ordinances regulating sources of urban and suburban air pollution.

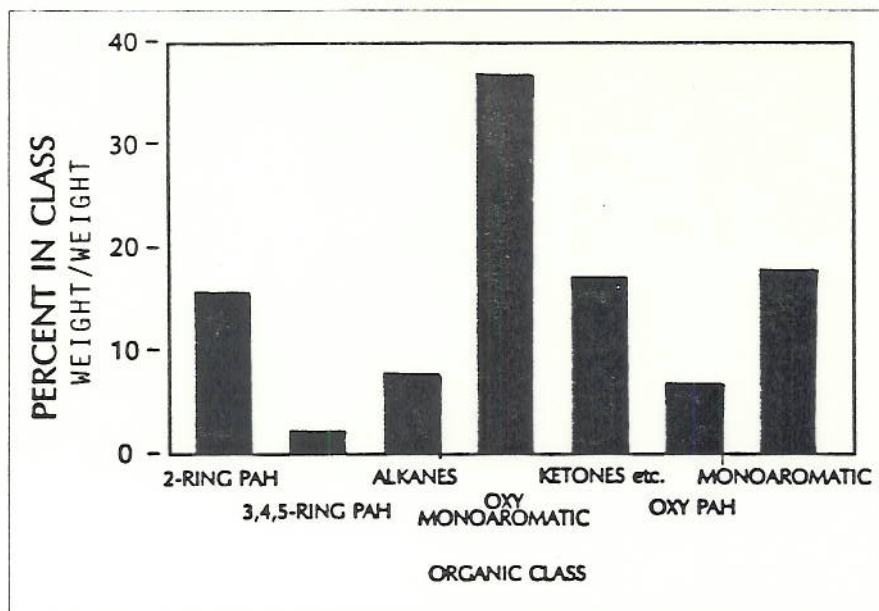


Figure 2. Distribution of compound classes in a residential woodstove stack (XAD-2 extract only).

and Steiber and Dorsey,⁷ the fracture of these structures during combustion tends to produce a wide variety of methoxy benzenes, methoxy phenols, and alkyl benzenes. In addition, the broad range of temperatures available in a woodfire provides the conditions for the transformation of some structures into naphthalenes, pyrenes and other condensed-ring aromatics (naphthalene, in fact, is the single most prevalent compound in woodfire effluents). However, for the purposes of fingerprinting it is the methoxylated compounds that are of the most interest.

Figure 2 shows the GC/MS results of the analyses of samples from a woodstove stack in bar graph form. The samples were taken in Boise, Idaho, during the Integrated Air Cancer Program (IACP) study in the winter of 1986-87. The feed material for the stove was a mixture of Douglas fir, ponderosa pine, and lodgepole pine, and the samples are typical of the ones acquired during the study. The graph shows an average of data for both a daytime (7 a.m. to 7 p.m.) and a nighttime (7 p.m. to 7 a.m.) sample.

The loading of oxygenated monoaromatics (e.g., methoxy benzene, methoxy phenol) is nearly twice that of any of the other classes. This paper will demonstrate that these methoxylated compounds are not found in the effluents of coal or oil fires, nor would one expect to see them as a by-product of the use of automotive fuels.⁸ In that sense they constitute a unique indicator for the presence of woodsmoke. The relationship of the methoxylated monoaromatics to the methyl-substituted monoaromatics is also

interesting. In this sample and in others there is an observed 2:1 weight/weight ratio between the two groups, and this ratio does not appear to be affected except by the most radical conditions in the firebox. That means that with caution this ratio can be used to provide a secondary verification of the presence of woodsmoke.

In none of the studies on which the previously mentioned information is based were woodstoves equipped with catalytic devices examined. However, other researchers have found that they emit the same range of methoxylated compounds.⁹

Coal Chemistry and Coalfire Effluents

As previously stated, the chief constituent of tree wood is lignin. In fact, it is the chief constituent of all woody plants and accounts for the majority of their organic carbon.

The lignin polymer is known to be long-lived. At the Petrified Forest National Monument in Arizona, Sigleo¹⁰ identified degraded lignin compounds in 200-million year old silicified wood. It should come as no surprise then that lignin-like structures persist in other artifacts of woody degradation, in particular in soft and hard coals. Figure 3 compares the lignin macromolecule with a general structure for coal proposed by Heredy and Wender.¹¹ This figure reveals that heat, pressure and time have resulted in the fusion of the original syringylpropane and guaiacylpropane skeletons into condensed hydroaromatic rings. Just as in the case of the single-ring structures of lignin, these fused-ring structures are joined by aliphatic bridges. The likely outcome when these bridges are sundered during combustion is the emission of fused-ring aromatics, methyl- and dimethyl-fused-ring aromatics, and phenolic compounds. Other likely compounds are the benzo- and dibenzo-furans, and since all coal contains at least some organic sulfur, the benzothiophenes.

Figure 4 shows the distribution of compound classes in a combined XAD-2/filter sample from an open-pit coal fire. Open-pit coal fires are a common method of home heating in Third World Asian countries, and these samples were acquired

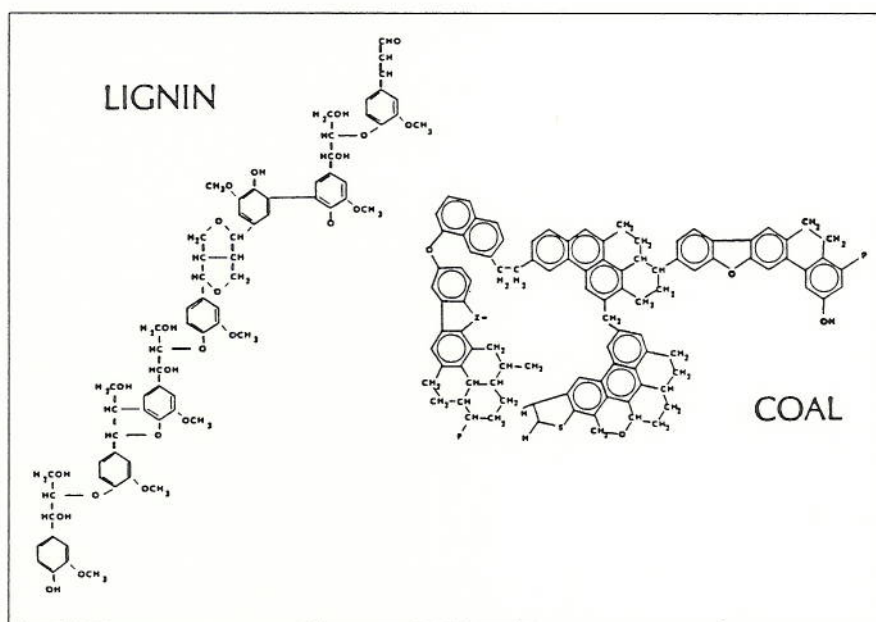


Figure 3. Comparison of coal and lignin macromolecules.

as part of a joint U.S.-Chinese epidemiological study.¹² The catches were extracted with dichloromethane, concentrated to an appropriate volume, and analyzed on a Finnigan Model 5100 quadrupole GC/MS.

The major compounds found in this sample fall into four basic categories: a homologous series of methyl-substituted naphthalenes; the classic three-, four-, and five-ring polynuclear aromatic hydrocarbons (PAH) including 9H-fluorene, chrysene, and benzo(a)- and benzo(k)pyrene; phenol and methyl-substituted phenols, and a homologous series of normal and substituted alkanes extending to C₂₆ and beyond. Also present are benzofuran, dibenzofuran, and several benzothiophene-type compounds. All these compounds are consistent with the fracture of the coal macromolecule during combustion and taken together constitute a kind of fingerprint for the presence of coal smoke.

In conclusion, the chief differences between the organic profiles of coalfire effluents and those of wood are the absence of methoxy benzenes and methoxy phenols and the greater prevalence of three-, four-, and five-ring PAH. This clearly reflects the differences in structure in the two macromolecules.

Oil Chemistry and Oilfire Effluents

The most frequently used home heating oil is No. 2 fuel oil, loosely defined as the cut in the distillation of crude oil that lies between 375 and 625 °F (the higher the number of the oil, the less volatile it is).

Unlike coal or wood, oil is not a polymer, but a mixture of closely related hydrocarbons. In the case of No. 2 fuel oil, this mixture is made up of four main groups of compounds: a homologous series of normal alkanes; a related series of substituted alkanes; a homologous series of alkyl benzenes; and, most importantly, a homologous series of substituted naphthalenes. A number of olefins are also present. The substituted alkanes are so many and various that on a chromatogram they form a kind of hump from which the normal alkanes and substituted naphthalenes protrude like the quills of a porcupine. (Figure 5)

When compared to woodstoves and coal furnaces, forced-draft central oil heaters are relatively clean burning. In the most common design, oil is sprayed from a nozzle into an accompanying toroid of air and ignited with an electric igniter. So long as the burner is well-maintained and the proper amount of air is present, the chief by-products of this process should be carbon dioxide and water. However, our analysis shows that in practice not all

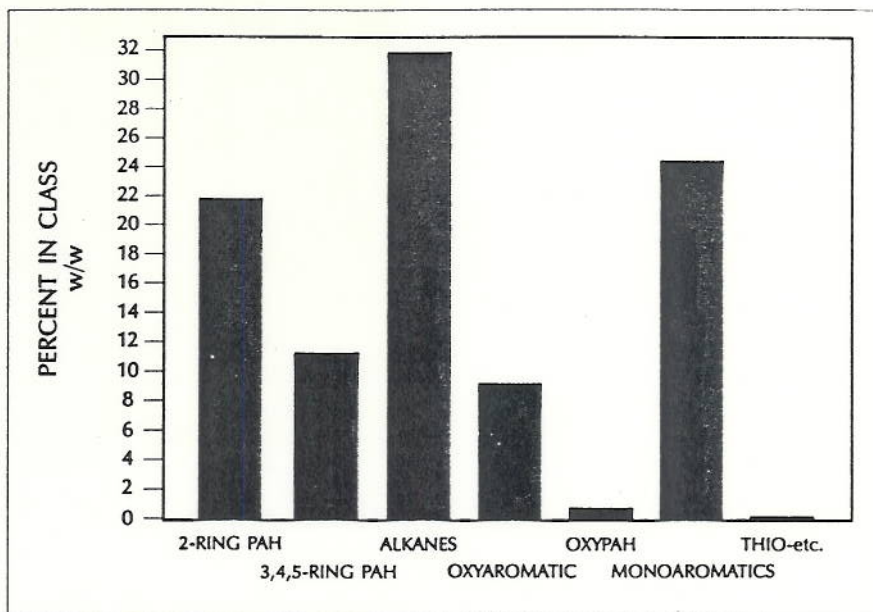


Figure 4. Distribution of compound classes in a coal smoke sample.

of the oil is combusted. Tiny droplets of it escape the flame and are carried up through the vent and out into the surrounding air.

Figure 5 compares the total ion chromatogram (TIC) of No. 2 fuel oil with the XAD-2 catch from the stack of the home heating apparatus in which it was subsequently burned. These samples were acquired as part of an IACP pilot study conducted by Robert C. McCrillis of the U.S. Environmental Protection Agency. Comparison of the two TICs confirms the fact that the chief organic effluent from the stack is the unburned oil itself. In fact, without any further knowledge, even the type of oil can be identified, simply by making note of the carbon numbers of the first and last alkanes to elute. Table I

presents a compound-by-compound comparison of the two TICs. Identifications were obtained using standard GC/MS search techniques and clearly support our contention that the two traces have a common organic source.

Figure 6 shows the distribution of compound classes in the stack sample. Note the relative prominence of the bar for the 2-ring PAH (naphthalene and substituted naphthalenes). As a weight-per-weight percentage of the sample there are 32 percent more 2-ring PAH in the oilfire extract than there are in the coalfire effluent and nearly double the percentage in the woodfire sample. The overall number of classes is also reduced. This is a reflection of the fact that No. 2 fuel oil is a refined

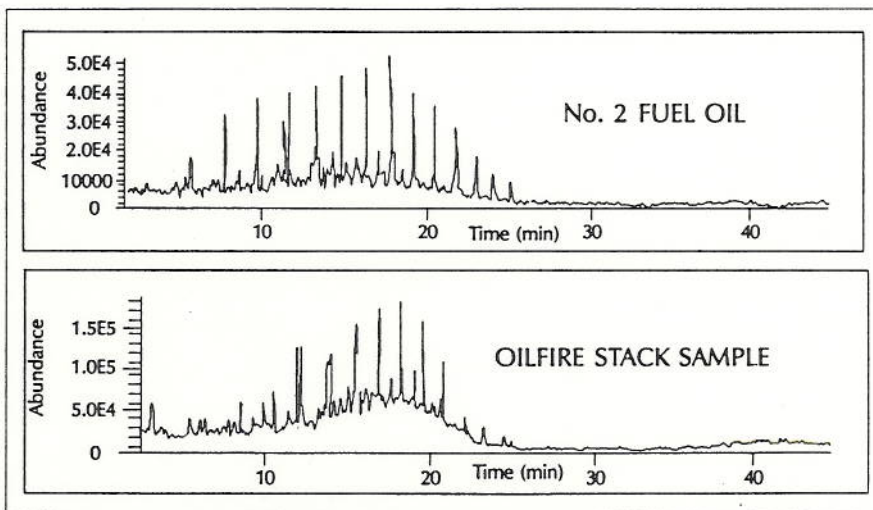


Figure 5. Comparison of TICs of No. 2 fuel oil and an oilfire stack sample.

product and that the portion that escapes the burner head is relatively unaffected by the combustion processes.

Discussion and Conclusion

The three bar graphs presented in this paper constitute a series of fingerprints for woodfire, coalfire and oilfire effluents. Each of these fingerprints is closely related to the structure of the fuels themselves. This is particularly true of the coal and wood polymers where thermal cleaving accounts for a significant portion of the emitted organics. In regard to specific classes of compounds, the monoaromatics (chiefly the alkyl benzenes) have roughly the same distribution in all three effluents, with slightly fewer, percentage-wise, being found in woodsmoke. Oxyaromatics, chiefly the methoxylated compounds, dominate the woodsmoke sample, and oxygenated compounds of all classes make up nearly 60 percent of the overall catch. This compares to roughly 12 percent for coal smoke, where they are mainly methyl-substituted phenols, and only 2 percent of the oilfire effluents. In woodsmoke, a single compound, naphthalene, accounts for almost the entirety of the 2-ring PAH and by itself constitutes nearly 13 percent of the overall effluents. In coal smoke and oilfire effluents it is the substituted naphthalenes that dominate the 2-ring PAH catch. Finally, there are the three-, four- and five-ring PAH, a class that contains benzo(a)pyrene and many of the other classic carcinogens. These make up nearly

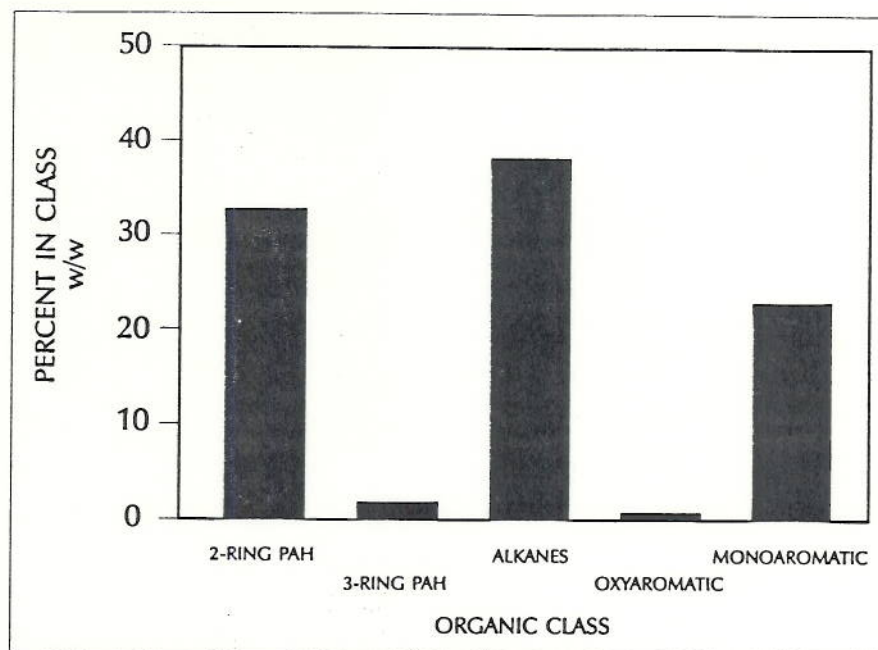


Figure 6. Distribution of compound classes in a residential oil furnace stack emission sample (XAD-2 extract only).

12 percent of the coal effluents, but only about 3 percent of the woodfire effluents and practically none of the oilfire emissions. In addition, within these fingerprints there are certain indicator compounds: the methoxylated aromatics for woodsmoke and the benzothiophenes for coalfire effluents. And where oilfire effluents are concerned there is still another indicator: the characteristic quilled hump

that shows up on GC chromatograms and GC/MS TICs.

All of the above information has been developed from stack samples, and its application as an apportionment tool for ambient samples awaits further study. Nevertheless, it is possible to speculate on a strategy for its use. Since coal is not often used as a home heating fuel in North America, the chief effluents of wintertime U.S. airsheds should result from either the burning of wood or the burning of oil. These are easily differentiated by their overall pattern and by specialized characteristics: methoxylated compounds in woodsmoke, the quilled hump in oilfire chromatograms. Where coalfire effluents are present, they are likely to be from industrial sources. However, there is no reason to believe that the types of compounds found in industrial effluents should differ markedly from those of home heating devices, however crude, and certainly both will contain benzothiophenes. It is the benzothiophenes that give coal its characteristic odor, and they are easily detectable at even the most minute concentrations, using selective ion GC/MS. Table II presents the above information in tabular form.

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Table I. Comparison of compounds found in No. 2 fuel oil with compounds found in stack.

No. 2 Fuel Oil	Stack
R.T.* Compound	R.T. Compound
5.24 trimethyl benzene	5.26 trimethyl benzene
5.55 decane	5.54 decane
9.23 naphthalene	9.24 naphthalene
9.78 dodecane	9.78 dodecane
11.34 1-methyl naphthalene	11.33 1-methyl naphthalene
11.62 2-methyl naphthalene	11.62 2-methyl naphthalene
13.35 tetradecane	13.33 tetradecane
13.48 1,2-dimethyl naphthalene	13.51 1,2-dimethyl naphthalene
13.79 1,8-dimethyl naphthalene	13.77 1,8-dimethyl naphthalene
14.05 2-ethyl naphthalene	14.03 2-ethyl naphthalene
14.61 2-methyl-1,1'-biphenyl	14.60 2-methyl-1,1'-biphenyl
15.26 2,3,6-trimethyl naphthalene	15.25 2,3,6-trimethyl naphthalene
15.52 trimethyl naphthalene**	15.54 trimethyl naphthalene**
15.78 trimethyl naphthalene**	15.77 trimethyl naphthalene**
16.19 1-(2-propenyl)-naphthalene	16.18 1-(2-propenyl)-naphthalene

*retention time, minutes

**isomer

Table II. Indicators for presence of effluents from three common home heating fuels.

Woodsmoke	<ul style="list-style-type: none"> — presence of methoxylated aromatics — 2.5:1 ratio* of methoxylated aromatics to the compound naphthalene — 2:1 ratio* of methoxylated aromatics to monoaromatics
Coalsmoke	<ul style="list-style-type: none"> — presence of benzothiophenes — presence of methyl substituted phenols, but absence of methoxylated phenols — 10 percent or more of the sample made up of 3-, 4- and 5-ring PAH
Oilfire Effluents	<ul style="list-style-type: none"> — characteristic quilled hump pattern in chromatogram — equal domination (within ± 5 percent) of sample by three classes of compounds: 2-ring PAH, alkanes, monoaromatics

*weight/weight

Disclaimer

Mention of commercially available products is for information purposes only and does not constitute an endorsement by the U.S. Environmental Protection Agency.

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