Chemical and Toxicological Characterization of Residential Oil Burner Emissions: I. Yields and Chemical Characterization of Extractables from Combustion of No. 2 Fuel Oil at Different Bacharach Smoke Numbers and Firing Cycles

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Particulates and complex organic mixtures were sampled from the exhaust of a flame retention head residential oil burner combusting No. 2 fuel oil at three firing conditions: continuous at Bacharach Smoke No. 1, and cyclic (5 min on, 10 min off) at Smoke Nos. 1 and 5. The complex mixtures were recovered by successive Soxhlet extraction of filtered particulates and XAD-2 sorbent resin with methylene chloride (DCM) and then methanol (MeOH). Bacterial mutagenicity [see Paper II (8)] was found in the DCM extractables. Samples of DCM extracts from the two cyclic firing conditions and of the raw fuel were separated by gravity column chromatography on alumina. The resulting fractions were further characterized by a range of instrumental methods.

Average yields of both unextracted particulates and of DCM extractables, normalized to a basis of per unit weight of fuel fired, were lower for continuous firing than for cyclic firing. For cyclic firing, decreasing the smoke number lowered the particulates emissions but only slightly reduced the average yield of DCM extractables. These and similar observations, here reported for two other oil burners, show that adjusting the burner to a lower smoke number has little effect on, or may actually increase, emissions of organic extractables of potential public health interest. Modifications of the burner firing cycle aimed at approaching continuous operation offer promise for reducing the amount of complex organic emissions.

Unburned fuel accounted for roughly half of the DCM extractables from cyclic firing of the flame retention head burner at high and low smoke number. Large (i.e., > 3 ring) polycyclic aromatic hydrocarbons (PAH) were not observed in the DCM extractables from cyclic firing. However, nitroaromatics, typified by alkylated nitroaromatics, alkyl-nitrophenyls, and alkyl-nitrophenanthrenes were found in a minor subfraction containing a significant portion of the total mutagenic activity of the cyclic low smoke samples (8). Oxygen-containing PAH, typified by phenalene-1-one and its alkyl derivatives, are important mutagens from cyclic firing at high smoke conditions. Thus, oil burner effluents differ markedly from those of several other combustors, including the automotive diesel engine, where multiring PAH, typified by fluoranthene and alkylated phenanthrenes, account for a significant portion of the effluent mutagenicity. Implications for combustion and emissions source identification are discussed.

Introduction

Residential oil burners are widely dispersed emissions sources that produce carbonaceous effluents. Fragmentary reports indicate that these effluents may be of public health interest, especially in densely populated neighborhoods or neighborhoods close to major population centers. For example, using information reported by Surprenant et al. (1) and more recent fuel utilization data (2), we estimate that approximately 50 million small scale (≤ 400,000 Btu/hr) stationary combustors, accounting for almost 10% of total national energy consumption, are used for residential space heating
in the United States, and that 10 to 15 million of these are residential oil burners, burning middle petroleum distillate (No. 2 fuel oil). About 60% of this fuel is consumed in the northeast, which contains about 35% of the United States population, but significant quantities of No. 2 fuel oil are used for residential heating in virtually all other regions of the United States, with the exception of the mountain and south central region (1).

Surprenant et al. (1) surveyed pre-1978 studies of oil burner emissions of \( \text{SO}_2 \), \( \text{NO}_x \), lighter hydrocarbons, \( \text{CO} \), \( \text{SO}_2 \), particulate sulfate, trace elements, and organic extractables, including selected polycyclic aromatic hydrocarbons (PAH), and other polycyclic compounds. They concluded that further data were required on \( \text{SO}_2 \), particulate sulfate, trace elements, and organics and performed their own field measurements of these emissions for several oil burners. Upon completing this study they called for further work on characterization of polycyclic organic matter in oil burner emissions. Such material is of particular interest for toxicological assessment since samples of complex organic mixtures recovered from other combustors have been shown to contain significant concentrations of chemicals capable of inducing mutagenic, carcinogenic, or teratogenic responses in cell and/or mammalian test systems (3–5).

Furthermore, Hangebrauck et al. (6), Kraus and Coburn (7), and Surprenant et al. (1) each demonstrated that residential oil burners emit polycyclic aromatic hydrocarbons.

The present study focused on determining the yields, chemical composition, and biological activity of particulates and complex organic mixtures in residential oil burner exhaust. Effluents from three different oil burners were studied. Specific questions of interest were:

1. What are the mass loadings of particulates and organic extractables in the oil burner exhaust for different operating conditions pertinent to residential practice?
2. To what extent can the biological activity of the whole mixtures of extractables be accounted for by the activities of specific fractions, compound classes, or compounds within those mixtures?
3. What organic compounds are found in these extractables?
4. How does a reduction in smoke emissions affect the chemistry and toxicity of co-emitted, complex organic mixtures?

Treatment of these questions required a multidisciplinary research team composed of expertise in combustion engineering, analytical chemistry, and toxicology. Our results are presented in this journal as two successive papers: this paper (1) describes the methods of sample acquisition from the oil burner and our results on particulates and extractables yields and on extractables chemical analysis, and Paper II by Braun et al. (8) presents our findings on toxicological analysis.

**Methods of Investigation**

**Measurement Strategy**

Integration of emissions sampling and yield measurements, chemical analysis, and toxicity testing was essential. Complex mixtures were therefore generated and recovered in sufficient quantities for chemical and biological testing by extended period sampling of the exhaust of an on-campus oil burner specifically purchased for this program and operated under controlled firing cycles.

**Oil Burner Emissions Test Facility**

As shown in Figure 1, this facility consists of a nominal 1 gallon/hr (GPH) flame-retention head, residential oil burner; a 144,000 Btu/hr forced hot air home furnace; and two interconnected 275 gallon capacity fuel tanks. This equipment is one form of space heating system commercially vended in the United States, and it is suitable for installation in small- to medium-size single family dwellings.

The furnace firing cycle, i.e., the length of time the burner was on and off, was controlled by an automatic timer. This allowed known and preselected on/off schedules to be continuously repeated over extended sampling periods of typically 6 to 8 hr and occasionally up to 12 hr. The fuel was commercial home heating oil (No. 2 petroleum distillate). One 550 gallon lot was purchased from a local supplier to meet the projected needs of the entire sample acquisition program. Chemical analysis of a sample of this fuel has been reported (9,10) and is discussed in more detail below.

During operation, fuel was fed to the burner from a 5 gallon safety canister. The fuel was atomized by forcing it under pressure (nominally 100 psig, developed by a fuel pump attached to the burner) through a small orifice in the burner nozzle. The nominal feed rate was 1.0 gallon/hr (GPH). The actual rate was determined by the delivery pressure and by the size and condition of the nozzle orifice. A 0.92 GPH nozzle was used throughout this program. The cumulative weight of fuel delivered to the burner over the known run period was used to normalize corresponding measured emissions yields to a standard basis of per unit weight of fuel fired. This weight of fuel was determined by weighing the feed canister (precision \( \pm 0.02 \) lb) before and after each run.

The atomized fuel droplets vaporized and burned as a turbulent diffusion flame (i.e., as a combusting mix-
ture, of reasonably well-defined shape and dimension, produced and maintained by energetic random mixing of air and fuel vapor). The flame was contained within a combustion chamber (fire box) with internal walls of refractory material; the walls were confined by the sheet metal shell of the furnace. The combustion process generated very high temperature flue (exhaust) gases, which consisted primarily (~ 99% by volume) of CO₂, water vapor, nitrogen, and oxygen that remained unreacted after combustion. Trace quantities of unburned fuel and of numerous other combustion products, many of which have toxic effects, were also present.

### Sampling Train

Our sampling train (Fig. 2) was based on a Battelle Columbus Laboratory (11—13) modification of the EPA Method 5 Sampling Train (14). It consisted of a 25-mm ID × 1 m long cylindrical quartz probe connected via a spherical ground glass ball joint to a 220-mm OD teflon-coated, glass fiber filter, followed successively by a condenser and approximately 150 g of XAD-2 sorbent resin confined in a 90-mm ID × 100-mm long cylindrical chamber. To prevent major temperature excursions, water at 55°C was circulated through jackets which surrounded the condenser and XAD-2 chamber. Nominal collection station temperatures were recorded by thermocouples placed near the upstream face of the filter and near the entrance and exit of the XAD-2 chamber. The last thermocouple was followed successively by a knockout trap, consisting of a pyrex flask surrounded by an ice bath, a throttling valve, a dry vacuum pump, and a dry test meter. The exhaust of the test meter was vented to the chimney. Glass components exposed to high temperatures were fabricated from pyrex or Vyco. The induced draft at the sampling region was determined by measuring the pressure difference between this location and the ambient atmosphere with a manometer. The flue gas temperature at the sampling zone was measured with a thermocouple and typically was > 400°F. Efficient performance of this sampler design has been reported in the literature (11—13).

### Sampling Procedure

In preparation for sampling, the air intake controls of the oil burner were adjusted to produce the desired Bacharach Smoke Number at the flue gas sampling location. This parameter was measured using a standard American Society for Testing and Materials (ASTM) method (No. D2165-65) for testing smoke density in flue gases from distillate fuel combustion (15) in home heating equipment. The color or shade of a test smoke spot, generated by drawing a known volume of flue gas through a section of filter paper of standard area, was compared with a set of 10 standard spot colors that constitute the Bacharach Oil Burner Smoke Scale. Each standard spot is assigned an integer smoke number ranging from 0 through 9 in order of increasing darkness. The Bacharach Smoke Number for the exhaust flow tested is then taken as the number for the standard spot closest to the color of the generated spot.

The two emissions of interest were complex mixtures of organic compounds and filterable particulates. The probe was connected to the assembled sampling train, and its open end was inserted radially into the exhaust duct to a depth of approximately 7.6 cm. This allowed near- and on-axis sampling at about 1.8 m from the exit of the furnace shell (and heat exchanger) and about 0.2 m upstream of the barometric damper. Samples of par-
ticulates and extractables were obtained simultaneously by actuating the sampling pump. Isokinetic sampling was omitted. At our sampling temperatures (typically > 400°F), most of the effluents of primary interest in this study (the materials recovered by methylene chloride and methanol extraction of the filter and XAD-2) should exist as vapors and thus follow the main gas flow without slip. Based on the discussions and correlations of May (16), our sampling conditions would also be expected to provide ≥ 66% recovery efficiencies for particulates of ≤ 5 μm aerodynamic diameter. Respirable particulates and most soot particles emitted by residential oil burners should fall in this size range.

Samples were obtained for cyclic operation of the burner at Smoke Nos. 1 and 5 and for continuous operation at Smoke No. 1. In the cyclic runs the burner was turned on for 5 min and off for 10 min, and this on/off cycle was continuously repeated, typically for 6 hr a day. Samples were drawn by continuously running the sampling line vacuum pump over a period that completely overlapped the on part of the burner cycle. This involved activating the vacuum pump approximately 10 sec prior to starting the burner and continuing to pump for 20 to 30 sec after stopping the burner.

The total time required for sampling under cyclic firing conditions was the time needed to obtain extractables in sufficient yields for detailed chemical analysis and biological testing. The maximum uninterrupted sampling time (typically ~ 6 hr) was dictated by the need to replace the filter before the pressure buildup due to particulates accumulation becoming so high that stable sampling conditions could no longer be maintained. The XAD-2 resin beds were replaced every 3 to 4 hr. One 4 to 12 hr operating day constituted one run. A large complex mixture sample from cyclic Smoke No. 5 operation was prepared by pooling the individual collections from eight such one-day runs. A similar sample for cyclic Smoke No. 1 firing was generated by pooling the output of 25 one-day runs.

**Methods of Yield Determination and Sample Preparation**

Each filter was weighed and stored in a dessicator before use in a sampling experiment. After sampling, each filter was removed from the collection train, dried, and reweighed. Both weighings were performed by bringing the filter to constant weight in a dessicated balance chamber. The yield of raw particulates sampled was then taken as the weight gain of the dry filter. Depending on burner and sampling train operating conditions, especially the filter temperature, this yield includes part of the complex organic compounds soluble in organic solvents.

Typically, sampling rates were 5.5 to 9 standard cubic feet per min (SFCM), and usually about 20 to 40% of the total exhaust was diverted into the sampling probe. The yields of particulates and extractables in the exhaust at the sampling location were calculated by correcting the measured yields of these products actually collected according to the fraction of the exhaust flow diverted through the sampling train. For each run, the required correction parameter (the sampling fraction)
was taken as the ratio of the cumulative standard volume of exhaust gas sampled throughout the run to the cumulative standard volume of gas emitted by the burner during the same period. The latter was calculated from the atomic hydrogen/carbon (H/C) ratio of the fuel, the cumulative weight of fuel used, and the amount of excess combustion air, which was calculated from the H/C ratio of the fuel and a measured value of the percentage of CO₂ in the oil burner exhaust. The exhaust CO₂ concentration was measured using a Fyrite KOH solution absorption cell (15). Emissions yields were normalized to a basis of per unit weight of fuel fired in the burner by dividing the calculated cumulative exhaust yields by the total weight of fuel delivered to the burner over the corresponding sampling period.

Separate yields of dichloromethane (DCM) and methanol (MeOH) extractables from the filters and the XAD-2 sorbent beds were measured in most runs. After re-weighing, the filters for a given run were combined and extracted for 24 hr in a Soxhlet apparatus initially charged with 500 mL of DCM. The XAD-2 sorbent resin was also extracted by the same procedure. Then the filters and XAD-2 resin were separately extracted with MeOH by the same procedure.

The DCM extracts from the cyclic Smoke No. 5 study were concentrated in a rotary evaporator. However, experiments on solvent concentration using a multiple plate distillation column (17) demonstrated significantly better recovery of more volatile extract components such as toluene. A large Kuderna-Danish (KD) apparatus consisting of a 1.5 L evaporation flask, a 25 mL receiver, and a 6-ball Snyder column was therefore used to concentrate the DCM extracts from the cyclic and continuous Smoke No. 1 experiments. The final volume of concentrated extract solution was 100 mL for both the KD and rotary evaporation techniques. Extract weights were determined by evaporating an aliquot of extract solution to dryness under a stream of nitrogen and weighing the residue. Normalized extract yields were calculated by the same procedure as described above for the particulates. Yields of DCM- and [DCM + MeOH]-extracted particulates were calculated by subtracting the corresponding extract yield from the yield of raw (unextracted) particulates.

**Fractionation of Whole Extracts**

Figure 3 summarizes the separations and analysis schemes used for chemical characterization of the raw extract samples. A simpler version of this protocol was used in earlier work (9) on fractionation and analysis of the No. 2 fuel oil employed in the present investigation. For each fractionation, a known amount of sample ranging from 50 to 250 mg was placed on 10 g of neutral aluminum oxide (Brockman activity I, 80–200 mesh) packed in hexane. The separations were performed according to previously reported methods (18,19). Figure 4 shows the specific fractions and subfractions collected from the cyclic Smoke 1 and Smoke 5 combustion extracts.

**Instrumental Methods of Analysis**

**GC/MS.** The mass spectrometer used for all GC/MS analyses was a Finnigan-MAT double-focusing instrument of reverse Nier-Johnson geometry interfaced to a Varian SS200 data system running on a DEC PDP-11/34A computer. Also interfaced to the mass spectrometer was a Varian model 3700 gas chromatograph equipped with a 15-m DB-5 fused silica capillary column which has an internal diameter of 0.32 mm and a film thickness of 0.25 μm. Operating conditions were: 70 eV electron energy, 4.5 A filament current, 3000 V accelerating potential, and an ion source temperature of 180°C. The resolution was set at 1:1000 and the mass range from 50 to 500 m/z was scanned in 2.2 or 1.1 sec
with an interscan time of 0.7 sec. The chromatographic column temperature program was: hold at 45°C for 45 sec, ramp at 4°C/min to 280°C, and then hold at final temperature for 2 min.

**HRMS.** The mass spectrometer used for obtaining high resolution data on whole samples or fractions was a CEC 21-110 double-focusing instrument of the Mattauch-Herzog type. It was set for 8000 V accelerating potential, 70 eV electron energy, 2.0 mA emission current, and a 3.0 A filament current. The ion source was maintained at 200°C. The resolution was set at 1:12,000. Mass spectra were recorded on a computerized mass-spectrometer interfaced to a PDP 11/45 computer system.

**GC/HRMS.** The gas chromatographic high resolution mass spectral data were obtained with the Finnigan-MAT 212 system. The GC columns used were 15-m DB-5 FSOT columns having a film thickness of either 0.25 or 1.0 μm. Analysis conditions were: mass range: 100 to 250 m/z; scan rate: 2.2 sec/decade with a 0.8 sec interscan period. Other instrumental parameters were the same as for low resolution GC/MS analysis.

**HPLC.** The liquid chromatographic system consisted of a Varian model 5000 ternary gradient pumping system coupled to a Hewlett-Packard model 8450A diode-array UV-VIS spectrophotometer. The model 8450A was interfaced to an HP 85B computer and a 7225B plotter. For reversed phase analysis of the chloroform fraction, two Apex-ODS 4.6-mm ID, 250-mm long columns (5 μm C-18 material) were connected in series. The mobile phase consisted of acetonitrile and water and the flow rate was 1.2 mL/min. Details of the analysis of the chloroform fraction have been published (20).

The HPLC separation procedure of benzene fractions was as follows: 100 μL of the fractionate, containing approximately 1.0 mg of material, was injected on a semipreparative (10-mm ID, 250-mm long) column packed with 10-μm particles of Alltech-CN cyanopropyl material. The hexane mobile phase was pumped isocratically at 4.0 mL/min. Under these conditions, a reference sample of chrysene eluted in 720 sec. Components eluting within 720 sec contained only aromatic hydrocarbons, while those eluting at longer times were shown to contain all of the nitroaromatics. The latter fraction was therefore designated the “nitro-subfraction” X-2(B) (Fig. 4).

**GC/TEA.** The nitrogen/NOx specific gas chromatograph (GC/TEA) was based on a Perkin-Elmer model 990 GC. It was equipped with a detector oven accessory normally used for GC/MS interfacing, and a 2.0-mm ID, 2.0-m long glass-lined, stainless-steel column packed with 3% Dexsil-300 on 100–120 mesh Chromosorb W-HP, and configured for on-column injection. The column was coupled to the pyrolyzer assembly of a Thermedics model 610N TEA Analyzer, a chemiluminescence-based nitrogen/NOx-specific detector (Thermedics Inc., 470 Wildwood Ave., Woburn, MA), using glass-lined, stainless-steel tubing and fittings. The detector signal was fed to a Perkin-Elmer LC/100 integrator serving as an interface to Chromatographics-III software running on a P-E model 7500 computer system. Operation of the GC/TEA has been described (21–23).

The present operating conditions were as follows. The injector was set at 275°C, the GC manifold at 350°C, the GC/TEA interface at 375°C, and the TEA pyrolyzer at 850°C. The carrier gas was helium at a flow rate of 25 mL/min. Oxygen flow to the ozonator was 10 mL/min, while combustion oxygen flow was 30 mL/min. Chamber pressure was approximately 7 mbar. The amount of sample injected was 10 μL. The GC temperature program was: column temperature was held initially at 100°C for 2 min followed by a ramp of 4°C/min to 300°C and a final temperature hold of 6 min at 300°C.

**Results and Discussion**

**Yields of Particulates and Extractables**

Table 1 presents the normalized exhaust yields of raw particulates, DCM- and [DCM + MeOH]-extracted particulates and of DCM, and of [DCM + MeOH]-extractables from the particulates and the XAD-2. Wide variability was found for all emissions except for raw and extracted particulates from continuous Smoke 1 operation. No clear correlation was found between any of these emissions and percentage excess air calculated as described above, and as shown in Table 2, a wide range of excess air values gave the same smoke number for different runs.

The goal of this work was not to investigate a carefully controlled research burner, but rather to study the effluents from a practical combustor operating under conditions pertinent to actual field practice. Our data (Table 1) show that extreme variability characterizes ordinary burner performance, and this variability must be accounted for in a testing strategy.

Possible causes for this variability include random distortions of the fuel spray pattern due to gradual accumulation and then erosion of carbon deposits on the feed nozzle and dripping of fuel from the nozzle between firing cycles, leading to crust formation and wide variability in fuel atomization and vaporization kinetics. Despite these wide variations, Table 1 confirms the expectation that the lower smoke number corresponds to lower emissions of particulates and also shows that at Smoke No. 1, continuous operation gives lower smoke emissions and lower average DCM extractables emissions than cyclic firing.

The methanol extractables generally did not exhibit statistically significant bacterial cell mutagenicity (See Paper II, (8)) and were not subjected to gravity column fractionation or detailed chemical analysis. Under cyclic firing, the mean DCM and [DCM + MeOH] extractables showed little difference between Smoke 1 and Smoke 5 operation.
**Table 1. Calculated oil burner emissions yields in mg per kg of fuel fired.**

| Emissions product                   | Burner operating condition | Burner operating condition | Burner operating condition |
|------------------------------------|----------------------------|----------------------------|----------------------------|
|                                    | Continuous Smoke 1         | Cyclic Smoke 1             | Cyclic Smoke 5             |
|                                    | Low | Mean | (n)b | High | Low | Mean | (n)b | High | Low | Mean | (n)b | High |
| Raw (unextracted) particulates     | 12  | 14   | (6)  | 17   | 31  | 59   | (36) | 96   | 129 | 227  | (33) | 370  |
| DCM-extracted particulates         | ---- | ---- | ---- | ---- | 30  | 55   | (10) | 89   | 127 | 207  | (12) | 310  |
| [DCM + MeOH]-extracted particulates| 5.5 | 6.1  | (3)  | 6.9  | 17  | 44   | (9)  | 85   | 107 | 201  | (11) | 294  |
| DCM extractablesf                 | 5.9 | 19   | (7)  | 39   | 24  | 34   | (9)  | 69   | 21  | 44   | (11) | 87   |
| [DCM + MeOH] extractablesf         | ---- | ---- | ---- | ---- | 54  | 78   | (8)  | 113  | 36  | 69   | (9)  | 112  |

*Flame retention head burner.

| Table 2. Ranges of percentage excess air giving equal smoke numbers. |
|---------------------------------------------------------------------|
| Smoke no. | Range of % excess air |
|-----------|-----------------------|
| 1 Continuous | 32–41 |
| 1 Cyclic    | 27–50 |
| 5 Cyclic    | 18–70 |

Table 1 thus suggests two conclusions of potential public health importance: (1) for cyclic firing, reducing smoke emissions by a substantial margin does not have a major effect on the total emission of organic extractables and (2) at a constant low smoke number (but not necessarily constant smoke loading, see Table 1), changing from cyclic to continuous operation reduces average extractables emissions.

Table 1, and its results (Table 3) show that for both burners (1) for continuous firing, reducing the smoke number from 5 to 1 reduces particulates evolution and does not diminish, but rather increases, emissions of DCM extractables; and at Smoke 5, cyclic firing emits more DCM extract and particulates than does continuous operation.

The absence of a correlation between extractables yield and smoke number for cyclic operation is noteworthy. For the DCM extractables (Table 1) this may reflect the fact (see below) that unburned fuel typically accounts for about 45 to 50 weight percent of their mass. The lower average yields of DCM and total extractables at continuous vs. cyclic operation imply that transient effects associated with burner startup and/or shutdown contribute to the increased emissions under nonsteady firing. One likely possibility is by-passing of unburned fuel, possibly modulated by condensation on and re-evaporation from thermally cycling furnace and burner components.

**Fractionation of Extracts**

The filters and XAD-2 resin from several cyclic Smoke No. 5 runs were extracted and concentrated. Portions of each were then separately fractionated. Tables 4A and 4B list the weights of these fractions for the XAD-2 and filter extracts, respectively. The recovered extractable mass is expressed as the weight percent of each fraction based on the total weight recovered from the alumina. The 65 mg of extractables from the filter with the 436 mg of XAD-2 extract constituted a total extractable mass of 501 mg available for chemical and biological characterization.

The 35 filters and 17 batches of XAD-2 resin collected from 119 hr of cyclic Smoke No. 1 operation were also
extracted and concentrated. The total amount of particulates collected was 2.35 g, of which 73 mg was extractable matter. After extraction, portions of the XAD-2 and filter extracts (168 mg and 20 mg, respectively) were each fractionated. The resulting weights for each of the collected fractions are shown in Table 5A and 5B.

### Chemical Characterization of DCM Extracts

Tables 6, 7, and 8 list the compounds found in the hexane, benzene, and chloroform fractions, respectively (see Figs. 3 and 4), from the DCM extractables from Cyclic Smoke 1 and 5 combustion and from the raw fuel. The components in the combustion samples produced by cyclic Smoke Nos. 1 and 5 were compared with those from the fuel itself in order to evaluate which compounds were actually produced during combustion and which compounds could be attributed to unburned fuel.

**Fraction 1—Hexane.** Examination of the data in Table 6 suggests that the alkane composition of both combustion samples was the same. The composition of this fraction from the fuel was also essentially identical to that from the combustion samples except for the presence of the C-24 and C-25 alkanes in the fuel. These findings suggest that fraction 1 from each of the samples analyzed contained mostly unburned fuel. The data in Tables 4A, 4B, 5A, and 5B show that the hexane fraction and hence, primarily unburned fuel, accounts for at least 37% and 29% of the total DCM extractables recovered under cyclic Smoke 5 and Smoke 1 firing, respectively.

**Fraction 2—Benzene.** The components found in this fraction are listed in Table 7. This eluent was of particular interest, since, as discussed in Paper II (8), it accounted for most of the bacterial mutagenicity in the cyclic Smoke No. 1 DCM extractables. Most compounds present in this fraction from the fuel were also present in the same fraction from the two combustion samples. There are small differences in the number of some isomeric components between the two combustion samples, but these are minor. Therefore, it is reasonable to assume that unburned fuel also accounts for most of the material in the benzene fraction from the DCM extractables recovered from the two cyclic combustion effluents. Again, using data from Tables 4A, 4B, 5A, and 5B, one calculates that the benzene fraction rep-
Table 7. Cyclic combustion: major components of benzene fraction.

| Isomers present | Quantity in fuel, % | Combustion samples |
|-----------------|--------------------|--------------------|
|                 |                    | Fuel | Smoke 1 | Smoke 2 |
| C-4 Benzene     | 1*                 | 1    | 1       |
| Tetralin        | + b                |     |         |
| Methy1 tetralin | 1                  | 1    | 1       | 1       |
| Dimethyl indan  | 2                  | 2    | 2       | 2       |
| Dimethyl tetralin | 2            | 2    | 2       | 2       |
| Naphthalene     | 1.2                | +    | +       | +       |
| Biphenyl        | 0.7                | +    | +       | +       |
| Phenanthrene    | 1.5                | +    | +       | +       |
| Methyl naphthalene | 9              | 2    | 2       | 2       |
| C-2 Naphthalenes| 15                 | 5    | 5       | 5       |
| C-3 Naphthalenes| 15                 | 6    | 5       | 5       |
| C-4 Naphthalenes| 12                 | 7    | 4       | 4       |
| C-5 Naphthalenes| 5                  | 1    | 1       |
| C-6 Naphthalenes| 4                  |     |         |
| C-7 Naphthalenes| 4                  |     |         |
| C-8 Naphthalenes| 4                  |     |         |
| C-4 Naphthalenes| 2                  |     |         |
| C-2 Bipheny1s   | 2                  | 2    | 2       | 2       |
| C-3 Bipheny1s   | 2                  | 3    | 2       |
| C-4 Bipheny1s   | 2                  | 2    | 2       |
| C-5 Bipheny1s   | 1                  | 1    | 1       |
| C-6 Bipheny1s   | +                  | 1    |         |
| C-7 Bipheny1s   | +                  | 1    |         |
| C-8 Bipheny1s   | +                  | 1    |         |
| C-9 Bipheny1s   | +                  | 1    |         |
| C-10 Bipheny1s  | +                  | 1    |         |
| C-11 Bipheny1s  | +                  | 1    |         |
| C-12 Bipheny1s  | +                  | 1    |         |

Dibenzothiophene | +                | +    | +       |
| C-1 Dibenzo1phenes | (40)          | 2    | 2       | 2       |
| C-2 Dibenzo1phenes | 4              | 3    | 3       |
| C-3 Dibenzo1phenes | 3              | 1    | 2       |
| C-4 Dibenzo1phenes | 2              | 2    |        |
| C-1 Phenanthrenes | 2              | 3    | 4       |
| C-2 Phenanthrenes | 3              | 3    | 6       |
| C-3 Phenanthrenes | 5              | 1    | 1       |
| Dibenzo1furan    | +                | +    | +       |
| C-1 Dibenzo1furans | +              | 3    | 3       |
| C-2 Dibenzo1furans | +              | 4    | 4       |
| C-3 Dibenzo1furans | +              | 4    | 4       |
| C-4 Dibenzo1furans | +              | 4    | 4       |
| C-5 Dibenzo1furans | +              | 4    | 4       |
| C-6 Dibenzo1furans | +              | 4    | 4       |
| C-7 Dibenzo1furans | +              | 4    | 4       |
| C-8 Dibenzo1furans | +              | 4    | 4       |
| C-9 Dibenzo1furans | +              | 4    | 4       |
| C-10 Dibenzo1furans | +             | 4    | 4       |
| C-11 Dibenzo1furans | +            | 4    | 4       |
| C-12 Dibenzo1furans | +           | 4    | 4       |

*Numerals refer to number of resolvable isomers.

(+ ) indicates compound present; only one isomer possible or isomers not resolved.

(- ) indicates not present or below detection limit.

Table 8. Cyclic combustion: major components of chloroform fractions.

| Isomers present | Compound | Combustion samples |
|-----------------|----------|--------------------|
|                 |          | Fuel | Smoke 1 |
| Alkylated carbazoles* | + | 1 |
| (Isobenzofuranone* | - | 1 |
| Methyl(1so)benzofuranones* | - | 1 |
| C-2 (iso)benzofuranones | - | 1 |
| C-3 (iso)benzofuranones | - | 1 |
| Acetophenone     | -       | +    |
| C-1 Benzo1dehyde | -       | 1    |
| C-3 Benzo1dehyde | -       | 5    |
| Methyl acetophenone | -   | -   |
| C-2 Acetophenone | -       | 2    |
| Naphthaldehyde   | -       | +    |
| Methyl naphthaldehyde | -   | 3    |
| Phenalenone      | -       | +    |
| Fluorenone       | -       | +    |
| Methyl phenalenone fluorenone | - | 4 |
| C-2 Phenalenone/fluorenone | - | 5 |
| C-3 Phenalenone/fluorenone | - | 5 |
| Anthraquinone    | -       | +    |
| C-1 Anthraquinone | -     | 4    |
| C-2 Anthraquinone | -     | 4    |
| Acetophenanthrone | +      | +    |
| Benzophenone     | -       | +    |
| Cyclopenta[ def]phenanthrene or cyclopenta[ ed]phenalenone | - | + |

*The fuel contained a large number of alky1ated carbazoles but no oxygenated species, whereas the combustion samples contained a large number of oxygenated species but no carbazoles.

(+ ) indicates compound present; only one isomer possible or isomers not resolved.

*Either isobenzofuranone or benzofuranone is possible.

(- ) indicates not present or below detection limit.

*Numerals refer to number of resolvable isomers.

Fraction 3—Chloroform. The largest difference in chemical composition between the fuel and cyclic combustion samples is found in the chloroform fraction. Compounds found in this fraction are listed in Table 8. The alky1ated carbazoles present in the fuel sample were not found in any combustion sample. However, a number of aromatic aldehydes, ketones, and quinones were found to be principal organic components in fraction 3 from the two cyclic combustion samples. The source of these compounds is not known, but oxidative pyrolysis of unreacted or partially reacted fuel in the post-flame regions of the oil burner combustion chamber is one possibility. This fraction is also of interest from a public health impact perspective since it accounted for a significant fraction of the bacterial mutagenicity of the cyclic Smoke No. 5 DCM extractables (8). It was therefore subjected to more detailed chemical analysis. It was found that phenalen-1-one and its alkylated derivatives accounted for a significant part of the bacterial mutagenicity of this fraction. Details of this work have been published (20).

Fraction 4—Methanol. The methanol fraction from both cyclic combustion samples was inactive in the bac-
terial and human cell mutagenicity assays (8). Detailed information on its chemical characterization is thus not directly pertinent to this paper, but can be found elsewhere (26). Some of the major components found in this fraction were phenol, cresol, and a number of C-2 phenol isomers which were by far the most abundant species.

Implications for Combustion and Emissions Source Identification

The present results suggest that reducing the amount of burner on/off cycling would reduce emissions of particulates, complex organics, and mutagens (8). Other studies have shown that reduced cycling would increase heating system efficiency. Down sizing of the burner or continuous modulation of the fuel input rate are strategies for diminishing or eliminating cyclic operation; however, practical implementation of these approaches would have their own difficulties; namely, inadequate heating capacity for extended cold spells and poor matching between the fixed surface area heat exchanges used in residential furnaces and the varying heat release rates accompanying continuous burner modulation.

Improved understanding of combustion sources of mutagens can be obtained by examining the present results, including the toxicological data reported in Paper II (8), in the light of literature on soot and PAH emissions from various research flames (27,28) and automotive diesel engines (4,29,30). It is clear that at different smoke numbers different chemical compounds contribute to the oil burner effluent mutagenicity. A variety of combustion and related processes are thus expected to be capable of generating mutagenic compounds such as nitropolynucleararomatics (cyclic Smoke 1), oxygenated polynucleararomatics (cyclic Smoke-5), and the more commonly studied mutagenic PAH such as benzof[al]pyrene, alkyl phenanthrenes, fluoranthene, and cyclopenta(cd)pyrene. Common multiring (i.e., > 3 rings) PAH were not observed in the oil burner DCM extracts, but have appeared in many combustion effluents (27,28), apparently being formed in- flame pyrolytic processes involving condensation of reactive, fuel-derived fragments. Nitroaromatics are expected to arise from post-flame reactions between NOx and fuel-derived aromatics. The alkyl naphthalenes, alkyl biphenyls, and alkyl phenanthrenes in benzene eluates from fractionation of the Smoke 1 and the Smoke 5 DCM extracts are believed to come from unburned fuel.

Oxygenated polynucleararomatics such as phenalene-1-one and its alkyl derivatives could rise from partial oxidation of fuel or fuel-derived products. These reactions would be expected in regions surrounding the flame where combustion chamber heat losses and/or partial depletion of oxygen create temperatures and oxidant potentials too low to sustain fuel ignition but still high enough to cause oxidative pyrolysis of organic reactants.

Since soot (smoke) formation is accompanied by formation of PAH (27,28), the absence at both cyclic smoke numbers of the more common multiring PAH often observed in combustion effluents was somewhat surpris-
Conclusions

For three residential oil burners, reduction of the Bacharach Smoke Number either had little effect on, or even increased the emissions of extractable complex organic mixtures.

Combustion modifications aimed at approaching continuous burner firing can reduce emissions of oil burner extractables and particulates.

About 45 to 50% of the total methylene chloride extractables emitted by cyclic firing of the flame retention head burner over a broad range of Smoke Nos. (1 and 5) appears to be unburned fuel. The fuel used was virtually free of multiring PAH (> 3 rings) and was not mutagenic to bacteria. Different results may have been obtained with fuels of different composition.

Multiring PAH (> 3 rings) were not observed in the effluents from cyclic firing of the flame retention head burner.

At least three compound classes that can be eluted from gravity fractionation columns contribute to bacterial cell mutagenicity in combustion effluents: (A) multiring PAH typified by fluoranthene and alkylated phenanthrenes; (B) alkylated nitroaromatics, typified by alkylated nitronaphthalenes, alkyl-nitrophenyls, and alkyl-nitro-phenanthrenes; and (C) oxygen-containing PAH, typified by phenalene-1-one and its alkyl derivatives. Classes A and B are relatively nonpolar and are eluted by benzene. Class A accounts for a significant portion of the mutagenicity in extracts of automotive diesel soot, and class B accounts for the retention head residential oil burner effluents evolved under cyclic, low smoke operation. The more polar class C is eluted by chloroform and contains a significant fraction of the mutagenicity in the retention head oil burner emissions from cyclic, high smoke firing.

Very different combustion processes can generate mutagenic effluents. In-flame pyro-synthesis by condensation reactions of fuel derived fragments, nitration (by NO₂) of unburned or partially burned fuel, and post-flame oxidative pyrolysis are believed to produce compound classes A to C, respectively.

The bacterial mutagenicity of effluent extracts from cyclic, low smoke oil burner operation was comparable to that of extracts from automotive diesel particulates. However, in contrast to the diesel extracts, common multiring mutagenic PAH were absent, and the oil burner samples were not mutagenic in our human cell assays. Per weight of fuel fired, diesel extract emissions exceed those of the oil burner by factors of about 10 to 100, and U.S. diesel fuel consumption is roughly twice U.S. home heating oil combustion. On the other hand, public exposure may be locally greater for oil burner effluents where population density is high.

Financial support of this research by the National Institute of Environmental Health Sciences under Grant Nos. 5 PO1 ES01640 and 5 P30 ES02109 is gratefully acknowledged. We also gratefully acknowledge the technical assistance of Robert Cukai in the acquisition of oil burner exhaust samples, the technical assistance of Michael Elia in chemical analysis of effluent extractables, and the collaboration of our colleagues in toxicology, A. G. Braun et al. (6).

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