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Project Summary

Waste Crankcase Oil Heater Study: Phase II: Organic and Inorganic Speciation Analyses

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This study involved measuring specific chemical species in emissions from two waste-oil-fired commercial heaters: one utilized a vaporizing pot; and the other, an air atomization combustion chamber. Polynuclear aromatic hydrocarbons (PAHs) were analyzed in the gaseous emissions of both units. Elemental analyses (including Pb, Fe, Cd, Zn, Cl, and Br) were performed on the air atomization discharges. In addition, several waste crankcase oils were tested for baseline levels of these species and to determine the effect on metal concentrations of both filtration and sedimentation during storage. Tests were also performed on emissions from the air atomization burner to measure the amount of organometallic lead species discharged from the burner, and to determine the distribution of iron oxidation states (Fe[II] versus Fe[III]) in gaseous emissions.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

This study is an extension of earlier work on residential appliances designed specifically for waste oil combustion. In that investigation, two reference waste crankcase oils were burned in residential waste heaters and a Level 1 analysis performed on the fuels, combustion residues, and gaseous emissions. The two types of space heaters tested, a vaporizing pot and an air atomization heater, were found to produce high levels of metallic discharges. The air atomizer generated the highest gas-phase metal discharges, and the vaporizing pot produced high levels of organic discharges along with a metal-rich pot residue. Among the metallic species identified for further study were Pb, Fe, Cd, and Zn: they were produced in high amounts and (in certain forms) are potentially harmful to humans. Since several researchers have proposed the use of waste oil as either a direct fuel or a blending agent to lower the cost of primary fuels, it is of great interest to investigate the environmental impacts of expanded waste oil use.

In this study, detailed investigations were performed on the species identified or suspected from the Level 1 data generated in the earlier program. In this study, samples were taken from both a vaporizing pot unit (Kroll) and a residential air atomization heater (Dravo). The experimental portion of this study consisted of:

(1) Analysis of five fuels to determine their metal content as a function of storage, batch differences, and fuel sources.

(2) Analysis of vaporizing pot and air atomization discharges for polynuclear aromatic hydrocarbons (PAHs).

(3) Analysis of air atomization gaseous discharges for organolead composition.

(4) Analysis of the Fe(II)/Fe(III) ratio in the air atomizer gaseous effluent.

(5) X-ray fluorescence analysis of the air atomizer particulate discharges to show concentration of inorganic species including Br, I, Fe, Cd, Pb, and Zn.

Figure 1 shows the two heaters schematically. The principal difference is the way the flame is sustained in each heater's firebox. The air atomization unit injects aerosolized oil vapor into the burn chamber, and the combustion gases are discharged in the gas phase into the flue. By contrast the vaporizing pot heater operates through volitilization of heated oil: the vapors are burned, and a heavy pot residue is left behind. In the initial study, this residue was found to contain a major portion of the metallic species from the fuel oil.

Experimental Procedures

PAHs were measured in both heaters by collecting Modified Method 5 samples and performing high-resolution capillary gas chromatography/ mass spectrometry (HRGC/MS) analysis on combustion sample extracts. An example of the complex organic matrix observed in these samples is shown in Figure 2, the total ion chromatogram from the HRGC/MS analysis of a vaporizing pot sample.

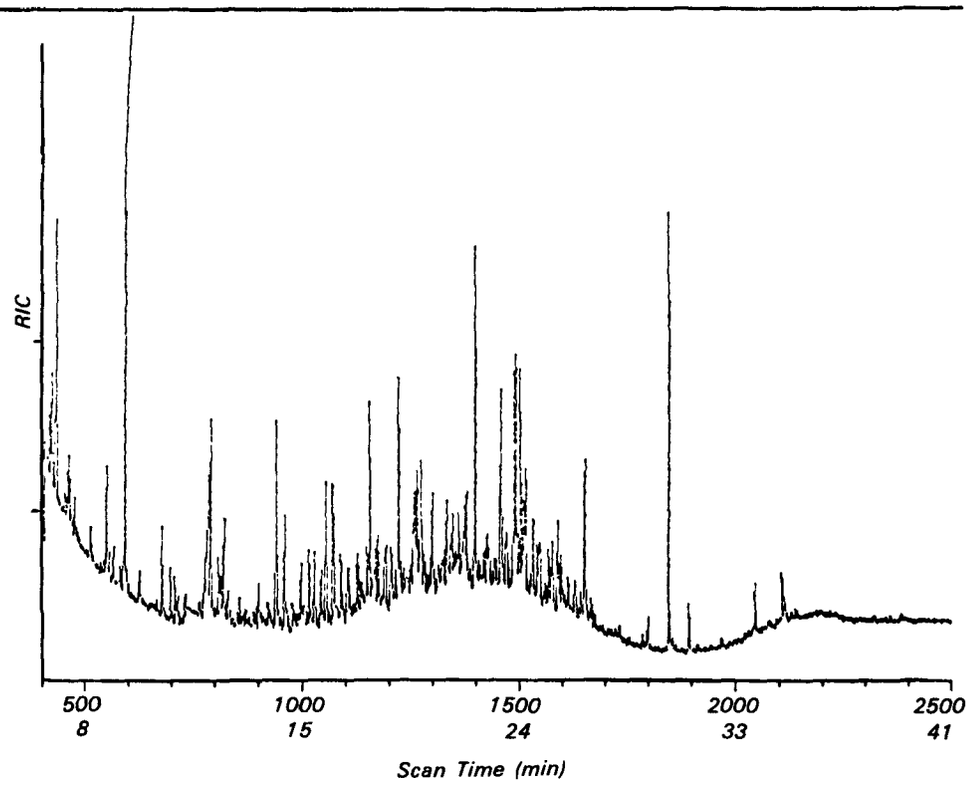

Figure 2. HRGC/MS chromatogram of vaporizing pot emission sample.

Volatile lead (alkyllead) compounds were analyzed by collecting cryogenic samples from the air atomization heater gas-phase discharges. High lead levels in engine waste oil probably arise from lead antiknocking agents added to gasoline. Analyzing volatile lead compounds in combustion emissions was important to determine if organolead compounds were stable in crankcase oil and subsequent combustion, or if ionic lead is converted to appreciable organometallic discharges during combustion. Figure 3 shows the cryogenic sampling train developed for this study. Samples were extracted with isooctane and analyzed by combined gas chromatography/atomic absorption spectrophotometry.

Metal species were analyzed by X-ray fluorescence (XRF) on filter samples of combustion gas from the air atomization heater, and also on raw crankcase oil samples. The XRF data were used to confirm the presence of metallic species that ostensibly arise from engine wear (e.g., Fe) and elements that are present in waste oil via contamination from fuel additives (e.g., Br). The fuel data also revealed comparative results for waste oil handling techniques; e.g., sedimentation and filtration.

Iron speciation was performed to determine which oxidation state (Fe[II] or Fe[III]) predominated in the air atomization discharges. Fe(II) was analyzed by photometric analysis of

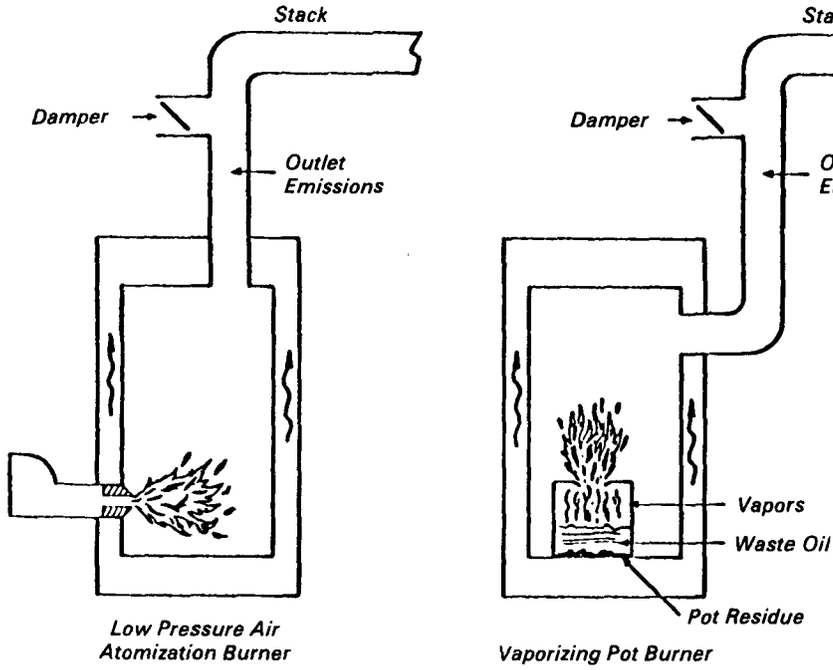

Figure 1. Test combustion systems.

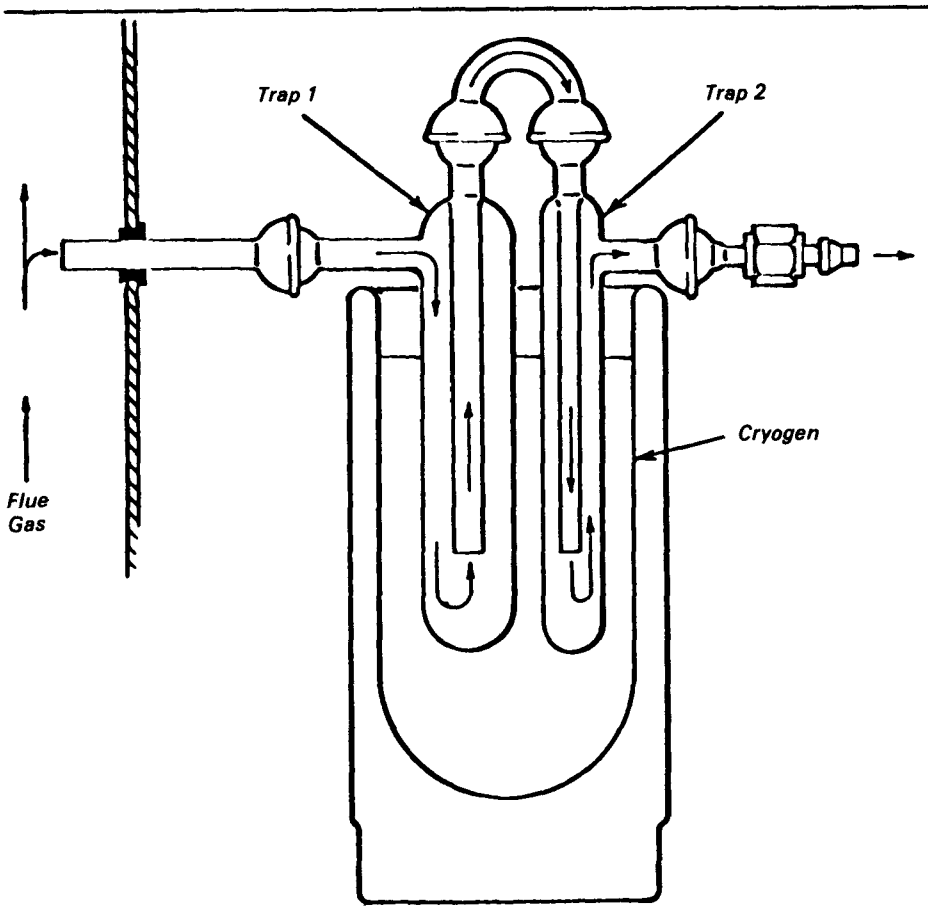

Figure 3. Cryogenic sampling train.

ferrous bathophenanthroline complex. Since ferric compounds and benzo(*a*)pyrene are known to produce a synergistic promotion of certain tumors, these two species were important to this study.

Conclusions

This study provided specific speciation data on major constituents indicated as being potentially harmful pollutants in the previous Level 1 analysis of vaporizing pot and air atomizer residential heater emissions. Conclusions of this study are summarized by chemical specie.

Polynuclear Aromatic Hydrocarbons

Several PAH compounds were found at elevated levels in the gas-phase emissions from the two combustion systems. As predicted from Level 1 data, the vaporizing pot system produced appreciably higher emissions than either the air atomizer heater or (based on literature estimates) residential heaters fired with commercial fuel oil.

Lead Species

No organolead species were detected in the cryogenic samples from the air atomization heater, indicating that lead exists essentially as Pb(II) in the air atomization emissions.

Metals/Halogens

X-ray fluorescence analysis of particulate emissions from the air atomization heater particulate matter confirmed the elevated Pb, Zn, and Fe found in earlier Level 1 analyses. In addition, high Br and Cl levels were found in gas-phase emissions. The Br level was several times the Cl level, indicating that Br from gasoline antiknocking additives exists as a major constituent of crankcase oil, and constitutes a major air contaminant from this source.

Fuel Studies

Filtration was shown to be effective for lowering metallic species (such as iron) in waste crankcase oil and should be a beneficial pretreatment procedure for this fuel. Settling by gravity over an extended period of time (11 months) had little or no effect on the level of metallic species in fuel obtained from the top of the tank.

Iron Speciation

The iron speciation tests indicated that most of the air atomizer iron emissions existed as Fe(III). This is a cause for great concern due to the presence of benzo(*a*) pyrene (BaP) in the PAH emissions. There is a documented synergistic effect between Fe(III) and BaP which promotes certain types of mammalian cancers and is believed to magnify the dangers associated with Fe(III) emissions.

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***Robert E. Hall** is the EPA Project Officer (see below).*
The complete report, entitled "Waste Crankcase Oil Heater Study: Phase II. Organic and Inorganic Speciation Analyses," (Order No. PB 84-212 224; Cost: $10.00, subject to change) will be available only from:
National Technical Information Service
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