

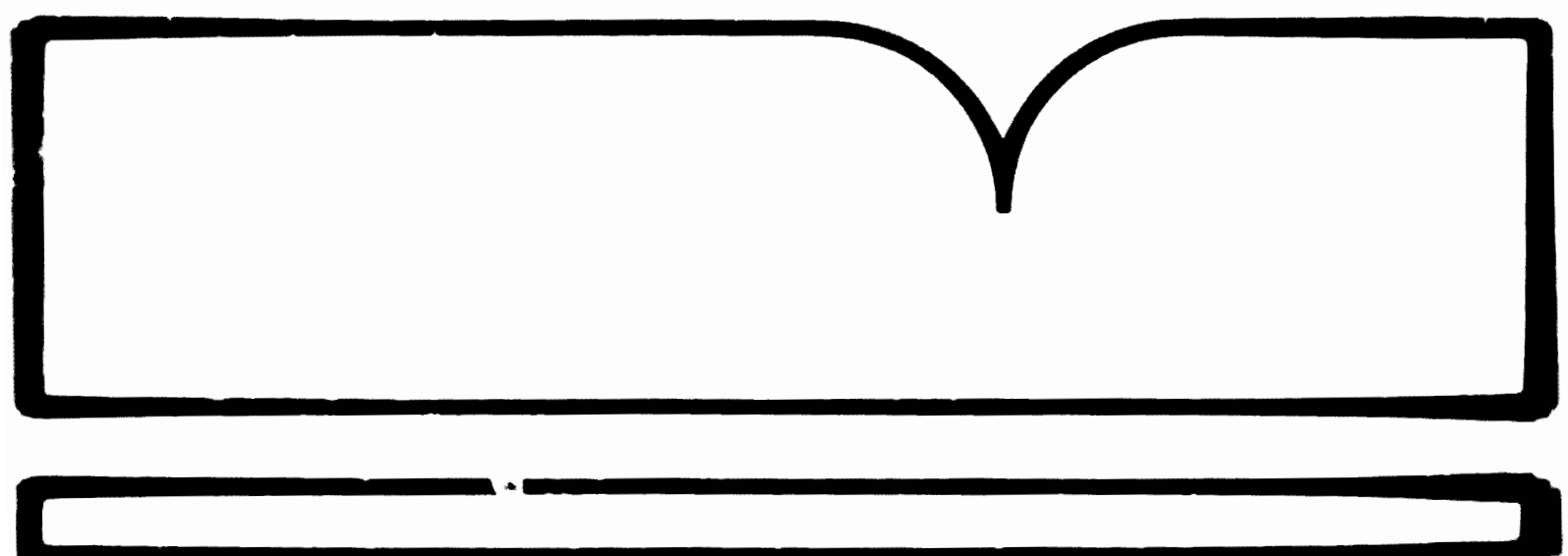
Waste Oil Heaters: Organic, Inorganic, and
Bioassay Analyses of Combustion Samples

Battelle Columbus Labs., OH

Prepared for

Industrial Environmental Research Lab.
Research Triangle Park, NC

May 84



**WASTE OIL HEATERS:
ORGANIC, INORGANIC, AND BIOASSAY
ANALYSES OF COMBUSTION SAMPLES**

by

**Marcus Cooke
Warren E. Bresler
Timothy L. Hayes**

**BATTELLE
Columbus Laboratories
Columbus, Ohio 43201**

**Robert E. Hall^{*}
Judy L. Mumford^{**}**

**U.S. ENVIRONMENTAL PROTECTION AGENCY
^{*} Industrial Environmental Research Laboratory
^{**} Health Effects Research Laboratory
Research Triangle Park, North Carolina 27711**

EPA Contract 68-02-1626

**INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711**

TECHNICAL REPORT DATA

(Please read instructions on the reverse before completing)

1 REPORT NO EPA-600/D-84-130		2		3 RECIPIENT'S ACCESSION NO NO 105346	
4 TITLE AND SUBTITLE Waste Oil Heaters: Organic, Inorganic, and Bioassay Analyses of Combustion Samples				5 REPORT DATE May 1984	
6 AUTHOR(S) M. Cooke, W.E. Bresler, and T.L. Hayes (Battelle); and R.E. Hall and J.L. Mumford* (EPA)				7 PERFORMING ORGANIZATION CODE	
8 PERFORMING ORGANIZATION NAME AND ADDRESS Battelle-Columbus Laboratories 505 King Ave. Columbus, OH 43201				9 PERFORMING ORGANIZATION REPORT NO	
12 SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711				10 PROGRAM ELEMENT NO	
				11 CONTRACT/GRANT NO 68-02-3628, Task 12	
				13 TYPE OF REPORT AND PERIOD COVERED Published paper; 9/82 - 3/84	
				14 SPONSORING AGENCY CODE EPA/600/13	
15 SUPPLEMENTARY NOTES					
16 ABSTRACT The paper describes tests on two typical designs of waste-oil space heaters, firing two different types of waste crankcase oils. Study results can be summarized according to the four substances investigated: particulates, polynuclear aromatic hydrocarbons (PAHs), organolead, and fuel samples. Analysis of samples from the air atomizing heater (AAH) confirmed previously identified elevated metal content of waste oil emissions. Bromine levels were exceptionally high. The ferrous ion (Fe(II)) content in particulate samples from the AAH was very low. Several PAHs were at elevated levels in gaseous emissions from both space heaters: the vaporizing pot heater (VPH) emissions had the higher PAH content. No organolead was detected in emissions from the AAH (organolead analyses were not performed on the VPH emissions). Mutagenicity assays of the particulate and the XAD samples from both heaters were mutagenic and contained direct-acting mutagens; emissions from the VPH were the more mutagenic. Comparison of the two types of fuels showed that emissions from the automobile waste crankcase oil were consistently more mutagenic than those from the truck waste crankcase oil.					
17 KEY WORDS AND DOCUMENT ANALYSIS					
5 DESCRIPTORS		6 IDENTIFIERS/OPEN ENDED TERMS		7 COSATI Term Group	
Pollution		Pollution Control		13B	
Vaporizing		Stationary Sources		11H	
Lubricating Oils		Waste Oil		21B	
Atomizing		Automotive Oil		13A	
Combustion		Air Atomizing Burners		06A	
Space Heaters		Vaporizing Pot Burners		21J	
Bioassay					
Crankcase					
18 DISTRIBUTION STATEMENT Release to Public				19 SECURITY CLASS (This Report) Unclassified	
				20 SECURITY CLASS (This page) Unclassified	

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

I. Introduction

In recent years federal, state, and local agencies have focused attention on emissions from the combustion of waste crankcase oil. Due to the sharp rise in the price of natural gas, fuel oil, and electricity, businesses that have an abundant supply of waste crankcase oil are using it for space heating in large areas, such as garages. Unfortunately, most waste crankcase oils contain large amounts of trace metals.

In order to obtain emissions data which could be used by concerned government agencies and industry, the U.S. Environmental Protection Agency's Office of Research and Development has sponsored tests on two typical designs of waste oil space heaters firing two different types of waste crankcase oils. The tests were performed by EPA's Industrial Environmental Research Laboratory in Research Triangle Park, NC.

II. Test Equipment and Fuels

Two types of waste oil heaters were tested while firing filtered, but otherwise untreated, waste crankcase oils. One was a Kroil Model W400L, waste oil heater rated at 35.2 kW (120,000 Btu/hr heat input). It uses a vaporizing pot burner in which only the heated vaporized fuel is combusted. With this type of burner the residue of unburned material, which accumulates in the bottom of the fuel pot, must be physically removed. This residue was also analyzed for organic and inorganic content. The second unit tested in this program was a Dravo Hastings Thermoflo Model 20-WO, waste oil heater rated at 73.3 kW (250,000 Btu/hr heat input), and it utilizes an air atomizing burner. With this type of burner, most of the fuel is burned and discharged as stack effluent.

Two different types of waste crankcase oils were tested during the Phase 1 study. One was an automotive waste crankcase oil that was obtained from a service station. The other was a truck crankcase oil that came from a diesel truck fleet. Since the emissions resulting from combustion of the automotive waste crankcase oil were higher, it was the only waste oil studied during the Phase 2 study.

III. Background

As a result of the Phase 1 tests (1,2), several trace metals were identified which were emitted into the atmosphere in high concentrations. It was found that burner design and fuel composition both have a significant effect on the levels of inorganic elements emitted. As shown in Figure 1, the air atomizing burner allowed high levels of trace elements to be carried by the flue gas into the stack. It also had particulate mass emission levels that were an order of magnitude higher than those of the

vaporizing pot burner. The vaporizing pot burner retained a significant amount of the trace elements in the pot residue. The study also showed that, even though total organic emissions from the two burners are similar, higher levels of polynuclear aromatic hydrocarbons (PAHs) were found in discharges of the vaporizing pot burner.

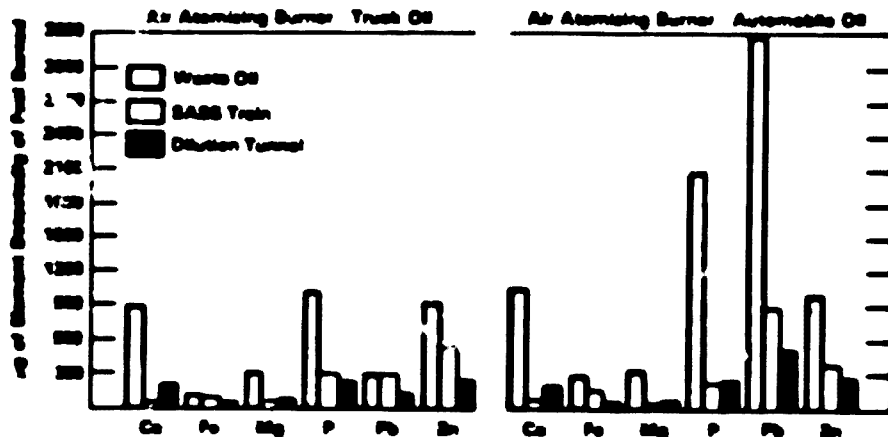


FIGURE 1 COMPARISON OF TOTAL MASS OF ELEMENTS DETERMINED BY ICAP FOR THE AIR ATOMIZING HEATER BURNING AUTOMOTIVE AND TRUCK CRANKCASE OIL.

As a result of the Phase 1 screening studies, it was decided that a Phase 2 follow-on study was needed to provide more information about specific chemical species in waste crankcase oil emissions. PAHs were analyzed in more detail, elemental analyses (including Pb, Fe, Cd, Zn, Cl, and Sr) were performed on the air atomization burner discharges, and analyses were conducted to measure possible organolead constituents and to determine the distribution of iron oxidation states (Fe(II) and Fe(III)).

In addition to the chemical analysis, a microbial mutagenicity assay was performed on the samples collected. The *Salmonella typhimurium* mutagenicity test developed by Ames et al. (3) has been widely used to evaluate the mutagenicity and potential carcinogenicity of pure chemicals and complex environmental samples. This assay detects substances that cause frameshift and base-pair substitution mutation in histidine-requiring mutants, that revert to prototrophy as a result of exposure to the mutagen. The Ames assay was used in this study to evaluate the potential carcinogenicity of the combustion products from the truck and automotive waste crankcase oils.

IV. Test Measurements

In addition, data were obtained for an EPA Level 1 assessment. This required the use of a glass Source Assessment Sampling System (SASS) train with subsequent data reduction by Battelle-Columbus Laboratories. The analysis included: spark source mass spectroscopy (SSMS) using an AEI Model MS-702R instrument to screen elemental constituents; inductively coupled argon plasma (ICAP) spectrometry using a Jarrell-Ash Model 975 instrument to analyze elemental species; and atomic absorption spectroscopy (AAS) using a Perkin-Elmer Model 5000 instrument to provide mercury (Hg), arsenic (As), and antimony (Sb) emissions data. Total chromatographable organic (TCO) analyses, gravimetric (GRAV) analyses, infrared (IR) analyses, and low resolution mass spectroscopic (LRMS) analyses were performed to obtain information about organic emissions.

A slipstream of the stack effluent was ducted into a dilution tunnel where a flow of filtered dilution air was allowed to mix with the heater discharge at a ratio of 10:1. The dilution tunnel effluent was collected in a Massive Air Volume Sampler (MAVS). The MAVS is a device normally used for ambient air sampling. It contains Teflon-coated metal plates which act as an electrostatic precipitator (ESP). This allows large amounts of particulate to be collected which can be easily removed for chemical and bioassay analysis. The dilution tunnel simulates the dilution and mixing that would occur if the flue gas were discharged directly into the environment. Organic bioassay samples used in this study were collected on a 51 cm x 51 cm (20 in. x 20 in.) Teflon-coated Paliflex filter.

The sampling conditions for the two stack effluent samplers (SASS train and dilution tunnel) are given in Table I for both types of waste oil heaters firing the automotive and truck waste crankcase oil fuels.

A comparison of total organic material collected in the Level 1 study is shown in Figure 2 where both burner types are compared for the two sampling strategies, SASS train and dilution tunnel.

The objective of the Phase 2 study was to perform detailed investigations on waste oil emission species identified or suspected from Level 1 data generated in the earlier program. The experimental portion of this study consisted of five parts:

- (1) Analysis of PAHs in gaseous emissions from a vaporizing pot heater (Kroll) and an air atomization combustion system (Dravo)
- (2) X-ray fluorescence analysis of inorganic species, including Br, I, Fe, Cd, Pb, and Zn, in particulate discharges from the air atomization heater.
- (3) Analysis of the Fe(II)/Fe(III) ratio in the air atomization gaseous effluent.

TABLE I SAMPLING DATA

Sampling Condition	Vaporizing Burner		Air Atomizing Burner	
	Automotive	Truck	Automotive	Truck
Average stack temperature, °C (°F)	414 (777)	416 (781)	339 (642)	332 (630)
Alnor reading, m/min (ft/min) at stack conditions	129 (424)	126 (412)	84 (275)	88 (288)
Stack diameter, cm (in.)	15.2 (5.98)	15.2 (5.98)	22.9 (9.02)	22.9 (9.02)
Total volume sampled, SASS, m ³ (ft ³)	30 (1060)	32 (1100)	15 (530)	29 (1020)
Total volume sampled, dilution tunnel, m ³ (ft ³)	126 (4450)	80 (2800)	77 (2700)	117 (4130)
Volumetric flow rate (Q) at STP (20°C, 1 atm.), m ³ /sec (ft ³ /sec)	0.015 (0.53)	0.014 (0.49)	0.024 (0.85)	0.024 (0.85)
Fuel feed rate, l/hr (gal/hr)	2.5 (0.66)	2.5 (0.65)	5.91 (1.56)	5.91 (1.56)

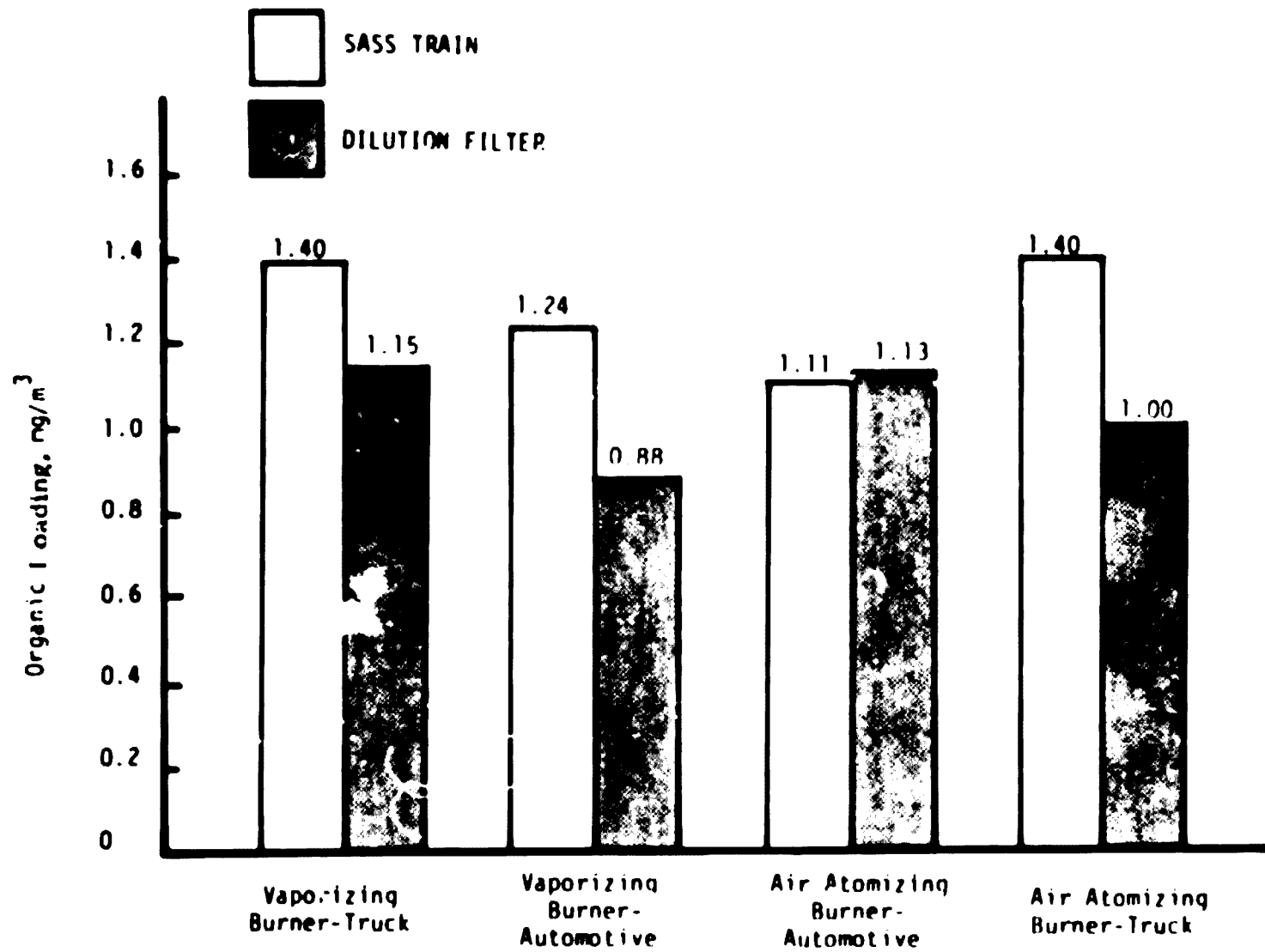


FIGURE 2. COMPARISON OF TOTAL ORGANICS FOR EACH TEST RUN SAMPLED BY SASS TRAIN AND DILUTION TUNNEL.

- (4) Analysis of air atomization gaseous discharges for organolead composition.
- (5) Detailed bioassay analyses of the SASS and dilution tunnel samples collected in the Level 1 study.

To complete the speciation measurements outlined above, two special sampling systems were used to collect suitable samples. A Modified Method 5 train (MM5), shown in figure 3, was used to collect the samples for PAH and metals analysis. MM5 samples were collected for both air atomization and vaporizing pot burners in order to measure PAH emission levels. Metals speciation tests were performed only in the air atomization tests since Level 1 data revealed elevated metal discharges from air atomization burning.

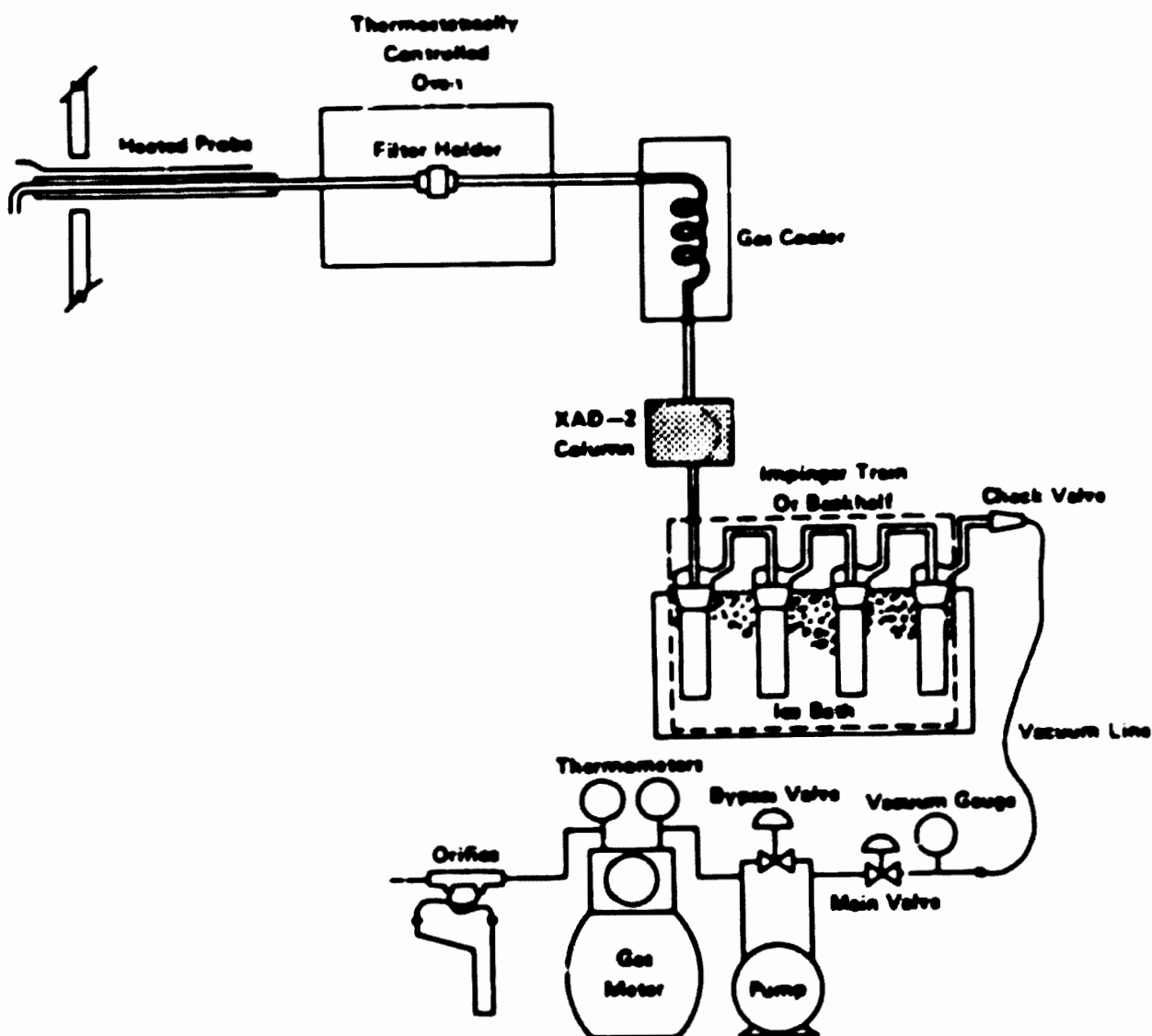


FIGURE 3. THE MODIFIED METHOD 5 (MM5) TRAIN.

The sampling conditions used for the vaporizing pot PM10 samples are given in Table II, while the air atomization PM10 sampling conditions are given in Table III.

The organolead samples required development of a cryogenic sampling system designed to condense the large amount of water found in a combustion source. Several designs tested would trap a plug of ice, thus closing off the flow stream. The cryogenic sampler used in this study is shown schematically in Figure 4 and is fully discussed in the EPA report describing this study (4).

V. Analytical Methods

Particulate Emissions

The substances of interest in the analysis of the PM10 particulate filter samples were those species which had been detected in the Phase I study at relatively high levels in waste oil combustion emissions: iodine (I), cadmium (Cd), iron (Fe), zinc (Zn), lead (Pb), chlorine (Cl), and bromine (Br). Since iron was identified as one of the predominant metallic elements in waste oil combustion emissions, an attempt was made to identify the relative amounts of the Fe species in the particulate emission samples. Consequently, two analyses were conducted on the PM10 particulate samples: X-ray fluorescence analysis of the seven elemental species of interest and a ferrous ion (Fe(II)) determination to allow a calculation of the Fe(II)/Fe(III) ratio in the emissions.

X-Ray Fluorescence Analyses--

X-ray fluorescence analyses were performed on three PM10 filter catches from the air atomization heater tests. Two of the filter samples, designated No. 3 and No. 5, were partial runs with weights of 0.6527 g and 0.5932 g, while No. 6 represented a complete test run and had a net weight of 0.8719 g. The analyses were conducted with a Kevex Energy Dispersive X-ray Analyzer. This instrument possesses the capability of a computer-controlled fundamental parameter program to obtain quantitative results.

Ferrous Ion Analysis--

The ferrous ion (Fe(II)) content of the three air atomization PM10 filter samples was determined using a bathophenanthroline photometric method. The principle of the method is based on the formation of ferrous bathophenanthroline complex in a solution buffered at pH 5 with subsequent extraction in chloroform. The absorbance of the complex at 533 nm was used to estimate the ferrous ion content from a previously prepared calibration curve. The calibration curve was constructed using ferrous ammonium sulfate as a standard. The filter samples were prepared by weighing the filter and

TABLE II. TEST CONDITIONS FOR VAPORIZING
POT COMBUSTION EXPERIMENTS

	Run 1		Run 2	
Barometric pressure, MPa (in. Hg)	0.102	(30.2)	0.102	(30.1)
Stack temperature, °C (°F)	411	(711)	419	(786)
Stack velocity, m/sec (ft/sec)	3.7	(12.2)	3.7	(12.2)
Meter temperature, °C (°F)	38	(101)	40	(104)
Isokinetic variation, %	112.7		109.7	
Corrected dry volume, scm (scf)	3.6	(126)	4.0	(143)
Moisture volume, scm (scf)	0.29	(10.4)	0.31	(11.1)
Flue gas composition				
H ₂ O, %	7.7		7.2	
CO ₂ , %	7.3		7.0	
O ₂ , %	11.7		11.8	
CO, ppm (v/v)	10		10	
Calculated molecular weight	28.67		28.87	
Auto crankcase oil used, l (gal)	15	(4)	14	(3.7)
Test time, minutes	280		330	
Rate, l/hr (gal/hr)	3.2	(0.85)	2.5	(0.66)
Pot residue, g	290		310	
Residue deposition rate				
g/cc	0.0193		0.0222	
g/min	1.03		0.94	
Average ΔP @ orifice plate, Pa (in. H ₂ O)	158	(0.635)	175	(0.703)

TABLE III. TEST CONDITIONS FOR AIR ATOMIZATION
COMBUSTION EXPERIMENTS

	Run 1		Run 2	
Barometric pressure, MPa (in. Hg)	0.102	(30.2)	0.102	(30.1)
Inlet temperature, °C (°F)	266	(511)	266	(511)
Velocity, m/sec (ft/sec)	1.4	(4.6)	1.4	(4.6)
Meter temperature, °C (°F)	40	(104)	40	(104)
Isokinetic variation, %	657		361	
Corrected dry volume, scm (scf)	4.3	(151)	3.3	(117)
Moisture volume, scm (scf)	0.40	(14)	0.34	(12)
Flue gas composition				
H ₂ O, %	8.3		9.3	
CO ₂ , %	10-11		10-11	
O ₂ , %	6.8		6.8	
CO, ppm (v/v)	50		50	
Calculated molecular weight	28.36		28.24	
Auto crankcase oil used, l (gal)	22	(5.81)	31	(3.21)
Test time, minutes	220		311	
Rate, l/hr (gal/hr)	7.3	(1.6)	7.3	(1.6)
Average ΔP @ orifice plate, Pa (in. H ₂ O)	520	(2.1)	92	(0.37)

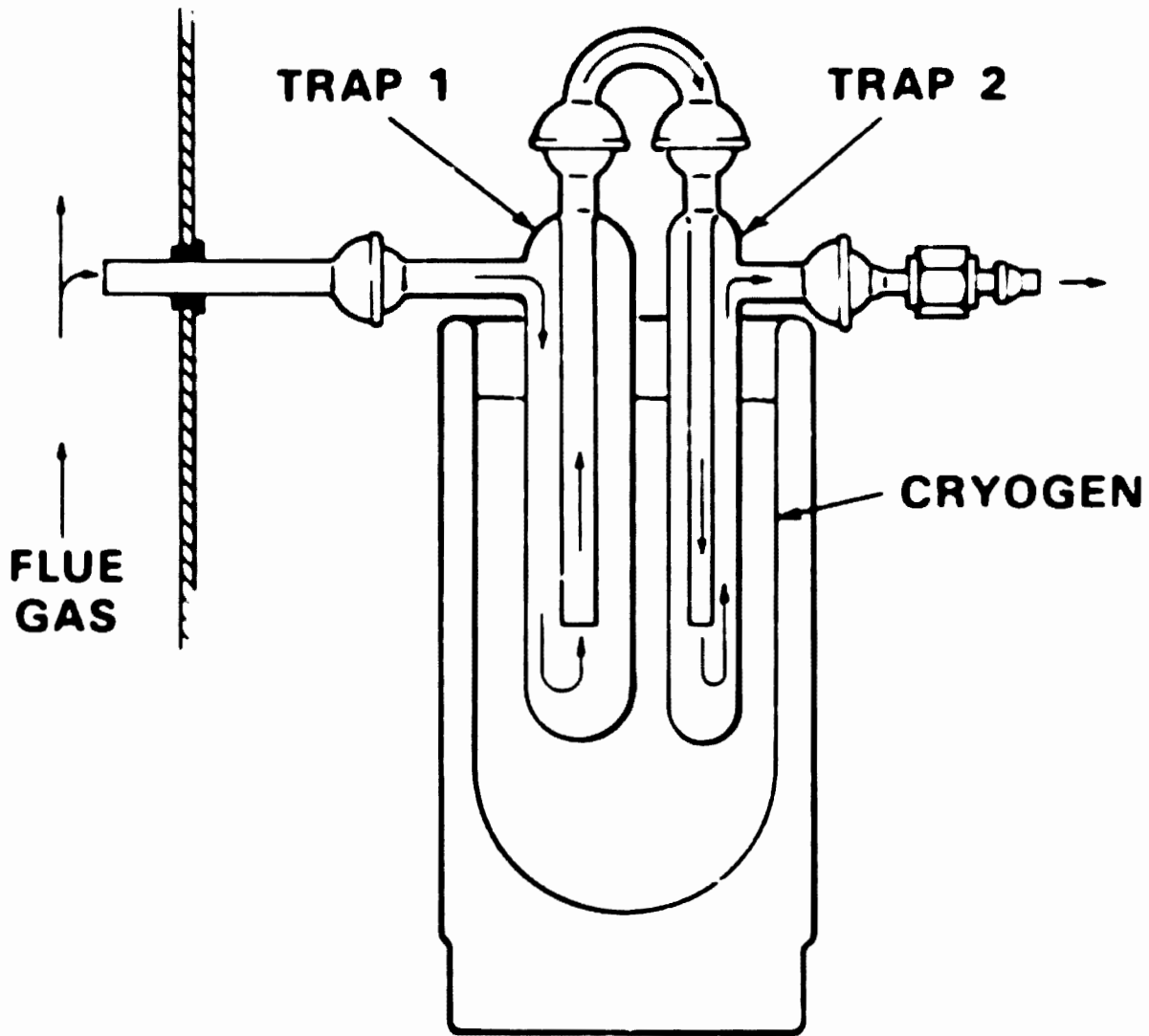


FIGURE 4. CRYOGENIC SAMPLING TRAIN FOR COLLECTING VOLATILE ORGANOLEAD EMISSIONS.

digesting the sample in 50 ml of 5% HCl under a CO₂ atmosphere. The cooled solution was diluted to 100 ml, from which a 20 ml aliquot was treated with the bathophenanthroline reagent.

PAH Emissions

The four MMS train samples collected in the combustion tests were analyzed for PAH by high resolution gas chromatography mass spectrometry (HRGC/MS). To prepare for this analysis, the XAD-2 resin sample was extracted with methylene chloride, along with the particulate-laden filter, in a Soxhlet extractor. The filter was re-extracted separately with benzene to remove PAH compounds not extracted by methylene chloride. The resin-filter extract was combined with the extracts of the aqueous impinger. This combined sample, which contained most of the organic burden, was analyzed by gas chromatography and gravimetry to determine condensible organics. The combined organics sample and the benzene filter extract were then combined and reduced to about 1 ml with a Kuderna-Danish concentrator, and to a final volume of 0.5 ml by directing a gentle stream of nitrogen across the top of the sample. An internal standard was spiked into the sample at this point before analyses by HRGC/MS.

Organolead Compounds

As with the sampling system for organolead compounds, an analytical method had to be developed for the determination of these compounds. Lead alkyls are a common fuel additive, used as an antiknocking ingredient in gasoline. The principal species used commercially are the methyl and ethyl substituents, predominantly tetramethyl (TML), trimethylethyl (TMEL), dimethyldiethyl (DMDEL), methyltriethyl (MTEL), and tetraethyl (TEL) lead.

The method most commonly used to measure alkyl lead compounds is gas chromatography (GC) coupled to an atomic absorption spectrometer (AAS) (5). The AAS acts as a sensitive detector for lead. Radziuk *et al.* used cryogenic sampling and GC/AAS to measure ambient alkyl lead with a graphite furnace technique to demonstrate instrument sensitivity of 40 pg Pb, which corresponded to about 0.5 ng/m³ in a 70 liter air sample (6). After experimenting with the GC/AAS interfaces proposed in the literature, a modification was used in this study which improved instrument sensitivity for direct flame atomization. This modified interface consisted of a 0.3 cm (1/8 in.) (O.D.), stainless steel GC tube mounted directly into the base of the AAS burner and attached to the GC column. The effluent from the GC column is passed through this tube and the entire effluent uniformly aspirated across the flame front.

The GC/AAS system used was a Varian Model 1400 GC interfaced to a Perkin Elmer Model 5000 AAS. The GC was equipped with a 0.9 m (3 ft) x 0.64 cm (0.25 in.) (O.D.) stainless steel column packed with 10% (W/W) Carbowax 20M on 100/120 mesh Porasil C. The column was held isothermal at 130°C and helium (120 ml/min) was the carrier gas. The reference standard

used for calibration was provided by the Ethyl Corporation (MLA-500(T313)) and contained 1.53 mg Pb per ml of solution in isooctane. The concentrations, retention times, and estimated detection limits for the individual tetraalkyl lead species in the reference mixture are given in Table IV.

TABLE IV. ALKYL LEAD REFERENCE MIXTURE -
MLA-500(T313)

Compound	Concentration, $\mu\text{g/ml}$	Retention Time, min.	Detection Limit, ng
TPL	114	0.61	11
TNEL	336	0.78	22
DMDEL	548	1.17	30
MTEL	408	1.78	47
TEL	123	3.00	81

Chromatograms showing the separation and rapid elution (<4 min) capabilities of the GC/AAS system are shown in Figure 5. The upper chromatogram shows a 50 μl injection representing 5.7-27.4 μg of the alkyl lead compounds. The lower chromatogram shows a 5 μl injection representing 0.6-2.7 μg of each compound. At high sample loading on the GC column, as shown in the upper chromatogram, TPL and TNEL show overlap and loss of resolution. Resolution is restored by reducing the amount of sample analyzed.

VI. Mutagenicity Bioassay Method

The fuel and organic extracts of the SASS samples (XAD only), and the filter samples from the dilution tunnel, for combustion of automotive and truck waste crankcase oils, using both atomizing and vaporizing burners were bioassayed for mutagenicity (7). The standard Salmonella typhimurium plate incorporation assay with minor modifications (3,8) was performed. The filter and resin samples were Soxhlet extracted with dichloromethane for 24 hours. The extract was then solvent-exchanged into dimethyl sulfoxide (DMSO). The organic extracts and the DMSO slurry of the waste oils were

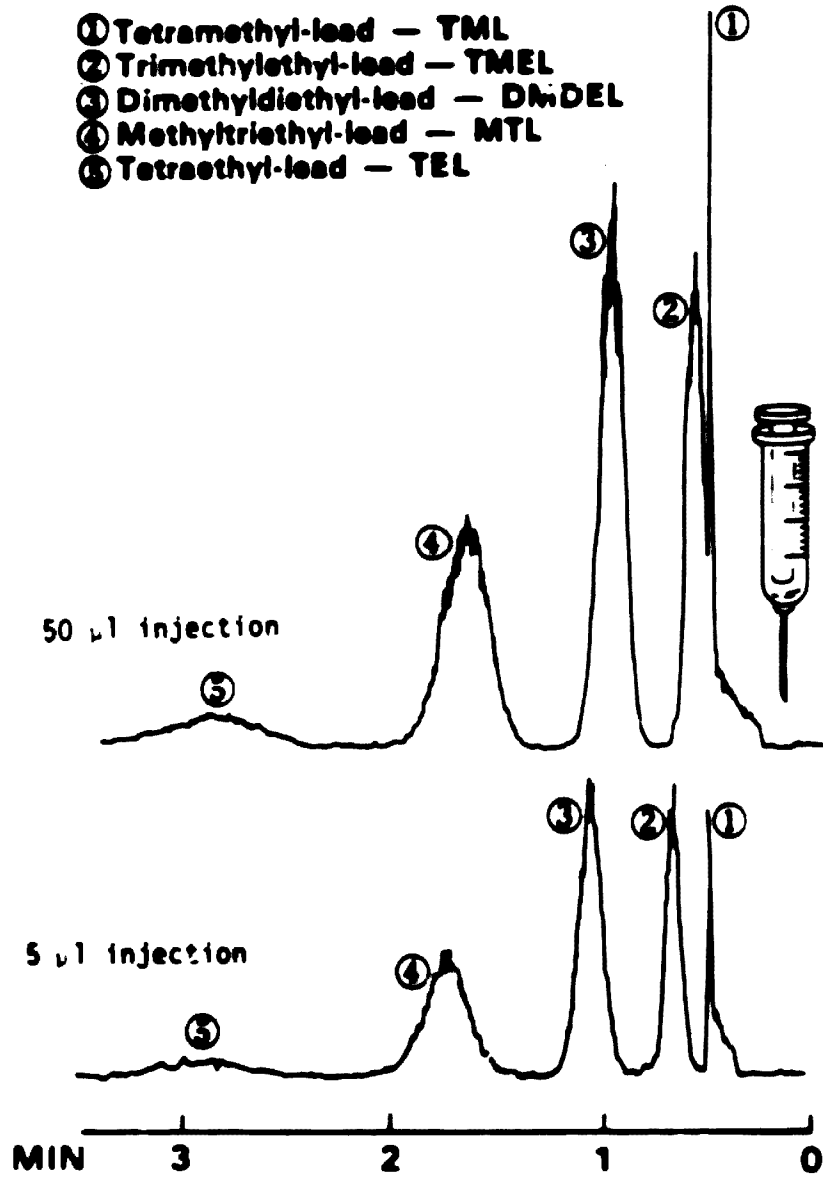


FIGURE 5. CHROMATOGRAMS OF TETRAALKYL LEAD COMPOUNDS IN THE GC/AAS SYSTEM.

tested, with and without S9 metabolic activation (the Aroclor-induced rat liver 9000 x g homogenate) in *Salmonella typhimurium* tester strain TA98. The data were analyzed using the nonlinear model to determine the slope of the dose response curve (9).

VII. Results

Organolead Compounds

Analysis of cryogenic samples from the air atomization burner tests indicated that no organolead compounds were present in the emissions. Since alkyl lead species are most likely not formed in the combustion conditions found in burning waste crankcase oil in the air atomizer combustor, the presence of these compounds would be an indication of unburned organolead additives in the waste oil fuel. To determine if organolead compounds were present in the crankcase oil used to fuel the air atomization burner, the waste oil was analyzed directly with the GC/AAS system and produced no measurable alkyl lead signal. The fuel oil then was spiked with a known addition of the Ethyl Reference Standard and analyzed by direct injection onto the GC/AAS analytical system. The chromatogram from that analysis is given in Figure 6. This chromatogram shows measurable peaks (except for TEL) near the detection limit.

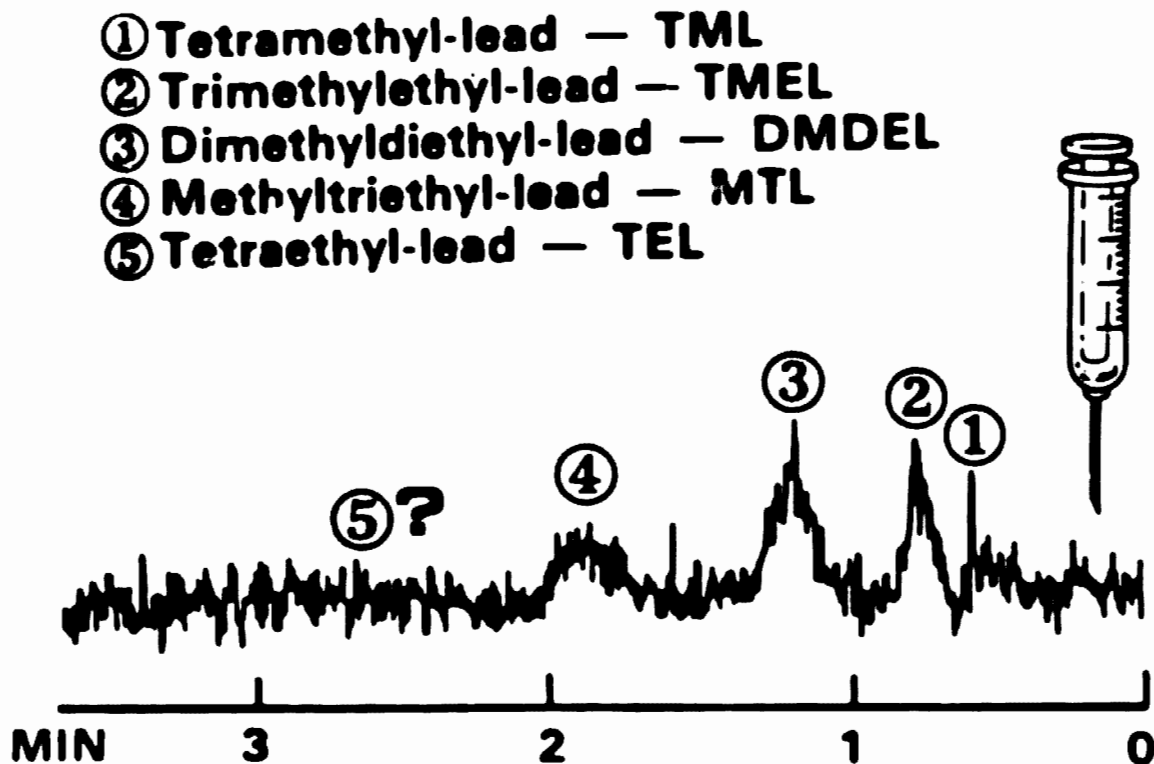


FIGURE 6. GC/AAS CHROMATOGRAM OF THE SPIKED WASTE OIL FUEL BY DIRECT INJECTION.

If organolead compounds were present in the fuel, they would be at extremely low levels. From the GC/AAS method detection limits cited earlier, this method should measure approximately 20 $\mu\text{g TML}/\text{m}^3$ in flue gas emissions and about 25 $\text{mg TML}/\text{l}$ in the waste oil fuel. From the previous Level 1 analysis of air atomization burners using the same automobile crankcase oil for fuel (1), a flue gas lead concentration of 140 mg/m^3 and a waste oil concentration of about 3 g/l were found. These concentrations, total lead in waste oil fuel and flue gas discharge, are far above the demonstrated method detection limits for the GC/AAS method. If lead were appreciably present in an organometallic form in these samples, it should be measurable. These data indicate that organolead compounds could be only a minor constituent of the air atomizer discharges measured in this study. No organolead analyses were made on vaporizing pot burner emissions.

Organolead compounds have been estimated to be a small percentage (0.1-14%) of total ambient lead (10-12). Radziuk *et al.* (6) found that tail-pipe emissions of alkyl lead are a minor fraction of ambient organolead levels. Volatile lead compounds in the ambient air arose from vaporization of gasoline and volatile lead losses from liquid fuels, not from combustion in internal combustion engines. The same effect would be expected from waste oil combustion. Waste crankcase oil combustion should be of minor concern for producing organolead emissions in the ambient air.

Ferrous Ion Analyses

The results of the analysis of the ferrous ion (Fe(II)) content in the MM5 particulate samples from the air atomization heater are given in Table V.

TABLE V. FERROUS ION CONTENT OF FILTER SAMPLES

Sample Number	Total Filter Weight, g	Fe(II) Content		Total Fe Content, ^a μg
		Total μg	$\mu\text{g}/\text{g}$ (ppm)	
3	0.6527	62	95	11,900
5	0.5932	52	88	9,100
6	0.8719	74	85	19,200

a As determined by X-ray fluorescence

These data indicate that Fe(II) is present at relatively insignificant levels in emissions from the air atomization heater fueled with automotive waste oil. Comparison of Fe(II) data with the X-ray fluorescence results for total Fe content shows that Fe(II) constitutes only a minor portion of the Fe content in these emissions. Since iron is expected to be converted primarily to ionic forms in combustion processes, an assumption can be made that only a relatively small amount of iron will be in the elemental state. Consequently, the amount of Fe(III) in the sample can be estimated by subtracting the Fe(II) content from the total Fe content. The resulting values for Fe(III) are relatively large, and the Fe(II)/Fe(III) ratios would, therefore, be small. The predominant form of Fe in the waste oil combustion emissions is, therefore, Fe(III).

PAH Emissions

PAH emissions are of concern since several members of this class of organic compounds are considered to be mammalian carcinogens. The results of PAH analyses are presented in Table VI. In general, the vaporizing pot samples showed higher concentrations of individual PAH species than the air atomization samples. Since Runs 1 and 2 were intended to be duplicates, and were very similar in test conditions and sampling parameters, the observed test-to-test differences reflect the variability of these data.

The data in Table VI are corrected for a system blank analysis, but are not corrected for method recoveries. Method losses were estimated by the technique of labeled isotope addition. In this method, a known amount of an atomic isotope of the compounds analyzed is spiked into the PM5 train after sampling. The recovery standard in this analysis was benzo(a)pyrene (BaP-d₁₂). These spikes were administered by liquid injection of 40 µg BaP-d₁₂ in benzene solution onto the XAD-2 resin. Quantitative (approximately 100%) recoveries were found for the BaP-d₁₂ spikes.

The complexity of the waste oil combustion discharges is illustrated by the total ion chromatogram of the air atomization sample shown in Figure 7. This chromatogram represents a simpler peak pattern where extracted ion chromatography is used to improve analytical sensitivity.

Salmonella Mutagenicity Assay

The uncombusted automotive oil showed low mutagenicity (0.09 revertants/µg with exogenous activation and 0.03 revertants/µg without activation in strain TA98) and the truck oil showed no mutagenic activity. The emissions from both burner types using automotive and truck oils were mutagenic and contained direct-acting mutagens. In comparison with other combustion emissions and based on revertants/µg organics, the mutagenicity of the organics extracted from the particles from waste oil combustion was comparable to or more mutagenic than the organics of the particles emitted from a residential wood stove, but

TABLE VI. RESULTS OF PAH ANALYSES

Compound	Amount Detected, $\mu\text{g}/\text{m}^3$ dry			
	VP-Run 1 ^a	VP-Run 2 ^a	AA-Run 1 ^a	AA-Run 2 ^a
Naphthalene	12	6	5	4
Acenaphthene	--	--	0.3	0.2
Acenaphthylene	2	--	--	--
Fluorene	6	0.6	0.8	0.7
Phenanthrene	70 ^b	5	6	4
Anthracene	--	2	0.2	0.2
Fluoranthene	--	--	0.4	0.5
Pyrene	3	2	0.5	0.5
Benzo(a)anthracene	--	4	0.2	0.4
Chrysene	--	--	0.2	0.4
Benzofluoranthenes	--	6	--	--
Benzo(e)pyrene	5	6	--	0.05
Benzo(a)pyrene	6	8	--	1
Perylene	--	6	--	0.6
Indeno(1,2,3-cd)pyrene	--	--	--	0.8
Benzo(ghi)perylene	--	--	0.1	0.6
Anthanthrene	--	--	0.1	1.1
Coronene	--	--	--	0.1

^a VP = Vaporizing Pot Sample; AA = Air Atomization Heater Sample

^b This apparent high result was verified by fragment ion patterns and appears to be an outlier.

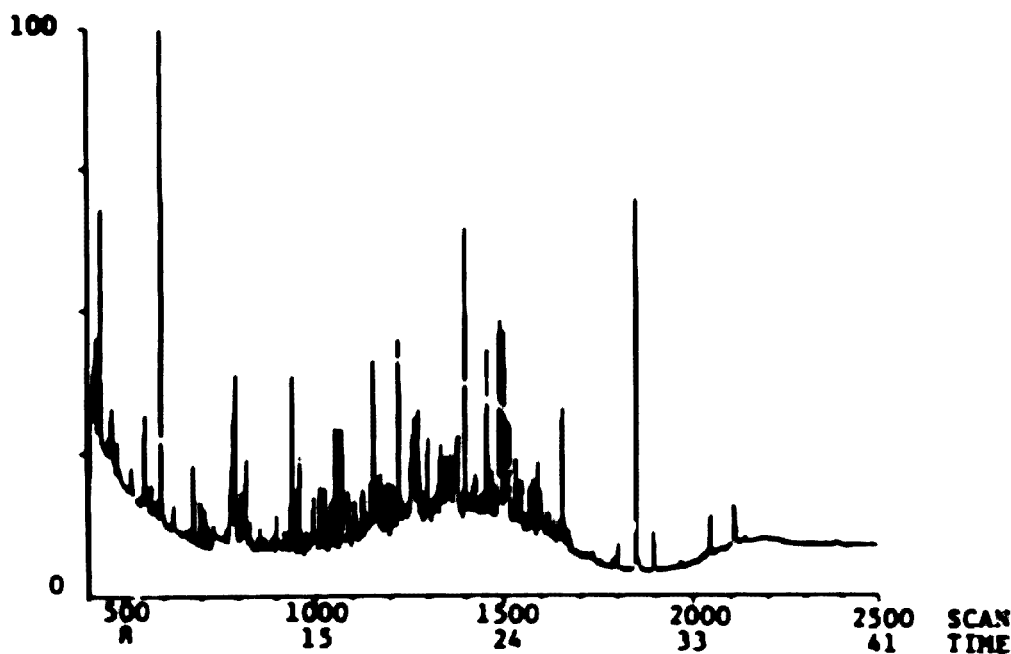


FIGURE 7. HRGC/MS TOTAL ION CHROMATOGRAM OF A VAPORIZING POT SAMPLE.

less mutagenic than from many diesel engine exhausts or a residential oil heater (13). In order to calculate the mutagenic emission rate, the mutagenicity of the organic extracts (revertants/ μg) was multiplied by the organic emission rate ($\mu\text{g}/\text{m}^3$). Figure 8 shows the mutagenic emission rate of the SASS XAD and the dilution tube samples from waste oil combustion in *Salmonella typhimurium* TA98 with and without metabolic activation. Comparison of the two types of fuels used shows that the emissions from automotive oil combustion were consistently more mutagenic than the emissions from truck oil combustion. Within the same type of fuel, either automotive or truck oil, the emissions from the vaporizing burner were more mutagenic than the emissions from the atomizing burner.

VIII. Discussion

The results from this study can be summarized according to the four substances investigated: particulate emissions, PAH emissions, organolead compounds, and fuel samples.