



Project Summary

Environmental Characterization of Disposal of Waste Oils by Combustion in Small Commercial Boilers

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In this project, air emission tests were conducted on seven boilers in the size range 0.4 to 15×10^6 Btu/hr while these boilers were firing waste oil. The main purpose of the project was to document the extent to which chemical contaminants in waste oil are destroyed during the combustion process. These data are of interest because one of the more common and widespread practices for disposing of waste oils is burning as a supplemental fuel.

Chemicals which were spiked into the waste oil before combustion included: chloroform, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, trichlorobenzene, 1-chloronaphthalene, 2,4,5-trichlorophenol, and chlorotoluene. Destruction efficiencies ranged from 99.4 to 99.99 percent. Concentrations of these chlorinated hydrocarbons in the flue gas ranged from 40 to $400 \mu\text{g}/\text{m}^3$. The concentrations of lead and zinc in the flue gas ranged between 5,000 and $72,000 \mu\text{g}/\text{m}^3$ and 3,000 and $34,000 \mu\text{g}/\text{m}^3$, respectively. The average emission rate of HCl from the seven boilers was 2.6 lb/hr.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Cincinnati, OH, 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).

Purpose and Scope of the Project

In recent years the environmental impact of the disposal of used oils has been a growing concern. Numerous studies conducted by state and Federal agencies have documented the presence of contaminants such as polynuclear aromatics (PNAs), chlorinated hydrocarbons and heavy metals in samples of used motor oils. One of the more common and widespread practices for disposing of used oils is burning as a supplemental fuel. In some cases, waste oil is burned directly; in others, it is blended with other fuel feedstocks.

The disposal of waste materials in boilers is of particular interest because to date, there has been little documentation of the extent to which chemical contaminants in waste oil are destroyed during the combustion process.

In this project, tests were conducted on boilers in the size range of 0.4 to 25×10^6 Btu/hr. These are commonly classified as commercial sources, as opposed to industrial or electric utility sources. Commercial boilers are of particular interest with regard to waste oil disposal for several reasons. These units generally would use untreated or poorly characterized waste fuels. They could be expected to provide less efficient combustion because of the generally intermittent mode of operation. In addition, their widespread distribution and their low stack heights makes their emissions more proximate to the general population.

Seven boilers were designated for testing in the program. The units were selected so as to provide a representative cross section of the commercial boiler population. A 4000-gallon lot of used automotive oil was obtained in order to maintain a consistent supply of waste fuel for the program. Portions of the base stock oil were spiked with predetermined amounts of selected organic compounds which are typically found in waste oil and in some cases are considered hazardous waste materials. The selected compounds were chloroform, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, trichlorobenzene, 1-chloronaphthalene, 2,4,5-trichlorophenol, and chlorotoluene.

Table 1 shows data comparing a typical spiked waste oil feed in this project with data from a cross section of representative waste oils.

Measurements were conducted at each of the sites to determine the atmospheric emissions of particulate, inorganic compounds (principally lead and HCl), and volatile organic and semivolatile organic material. The destruction and removal efficiencies (DRE) for each of the spiked components were also determined. A listing of the boilers and a summary of the tests conducted at each site are presented in Table 2.

Test Results

Destruction and Removal Efficiencies

In general, the data of the principal atmospheric emissions indicate that the emission rates of the principal inorganic components, lead and HCl, were substantially higher than the organic emissions from the six boilers tested. The average particulate emissions for the six boilers tested was determined to be 0.7 lb/hr (0.3 lb/10⁶ Btu heat input). Combustion efficiencies, calculated for each of the boilers, ranged from 99 to greater than 99.9 percent.

The flue gas emissions of the organic compounds of interest correspond to destruction and removal efficiencies of 99.4 to 99.99 percent as indicated in Table 3. There were no strong correlations between destruction efficiency and boiler size or firing technique. One trend that is apparent from the data is that the destruction efficiencies for the semivolatile compounds are consistently higher than those of the volatile compounds. The fact that generally higher DREs were achieved for the semivolatile components, trichloroben-

Table 1. Concentrations of Selected Contaminants in 24 Representative Waste Oils—Compared With a Typical Spiked Oil Used in This Project

Contaminant	Concentration (μg/g)		
	Representative oils ^a		Typical "spiked oil," (this project)
	Average	Range	
<i>Elements</i>			
Aluminum	45	1-640	10.2
Arsenic	12	<1-100	14.0
Barium	66	10-160	59.5
Cadmium	1	<1-2.8	2.2
Chlorine	2260 ^b	50-27,000	12,000
Chromium	6	<1-37	7.1
Iron	240	60-980	168
Lead	1100	350-2060	1,520
Magnesium	260	5-590	200
Vanadium	3	<1-13	2.2
Zinc	800	90-1550	743
<i>Volatile Organics</i>			
Trichlorotrifluoroethanes	410	<20-1900	—
1,1,1-trichloroethane	700 ^b	<20-14,800	3,500
Trichloroethylene	600	<20-4900	50
Tetrachloroethylene	400 ^b	<20-13,000	3,100
Toluene	3100	380-12,000	2,800
Chloroform	—	—	2,500
<i>Semivolatile Organics</i>			
Phenol	25	<5-70	10
2,4,6-trichlorophenol	<5	<5-<10	1,000
N-nitrosodiphenylamine	<5	<5-<10	<10
Benz(a)anthracene	20	<5-40	16
Benzo(a)pyrene	<5	<5-30	—
4,4'-DDE	<5	<5-<10	—
PCBs	<5	<0.1-65	<6
Trichlorobenzene	—	—	1,800
1-chloronaphthalene	—	—	1,500

^aTaken from U.S. DOE Report. No. DOE/BC/10375-6, Oct. 1983.

^bAverage value does not include maximum value shown in range.

—Denotes data not available or not investigated.

zene, 1-chloronaphthalene and trichlorophenol, is consistent with the ranking of the spike compounds on the EPA Hierarchy of Waste Incinerability.

Generally the lowest DREs were found in site A, the only boiler rated at less than 1 x 10⁶ Btu/hr. This unit normally fires a No. 2 fuel oil and its adaption to firing waste oil proved difficult. Eventually dilution of the waste oil on a 1:1 basis with No. 2 oil was required for acceptable operation. Even with this modification, the combustion efficiency and destruction efficiencies were significantly lower than the other units.

Concentrations of Contaminants in Combustion Gases

The concentration ranges in the stack gas of the compounds studied within the program are given in the full report.

In general, concentrations ranged from 40 to 400 μg/m³ for the volatile compounds and from about 10 to 50 μg/m³ for the semivolatile compounds. On a volume/volume (v/v) basis, these are very low concentrations. As an example, a range of 40 to 400 μg/m³ for a compound such as trichloroethylene corresponds to a concentration of 7.4 to 74 parts per billion (ppb) on a volume/volume basis. Conducting emission tests at these low concentrations required extensive refinement of available emission source testing techniques.

Lead and Other Metal Emissions

The samples of flue gas particulate collected at each site were analyzed for a total of 27 metals by Inductively Coupled Argon Plasma Emissions Spectroscopy (ICAP) techniques. Lead

Table 2. Boiler Descriptions

Site description	Rated capacity 10 ⁶ Btu/hr	Boiler type	Method of atomization	Site description	Spike level of each component (ppm)	Total number of test runs
A	0.5	Cast iron	Mechanical	Office building	1,500, 3,000	3 3
B*	1.0	Scotch firetube 2 pass	Rotary cup	Dairy complex		
C	2.4	Horizontal return tube	Rotary cup	Greenhouse	3,000	3
D	2.7	Scotch firetube 3 pass	Air	Office building	3,000, 10,000	3 3
E	3.4	Scotch firetube 4 pass	Rotary cup	Greenhouse	3,000, 5,000	3 3
F	4.2	Scotch firetube 3 pass	Air	Greenhouse	3,000, 5,000	3 3
G	12.5	Scotch firetube 4 pass	Air	Greenhouse	3,000, 10,000	3 1

*Boiler not available for testing in the program due to problems with the burner assembly and fuel feed system.

Table 3. Calculated Destruction and Removal Efficiencies (%)

	A	C	D	E	F	G	Average by compound
Volatile Compounds							
Chloroform	99.65	99.91	99.96	99.90	99.94	99.95	99.88
Trichloroethane	99.78	99.95	99.97	99.37	99.80	99.93	99.80
Trichloroethylene	99.45	99.92	99.89	99.85	99.92	99.87	99.82
Perchloroethylene	99.74	99.91	99.86	99.73	99.85	99.96	99.84
Semivolatile Compounds							
Trichlorobenzene	99.84	99.98	99.96	99.90	≥99.96	99.89	>99.92
1-chloronaphthalene	99.95	99.95	99.95	>99.94	99.98	99.92	>99.95
2,4,5-Trichlorophenol	>99.97	>99.99	—	≥99.92	≥99.98	—	>99.97

and zinc were present at concentrations substantially higher than any other trace metals. The lead concentrations in the flue gas samples ranged from 5,380 µg/m³ to 72,400 µg/m³ corresponding to an average emission rate of 0.12 lb/hr. Calculations based on simplified models have shown in some cases, lead emissions at these levels could cause violations of ambient air quality standards for lead. The concentrations of zinc in the flue gas ranged from 3,100 to 34,000 µg/m³, corresponding to an average emission rate of 0.06 lb/hr. The ratio between lead and zinc emissions was generally 2:1, consistent with their concentration in base stock oil, which was 1,550 ppm and 760 ppm by weight, respectively. Lead and zinc compounds are commonly found in waste automotive oil and result from both gasoline and oil additives.

Other metals that received special attention were arsenic, cadmium and chromium. These were generally at low enough concentrations in the stack gas so that when diluted in the atmosphere they should not cause major problems, but the situation is still of some concern as the concentration of these metals could be substantially higher in other waste oil base stocks (e.g., see Table 1).

The results of metal emissions are summarized in Table 4.

Particulate and Chloride Emission

Particulate emission rates at the six sites ranged from 0.07 to 1.2 lb/hr with an average value of 0.73 lb/hr (0.34 lb/10⁶ Btu heat input). This is significantly higher than the literature value of 0.09 lb/10⁶ Btu for commercial boilers firing residual oil, but the higher value is con-

sistent with the much higher ash content of waste oil, which can range from 0.15 to 1.5 percent. Particulate sizing measurements conducted at four test sites indicated that 80 to 90 percent of the particulates containing lead are sub-micron in nature and would be readily inhalable.

The flue gas emissions of HCl from the six boilers averaged 2.6 lb/hr. This is a relatively high emission rate for such small units, but it is below the 4.0 lb/hr air emission standard established for hazardous waste incinerators, which would typically burn large quantities of chlorinated compounds similar to those used in this program.

Mass flow calculations indicate that 50 to 60 percent of the lead and chloride introduced into the boilers exists from the system in the flue gas streams. The analysis of samples of firetube ash col-

lected at a single site indicates concentration levels of lead and chloride in the ash on the order of 1 to 2 percent. Data from the stack gas emissions coupled with the chemical analysis of the fire-tube fly ash and the waste oil provide for material balance closures at about 65 percent for the total system. This was considered a reasonable closure for the purpose of this project and further investigative work on the remaining 35 percent was not performed.

Products of Incomplete Combustion

The flue gas samples from each site were screened by gas chromatography/mass spectrometry (GC/MS) for additional organic components considered to be potential products of incomplete combustion. The types of compounds which were identified are given in the full report. In general, the components were nonchlorinated in nature and were representative of the types of compounds that result from the combustion of traditional fossil fuels. These compounds were also very typical of contaminants sometimes found on the blank sample adsorbing medium, XAD-2 resin. The extent to which these compounds, when detected, resulted from combustion byproducts or from resin contaminants could not be determined; hence, the concentrations could be viewed as upper limits for many of the nonchlorinated products of incomplete combustion. During the course of this program, there were some baseline runs done on conventional No. 4 fuel oil. As expected, no chlorinated hydrocarbons were detected in the stack gas, with detection limits being $8 \mu\text{g}/\text{m}^3$. With conventional No. 4 oil, combustion products such as naphthalene and similar PAH compounds were $100 \mu\text{g}/\text{m}^3$ or less.

Chlorinated dibenzofuran (PCDF) or chlorinated dioxin (PCDD) species were detected in 15 of the 25 samples analyzed as shown in Table 5. The concentration of these compounds ranged from 0.07 to $17 \mu\text{g}/\text{m}^3$. On a volume/volume basis, this corresponds to a range of 7 to 470 parts per trillion (ppt).

Bulk samples of firetube ash collected at one of the sites contained parts per billion levels of 11 PCDF and PCDD isomers on a weight by weight basis. Because chlorinated dioxins and chlorinated dibenzofurans were found in the flue gas, tests were also conducted on the waste oil base stock, both spiked

Table 4. Concentrations of Metals in Flue Gas ($\mu\text{g}/\text{m}^3$)

Site	A	C	D	E	F	G
Arsenic	11.2	655	26.1	106	251	286
Cadmium	31.2	102	8.3	182	350	81
Chromium	62.2	166	112	230	205	263
Lead	9,680	72,400	5,390	20,300	49,800	51,000
Zinc	5,150	33,700	3,134	12,100	26,800	27,000

Table 5. Average Concentrations in Stack Gas of Dibenzofuran and Dioxin Species from Tests Exhibiting Detectable Levels ($\mu\text{g}/\text{m}^3$)

	A ^a	C ^b	D ^a	E ^a	F ^a	G ^c
Dibenzofuran	62(5)	5.4(2)	3.4(5)	8.0(5)	16(3)	2.7(3)
Chlorodibenzofuran	0.8(3)	0.52(1) ^d	0.7(3)	0.4(2)	2.1(1) ^d	
Dichlorodibenzofuran	1.9(2)	0.07(1)		0.24(1)		
Trichlorodibenzofuran		0.43(2)				
Tetrachlorodibenzofuran				0.17(1)		
Dibenzodioxin	1.3(3)			0.73(1)		
Chlorodibenzodioxin		0.27(1)				
Dichlorodibenzodioxin		0.18(1)		1.6(1)	2.4(1)	
Tetrachlorodibenzodioxin						1.4(1)
Octachlorodibenzodioxin		4.5(1) ^d			17(1) ^d	

^aSamples from 5 tests analyzed.

^bSamples from 2 tests analyzed.

^cSamples from 3 tests analyzed.

^dQuality assurance samples indicate potential loss.

() number of tests in which component was detected.

and unspiked to determine the extent to which these types of compounds might be present in the oil. No chlorinated dioxins or chlorinated dibenzofurans were found in either the spiked or unspiked oil.

Test Methods

Waste Oil Analysis

Waste feed samples were analyzed for chloride, metals and the organic spike components. The chloride content of the fuel was determined by Parr Oxygen Bomb Combustion followed by Ion Chromatography (IC) analyses. Metals concentrations were determined by means of ICAP. The samples were prepared for ICAP analysis by a controlled dry ashing procedure utilizing IR lamps.

The volatile organic analysis of the waste fuel was accomplished by extraction followed by purge and trap GC/MS techniques in accordance with EPA Method 624 procedures. Sample preparation followed procedures as given in Method A101B5, with the substitution of tetraglyme (tetraethylene glycol di-

methylether) for the polyethylene glycol normally specified. Tetraglyme is similar in nature to polyethylene glycol, but was found to contain fewer potentially interfering contaminants.

The analysis of the waste oil for the semivolatile components of interest was performed using a gas chromatograph equipped with an electron capture detector (GC/ECD). Initial analysis of the waste oil employing silica gel chromatographic cleanup and GC/MS techniques was determined to be inappropriate due to the unacceptable sample recoveries for trichlorobenzene and trichlorophenol.

Combustion Gas Sampling and Analysis

The determination of volatile organic concentrations in the flue gas was carried out using a gas chromatograph equipped with an electron capture detector (GC/ECD). Duplicate, integrated samples of flue gas were collected in nonreactive Tedlar bags and injected into the instrument using a heated gas sampling loop. Each of the samples

were analyzed in duplicate, with replication sample values to within ± 10 percent as the criterion for acceptance. The accuracy of the calibration standards developed for the analysis were verified by comparison of NBS traceable standards.

A modified Method 5 train equipped with an XAD-2 resin trap was used to collect particulate, semivolatile organic compounds, metals and HCl components from the flue gas of the boilers. The particulate, XAD-2 resin and flue gas condensate samples from the train were combined and solvent extracted; analysis of solvent extracts was conducted using capillary GC/MS. Aliquots of these sample aliquots were further concentrated for subsequent analysis for polychlorinated dibenzofuran and polychlorinated dibenzodioxin species. The analysis was conducted using a quadrupole Hewlett Packard 5985 GC/MS system fitted with a fused silica capillary column.

A single set of Method 5 samples from each site was subjected to inorganic analysis for chloride and particulate metal determinations. Samples of the collected gas condensate were analyzed for chloride by direct injection on an Ion Chromatograph. Particulate samples from the train were prepared for metal determinations by a hot nitric acid leach followed by ICAP analysis.

Additional samples of particulate were collected at four sites using an Andersen High Capacity Sampling System (HCSS) for particle size determinations. The size fractionated particulate (10 μm , 10-3 μm , 3-1 μm and 1 μm) were extracted using 3M nitric acid and analyzed for lead using atomic absorption spectrophotometry.

Samples of firetube ash were collected for chloride, metals and semivolatile organic analysis. The methods for the trace metal and organic determinations are as described above. Aliquots of the samples were subjected to a hot aqueous leach to extract soluble chloride species followed by IC analysis. Additional samples were analyzed by EP Toxicity in accordance with the procedures outlined in §260.20 and §260.21

Quality Assurance Procedures

Quality control checks were performed to ensure the collection of representative samples and the generation of valid analytical results. Blank samples including field biased blanks and

method blanks, were used to assess the possible contamination of the samples. Duplicate and spiked samples were routinely employed during the program to verify the precision and accuracy of the analysis.

EPA quality control concentrates and NBS Standard Reference Materials were used where appropriate to assess the analytical work. A comprehensive systems audit was conducted during the program to ensure that the project goals and requirements set forth in the Quality Assurance Plan were met.

Conclusions

Although a sample population of six boilers is very limited, several general conclusions can be reached regarding the combustion of waste automotive fuels in boilers in this size range.

1. It is possible to achieve combustion efficiencies greater than 99.9 percent for small commercial boilers firing waste oils.
2. Destruction and removal efficiencies of greater than 99.9 percent can be obtained for chlorinated organic contaminants typically present in waste oils. For the volatile compounds studied (chloroform, trichloroethylene, trichloroethane and perchloroethylene), destruction and removal efficiencies were on the order of 99.9 percent. For the semivolatile compounds, (trichlorobenzene, 1-chloronaphthalene, and trichlorophenol), destruction and removal efficiencies were on the order of 99.95 percent.
3. For boilers above 1×10^6 Btu/hr input, there were no apparent correlations between boiler size or firing method and destruction efficiency of organic contaminants.
4. Inorganic components, as opposed to organic components of waste oil, have substantially greater mass emission rates to the atmosphere as a result of the combustion of automotive waste oils. The principal inorganic components of concern are lead, hydrochloric acid and total particulate. Also of potential concern are arsenic, cadmium and chromium. The particulate lead emissions from a source may, during the peak heating season, affect the compliance with the primary ambient air standard for lead. A significant percentage of the particulate lead emis-

sions is submicron in nature and would be readily inhalable.

5. Detectable levels of emissions of polychlorinated dibenzofurans and polychlorinated dibenzodioxins compounds were found in some of the boilers tested. These compounds, when present, were usually at levels less than $5 \mu\text{g}/\text{m}^3$, which is less than 0.5 part per billion by volume in the stack gas. The extent to which these compounds pose a hazard at these low levels is undetermined.

Tests were done on the base stock waste oil, with and without the spiked contaminants, to determine the extent to which the oil may have contained trace levels of dioxin. No dioxin or dibenzofuran compounds were detected in any of the oil samples; detection limits were 200 ppb by weight for TCDD and TCDF. If dioxin compounds were present at or below their detection limits, such a quantity would not be large enough to account for the observed levels in the stack gas even with zero percent destruction. Therefore, dioxin and dibenzofuran found in the stack gas most probably was formed during the combustion process.

6. The fly ash deposited in the fire-tubes of the boilers may contain percent levels of lead and parts per billion levels of chlorinated dibenzofuran and dioxin compounds. The ash has the potential for being classified as hazardous on this basis, and may be subject to hazardous waste regulations for disposal.

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Harry Freeman and Michael Petruska are the EPA Project Officers (see below)
*The complete report, entitled "Environmental Characterization of Disposal of
Waste Oils by Combustion in Small Commercial Boilers," (Order No. PB 85-105
880, Cost: \$17.50, subject to change) will be available only from:*

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