

VERMONT USED OIL ANALYSIS AND WASTE OIL FURNACE EMISSIONS STUDY

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Executive Summary

In response to regulatory changes in 1993 and at the direction of the Vermont General Assembly, the Agency of Natural Resources Department of Environmental Conservation proposed to conduct a study to characterize the constituents and properties of used oils generated in the state and the resultant emissions and ambient impacts associated with the combustion of these used oils in small waste oil furnaces. The study results were intended to determine whether the combustion of used oil in air atomizing space heaters complied with existing Air Pollution Control and Hazardous Waste Management Regulations. Based on the results of the study, the Agency was to make recommendations for any necessary changes in the laws and regulations.

Used oil samples from 21 sites, including gasoline and diesel vehicle maintenance facilities as well as do-it-yourself drop off sites, were collected and analyzed to determine the concentrations of several contaminants known or suspected to be present in used oils. The majority of used oil samples were collected from gasoline maintenance facilities. These facilities are believed to represent the largest sector of used oil generation and subsequent burning in the state. The results of the used oil sample testing revealed higher levels of several contaminants over levels found in No. 2 home heating fuel oil, including barium, cadmium, chromium, lead, zinc, ash and halogens such as chlorine and bromine. Some of these contaminants are also found in the virgin lubricating oil as a result of performance additives and are not necessarily the result of contamination through the use of the oil. The majority of the used oil samples complied with the existing waste oil constituents and properties limitations contained in the Vermont Air Pollution Control (Table A, §5-221(2) APCR) and Hazardous Waste Management Regulations (Table 1, §7-606(4) HWMR).

Stack emissions testing was conducted on several waste oil furnaces to more accurately assess the emissions from used oil combustion and determine compliance with the recently amended Control of Hazardous Air Contaminants Rule of the Vermont Air Pollution Control Regulations (§5-261). Testing was conducted for the following pollutants determined to be of most concern: hydrochloric acid, total particulates, arsenic, cadmium, chromium, and lead. Stack emission samples were collected from five atomizing waste oil furnaces currently in service and one No. 2 fuel oil furnace. All units were less than 280,000 BTU per hour. These waste oil furnaces represent the latest generation of improved units that are presently in the marketplace. A sample of the fuel being combusted at each site during the emission testing was also collected and analyzed.

Stack emissions testing results indicated higher levels of several contaminants over that of No. 2 fuel oil. Emissions of hydrochloric acid, total particulates and lead were all higher from the combustion of the used oils than No. 2 fuel oil. The emission results from these specific units tested were determined through atmospheric dispersion modeling to comply with their respective ambient air quality standard contained in the Vermont Air Pollution Control Regulations.

Emissions of chromium were also higher from the combustion of used oil than No. 2 fuel oil and

again were determined to comply with the total chromium ambient standard. Compliance or noncompliance with the hexavalent chromium ambient standard could not be demonstrated for the used oil combustion units due to the unknown portion of the total chromium measured that is present in the hexavalent form and the difficulties with accurately quantifying contaminant concentrations at the levels necessary. However, hexavalent chromium emissions can reasonably be expected to comply with its ambient standard based on the likely minor amount of hexavalent chromium in the total chromium emissions. Emissions of hexavalent chromium from the No. 2 fuel oil combustion could be shown to comply with the hexavalent chromium ambient standard even when all the chromium was assumed to be in the hexavalent form. Emissions of arsenic and cadmium were not detected in any of the samples. Even if these two metals were assumed to be present at levels equal to the detection limit they were shown to comply with the ambient standards for both No. 2 fuel oil and used oil combustion.

The fuel analyses and emissions testing clearly shows that used oil combustion has higher emissions than No. 2 fuel oil combustion for most contaminants. A prohibition on the burning of used oils would thus have an air quality benefit near facilities currently burning these oils. However, since the emissions from these waste oil furnaces were reasonably able to demonstrate compliance with the ambient standards, it would not be prudent public policy to regulate these fuels differently based on these emissions. Larger units than those tested however may need to be subjected to more stringent requirements. A prohibition on the burning of used oils would also have an adverse economic impact on the facilities currently burning their used oil for energy recovery. It would also eliminate the incentive for these facilities to collect do-it-yourself oil.

In consideration of these factors, the Agency recommends a policy to conditionally allow the burning of used oils in small waste oil furnaces with a maximum rating of 500,000 BTU per hour. The Agency recommends that used oil combustion in these units be excluded from the air toxics demonstration for all contaminants except hydrochloric acid. This exclusion would be similar to that already in existence for virgin fuel oils. Permits would be in the form of a general permit for specific makes and models of waste oil furnaces and would be issued after that specific make and model (not each installation) has been demonstrated to meet certain requirements, including possible particulate and hydrochloric acid compliance testing and being equipped with an air atomizing burner. Conditions may also be placed on the size of the units, number of units at a facility, amount of fuel consumed per year, contaminant concentrations and recordkeeping and reporting requirements. The Agency will also review and amend all current Department regulations and explore the option of combining all Department regulations into one combined regulation to ensure there are no longer any inconsistencies between program regulations. The allowed contaminant concentrations would be reviewed and revised if necessary. Finally the Agency recommends enhanced information and education outreach programs be conducted to minimize the contamination of the used oil fuel and to promote the voluntary re-refining of used oils back into usable lubricating oils.

1. INTRODUCTION

The environmental benefits and consequences of the combustion of used oils in waste oil furnaces has been the subject of contentious debate in the state and elsewhere over the past years. Waste oil combustion is regulated under both the Air Pollution Control Regulations (hereinafter "APCR") and the Hazardous Waste Management Regulations (hereinafter "HWMR"). The HWMR (§7-606 through §7-610 HWMR) restrict the burning of waste oils for energy recovery if they are mixed with hazardous wastes; requiring it to be managed in accordance with federal regulations (40 CFR §226.30-226.35) unless the waste oil is hazardous solely due to ignitability, corrosivity, reactivity, or toxicity or if it contains hazardous waste generated only by a Conditionally Exempt Small Quantity Generator as defined in the HWMR. Waste oil not restricted by the above is then classified as either specification or off-specification waste oil in accordance with Table 1 of §7-606 (see Table A of Appendices) which establishes allowable levels for arsenic, cadmium, chromium, lead, flash point and total halogens in the waste oil. However, specification and off-specification waste oils may be burned for energy recovery in small waste oil furnaces less than 500,000 BTU per hour.

The APCR prohibit the combustion of waste oils not meeting the constituent and property limitations as set forth in Table A of §5-221 (see Table A of Appendices). Table A establishes allowable levels for PCBs, total organic halogens, total inorganic chloride, lead, net heat of combustion and flash point. In addition, as a result of increasing concerns and a general lack of detailed information regarding the air quality impacts from the combustion of used oils in waste oil furnaces, the APCR were amended in January of 1993 making these units subject to the Control of Hazardous Air Contaminant rule (§5-261 APCR). The Vermont General Assembly subsequently passed a bill, S.107, in the spring of 1993 which provided for the curbside collection of used oils and exempted waste oil furnaces from the Control of Hazardous Air Contaminant rule. This bill was vetoed by the Governor due in part to concerns over air quality. The Agency of Natural Resources Department of Environmental Conservation (hereinafter "Agency") was then directed to study the issue and report on its findings.

During the following 1994 legislative session, bill S.335 was passed and signed into law by the Governor. This bill exempted small waste oil furnaces from regulation under the Control of Hazardous Air Contaminant rule (§5-261 APCR) if they were installed prior to January 21, 1994. The bill did, however, prohibit the sale and use of vaporizing waste oil furnaces or "pot burners" effective July 1, 1997. The Agency was directed to develop rules creating a general permit allowing for used oil combustion in small waste oil furnaces and to consider the full environmental and economic impacts of various options for used oil management. Finally, the Agency was required to report to the natural resources and energy committees of the House and Senate the results of this used oil testing program and any recommendations for rules governing the burning of used oil in small waste oil furnaces.

As a result of the regulatory changes to the APCR in 1993 and at the direction of the General Assembly, the Agency proposed in August of 1993 to conduct a study to characterize the constituents and properties of used oils generated in the state and the resultant emissions and

impacts associated with the combustion of these used oils in small waste oil furnaces. The study results were intended to determine whether the combustion of used oil in these space heaters complied with existing Air Pollution Control and Hazardous Waste Management Regulations.

The study was divided into three separate phases. The first phase involved a literature search to identify the contaminants of concern and determine their respective concentrations in used oils. Due to the highly variable nature of contaminants and their respective concentrations in used oils and limitations in available existing data, the second phase of the study involved a used oil sample collection and analysis survey of the used oil streams in the state. The third phase of the study involved stack emissions testing of several waste oil furnaces to determine the actual emissions of those contaminants determined to be of greatest concern.

2. LITERATURE SEARCH

The Agency tried to concentrate the literature search on recent studies and reports relating to waste oil contaminant concentrations and the resultant combustion emissions. A substantial amount of information was available from the late 1970's and early 1980's. The Agency felt this data was of limited use, however, due to changes in the waste oil furnaces themselves as well as waste oil characteristics since that time, such as the gradual phase out of lead in gasoline and the discontinued use of PCBs in oils as a result of legislation including the 1976 Toxic Substances Control Act. While the specific data and results of these studies were dated, the Agency was able to identify potential contaminants of concern that could be addressed in the next stage of this study.

The literature indicated that the constituents and properties of waste oils can vary considerably from source to source. Whereas some contaminants in fuel oils and lubricating oils are present in the virgin stock, waste lubricating oils are often contaminated as a result of their specific use. Lead levels in waste crankcase oils are attributable mainly to piston blow-by in engines using leaded gasoline. Arsenic, cadmium and chromium are believed to be largely a result of engine wear. In addition to being contaminated through use, hazardous wastes such as degreasing solvents may also be mixed with the waste oils. Lubricating oils also typically have performance enhancing additive packages such as detergents, dispersants, extreme pressure additives and anti-wear additives blended into the oils before use. Gasoline and oil additives are also added by the consumer. Barium, phosphorus, zinc and some chlorine and bromine compounds are present in lubricating oils in significant concentrations as a result of additives. Numerous other inorganic compounds are present in used oils such as nitrogen, sulfur, aluminum, calcium, copper, iron, magnesium, manganese, potassium, silicon, sodium and tin. Many of these compounds are not generally given much attention due to their low levels and low toxicity.

A private laboratory in the state was able to provide the Agency with copies of the actual results of waste oil analysis they had performed for facilities over the past several years. While the constituents and properties analyzed for were limited in scope to those required under the APCR and HWMR, the data was useful in that it provided current compliance information with respect

to the waste oil constituent and property limitations contained in the APCR (Table A, §5-221(2) APCR) and HWMR (Table 1, §7-606(4) HWMR). The information indicated that most of the oil submitted for analysis met the requirements for burning outlined by these regulations. However, the analyses did not provide information that could be used to determine if burning the used oil would generate emissions that would comply with the ambient air standards contained in the Control of Hazardous Air Contaminant rule (§5-261 APCR). This is because the results were often reported as simply being less than the allowable constituent limitation in Table A or Table 1 of the applicable regulation and constituent concentrations at that level would not necessarily comply with the ambient standards. Preliminary modeling using the current allowable constituent levels indicate that very small amounts of contaminants present in the used oil may result in emissions that exceed the limit set in the Control of Hazardous Air Contaminants rule.

Another source of information for this phase of the study was the promotional material developed by the waste oil heater manufacturers. Several news releases and magazine articles were utilized as sources of information. These articles and releases document the falling lead concentrations in used oil in the past ten years, due to the phase-out of leaded gasoline.

Based on a review of the available literature, the final list of contaminants in used oil that would be sampled for in the second phase of this study was compiled. This list consists of the following:

Metals: arsenic, barium, beryllium, cadmium, chromium, lead, nickel, zinc
Others: Total halogens (HCl formation), total organic halogens (HCl formation), sulfur, nitrogen, PCBs, and ash.

Arsenic is identified in the HWMR as a regulated contaminant in used oils. The source of arsenic and the potential concentrations of the contaminant in used oils was not able to be determined from the literature search that was completed. Therefore, in an effort to obtain more reliable data on the concentration of arsenic in the Vermont used oil stream and to determine compliance with the arsenic constituent level in the HWMR, arsenic was selected to be analyzed for in the second phase of this study. Barium and zinc were identified as possible additives in lubricating oils and were also selected to be analyzed for in the second phase of the study to determine their respective concentrations in used oils. Beryllium and nickel are trace metals found in low concentrations in most oils. No information was available on their concentrations in used oils therefore these contaminants were also determined to require further analysis in the next phase of the study. Cadmium is also identified in the HWMR as a regulated contaminant in used oils and is believed to be mainly from engine wear. Cadmium was analyzed for in the next phase of the study to determine its concentration in used oils and to determine compliance with the constituent level in the HWMR.

Chromium is also identified in the HWMR as a regulated contaminant in used oils. The toxicity of chromium is dependant on the form in which it is present. Chromium may be present in eight different oxidation states ranging from Cr^{-2} to Cr^{+6} . The most stable and therefore important forms of chromium are the trivalent (Cr^{+3}) and the hexavalent (Cr^{+6}) forms, respectively.

Hexavalent chromium is considered the most toxic form of chromium and rarely occurs naturally but rather is produced by anthropogenic sources such as chrome electroplating and cooling towers. The relevant concentration of trivalent and hexavalent chromium in waste oils was not determined from the literature search and is of limited value since the combustion of the fuel would be expected to alter the percentages of each. In addition, since chromium compounds can be readily oxidized or reduced to other forms under certain conditions, special sampling and analytical techniques would be required to ensure accurate results. Therefore, only total chromium was analyzed for in the next phase of the study. These results will be used to determine compliance with the total chromium constituent level in the HWMR and to determine if chromium is present in the used oil in high enough concentrations to warrant further study under the emission testing phase of this study.

Total halogens are regulated under the HWMR and total organic halogens and total inorganic chloride are regulated under the APCR. The halogens include bromine, chlorine and fluorine. Chlorine is believed to be the halogen of highest concentration in used oils as a result of additives to the oil and gasoline. Chlorine is of concern when it is combusted due to the formation of hydrochloric acid. Total halogens and total organic halogens will be analyzed for to determine compliance with the constituent levels in the HWMR and APCD. The results will also give an indication of the chlorine concentration in used oils and therefore the hydrochloric acid emission potential when burned. A direct analysis for chlorine was not required since it is not directly regulated as a constituent.

Sulfur and nitrogen in fuels form sulfur oxides and nitrogen oxides respectively when burned, both of which are regulated air pollutants under the APCR. The sulfur and nitrogen contents of the used oil and virgin fuel oil samples will be analyzed for in the next phase of the study to determine if there is any notable difference between the fuels.

Even though PCBs are not expected to be present in the general used oil stream due to their discontinued use, they will be tested for to verify this assumption. Any electrical transformer oils thought to still contain PCBs would be expected to be handled separately from the used oil stream being combusted in small waste oil furnaces. Therefore no transformer oil samples were collected as part of this study.

The ash content of a fuel refers to the mineral matter that is noncombustible. This would include silica, iron, other metals, dirt, etc. that may be present in the oils. The ash content would contribute directly to particulate matter emissions when the fuel is burned. The ash content will be analyzed for in the next phase to determine if any notable difference exists between the fuels.

3. USED OIL SAMPLE COLLECTION AND ANALYSIS

Used oil samples from 21 locations, including gasoline and diesel vehicle maintenance facilities as well as do-it-yourself drop off sites, were collected and analyzed to determine the concentrations of the contaminants identified in the previous phase of the study. Since gasoline vehicle maintenance facilities are believed to represent the largest sector of used oil generation and subsequent burning, the majority of used oil samples were collected from these facilities. The facilities included 15 automobile service/sales operations, four diesel equipment operations and two do-it-yourself drop off sites. In addition, virgin lubricating oil samples were purchased off the shelf, and a sample of No. 2 home heating fuel oil as well as No. 4 fuel oil were obtained from a commercial facility using these virgin fuels. The sample collection methods are described in the study proposal dated August 1993.

3.1 Used Oil Analysis Results

Average results of analysis of used oil samples are listed in Table 1. More detailed results for individual samples are contained in Table B of the Appendices. The table is arranged so that contaminants in used oil can be readily compared to contaminants in the virgin fuel and lubricating oil. Samples of virgin lubricating oil were analyzed to determine if contaminants were present in the oil before use in a vehicle engine. The only metal discovered in substantial quantity in the virgin lubricating oil was zinc, which is an additive. Barium, cadmium, chromium, lead, and nickel and ash all appear in higher concentrations in the used oil than the unused lubricating oil as a result of its use in the engine. These same contaminants as well as zinc and halogens were all notably higher in the used oil than the fuel oils, with the exception of the No.4 fuel oil ash content which was comparable to the used oil. There were no notable differences in sulfur or nitrogen contents between the various oil types. Arsenic and beryllium were not present in either the virgin oils or used oils in quantities sufficient for reliable measurement. All samples were analyzed for PCBs, however no PCBs were detected at the minimum detection limit of the analytical equipment (5 ppm).

The only average contaminant concentration in excess of current constituent standards is the cadmium in diesel crankcase oil (2.34 ppm; HWMR standard 2.0 ppm). It should be noted that this average is based on only four diesel samples, and that one sample had a cadmium concentration of 6.61 ppm and the three remaining diesel crankcase oil samples all complied with the 2.0 ppm limit. Examination of individual results also show that a total of four gasoline crankcase oil samples also exceed the HWMR cadmium standard of 2.0 ppm. These exceedances simply mean that the oil would be classified as off-specification oil and not prohibited from being combusted in a waste oil furnace for energy recovery.

Table 1
Used Oil Samples Average Analytical Results

contaminant	gasoline engine oil	diesel engine oil	virgin engine oil	No. 2 fuel oil	No. 4 fuel oil
arsenic (ppm) ¹	--	--	--	--	--
barium (ppm)	2.73	3.39	< 1.00	< 1.00	< 1.00
beryllium (ppm)	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
cadmium (ppm)	< 1.51	2.34	< 0.25	< 0.25	< 0.25
chromium (ppm)	3.19	3.91	< 2.00	< 2.00	< 2.00
lead (ppm)	47.23	57.00	< 20.00	< 10.00	< 10.00
nickel (ppm)	< 1.40	1.85	< 1.20	< 1.20	8.34
zinc (ppm)	1161	1114	1210	5.00	9.05
ash (% w/w)	0.54	0.46	0.135	0.13	0.55
PCBs (ppm)	< 5	< 5	< 5	< 5	< 5
total halogens (ppm)	< 350	< 234	< 300	< 200	< 200
total organic halogens (ppm)	< 301	< 217	< 292	< 200	< 200
flash point (°F)	> 200	> 200	> 200	> 200	> 200
sulfur (% w/w)	0.36	0.25	0.36	0.12	0.19
nitrogen (% w/w)	0.04	0.02	0.02	< 0.01	0.03

¹ arsenic concentrations are not reported due to analytical difficulties with accurately determining arsenic concentrations at the necessary levels. While the laboratory can quantify arsenic concentrations in oil greater than 250 ppb, under the procedures of method 3050 some organic arsenic compounds are lost through volatilization, resulting in poor spike recoveries and the possibility of false negative results. Only one sample had an arsenic concentration > 250 ppb and that concentration was reported as > 2 ppm.

The only other constituent standard to be exceeded by an individual sample was lead. In this case two gasoline crankcase oil samples exceeded the 100 ppm HWMR limit but not the 200 ppm APCR limit, thus the oil would not be prohibited from being burned and would be considered in compliance. Concentration of the contaminants in the individual samples ranged as follows: barium < 1.0 ppm to 6.9 ppm; cadmium < 0.25 ppm to 6.6 ppm; chromium < 2.0 ppm to 6.8 ppm; lead < 20 ppm to 146 ppm; nickel < 1.2 ppm to 3.0 ppm; halogens < 200 ppm to 877 ppm.

3.2 Conclusions

The used oils sampled largely demonstrated compliance with the waste oil constituent and property limitations governing the burning of used oils. In addition, the contaminants barium, beryllium, nickel, zinc, PCBs, nitrogen and sulfur were not found to be of significant concern with respect to potential air emissions based on their reported concentrations and respective toxicity levels. The toxicity of arsenic and the difficulty in obtaining accurate and reliable data on its concentration in the used oils warrants further study of this contaminant in the next phase of the study. The concentrations of lead and halogens in the used oils are also high enough to warrant further study of the potential emissions and impacts on air quality. Cadmium and chromium concentrations were high enough such that projected emission and ambient impacts would not comply with the ambient air standards contained in the Control of Hazardous Air Contaminant rule (§5-261 of the APCR).

4. STACK EMISSION TESTING

Stack emissions testing was conducted on several waste oil furnaces for the contaminants of most concern. These contaminants were identified from the concentration of contaminants found in the previous phase of the study and their relative toxicity; these being hydrochloric acid, total particulates, arsenic, cadmium, chromium, and lead. Volatile and semi-volatile organics were not considered in this study. Stack emission samples were collected from five existing atomizing waste oil furnaces currently in service at the selected facilities and one No. 2 fuel oil furnace. Four of the used oil sites burned predominately waste automotive crankcase oils and the fifth burned exclusively diesel waste crankcase oils. The units were all of similar size, ranging from 185,000 BTU to 280,000 BTU. All units were of the air atomizing type. No vaporizing burners were tested. The specifications of the units tested are presented in Table C of the Appendices.

Samples of the fuels being combusted were also collected and analyzed for each of the sites and these results are presented in Table D of the Appendices. Caution should be used in attempting to correlate used oil contaminant concentrations with emission test results due to the non-homogenous nature of waste oils and the difficulty in obtaining the exact contaminant concentrations entering the burner over the test period.

4.1 Stack Emission Sampling Methods

Stack emission samples were collected from the outlet stack for each facility. EPA stack sampling requirements specify that samples must be collected from a location a minimum of four stack diameters downstream and one stack diameter upstream of any stack flow disturbance. An eight inch in diameter by three foot long galvanized stack extension pipe was added to each of the used oil heater stacks to ensure compliance with this requirement.

Stack emission samples for hydrochloric acid, particulates and metals were all collected in accordance with EPA's modified method 5 for multiple metals sampling method (MM5-MM,

Draft EPA Method 29 and 0050). Stack gas moisture content, temperature and velocity were also determined in accordance with this EPA sampling method. EPA method 3B was used for the determination of stack gas oxygen and carbon dioxide content. Table F of the Appendices presents the waste oil furnace operating parameters.

To account for the potential cycling of the burner on and off during the test run, the units (which were all thermostatically controlled) were turned on by setting the thermostat to a point where the unit would not shut off during the testing. The units were periodically monitored to ensure that they were running constantly during the testing. The fact that the units would not run continuously during normal operation and therefore would not have as high of emissions due to shut-off periods is accounted for in the estimation of ambient impacts discussed later in this report. A burner that cycles on and off frequently would be expected to have a slightly lower combustion efficiency than a unit that runs for longer periods of time. However, with respect to metal emissions and hydrochloric acid formation, this would not be expected to significantly alter the results. Combustion efficiency would have a more significant effect on organic and semi-organic emissions which are not addressed in this study. Total particulates could also be expected to increase slightly with lower combustion efficiency.

Standard stack emission compliance testing requires three one-hour samples runs where the three runs are averaged to determine compliance. However, due to the relatively small size of waste oil furnaces in general, the stack sample collection times were extended to ensure an adequate sample size was collected for analysis. Stack sampling times were extended to four-hours each and reduced to only two runs per facility. Only facility WO/1 had sample collection times less than four-hours (two-hours and three-hours respectively). This was due to an increase in the vacuum pressure required for sampling and a visual inspection of the sampling nozzle which indicated heavy particulate loading.

4.2 Stack Emission Testing Results

Average results for the stack emission testing are presented in Table 2. Table E of the Appendix contains the actual results for each test run. As indicated in Table 2, emissions of hydrochloric acid, particulates, chromium and lead were all significantly greater from the used oil combustion than from No. 2 fuel oil combustion. The average hydrochloric acid emissions from the used oil combustion were 15 times higher than from No. 2 fuel oil combustion. Particulate emissions were also much greater from the used oil combustion, averaging 467 mg/min versus no quantifiable amount of particulates from No. 2 fuel oil combustion. Chromium emissions were 8.5 times higher and lead emissions were 70 times higher from used oil combustion than from No. 2 fuel oil combustion. These results are not unexpected given the contaminant concentrations of chlorine, ash, chromium and lead in the used oils. In addition, the higher molecular weights of the lubricating oil hydrocarbon chains could be more difficult to completely combust and thus could result in increased total particulate emissions.

Emissions of arsenic and cadmium were not detected in any of the samples despite the increased sample collection times. The values presented in Table 2 for arsenic and cadmium are the

detection limits for the specific samples collected and vary from sample to sample since the detection limit is a function of the sample mass and is not a fixed analytical number.

Table 2 Emission Testing Actual Results (mg/min)						
Facility	HCl	Particulate	Arsenic ¹	Cadmium ¹	Chromium	Lead
	(mg/min)	(mg/min)	(mg/min)	(mg/min)	(mg/min)	(mg/min)
No. 2 oil	2.3	0	< 0.02	< 0.03	0.02	0.03
WO/1	55.7	416.5	< 0.04	< 0.07	0.13	1.55
WO/2	16.7	333.0	< 0.02	< 0.04	0.12	1.32
WO/3	45.3	500.0	< 0.03	< 0.13	0.21	2.58
WO/4	19.2	667.0	< 0.04	< 0.08	0.24	2.73
WO/5	36.3	416.5	< 0.02	< 0.07	0.14	2.25
average ²	34.6	466.6	< 0.03	< 0.08	0.17	2.09

¹ Arsenic and cadmium results were all reported as non detectable. The values presented represent the varying levels of detection for each specific sample collected which is a function of the sample mass.

² Values are for waste oil testing results only.

4.3 Comparison to Regulatory Levels Under §5-261 of the APCR

In order to determine compliance with the Control of Hazardous Air Contaminant rule (§5-261 of the APCR), emissions from the waste oil furnaces must first be compared to the regulatory Action Level for the respective pollutants. These Action Levels are listed in Appendix C of the APCR and are used to determine applicability to the rule. If emissions of a contaminant exceeds its respective Action Level, then that contaminant is subject to the rule. Once a pollutant is subject to the rule its emissions must be demonstrated to be reduced to the Hazardous Most Stringent Emission Rate ("HMSE"). HMSE is defined in the APCR as the lowest rate of emissions that the Agency determines is achievable for the source, taking into account economics. HMSE may be achieved through the application of pollution control equipment, equipment design changes, operating practice changes or even product substitution. For the purposes of this study, it was assumed that HMSE would not prohibit the combustion of used oil in favor of virgin oil. Once HMSE is determined, the source must demonstrate compliance with the Hazardous Ambient Air Standard if the emissions are still over the Action Level after achieving HMSE. These standards are also presented in Appendix C of the APCR.

The average milligrams per minute emission results presented in Table 2 above were converted to emission in pounds per eight hours for comparison to the regulatory Action Levels and are presented in Table 3 below. Emissions of particulates are not compared to an Action Level since particulates are not regulated under the Control of Hazardous Air Contaminant rule.

Table 3 Comparison to Regulatory Action Levels						
Facility	HCl	Particulate	Arsenic ¹	Cadmium ¹	Chromium	Lead
	(lb/8hr)	(lb/8hr)	(lb/8hr)	(lb/8hr)	(lb/8hr)	(lb/8hr)
No. 2 oil	0.002	--	< 0.000021	< 0.000032	0.000021	0.00003
WO/1	0.059	--	< 0.000042	< 0.000074	0.000138	0.00164
WO/2	0.018	--	< 0.000021	< 0.000042	0.000127	0.00140
WO/3	0.048	--	< 0.000032	< 0.000138	0.000222	0.00273
WO/4	0.020	--	< 0.000042	< 0.000085	0.000254	0.00289
WO/5	0.038	--	< 0.000021	< 0.000074	0.000148	0.00238
average ²	0.04	--	< 0.000032	< 0.000083	0.000178	0.002
Action Level (lbs/8hrs)	0.87	--	0.000019	0.000047	0.01 (total) 0.0000071 (+6)	0.014

¹ Arsenic and cadmium results were all reported as non detectable. The values given are based on the sample detection limits.

² Values are for waste oil testing results only.

As shown in Table 3 above, emissions of hydrochloric acid and lead from both used oil and No. 2 fuel oil combustion do not exceed their respective regulatory Action Level for the size units tested in this study. The average hydrochloric acid emission from the waste oil furnaces was approximately one-twentieth the Action Level. The average lead emission from the waste oil furnaces was approximately one-seventh the Action Level. Emissions of chromium from both used oil and No. 2 fuel oil combustion can be shown to be less than the "total" chromium Action Level. However, compliance with the hexavalent chromium Action Level could not be determined for either fuel since the hexavalent chromium percentage of the total chromium value is not known. According to the U.S. Department of Health's Toxicological Profile for Chromium (Update) (USDH 1993. Toxicological Profile for Chromium (Update). U.S. Department of Health & Human Services, Agency for Toxic Substances and Disease Registry, Atlanta, GA.) special sample collection and analytical

procedures are required to accurately quantify concentrations of trivalent and hexavalent chromium in air samples, especially when present at concentrations below 1 ug/m³. This document indicated that chromium emissions from the combustion of coal and virgin oil are believed to be emitted predominantly in trivalent forms, however minor amounts of hexavalent chromium, in the range of 0.2 percent of the total chromium, is also believed to be emitted. A separate unidentified emission test of an unknown sized multi oil furnace reported the hexavalent chromium percentage to be approximately 6 percent. Based on the emission rates of total chromium from the waste oil furnaces tested in this study, hexavalent chromium would need to comprise less than 4 percent of the total chromium in order for emissions to be less than the hexavalent chromium Action Level.

Since arsenic and cadmium were not detected in the emission test samples, an emission rate equal to the individual sample detection limit was assumed. This emission rate would represent worst case emissions. Based on these assumed emission rates, both fuels show arsenic emissions will exceed its Action Level. No. 2 fuel oil had an arsenic emission rate of 0.000021 pounds per eight hours compared the Action Level of 0.000019 pounds per eight hours. Arsenic emissions from waste oil combustion were predicted to exceed the Action Level by approximately two times. Based on the assumed worst case emission rates, cadmium emissions were shown to be less than the Action Level for No. 2 fuel oil combustion but exceed the Action Level for waste oil combustion by approximately two times.

The actual ambient impacts associated with a given emission rate of a contaminant must be predicted or estimated through the use of atmospheric dispersion models for comparison to the applicable state Hazardous Ambient Air Standard. The atmospheric dispersion modeling requires certain assumptions in order to estimate ambient impacts from the reported mass per unit time emission rates determined from the testing. The model inputs include the contaminant emission rate in grams per second, the stack height and diameter, exhaust gas flow rate, velocity, and temperature, and the building dimensions where the stack is located. Since the model is used to estimate the average ground level ambient impact over a period of time equivalent to the averaging period for the contaminants respective Hazardous Ambient Standard (HCl 24-hours, lead 3-months, arsenic, cadmium and chromium 1-year), an assumption as to how much fuel is burned over a given period of time must be made since the units do not operate continuously at full capacity. The assumption used here is 3,000 gallons of used oil is burned by a facility in a year and potentially in a three month period as well. It is also assumed that the unit could operate continuously for a 24-hour period.

The stack parameters used in the modeling are taken from the average stack parameters determined from the emissions testing and are given in Table F of the Appendices. Since building dimensions vary from facility to facility, two different building dimension scenarios were analyzed. One building was assumed to have dimensions of 40 feet wide, 60 feet long and 15 feet high with a stack 5 feet above the roofline. The second building was assumed to have dimensions of 40 x 60 and 25 feet high with a stack height again 5 feet above the roofline.

The U.S. EPA Screen2 Model was used to predict the ambient impacts. A maximum one-hour

concentration of 4,597 ug/m³ was calculated using the above parameters and assuming an emission rate of 1 g/sec. This value was then scaled for the various contaminant emission rates and averaging times. The results are presented in Table 4.

Table 4 Comparison to Regulatory Hazardous Ambient Air Standards						
Facility	HCl	Particulate ¹	Arsenic ²	Cadmium ²	Chromium	Lead
	(ug/m ³)	(ug/m ³)	(ug/m ³)	(ug/m ³)	(ug/m ³)	(ug/m ³)
No. 2 oil	0.07	0/0	< 0.000026	< 0.000039	0.000026	0.00
WO/1	1.71	0.7/12.8	< 0.000063	< 0.000109	0.000203	0.015
WO/2	0.51	0.7/10.2	< 0.000040	< 0.000079	0.000238	0.016
WO/3	1.39	0.7/15.3	< 0.000039	< 0.000171	0.000276	0.020
WO/4	0.59	0.9/20.4	< 0.000052	< 0.000105	0.000315	0.021
WO/5	1.11	0.8/12.8	< 0.000040	< 0.000139	0.000278	0.027
average ³	1.1	0.8/14.3	< 0.00005	< 0.00012	0.000262	0.02
HAAS (ug/m ³)	16.7	50/150 17/30	0.00023	0.00057	0.12 (total) 0.000085 (* 6)	0.25

¹ Particulate matter emissions are regulated separately from the hazardous air pollutants under the Vermont Air Pollution Control Regulations. There is an annual and 24 hour averaging period National Ambient Air Quality Standard for particulate matter (PM₁₀). The values given in the left and right side of the column represent annual and 24 hour impacts respectively with the NAAQS and full PSD increments given in the bottom row.

² Arsenic and cadmium results were all reported as non detectable. The values given are based on the sample detection limits.

³ Values are for waste oil testing results only.

Calculations to predict ambient impacts are based on the following formula:

$$\text{ambient impact} = (\text{mg/min}) (1 \text{ min}/60\text{sec}) (1\text{g}/1000\text{mg}) (4597) (\text{scaling factor}) (\text{capacity factor})$$

where,

mg/min = emission rate from Table 2 (page 9)

4597 = ambient impact from U.S. EPA SCREEN2 model based on unit emission rate of 1g/sec

scaling factor = 0.4 for 24 hr stds (HCl, PM₁₀); 0.15 for 3 month stds (lead); and 0.1 for annual stds. (PM₁₀, As, Cd, Cr)

capacity factor = for 24 hr stds. there is no factor, assume value of 1

= for 3month stds: (3000gal) / [(BTU/hr rating of unit) (2190hrs) / (140,000BTU/gal)]

= for annual stds: (3000gal) / [(BTU/hr rating of unit) (8760hrs) / (140,000BTU/gal)]

The results in Table 4 indicate that even though the predicted ambient impacts from waste oils combustion are significantly higher than impacts from No. 2 fuel oil combustion, both fuels easily complied with the respective state Hazardous Ambient Air Standard for the size units tested. Only hexavalent chromium impacts from the waste oil combustion could not be conclusively determined to comply with its ambient standard due to the unknown percentage of hexavalent chromium to total chromium. Hexavalent chromium impacts can reasonably be expected to comply with the ambient standard since the hexavalent chromium percentage of the total chromium would need to exceed 32 percent before the standard would be exceeded. While the actual percentage is not known, the literature indicates that hexavalent chromium comprises less than 6 percent. The ambient impacts in Table 4 do not include any existing background concentrations for the pollutants. When available, existing background concentrations of the respective pollutant must be added to the predicted impact for comparison to the ambient standard.

Hydrochloric acid emissions from the waste oil furnaces were shown to cause an average ambient impact of 1.1 ug/m^3 versus a standard of 16.7 ug/m^3 . Hydrochloric acid emissions and the predicted ambient impact from the No. 2 fuel oil unit were significantly less than the waste oil units. Particulate emissions from these same units had an average ambient impact of 14.3 ug/m^3 for a 24 hour average and 0.8 ug/m^3 for an annual average compared to the NAAQS of 150 ug/m^3 and 50 ug/m^3 respectively. Arsenic and cadmium emissions were not detected in any of the samples, however when it was assumed that the emissions were equal to the sample detection limits the Action Levels for these pollutants were triggered. The resulting predicted ambient impacts based on these detection limit emission rates indicates that both pollutants comply with their respective ambient standard. Arsenic emissions from the waste oil furnaces were estimated to cause an average impact of $< 0.00005 \text{ ug/m}^3$ compared to a standard of 0.00023 ug/m^3 . Cadmium emissions were estimated to cause an average impact of $< 0.00012 \text{ ug/m}^3$ compared to its standard of 0.00057 ug/m^3 . Lead emissions from the waste oil furnaces were shown to cause an average ambient impact of 0.02 ug/m^3 versus a standard of 0.25 ug/m^3 .

4.4 Conclusions

The results of the emission testing show that the combustion of these used oils in small waste oil furnaces have higher emissions and consequently higher predicted ambient impacts for most pollutants than the combustion of No. 2 home heating fuel oil. Despite the greater emission rates, the waste oil furnaces tested in this study were all reasonably shown to comply with the respective ambient standards. All units testing in this study were less than 280,000 BTU per hour.

5. POLICY ANALYSIS AND CONCLUSIONS

The policy decision to allow the continued use of used oil fuel in space heaters is based on an analysis of the emission testing results, the economic impact to the generators and users of used oil, and alternative disposal methods available to generators of used oil.

The fuel analyses and emissions testing clearly shows that used oil combustion has higher emissions than No. 2 fuel oil combustion for most contaminants. A prohibition on the burning of used oils would thus have an air quality benefit near facilities currently burning these oils. However, since the emissions from these waste oil furnaces were reasonably able to demonstrate compliance with the ambient standards, it would not be prudent public policy to regulate these fuels differently based on these emissions. It is extremely difficult to quantify the overall impact of used oil combustion since the number and distribution of used oil furnaces currently operating in the state is unknown. While an adverse impact to air quality does occur, the on-site management of used oils for energy recovery reduces the potential for other environmental impact caused by spills, improper disposal, and vehicle emissions generated during transport of the used oil off-site.

Economic impact to burners is possible to quantify, using assumptions about costs for disposal of used oil, costs for virgin fuel oil, and the amount of oil generated by a facility. For example, a facility that generates 1000 gallons of used oil per year and burns that oil on-site could save \$900 in fuel costs, and \$200 in disposal costs per year (assuming the cost of virgin fuel oil at \$.90/gallon and disposal costs of \$.20/gallon). In contrast, if a facility that currently burns used oil on-site has to discontinue the practice, they would incur costs of \$1100 in fuel and disposal costs in addition to their operating expenses. In addition, there is a potential risk that generators may improperly dispose of their used oil if they are unwilling or unable to accept the financial responsibility of proper disposal.

The economic benefit to used oil burners may be an incentive for facilities to accept used oil from do-it-yourselfers (DIY). Facility acceptance of used oil as "free fuel" provides a disposal option to DIY, and may reduce improper disposal of DIY oil.

There are currently three primary disposal options available to generators of used oil in Vermont. The disposal method used by most generators (384,000 gallons in 1993) is shipment out of state for fuel blending and subsequent burning for energy recovery by industrial facilities. The second option is shipment to a re-refinery. In 1993 approximately 20,000 gallons were collected and shipped to out of state re-refineries in either Illinois or Ontario, Canada. The final disposal option available is on-site burning for energy recovery. The amount of used oil disposed of in this manner is currently unknown as there are no accurate records of the number of these facilities or how much each facility generates.

Based on the current market distribution of used oils being disposed of, a prohibition of on-site burning would likely result in only a small increase in the amount of used oil being re-refined if the market share proportions were assumed to remain unchanged between out of state shipment to industrial facilities and re-refining. Mandating re-refining with the intent of attracting a re-refinery to the area may not be practicable without governmental assistance or incentives given the relatively small amount of used oil generated in Vermont.

6. RECOMMENDATIONS

In consideration of the level of emissions resulting from used oil combustion, the economic impacts to the facilities currently burning their used oil, and current disposal practices and their respective share of the used oil disposal market, the Agency recommends a policy to conditionally allow the burning of used oils in small waste oil furnaces. The Agency offers the following recommendations for achieving this end.

- A. Issue general permits for specific makes and models of waste oil furnaces after the units have been demonstrated to meet certain minimum requirements, including particulate and hydrochloric acid air toxic compliance testing and being equipped with an air atomizing burner. Conditions may also be placed on the size of the units, number of units allowed at a facility, amount of fuel consumed per year, contaminant concentrations and recordkeeping and reporting requirements. Units greater than 500,000 BTU per hour would likely be subject to more stringent requirements.
- B. Review and amend current Department of Environmental Conservation (DEC) regulations regarding used oil and explore the option of combining all Department regulations into one combined regulation to ensure there are no inconsistencies between federal and state regulations. Currently, there are three separate Divisions within DEC that regulate used oil (Air Pollution Control Division, Hazardous Materials Management Division, and Solid Waste Management Division). These amendments include, in part, an examination of the current allowable contaminant levels for oil that is burned. The goal of this examination is to determine if current levels should be reduced for selected contaminants. The allowed levels will be set to ensure compliance with air quality goals while facilitating compliance with material standards.
- C. Enhance information and education outreach programs to generators of used oil, to ensure that the oil is not contaminated with hazardous constituents and to promote the voluntary re-refining of used oils back into usable lubricating oils. This includes the development of specific quality assurance plans to be used where oil is collected for combustion.

APPENDICES

Table A: Waste Oil Constituent and Property Regulatory Limits

Table B: Used Oil Sample Analytical Results (by facility)

Table C: Waste Oil Furnace Specifications

Table D: Used Oil Sample Analytical Results from Stack Test Sources

Table E: Emission Testing Actual Results for Each Test Run (mg/min)

Table F: Waste Oil Furnace Operating Parameters

Table A
Waste Oil Constituent and Property Regulatory Limits

oil constituent/property	APCR	HWMR
unit size	1 MMBtu (max)	no limit for spec oil 500,000 BTU off-spec (max)
PCBs	50 ppm (max)	50 ppm (max)
halogens total organic halogens total inorganic chloride total halogens	500 ppm (max) 1,000 ppm (max)	4,000 ppm (max-spec)
lead	200 ppm (max)	100 ppm (max-spec)
net heat of combustion	8,000 BTU/lbs (min)	--
flash point	140 ⁰ F (min)	100 ⁰ F (min-spec)
arsenic	--	5 ppm (max-spec)
cadmium	--	2 ppm (max-spec)
chromium	--	10 ppm (max-spec)

Table B
Used Oil Sample Analytical Results (by facility)

used oil type	arsenic	barium	beryllium	cadmium	chromium	lead	nickel	zinc	ash	PCBs	TX	TOX	flash point	Sulfur	N
	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(% w/w)	(ppm)	(ppm)	(ppm)	(°F)	(%w/w)	(% w/w)
diesel	-	2.240	< 0.020	1.040	2.970	146.0	1.590	1120	0.461	< 5	226	< 200	> 200	0.411	0.015
diesel	> 250	3.420	< 0.020	6.610	6.850	41.90	1.050	2370	0.370	< 5	< 200	< 200	> 200	0.224	0.029
diesel	-	2.340	< 0.020	0.847	3.500	23.60	3.020	568	0.406	< 5	< 200	< 200	> 200	0.212	0.021
diesel duplicate	-	3.030	< 0.020	-	3.810	33.80	2.370	790	0.516	< 5	< 200	< 200	> 200	0.133	0.022
diesel	-	5.900	< 0.020	0.855	2.400	39.70	< 1.20	724	0.523	< 5	342	283	> 200	0.260	0.017
gasoline	-	2.610	< 0.020	1.610	4.230	57.10	1.430	1160	0.592	< 5	230	< 200	> 200	0.345	0.054
gasoline	-	1.650	< 0.020	1.210	2.690	22.30	1.190	1230	0.685	< 5	239	< 200	> 200	0.395	0.057
gasoline	-	3.380	< 0.020	1.340	3.520	58.70	1.600	1150	0.517	< 5	217	218	> 200	0.445	0.041
gasoline	-	2.490	< 0.020	1.470	4.100	44.70	< 1.20	1180	0.521	< 5	< 200	< 200	> 200	0.396	0.054
gasoline	-	3.170	< 0.020	1.240	3.040	42.30	< 1.20	1180	0.473	< 5	309	< 200	> 200	0.303	0.038
gasoline duplicate	-	1.890	< 0.020	1.260	3.450	38.40	< 1.20	1300	0.399	< 5	297	252	> 200	0.448	0.063
gasoline	-	1.620	< 0.020	2.520	2.320	50.20	1.830	1100	0.870	< 5	877	568	> 200	0.460	0.046
gasoline	-	< 1.00	< 0.020	1.130	< 2.00	51.70	1.590	1190	0.417	< 5	< 200	< 200	> 200	0.331	0.032
gasoline	-	1.890	< 0.020	< 0.250	2.870	84.00	< 1.20	1310	0.528	< 5	< 200	< 200	> 200	0.359	0.041
gasoline	-	4.480	< 0.020	2.180	3.000	47.90	1.500	1120	0.317	< 5	622	598	> 200	0.334	0.063
gasoline	-	1.400	< 0.020	< 0.250	2.120	< 20.	< 1.20	1150	0.533	< 5	< 200	< 200	> 200	0.337	0.038
gasoline	-	1.940	< 0.020	0.506	3.000	42.60	1.000	1010	0.834	< 5	< 200	< 200	> 200	0.406	0.040
gasoline	-	4.980	< 0.020	1.830	4.210	40.20	1.720	867	0.486	< 5	< 200	< 200	> 200	0.287	0.027
DIY	-	6.990	< 0.020	0.711	3.020	104.0	1.540	1090	0.457	< 5	352	240	> 200	0.250	0.027

used oil type	arsenic	barium	beryllium	cadmium	chromium	lead	nickel	zinc	ash	PCBs	TX	TOX	flash point	sulfur	N
	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(% w/w)	(ppm)	(ppm)	(ppm)	(°F)	(% w/w)	(% w/w)
gasoline	-	2.040	< 0.020	3.330	3.980	41.30	1.290	1140	0.516	< 5	577	586	> 200	0.243	0.041
gasoline duplicate	-	1.810	< 0.020	2.720	3.130	35.80	1.800	1230	0.486	< 5	799	591	> 200	0.370	0.019
DIY	-	2.340	< 0.020	0.490	2.820	57.50	1.320	1240	0.432	< 5	216	202	> 200	0.316	0.040
gasoline	-	4.040	< 0.020	2.640	2.910	40.20	1.400	1130	0.556	< 5	432	454	> 200	0.317	0.052
gasoline duplicate	-	3.680	< 0.020	2.410	3.620	34.70	1.780	1130	0.616	< 5	424	301	> 200	0.384	0.047
gasoline	-	1.260	< 0.020	1.190	3.760	31.00	1.000	1330	0.627	< 5	< 200	< 200	> 200	0.404	0.055
v. lube	-	< 1.00	< 0.020	< 0.250	< 2.00	< 20.0	< 1.20	1270	0.151	< 5	< 200	< 200	> 200	0.328	0.019
v. lube	-	< 1.00	< 0.020	< 0.250	< 2.00	< 20.0	< 1.20	1150	0.119	< 5	400	385	> 200	0.400	0.016
No. 2	-	< 1.00	< 0.020	< 0.250	< 2.00	< 10.0	< 1.20	5.00	0.125	< 5	< 200	< 200	> 200	0.118	< 0.01
No. 4	-	< 1.00	< 0.020	< 0.250	< 2.00	< 10.0	8.340	9.05	0.549	< 5	< 200	< 200	> 200	0.186	0.033
high	-	6.990	< 0.020	6.610	6.850	146.0	3.020	2370	0.870	< 5	877	598	> 200	0.460	0.063
avg all ²	-	2.864	< 0.020	1.652	3.333	49.18	1.484	1152	0.525	< 5	< 327	< 284	> 200	0.335	0.039
avg gas	-	2.733	< 0.020	1.514	3.190	47.23	1.400	1161	0.543	< 5	< 350	< 301	> 200	0.357	0.044
avg dies	-	3.386	< 0.020	2.338	3.906	57.00	1.846	1114	0.455	< 5	< 234	< 217	> 200	0.248	0.021
low	-	< 1.00	< 0.020	< 0.250	< 2.00	< 20.0	1.00	568	0.317	< 5	< 200	< 200	> 200	0.133	0.017

¹ arsenic concentrations are not reported due to analytical difficulties with accurately determining arsenic concentrations at the necessary levels . While the laboratory can quantify arsenic concentrations in oil greater than 250 ppb, under the procedures of method 3050 some organic arsenic compounds are lost through volatilization, resulting in poor spike recoveries and the possibility of false negative results. Only one sample had an arsenic concentration > 250 ppb and that concentration was reported as > 2 ppm.

² does not include virgin lube oil or virgin fuel oil samples.

Table C
Waste Oil Furnace Specifications

Facility	Make	Model	Burner	Size Input (BTU/hr)	gph	oil psi
No. 2 oil	Oneida Royal	0-224B-5	Beckett-AF AK-076880	280,000	2	7
WO/1	Shenandoah	200	Shenandoah GB3.50	235,200	1.68	9
WO/2	Clean Burn	CB86AH	Clean Burn CB85HS	185,000	1.33	1
WO/3	Clean Burn	CB86BH	Clean Burn CB85HS	280,000	2.0	3.5
WO/4	Clean Burn	CB86BH	Clean Burn CB85HS	280,000	2.0	3
WO/5	Clean Burn	CB90AH	--	185,000	1.3	-

Table D
Used Oil Sample Analytical Results for Stack Test Sources

Facility	arsenic ¹	barium	cadmium	chromium	lead	nickel	zinc	TX	TOX	Chloride	Bromide	flash point ³	
	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(°F)	
No.2 oil	-	< 1.00	< 1.00	1.02	< 20.0	< 1.00	< 5.0	< 250	< 250	33.2	64.2	102	68
WO/1	-	3.43	1.20	3.85	31.8	1.63	1,100	< 250	< 250	< 26.0	< 26.0	--	> 200
WO/2	-	< 1.00	< 1.00	3.67	40.5	1.53	1,020	< 250	< 250	101.0	68.9	--	189
WO/3	-	1.75	1.75	4.23	29.9	2.03	1,280	< 250	< 250	75.2	60.6	100	88
WO/4	-	63.40	< 1.00	2.10	11.9	< 1.00	709	< 250	< 250	62.0	62.2	133	> 200
WO/5	-	2.14	2.14	4.73	96.8	3.69	868	500	460	106.0	61.0	102	91
high ²	-	63.40	2.14	4.73	96.8	3.69	1,280	500	460	106.0	68.9	> 200	
average ²	-							< 300	< 292	< 74.0	< 55.7	--	
low ²	-	1.00	< 1.00	2.10	11.9	< 1.00	709	< 250	< 250	< 26.0	< 26.0	68	

¹ arsenic concentrations are not reported due to analytical difficulties with accurately determining arsenic concentrations at the necessary levels . While the laboratory can quantify arsenic concentrations in oil greater than 250 ppb, under the procedures of method 3050 some organic arsenic compounds are lost through volatilization, resulting in poor spike recoveries and the possibility of false negative results.

² Values are for waste oil testing results only.

³ The waste oil samples were analyzed by two separate laboratories for flash point.

Table E
Emission Testing Actual Results For Each Test Run (mg/min)

Facility	HCl	Particulate	Arsenic ¹	Cadmium ¹	Chromium	Lead
	(mg/min)	(mg/min)	(mg/min)	(mg/min)	(mg/min)	(mg/min)
No. 2 oil	2.6	0	< 0.01	< 0.02	0.02	0.03
	1.9	0	< 0.02	< 0.03	0.02	0.03
WO/1	52.8	500	< 0.05	< 0.07	0.15	1.58
	58.6	333	< 0.02	< 0.07	0.11	1.52
WO/2	18.7	333	< 0.02	< 0.04	0.13	1.47
	14.6	333	< 0.02	< 0.03	0.10	1.17
WO/3	68.9	667	< 0.03	< 0.19	0.33	3.83
	21.7	333	< 0.02	< 0.06	0.09	1.32
WO/4	20.5	667	< 0.05	< 0.09	0.28	2.92
	17.9	667	< 0.02	< 0.07	0.19	2.53
WO/5	40.3	500	< 0.02	< 0.07	0.15	2.60
	32.2	333	< 0.02	< 0.06	0.12	1.90
average ²	34.6	467	< 0.03	< 0.08	0.17	2.09

¹ Arsenic and cadmium results are all reported as non detectable. The values presented represent the varying levels of detection for each specific sample collected which is a function of the sample mass.

² Values are for waste oil testing results only.

Table F
Waste Oil Furnace Operating Parameters

Facility	Temp	Moisture	Flow Rate	Velocity	Oxygen	Stk diam.	unit size
	(°F °C)	(% by vol)	(acfm acmm)	(ft/min m/min)	(% by vol)	(in m)	(MBTU/hr)
No. 2 oil	446/230	9.0	160/5	457/139	8.2	8/0.203	280
	479/248	9.1	154/4	440/134	8.2	"	
WO/1	516/269	2.2	267/8	766/233	9.0	"	235
	475/246	2.0	285/8	816/249	2.6	"	
WO/2	274/134	1.9	258/7	740/226	11.2	"	185
	426/219	3.1	212/6	608/185	11.3	"	
WO/3	470/243	7.6	177/5	507/155	11.4	"	280
	618/326	8.8	111/3	317/97	11.0	"	
WO/4	358/181	4.6	288/8	826/252	15.2	"	280
	385/196	0.1	253/7	725/221	15.2	"	
WO/5	287/142	4.4	205/6	587/179	11.4	"	185
	305/152	5.1	151/4	434/132	10.8	"	
average ¹	411/210	4.0	221/6.2	633/193	10.9	8/0.203	

¹ Values are for waste oil testing results only.

This starts the second part of the report.

Vermont Used Oil Study

Report

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Vermont Used Oil Study

Report

**Prepared for
U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Technical Support Division (MD-19)
Emission Measurement Branch
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PREFACE

This report was prepared by Midwest Research Institute (MRI) for the U.S. Environmental Protection Agency (EPA) under EPA Contract No. 68-D2-0165, Work Assignment No. I-28. Mr. Solomon Ricks was the EPA Work Assignment Manager (WAM) for the EMB. The report contains summary of test results, description of field activities, and QA/QC procedures, as well as analytical results and copies of pertinent calculations.

The project was conducted under the leadership of Mr. Slawomir Szydlo of MRI's Engineering and Environmental Technology Department.

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SECTION 1

INTRODUCTION

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1.1 SUMMARY OF TEST PROGRAM

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The U.S. Environmental Protection Agency (EPA), in cooperation with the Air Pollution Control Division and the Hazardous Materials Management Division of the State of Vermont Agency of Natural Resources (ANR), conducted a joint study to characterize the constituents and properties of used oils generated in the State and the resultant emissions from the combustion of used oil in small space heaters. The study results are intended to provide the information necessary to gauge compliance of burning used oil in these heaters with existing Air Pollution Control Regulations and Hazardous Waste Management Regulations. The study results will be used to assess the environmental impact of current used oil combustion practices versus alternative management practices such as more stringent burning regulations, re-refining, or fuel blending in order to provide the basis for developing a used oil management policy.

This report summarizes the results of stack testing performed at six facilities operating used oil burners. The testing was performed by MRI from April 18 to 29, 1994. The tests were performed to determine the following:

- the emission rate of HCl in the exhaust gas from the used oil space heaters,
- total particulate matter (TPM),
- the emission rate of arsenic, cadmium, chromium, and lead in the exhaust gas from the used oil space heaters.

Section 2 provides a brief description of the facilities tested. Section 3 of this report contains a summary of the test objectives and results. It also describes changes and modifications implemented during field testing. The sampling equipment used is described in detail in Section 4. Section 5 presents the quality assurance activities.

1.2 KEY PERSONNEL

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The key personnel who coordinated the test program and their phone numbers are presented in Figure 1-1.

Figure 1-1. Organizational chart.

SECTION 2

FACILITY AND SAMPLING LOCATION DESCRIPTIONS

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2.1 FACILITY DESCRIPTIONS

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The facilities tested included service stations, an automobile dealership, and a diesel truck maintenance shop. At all facilities, used crankcase oil is generated when servicing the vehicles. The used crankcase oil is stored for later use in small space heaters during the cold months of the year.

None of the facilities tested had pollution control equipment installed on the heaters.

2.2 SAMPLING LOCATIONS

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Emission sampling was conducted on the outlet stack of all six facilities. After installing the stack extension, all six sampling locations met the EPA criteria of 4 diameters downstream and 1 diameter upstream. A schematic diagram of a typical sampling location is presented in Figure 2-1.

Figure 2-1. Location of sampling ports and isokinetic points.

SECTION 3

TEST RESULTS

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The purpose of this study was to characterize emissions from the combustion of used oil in small space heaters.

3.1 OBJECTIVES AND TEST MATRIX

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The specific objectives of this project were as follows:

- To collect and analyze stack samples for particulate matter, HCl, arsenic, cadmium, chromium, and lead at five facilities utilizing used oil space heaters and one facility utilizing a No. 2 (diesel) fuel space heater. The heater utilizing No. 2 fuel was located at Barre Sunoco.
- To calculate emission rates of HCl, arsenic, cadmium, chromium, and lead for each facility tested.
- To prepare a concise report containing testing and analytical results.

Table 3-1 summarizes the sampling and analysis matrix for the project. The components and utilization of the sampling train are discussed in Section 4.

3.2 FIELD TEST CHANGES AND PROBLEMS

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The changes instituted during the testing were related mainly to the length of the sampling run. Since there were no previous tests done on these used oil space heaters, the time required to collect appropriate amount of sample was unknown. Thus, it was decided that a 4-h run should be necessary to collect enough sample to meet detection limits of the analytical methods. However, if there was evidence that enough sample was collected in a shorter period of time (i.e., heavy particulate loading), the length of the run was reduced.

During the two sampling runs at Bayview Cadillac, visual inspection of the sampling nozzle revealed very heavy particulate loading and a slight increase in the vacuum pressure required for sampling. For that reason, the sampling time for the first and second runs at Bayview Cadillac were shortened to 2 and 3 h,

respectively. All runs at other locations were 4 h in length. The lengths of sampling runs and their corresponding locations are presented in Table 3-2.

TABLE 3-1. SUMMARY OF SAMPLING AND ANALYSIS PARAMETERS AND METHODS

Sample	Sampling frequency for each run	Sampling method ^a	Sample size	Analytical parameters	Preparation method ^a	Analytical method ^a
Stack gas	2-h composite per run	MM5-MM ^b (Draft EPA Method 29 and EPA Method 0050)	60 to 100 ft ³ ^c	Metals ^d	Acid digestion (Draft EPA Method 29)	ICP (SW846, 6010A)
				Moisture	NA	Gravimetric
				Temperature	NA	Thermocouple
				Velocity	NA	Pitot tube
				Particulate	Desiccation	Gravimetric (EPA Method 5)
	HCl	NA	Ion chromatography (SW846, 9057)			
	2-h composite per run	EPA Method 3B	~ 20 L	Oxygen, carbon dioxide	NA	Orsat

^a "SW846" refers to *Test Methods for Evaluating Solid Waste*, Third Edition, November 1986, and updates. "EPA Method" refers to *New Source Performance Standards, Test Methods and Procedures*, Appendix A, 40 CFR 60.

^b MM5-MM = Modified Method 5 for multiple metals as specified in the draft EPA Method 29, "Determination of Metals Emissions from Stationary Sources."

^c Exact volume of gas sampled was dependent on isokinetic sampling rate.

^d Metals to be included in analysis were As, Cd, Cr, and Pb.

TABLE 3-2. TIMES AND LOCATIONS OF SAMPLING RUNS

Location	Run	Time (h)
Clarke's Sunoco	1	4
Clarke's Sunoco	2	4
Bayview Cadillac	1	2
Bayview Cadillac	2	3
Barre Sunoco	1	4
Barre Sunoco	2	4
Walker Motors	1	4
Walker Motors	2	4
Green Mtn. Kenworth	1	4
Green Mtn. Kenworth	2	4
Cody Chevrolet	1	4
Cody Chevrolet	2	4

The flow rate of the flue gas during the first sampling run at Cody Chevrolet was considerably different from the flow during the second run, with the flow during the second sampling run being much lower. The difference in flows between runs 1 and 2 was caused by a different fuel flow during each run. Also, the average flue gas temperature during the first run was 148°F lower than the average temperature during the second run. The difference in flow rates between runs resulted in considerably different volumes collected during both runs. The gas volume collected during the first run is approximately twice the volume collected during the second run.

3.3 SUMMARY OF RESULTS

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The emission rates of HCl for every facility tested are presented in Table 3-3. The rates of HCl emissions from heaters burning used crankcase oil vary widely from facility to facility, with the lowest emission rate of 1.46 mg/min at Clarke's Sunoco and the highest of 68.90 mg/min at the Cody Chevrolet. The emissions of HCl from No. 2 fuel were much lower with an average value of 2.20 mg/min. For calculations used, see Section 4.1.

The metal emission rates were calculated for arsenic, cadmium, chromium, and lead and are presented in Table 3-4. Some of the metal emission rates are reported with "<" value because either the front-half concentration or the back-half concentration was having concentrations below the instrumental detection limit. The calculations of metal emission rates are presented in Appendix B. The equations used for metals calculations are presented in Section 4.2.

The emission rates of all metals from the first run at Cody Chevrolet are roughly three times higher than the emission rates from the second run. The difference in the emission rates was due to different operating conditions of the used oil burner during the first and second run as noted previously.

All of the back-half blank concentrations were below the instrumental detection limit. Except for cadmium, all of the front-half blank concentrations were either below or very near the detection limit.

The front-half reagent blank for cadmium was 6.57 µg. The amount of cadmium ranged from 17.1 to 142 mg. The contribution of cadmium blank ranged from 5% to 38% for the total cadmium mass.

Because most of the blank values were below detection limit, and in the case of cadmium the blank contribution was unusually high, the metal emissions

were not blank corrected.

The particulate emissions for each run are presented in Table 3-5.

TABLE 3-3. HCI EMISSION RATES

TABLE 3-4. SUMMARY OF METALS EMISSION RATES

Location	Run No.	Emission rate (mg/min)			
		Arsenic	Cadmium	Chromium	Lead
Clarke's Sunoco	1	< 0.02	< 0.04	0.13	1.47
	2	< 0.02	< 0.3	0.10	1.17
Bayview Cadillac	1	< 0.05	< 0.07	0.15	1.58
	2	< 0.02	< 0.07	0.11	1.52
Barre Sunoco ^a	1	< 0.01	< 0.02	0.02	0.03
	2	< 0.02	< 0.03	0.02	0.03
Walker Motors	1	< 0.02	< 0.07	0.15	2.60
	2	< 0.02	< 0.06	0.12	1.90
Green Mtn. Kenworth	1	< 0.05	< 0.09	0.28	2.92
	2	< 0.02	< 0.07	0.19	2.53
Cody Chevrolet	1	< 0.03	< 0.19	0.33	3.83
	2	< 0.02	< 0.06	0.09	1.32

^a The heater operates on No. 2 fuel.

TABLE 3-5. SUMMARY OF PARTICULATE EMISSIONS

Location	Run	(kg/h)
Clarke's Sunoco	1	0.02
Clarke's Sunoco	2	0.02
Bayview Cadillac	1	0.03
Bayview Cadillac	2	0.02
Barre Sunoco ^a	1	0.00
Barre Sunoco ^a	2	0.00
Walker Motors	1	0.03
Walker Motors	2	0.02
Green Mtn. Kenworth	1	0.04
Green Mtn. Kenworth	2	0.04
Cody Chevrolet	1	0.04
Cody Chevrolet	2	0.02

^a The facility burns No. 2 fuel.

Similar to the metal emission rates, the HCl emission rates from the first run at Cody Chevrolet are approximately three times higher than those from the second run. Also, the sample collected from the first run at Bayview Cadillac was diluted during recovery by a factor of 3. The concentration was readjusted for the dilution factor.

Data on the usage of fuel was collected by representatives of the State of Vermont.

SECTION 4

SAMPLING AND ANALYTICAL PROCEDURES

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Ordinarily, testing for TPM, HCl, and metals requires at least two separate samplings. However, for this project, it was decided to utilize a modified Method 5 train able to test for all of the three parameters of interest at the same time.

4.1 PARTICULATE MATTER, HCl, AND METALS EMISSIONS TESTING METHOD

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The modified Method 5 train used in this study was designed to collect TPM, HCl, and multiple metals simultaneously in the same train. This method is applicable for the determination of TPM, HCl, Pb, Ni, Zn, P, Cr, Cu, Mn, Se, Be, TL, Ag, SG, Ba, Cd, and As from various types of processes. In this particular study, the test samples were analyzed only for As, Cd, Cr, and Pb. Particulate emissions were based on the weight gain of the filter and the front half acetone rinses of the probe, nozzle, and the front half of the filter holder. After the gravimetric analyses were completed, the sample fractions were analyzed for the target metals. During the recovery of the train, an aliquot of the impinger solution was removed for HCl analysis.

4.1.1 Sampling Equipment for Total Particulate Matter, HCl, and Metals

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This methodology used the sampling train shown in Figure 4-1. The sampling train consisted of a quartz nozzle/probe liner followed by a heated filter assembly with a Teflon[®] filter support, a series of six impingers, and the standard EPA Method 5 meterbox and vacuum pump. The sample was not exposed to any metals surfaces in this train. The first two impingers contained 100 mL of 0.1 N H₂SO₄ each. The third impinger was empty. The fourth and fifth impingers contained 100 mL of 5 percent nitric acid (HNO₃)/10 percent hydrogen peroxide (H₂O₂) solution, and the sixth impinger contained approximately 250 g of silica gel. The impingers were connected together with clean glass U-tube connectors and were arranged in an impinger bucket. Sampling train components were recovered and analyzed in separate front and back half fractions.

Figure 4-1. Modified Method 29 Sampling Train.

4.1.2 Equipment Preparation for Particulate Matter and Metals Sampling

p

4.1.2.1 Glassware Preparation—p

Glassware was washed in hot, soapy water, rinsed 3 times with tap water and then rinsed 3 times with deionized distilled water. The glassware was then subjected to the following series of soaks and rinses:

- Soaked in a 10 percent HNO₃ solution for a minimum of 4 h;
- Rinsed 3 times with deionized distilled water rinse; and
- Rinsed with acetone rinse.

The cleaned glassware was allowed to air dry in a contamination-free environment. The ends were then covered with parafilm. All glass components of the sampling train plus any other sample bottles, petri dishes, graduated cylinders, and other laboratory glassware used during sample preparation, recovery, and analysis were cleaned according to this procedure.

4.1.2.2 Reagent Preparation—p

The sample train filters were Whatman QM-4 filters. The acids and H₂O₂ were Baker "Instra-analyzed" grade or equivalent. The H₂O₂ was purchased specifically for this test site.

The reagent water was Baker "Analyzed HPLC" grade or equivalent. The H₂SO₄ solution for HCl determination was prepared according to Section 3.3.1.5 of the 40 *CFR*, Part 266, Appendix IX, p. 559.

The HNO₃/H₂O₂ absorbing solution was prepared fresh daily according to Section 3.1.4.2 of the 40 *CFR*, Part 266, Appendix IX, p. 530. The analyst wore both safety glasses and protective gloves when the reagents were mixed and handled. Each reagent had its own designated transfer and dilution glassware. To avoid contamination, this glassware was marked for identification with a felt tip glass-marking pen and used only for the reagent for which it was designated.

4.1.2.3 Equipment Preparation—p

The remaining preparation included calibration and leak checking of all the train equipment, which included meterboxes, thermocouples, nozzles, pitot tubes, and umbilicals. Referenced calibration procedures were followed when available, and the results were properly documented and retained. A discussion of the techniques used to calibrate this equipment is presented below.

Standard Pitot Tube Calibration. The EPA has specified guidelines

concerning the construction and geometry of an acceptable standard pitot tube. A pitot tube coefficient of 0.99 is used if the specified design and construction guidelines are met. Information pertaining to the design and construction of the standard pitot tubes meeting the required EPA specifications were used. Pitot tubes were inspected and documented as meeting EPA specifications prior to field sampling.

Sampling Nozzle Calibration. Glass nozzles were used for isokinetic sampling. Calculation of the isokinetic sampling rate required that the cross-sectional area of the sampling nozzle be accurately and precisely known. All nozzles were thoroughly cleaned, visually inspected, and calibrated according to the procedure outlined in Section 3.4.2 of EPA Document 600/4-77-027b.

Temperature Measuring Device Calibration. Accurate temperature measurements were required during source sampling. Thermocouple temperature sensors were calibrated using the procedure described in Section 3.4.2 of EPA document 600/4-77-027b. Each temperature sensor was calibrated at a minimum of two points over the anticipated range of use against an NBS-traceable mercury-in-glass thermometer. All sensors were calibrated prior to field sampling.

Dry Gas Meter Calibration. Dry gas meters (DGMs) were used in the sample trains to monitor the sampling rate and to measure the sample volume. All DGMs were calibrated to document the volume correction factor using the procedure outlined in Section 3.3.2 of EPA document 600/4-77-207b.

4.1.3 Total Particulate Matter, HCl, and Metals Sampling Operations

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4.1.3.1 Preliminary Measurements—b

Before sampling began, preliminary measurements were required to ensure isokinetic sampling. These included determining the traverse point locations and performing a preliminary velocity traverse and moisture determination. These measurements were used to determine an isokinetic sampling rate from stack gas flow readings taken during sampling.

Measurements made during the pretest site survey were then checked for accuracy. Measurements were made of the duct inside diameter, port nozzle length, and the distances to the nearest upstream and downstream flow disturbances. These measurements were used to verify sampling point locations by following EPA Reference Method 1 guidelines. The distances were then marked on the sampling probe using an indelible marker.

4.1.3.2 Assembling the Train—p

Assembling the PM, HCl, and metals sampling train components was initiated in the recovery trailer, and final train assembly was completed at the stack location. First, the empty, clean impingers were assembled and laid out in the proper order in the recovery trailer. Each joint was carefully inspected for hairline cracks. After the impingers were loaded, each impinger was weighed, and the initial weight and contents of each impinger were recorded on a recovery data sheet. The impingers were connected together by clean glass U-tube connectors and arranged in the impinger bucket. The height of all the impingers was approximately the same to obtain a leak-free seal. The open ends of the train were sealed with parafilm or teflon tape.

The second step was to load the filter into the filter holder in the recovery trailer. The filter holder was then capped off and placed into the impinger bucket. A supply of parafilm and joints was also placed in the bucket in a clean plastic bag for use by the samplers. The train components were transferred to the sampling location and assembled as previously shown in Figure 4-1.

4.1.3.3 Sampling Procedures—p

After the train was assembled, the heaters for the probe liner and heated filter box were turned on. When the system reached the appropriate temperatures, the sampling train was ready for pretest leak checking. The filter skin temperature was maintained at $120 \pm 14^\circ\text{F}$ ($248 \pm 25^\circ\text{F}$). The probe temperature was maintained above 100°C (212°F).

The sampling trains were leak checked at the start and finish of sampling. (EPA Method 5 protocol required posttest leak checks and recommended pretest leak checks.) An acceptable pretest leak rate was less than 0.02 acfm (ft^3/min) at approximately 15 inches of mercury (inHg).

To leak check the assembled train, the nozzle end was capped off and a vacuum of 15 inHg was pulled in the system. When the system was evacuated, the volume of gas flowing through the system was timed for 60 s. After the leak rate was determined, the cap was slowly removed from the nozzle end until the vacuum dropped off, and then the pump was turned off. If the leak rate requirement was not met, the train was systematically checked by first capping the train at the filter, at the first impinger, etc., until the leak was located and corrected.

After a successful pretest leak check had been conducted, all train components were at their specified temperatures and initial data were recorded (DGM reading), the test was initiated. Sampling train data were recorded

periodically on standard data forms.

The leak rates and sampling start and stop times were recorded on the sampling data terms. Also, any other events that occurred during sampling were recorded on the task log such as pitot cleaning, thermocouple malfunctions, heater malfunctions, or any other unusual occurrences.

At the conclusion of the test run, the sample pump (or flow) was turned off, the probe was removed from the duct, a final DGM reading was taken, and a posttest leak check was completed. (The posttest leak check procedure is identical to the pretest procedure; however, the vacuum should be at least 1 inHg higher than the highest vacuum attained during sampling.) An acceptable leak rate was less than 4 percent of the average sample rate, or 0.02 acfm (whichever was lower).

4.1.4 Particulate Matter, HCl, and Metals Sample Recovery

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Recovery procedures began as soon as the probe was removed from the stack and the posttest leak check was completed.

To facilitate its transfer from the sampling location to the recovery trailer, the sampling train was disassembled into two sections: the nozzle/probe liner and filter holder, and impingers bucket. Each of these sections was capped with Teflon[®] tape or parafilm before being transported to the recovery trailer.

Once in the trailers, the sampling train was recovered as separate front and back half fractions. Figure 4-2 is a diagram illustrating front half and back half sample recovery procedures. No equipment with exposed metal surfaces was used in the sample recovery procedures. The weight gain in each of the impingers was recorded to determine the moisture content in the flue gas. Following weighing of the impingers, the front half of the train was recovered, which included the filter and all sample-exposed surfaces forward of the filter. The probe liner was rinsed with acetone by tilting and rotating the probe while squirting acetone into its upper end so that all inside surfaces were wetted. The acetone was quantitatively collected into the appropriate sample bottle. This rinse was followed by additional brush/rinse procedures using a nonmetallic brush; the probe was held in an inclined position, and acetone was squirted into the upper end as the brush was pushed through with a twisting action. All of the acetone and particulate was caught in the sample container. This procedure was repeated until no visible particulate remained and was finished with a final acetone rinse of the probe and brush. The front half of the filter was also rinsed with acetone until all visible

particulate was removed. After all front half acetone washes were collected, the cap was tightened, the liquid level marked, and the bottle weighed to determine the acetone rinse volume. The method specifies that a total of 100 mL of acetone must be used for rinsing these components. However, a thorough rinse usually requires more reagent. For blank correction purposes, the exact weight or volume of acetone used was measured. An acetone reagent blank of approximately the same volume as the acetone rinses was analyzed with the samples.

Figure 4-2. Analysis Scheme for Sampling Train Components.

The nozzle/probe liner and front half of the filter holder was rinsed 3 times with 0.1 N HNO₃, and the rinse was placed into a separate amber bottle. The container was capped tightly, the weight of the combined rinse was recorded, and the liquid level was marked on the bottle. The filter was placed in a clean, well-marked glass petri dish and sealed with Teflon[®] tape.

Prior to recovering the back half impingers, the contents were weighed for moisture content. Any unusual appearance of the filter or impinger contents was noted in the logbook.

The contents of the first two impingers were recovered into a preweighed, prelabeled bottle and combined with H₂O rinses of the first two impingers. An aliquot of the impingers' content was saved for HCl analysis. The impingers were rinsed with 0.1 N HNO₃, and the rinsate saved for metals analysis. The remaining impingers and connecting glassware were rinsed thoroughly with 0.1 N HNO₃, the rinse was captured in the impinger contents bottle, and a final weight was taken. Again, the method specifies a total of 100 mL of 0.1 N HNO₃ be used to rinse these components. The weight of reagent used for rinsing was determined by weighing the impinger contents bottle before and after rinsing the glassware. A nitric acid reagent blank of approximately the same volume as the rinse volume was analyzed with the samples.

After final weighing, the silica gel from the train was saved for regeneration.

A reagent blank was recovered in the field for each of the following reagents:

- Acetone blank
- 0.1 N HNO₃ blank
- 5 percent HNO₃/10 percent H₂O₂ blank
- Dionized water
- Filter blank
- 0.1 N H₂SO₄

Each reagent blank was from the same lot used during the sampling program.

The liquid level of each sample container was marked on the bottle in order to determine if any sample loss occurred during shipment. If sample loss had occurred, the sample might have been voided or a method could have been used to incorporate a correction factor to scale the final results depending on the volume of the loss.

4.1.5 Particulate, HCl, and Metals Analysis

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The analytical approach is shown schematically in Figure 4-2. The general gravimetric procedure described in EPA Method 5, Section 4.3, was followed. Both filters and precleaned beakers were weighed to a constant weight. The same balance used for taring was used for weighing the samples.

The acetone rinses were evaporated under a clean hood at room temperature to dryness in a tared beaker. The residue was desiccated for 24 h in a desiccator containing fresh room temperature silica gel. The filter was also desiccated to a constant weight under the same conditions. Weight gain was reported to the nearest 0.1 mg. Each replicate weighing agreed to within 0.5 mg or 1 percent of total weight less tare weight, whichever was greater, between two consecutive weighings, and was at least 6 h apart. The metals analysis followed the procedure of SW-846 Method 6010A. Detailed description of metals analysis can be found in Appendix D of this report: "Metals Analysis Report." The HCl samples were analyzed according to Method 3057, 40 *CFR*, Part 266, Appendix IX, pp. 573-575.

4.2 EMISSION CALCULATIONS

b

The sampling train used in this study was designed to collect TPM, HCl, and metals. During the recovery of train after the testing, an aliquot of the absorbing solution from the first two impingers was taken for HCl analysis. The solution taken for HCl analysis was not analyzed for metals. Thus, in order to achieve true representation of metal emissions, the missing volume of the aliquot had to be accounted for. The following approach was used to calculate metal emissions.

where:

$V_{m(\text{std})}$	=	Gas volume collected [dscm ³]
Vol_A	=	Volume of impinger solutions before aliquot was taken [mL]
Vol_B	=	Volume of impinger solution after [mL] aliquot was taken
M_4	=	Constant [10^{-3} mg/ μ g]
M_T	=	Total mass of metal (sum of front half and back half analysis) [μ g]
M_{TC}	=	Corrected total mass of metal [μ g]
C_S	=	Metal emission rate [mg/dscm]
G_R	=	Volumetric gas flow rate [dscm/min]
E_R	=	Metal emission rate [mg/min]

The metal emissions are calculated as follows:

$$M_{TC} = M_T \times \frac{Vol_A}{Vol_B} \quad (4-1)$$

$$C_S = K_4 \left(\frac{M_{TC}}{V_{M(std)}} \right) \quad (4-2)$$

$$E_R = C_S \times G_R \quad (4-3)$$

The HCl emissions were collected in the first two impingers containing 0.1 N H₂SO₄ solution. The HCl concentrations were analyzed from the aliquot taken during the sampling which was only a fraction of the total impinger solution. The total HCl were calculated as follows:

where:

- C_{HCl} = Concentration of HCl [$\mu\text{g/mL}$]
- V_I = Volume of solution in the impingers [mL]
- $V_{M(std)}$ = Gas volume collected [dscm]
- G_R = Gas flow rate [dscm/min]
- CR_{HCl} = Concentration of the HCl in the gas [mg/dscm]
- E_{HCl} = Emission rate of HCl [mg/min]
- K = Constant ($10^{-3} \text{ mg}/\mu\text{g}$)

$$CR_{HCl} = (K \times C_{HCl} \times V_I) / V_{m(std)} \quad (4-4)$$

$$E_{HCl} = CR_{HCl} \times G_R \quad (4-5)$$

SECTION 5

QA/QC REPORT

b

The subject report and appendices (in final draft form) were independently reviewed by the project QA coordinator. Data for Run 1 from the Clarke's Sunoco facility were audited versus the field sampling records and analytical reports. Derived emission rates for Pb and HCl in this run were checked for accuracy by manual calculation.

In addition, the metals data are supported by QC analyses of a NIST filter (85% to 124% of certified values) and a spiked simulated matrix sample (102% to 111% recovery of spiked amount) for the front and back half fractions, respectively. Accuracy of the chloride data were demonstrated with an independent check standard (102% accuracy) and a spiked matrix sample (102% recovery). Gravimetric measurements for particulate data were monitored by weighing control samples and a standard weight to within 2% tolerance.

Based on the review of representative sample and QC data described above, test results were found to be complete, traceable, and correctly reported. Minor editorial and significant figure reporting changes were recommended for the final report.

APPENDIX A

LIST OF SAMPLES COLLECTED

The following represents samples collected in the field:

Front Half Acetone Rinse:

Samples: 1001, 2001, 3001, 4001, 5001, 6001, 7001, 8001, 9001,
10001, 11001, 12001

Front Half HNO₃ Rinse:

Samples: 1002, 2002, 3002, 4002, 5002, 6002, 7002, 8002, 9002,
10002, 11002, 12002

Particulate Filter:

Samples: 1003, 2003, 3003, 4003, 5003, 6003, 7003, 8003, 9003,
10003, 11003, 12003

Galbright HCl Aliquot:

Samples: 1004, 2004, 3004, 4004, 5004, 6004, 7004, 8004, 9004,
10004, 11004, 12004

HNO₃ Rinse of Impingers 1 and 2:

Samples: 1005, 2005, 3005, 4005, 5005, 6005, 7005, 8005, 9005,
10005, 11005, 12005

Condensate from Impingers 1 and 2 Plus H₂O Rinse:

Samples: 1006, 2006, 3006, 4006, 5006, 6006, 7006, 8006, 9006,
10006, 11006, 12006

Condensate from Impingers 3, 4, and 5 Plus HNO₃ Rinse:

Samples: 1007, 2007, 3007, 4007, 5007, 6007, 7007, 8007, 9007,
10007, 11007, 12007

D1 H₂O Blank—Sample 3012

0.1 N H₂SO₄ Blank—Samples 3015

5% HNO₃/10% H₂O₂ Blank—Sample 3016

Acetone Blank—Sample 3011

Filter Blank—Sample 3013

0.1 N HNO₃ Blank—Sample 3014

APPENDIX B

METALS EMISSION RESULTS PER FACILITY

APPENDIX C

SAMPLING DATA

APPENDIX D

PARTICULATE ANALYSIS DATA

APPENDIX E

METALS ANALYSIS REPORT

APPENDIX F

HCI ANALYSIS RESULTS

APPENDIX G

TRACEABILITY FORMS

APPENDIX H

EQUIPMENT CALIBRATION FORMS

APPENDIX I

MODIFIED METHOD 5 CALCULATIONS