

Quantification of Metals Emissions From Burning Used Oil Fuel

Entropy, Inc.



Performed For: Used Oil Recycling Coalition

July, 1996

National
Oil
Recyclers
Association



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STATIONARY SOURCE SAMPLING REPORT

REFERENCE NO. 14505C

VOLUME 1

EMISSIONS TESTING FOR:

Particulate

Arsenic

Barium

Cadmium

Chromium

Hexavalent Chromium

Lead

Zinc

PERFORMED FOR: USED OIL RECYCLING COALITION

JULY 1995

REPORT CERTIFICATION

El Reference Number 14505C

The sampling and analysis performed for this report were carried out under my direction and supervision, and I hereby certify that the test report is authentic and accurate.

Signature:

Tom E. Holder

Date:

4/12/96

Tom E. Holder
Project Director
Test Operations Division

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EXECUTIVE SUMMARY

The Used Oil Recycling Coalition (UORC) contracted with Entropy, Inc. to evaluate metals emissions from used oil combustion. The primary objective of the study was to compile accurate data on emissions of lead for combustion sources utilizing used oil as a fuel. The secondary objective was to compile accurate emissions data for other metals including barium, cadmium, chromium, arsenic, and zinc.

The project was divided into two phases. In Phase I, Entropy, Inc. conducted a comprehensive literature search to determine if there were significant gaps in the available technical information regarding the emissions of metals from the combustion of used oil. In addition, an emissions inventory for used oil combustion sources was compiled to evaluate the emission quantities of each source category. Portions of the conclusions and recommendations for Entropy's Phase I report (dated April 27, 1994) are excerpted below.

In Phase II of the project, Entropy, Inc. conducted emissions test programs at two asphalt plants that combust used oil. Testing at one of the plants also involved the combustion of virgin oil. Asphalt plants were chosen for emissions testing because they are the single largest category of sources that burn used oil, and they consume approximately 43 percent of the total used oil collected and used as fuel in the United States.

The information from the study demonstrates that the combustion of used oil in asphalt plants equipped with baghouses in good working condition resulted in emissions of lead below detection limits. In fact, the emissions of lead and other metals from the combustion of used oil at both test facilities did not differ significantly from the emissions associated with the combustion of number 2 virgin oil at one of the test facilities.

Phase I Conclusions:

1. Due to significant reductions in the concentrations of some of the metals in used oils, most of the metals emission test data obtained prior to 1985 is not representative of present-day emissions.
2. Due to the lead-in-gasoline phase-down requirements, lead levels in automotive used oil after processing have decreased substantially. Average levels are now in the range of 40 ppm, well below the pre-1985 levels of 200 to 1000 ppm.
3. Barium levels in used oil have decreased substantially due to changes in the composition of additive packages used for lubricating oils. Average levels in automotive used oils are now in the range of 10 ppm.
4. A large fraction of the metals contained in used oil fuel stays within the combustion chamber and is not emitted into the effluent stream. The metals are trapped as deposits on combustion chamber walls and heat exchange surfaces. For industrial boilers, commercial boilers, space heaters, and other small combustion sources, the quantities retained as permanent deposits are probably 50 percent of the total quantity of metals entering with the fuel.

5. A significant fraction of the metals contained in used oil fuel for industrial furnaces is captured by the product streams processed in the furnaces. These metals are trapped as permanent solid deposits in the surfaces of the product materials and are not emitted to the atmosphere. For cement kilns and asphalt plant rotary dryers, metal capture by-product materials can range from 20 percent to 90 percent.
6. Metal-containing particles formed due to vaporization in the combustion chamber and nucleation during gas stream cooling are primarily in the submicron size range. Multicyclone collectors are ineffective for this particle size range. The collection efficiencies for the types of wet scrubbers, electrostatic precipitators, and fabric filters employed on used oil combustion sources range from approximately 50 percent to greater than 99 percent.
7. Asphalt plants are the largest single category of sources burning used oil. They consume approximately 43 percent of the total used oil collected and used as fuel in the United States, and there are indications that the consumption rates are increasing. Metals removal in baghouse-controlled plants is very high. There is considerable uncertainty regarding the capability of wet scrubber controlled plants to collect metals-containing particles efficiently.
8. Utility boilers are an important consumer of used oil. More data are needed regarding the types of boilers that burn used oil, the types of fuels co-fired with used oil, the types of air pollution control systems on these boilers, and the used oil firing practices. There are no previously conducted air emissions studies on utility boilers regarding the potential metals emissions attributable to the burning of used oil.
9. Industrial boilers used for space heating and steam generation are important because of the quantities of used oil consumed and the limited air pollution control system capability. Emissions data are needed to evaluate the metals retention as deposits in the boilers and to evaluate the fractions removed as part of bottom ash or flyash streams. There are no relevant, up-to-date data concerning metals emissions from industrial boilers.
10. Space heaters are an important category due to the quantities of used oil burned and the lack of air pollution control systems. There is very little relevant, up-to-date emissions data. However, a study being coordinated by the State of Vermont is likely to provide valuable data. (See Volume 1, Appendix A of this report).
11. The NORA survey data indicates that small commercial boilers, apartment house boilers, and school boilers (collectively termed "residential/commercial" boilers) receive a relatively small fraction of the overall used oil generated in the United States.
12. Cement kilns and other types of industrial processes do not appear to be significant sources of metals emissions due to high particulate collection efficiencies and to metal capture in the product streams.

Phase I Recommendations:

1. An emission test program should be conducted to characterize emissions from three types of used oil combustion sources: (1) asphalt plants, (2) utility boilers, and (3) industrial boilers. The tests should include analyses of the used oil fuel and the accumulation of metals on heat exchange surfaces and refractory within the boilers. The scope of the tests should include lead, barium, cadmium, chromium, arsenic, and zinc.
2. Air pollution emission data obtained as part of the State of Vermont study of space heaters should be requested as soon as it is available to further evaluate the environmental aspects of used oil combustion in space heaters. (See Volume 1, Appendix A of this report).

Phase II:

Pursuant to the Phase I recommendations, extensive efforts were made to locate suitable combustion sources from all three recommended categories, but no suitable utility or industrial boilers were identified as test subjects. No utility boilers were identified that co-burned used oil with virgin oil. Although many utility boilers co-burn used oil with coal, these burners were determined not to be appropriate test subjects because the used oil generally constitutes a small constituent of the fuel load and because of the difficulties inherent in differentiating the very slight impact of metals associated with the combustion of used oil from the metals associated with the combustion of coal. A small number of potential industrial boiler candidates were identified and contacted. Ultimately, however, none would allow the testing to be performed. Thus, Phase II testing was limited to two asphalt plants.

Stack testing was conducted at two asphalt plants, designated as Facility A and B throughout this report, to determine the emissions of lead, barium, cadmium, chromium (hexavalent and total), arsenic, and zinc. At Facility A, tests were conducted during the combustion of virgin number 2 fuel oil (designated as Condition I) as well as used oil, which is referred to by the asphalt plants as number 4 recycled oil (designated as Condition II). At Facility B, tests were conducted during the combustion of number 4 recycled oil.

Comparison of the emissions from the different fuels fully supports the contention that metals removal in baghouse-controlled plants is very high. At Facility A, lead content of the recycled oil was 50 times higher than that of the virgin oil, yet emissions remained at or below the detection limit with corresponding removal efficiencies greater than 99.98 percent. A comparison of the average percent removal efficiencies for each metal under each of the test conditions is presented in the following table.

Metals Removal Efficiency - Average of Three Test Runs

Arsenic	Barium	Cadmium	Chromium	Lead	Zinc
Facility A Virgin Number 2 Fuel Oil					
> 98.63	> 92.06	> 97.86	> 96.07	> 95.33	> 70.49
Facility A Recycled Number 4 Fuel Oil					
> 98.70	98.72	> 99.42	99.05	> 99.98	99.97
Facility B Recycled Number 4 Fuel Oil					
> 98.03	96.59	> 98.56	98.74	> 99.95	99.96

At Facility B, lead content in the recycled oil was slightly lower than that in the recycled oil at Facility A, and removal efficiencies remained high - greater than 99.95 percent. At both facilities, removal efficiencies of the other metals tested were similarly high.

The information from the study indicates that the combustion of used oil in asphalt plants equipped with baghouses in good working condition resulted in low levels of emissions of lead and other metals at or below detection limits. In fact, the emissions of lead and other metals from the combustion of used oil at these facilities did not differ significantly from the emissions associated with the combustion of number 2 virgin fuel oil at Facility A. The mass balance calculations indicate overall removal efficiencies of 96.05 percent to 99.98 percent of the metals tested. Thus, the study demonstrates that the combustion of used oil in these types of asphalt plants is a good option for resource recovery.

1.0 INTRODUCTION

1.1 Overview of Project Objectives

The Used Oil Recycling Coalition (UORC) contracted with Entropy, Inc. to evaluate metals emissions from used oil combustion. The primary objective of the study was to compile accurate data on emissions of lead for combustion sources utilizing used oil as a fuel. The secondary objective was to compile accurate emissions data for other metals including barium, cadmium, chromium, arsenic, and zinc.

The project was divided into two phases. In Phase I, Entropy, Inc. conducted a comprehensive literature search to determine if there were significant gaps in the available technical information regarding the emissions of metals from the combustion of used oil. In addition, an emissions inventory for used oil combustion sources was compiled to evaluate the emission quantities of each source category.

In Phase II of the project, Entropy, Inc. conducted emissions test programs at two asphalt plants that combust used oil. Testing at one of the plants also involved the combustion of virgin oil to make a direct comparison of the metals emissions from the same system. Asphalt plants were chosen for emissions testing because they are the single largest category of sources that combust used oil, and they consume approximately 43 percent of the total used oil collected and used as fuel in the United States.

The Phase I report was submitted to the UORC on April 27, 1994. This report is the result of the tests conducted under Phase II.

1.2 Outline of Test Program

The testing was conducted using well-established U.S. EPA Reference Methods under carefully controlled conditions fully documented in the Quality Assurance Project Plan (QAPP) submitted June 14, 1995 to the Used Oil Recycling Coalition. The QAPP was also submitted to the USEPA for review and comments. During each of the tests, fuel samples and solid waste samples were collected and analyzed to support the findings of the air emissions tests.

Pursuant to the Phase I recommendations, extensive efforts were made to locate suitable combustion sources from all three recommended categories, but no suitable utility or industrial boilers were identified as test subjects. No utility boilers were identified that co-burned used oil with virgin oil. Although many utility boilers co-burn used oil with coal, these burners were determined not to be appropriate test subjects because the used oil generally constitutes a small constituent of the fuel load and because of the difficulties inherent in differentiating the very slight impact of metals associated with the combustion of used oil from the metals associated with the

combustion of coal. A small number of potential industrial boiler candidates were identified and contacted. Ultimately, however, none would allow the testing to be performed. Thus, Phase II testing was limited to two asphalt plants.

This portion of the test program was conducted at two asphalt plants. **Table 1-1** is a test log that presents the test conditions, sampling locations, sampling objectives, sampling methods, test dates, and run numbers for the test program. Several runs utilized flue gas composition data from other runs; refer to **Table 1-1**.

Asphalt plants are the largest single category of sources that burn used oil. They consume approximately 43 percent of the total used oil collected and used as fuel. Fuel oil is burned in asphalt plants to heat and dry the aggregate prior to the addition of asphaltic binder. A single oil burner is mounted in a short rotary drier. The aggregate passes through the drier and is showered across the path of the hot combustion gas using a large number of flights (scoops) mounted on the interior surface of the drier. The plants tested were equipped with high-efficiency fabric filters for particulate emissions control.

At Facility A, during Condition I, the asphalt plant was burning virgin Number 2 fuel oil. During Condition II, recycled number 4 fuel oil was burned. At Facility B, a single condition was tested during the combustion of recycled number 4 fuel oil. Analysis of each of the fuels is included in this report.

**TABLE 1-1
TEST LOG**

Test Location	Sampling Objective	Test Method	Test Date	Run Numbers	Flue Gas Composition
Facility A Condition I	Cr ⁺⁶	SW-846 0013	07/10	I-M0013-1	I-M3-1
			07/10	I-M0013-2	I-M3-2
			07/10	I-M0013-3	I-M3-3
	Particulate and Metals	EPA 5/29	07/10	I-M5/29-1	I-M3-1
			07/10	I-M5/29-2	I-M3-2
			07/10	I-M5/29-3	I-M3-3
Facility A Condition II	Cr ⁺⁶	SW-846 0013	07/11	II-M0013-1	II-M3-1
			07/11	II-M0013-2	II-M3-2
			07/11	II-M0013-3	II-M3-3
	Particulate and Metals	EPA 5/29	07/11	II-M5/29-1	II-M3-1
			07/11	II-M5/29-2	II-M3-2
			07/11	II-M5/29-3	II-M3-3
Facility B	Cr ⁺⁶	SW-846 0013	07/13	M0013-1	M3-1
			07/13	M0013-2	M3-2
			07/14	M0013-3	M3-3
	Particulate and Metals	EPA 5/29	07/13	M5/29-1	M3-1
			07/13	M5/29-2	M3-2
			07/14	M5/29-3	M3-3

1.3 Test Participants

Table 1-2 lists the personnel involved in the test program.

**TABLE 1-2
TEST PARTICIPANTS
JULY 1995**

Entropy, Inc.	Tom E. Holder Project Director
	Lafayette B. Johnson Sampling Team Leader
	Donald J. Garnet Sampling Team Leader
	Joseph R. Winslow Laboratory Technician

2.0 SUMMARY OF RESULTS

2.1 Presentation

Tables 2-1 through 2-5 present test summaries; refer to the "List of Tables and Figures" of the "Table of Contents." Detailed test results are presented in Appendix B. Field data are given in Appendix C. Analytical data can be found in Appendix D.

2.2 Discussion

Asphalt plants consume approximately 43 percent of the used oil fuels generated in the United States. The National Asphalt Paving Association (NAPA) has estimated that the industry consumes as much as 200 million gallons per year. That consumption rate has increased during the last few years.

The data in this report show that metals in used oil fuels burned in asphalt plants are captured with high efficiency at units equipped with well-operated baghouses. Comparison of the emissions from the different fuels fully supports the contention that metals removal in baghouse-controlled plants is very high. At Facility A, lead content of the recycled oil was 50 times higher than that in the virgin oil, yet emissions remained at or below the detection limit with corresponding removal efficiencies greater than 99.98 percent. A comparison of the average percent removal efficiencies for each metal under each of the test conditions is presented in the following table.

Metals Removal Efficiency - Average of Three Test Runs

Arsenic	Barium	Cadmium	Chromium	Lead	Zinc
Facility A Virgin Number 2 Fuel Oil					
> 98.63	> 92.06	> 97.86	> 96.07	> 95.33	> 70.49
Facility A Recycled Number 4 Fuel Oil					
> 98.70	98.72	> 99.42	99.05	> 99.98	99.97
Facility B Recycled Number 4 Fuel Oil					
> 98.03	96.59	> 98.56	98.74	> 99.95	99.96

At Facility B, lead content in the recycled oil was slightly lower than that in the recycled oil at Facility A, and removal efficiencies remained high - greater than 99.95 percent. At both facilities, removal efficiencies of the other metals tested were similarly high.

The high metal removal efficiencies of this study can be attributed to the characteristics of the combustion process and fabric filter collection. The metals vaporized in the burner flame have

ample opportunity to nucleate on the surfaces of the aggregate and the aggregate dust circulating through the combustion gas stream. The aggregate surface temperatures are much lower than the dewpoint temperatures for the metal vapors. In fact, the aggregate temperatures are far below the normal surface temperatures of the combustion chamber surfaces. Accordingly, condensation of these vapors is likely on the aggregate as well as on the aggregate dust. Metals captured by the aggregate are removed from the mass balance equation as part of the hardened asphaltic concrete. Metal emissions are further reduced in the equation by the fabric filters used at these plants. Because fabric filter efficiency is high even in the submicron range, metal vapor that nucleates on the aggregate dust is captured by the fabric filters.

2.3 Cyclonic Flow Checks

A cyclonic flow check was performed at the Facility A sampling location to determine if any cyclonic flow existed. An average yaw angle of $< 0.5^\circ$ was measured, indicating an acceptable location with respect to EPA Method 1 requirements.

TABLE 2-1
EMISSION RATES AND CONCENTRATIONS
FACILITY A, CONDITION I
JULY 1995

	Rep 1	Rep 2	Rep 3	Average
Concentration, gr/DSCF				
Filterable Particulate	0.00174	0.00259	0.00245	0.00226
Arsenic	< 1.55E-07	< 2.27E-07	< 2.32E-07	< 2.05E-07
Barium	2.39E-06	1.54E-06	1.13E-06	1.69E-06
Cadmium	3.75E-07	5.69E-07	1.51E-07	3.65E-07
Chromium	4.66E-07	7.60E-07	5.58E-07	5.95E-07
Hexavalent Chromium	< 3.67E-07	< 4.80E-07	< 4.55E-07	< 4.34E-07
Lead	2.71E-07	< 1.34E-06	< 2.32E-07	< 6.14E-07
Zinc	5.27E-06	1.64E-05	4.63E-06	8.77E-06
Concentration, gr/DSCF @ 12% CO2				
Filterable Particulate	0.00317	0.00457	0.00420	0.00398
Arsenic	< 2.82E-07	< 4.01E-07	< 3.97E-07	< 3.60E-07
Barium	4.34E-06	2.71E-06	1.93E-06	2.99E-06
Cadmium	6.82E-07	1.00E-06	2.58E-07	6.47E-07
Chromium	8.48E-07	1.34E-06	9.57E-07	1.05E-06
Hexavalent Chromium	< 6.67E-07	< 8.47E-07	< 7.80E-07	< 7.65E-07
Lead	4.93E-07	< 2.37E-06	< 3.97E-07	< 1.09E-06
Zinc	9.58E-06	2.89E-05	7.94E-06	1.55E-05
Concentration, gr/DSCF @ 7% O2				
Filterable Particulate	0.00269	0.00414	0.00382	0.00335
Arsenic	< 2.39E-07	< 3.63E-07	< 3.62E-07	< 3.21E-07
Barium	3.68E-06	2.45E-06	1.76E-06	2.63E-06
Cadmium	5.79E-07	9.09E-07	2.35E-07	5.74E-07
Chromium	7.20E-07	1.21E-06	8.72E-07	9.34E-07
Hexavalent Chromium	< 5.67E-07	< 7.67E-07	< 7.10E-07	< 6.81E-07
Lead	4.19E-07	< 2.14E-06	< 3.62E-07	< 9.74E-07
Zinc	8.13E-06	2.62E-05	7.23E-06	1.39E-05
Emission Rate, lb/hr				
Filterable Particulate	0.334	0.503	0.470	0.436
Arsenic	< 2.97E-05	< 4.42E-05	< 4.45E-05	< 3.95E-05
Barium	4.57E-04	2.99E-04	2.16E-04	3.24E-04
Cadmium	7.18E-05	1.11E-04	2.89E-05	7.06E-05
Chromium	8.92E-05	1.48E-04	1.07E-04	1.15E-04
Hexavalent Chromium	< 6.94E-05	< 8.84E-05	< 8.39E-05	< 8.06E-05
Lead	5.19E-05	< 2.61E-04	< 4.45E-05	< 1.19E-04
Zinc	1.01E-03	3.18E-03	8.90E-04	1.69E-03

TABLE 2-2
EMISSION RATES AND CONCENTRATIONS
FACILITY A, CONDITION II
JULY 1995

	Rep 1	Rep 2	Rep 3	Average
Concentration, gr/DSCF				
Filterable Particulate	1.18E-03	1.19E-03	7.37E-04	1.04E-03
Arsenic	< 2.51E-07	< 2.10E-07	< 2.17E-07	< 2.26E-07
Barium	1.31E-06	9.79E-07	3.32E-06	1.87E-06
Cadmium	1.09E-07	1.15E-07	< 8.67E-08	< 1.04E-07
Chromium	9.88E-07	4.72E-07	4.16E-07	6.25E-07
Hexavalent Chromium	< 5.38E-07	< 4.13E-07	< 3.35E-07	< 4.29E-07
Lead	< 2.51E-07	< 2.10E-07	< 2.17E-07	< 2.26E-07
Zinc	3.52E-06	2.93E-06	4.77E-06	3.74E-06
Concentration, gr/DSCF @ 12% CO2				
Filterable Particulate	0.00188	0.00256	0.00170	0.00205
Arsenic	< 4.02E-07	< 4.49E-07	< 5.00E-07	< 4.50E-07
Barium	2.09E-06	2.10E-06	7.66E-06	3.95E-06
Cadmium	1.75E-07	2.47E-07	< 2.00E-07	< 2.07E-07
Chromium	1.58E-06	1.01E-06	9.61E-07	1.18E-06
Hexavalent Chromium	< 8.60E-07	< 8.86E-07	< 7.73E-07	< 8.40E-07
Lead	< 4.02E-07	< 4.49E-07	< 5.00E-07	< 4.50E-07
Zinc	5.63E-06	6.29E-06	1.10E-05	7.64E-06
Concentration, gr/DSCF @ 7% O2				
Filterable Particulate	0.00169	0.00218	0.00149	0.00179
Arsenic	< 3.60E-07	< 3.83E-07	< 4.37E-07	< 3.93E-07
Barium	1.87E-06	1.79E-06	6.68E-06	3.45E-06
Cadmium	1.56E-07	2.11E-07	< 1.75E-07	< 1.81E-07
Chromium	1.42E-06	8.63E-07	8.39E-07	1.04E-06
Hexavalent Chromium	< 7.71E-07	< 7.56E-07	< 6.75E-07	< 7.34E-07
Lead	< 3.60E-07	< 3.83E-07	< 4.37E-07	< 3.93E-07
Zinc	5.04E-06	5.37E-06	9.61E-06	6.67E-06
Emission Rate, lb/hr				
Filterable Particulate	0.202	0.172	0.103	0.159
Arsenic	< 4.33E-05	< 3.02E-05	< 3.04E-05	< 3.46E-05
Barium	2.25E-04	1.41E-04	4.64E-04	2.77E-04
Cadmium	1.88E-05	1.66E-05	< 1.21E-05	< 1.58E-05
Chromium	1.70E-04	6.79E-05	5.83E-05	9.87E-05
Hexavalent Chromium	< 8.63E-05	< 5.63E-05	< 4.58E-05	< 6.28E-05
Lead	< 4.33E-05	< 3.02E-05	< 3.04E-05	< 3.46E-05
Zinc	6.06E-04	4.23E-04	6.68E-04	5.66E-04

TABLE 2-3
PERCENT REMOVAL EFFICIENCIES, lb/hr
FACILITY A
JULY 1995

	Arsenic	Barium	Cadmium	Chromium	Lead	Zinc
CONDITION I						
Run 1						
Fuel	< 0.0032	< 0.0032	< 0.0032	< 0.0032	< 0.0032	< 0.0032
Stack Emissions	< 0.0000297	0.000457	0.0000718	0.0000892	0.0000519	0.00101
Removal Efficiency	> 99.08	> 85.88	> 97.78	> 97.21	> 98.40	> 68.80
Run 2						
Fuel	< 0.0033	< 0.0033	< 0.0033	< 0.0033	< 0.0033	0.0062
Stack Emissions	< 0.0000442	0.000299	0.000111	0.000148	< 0.000261	0.00318
Removal Efficiency	> 98.65	> 90.88	> 96.62	> 95.49	> 92.04	48.71
Run 3						
Fuel	< 0.0032	< 0.0032	< 0.0032	< 0.0032	< 0.0032	0.0115
Stack Emissions	< 0.0000445	0.000216	0.0000289	0.000107	< 0.0000445	0.00089
Removal Efficiency	> 98.61	> 93.24	> 99.10	> 96.65	> 98.61	92.26
CONDITION II						
Run 1						
Fuel	< 0.0030	0.0320	0.0030	0.0091	0.1872	2.520
Stack Emissions	< 0.0000433	0.000225	0.0000188	0.000170	< 0.0000433	0.000606
Removal Efficiency	> 98.58	99.30	99.37	98.13	> 99.98	99.98
Run 2						
Fuel	< 0.0025	0.0267	0.0026	0.0069	0.1574	2.107
Stack Emissions	< 0.0000302	0.000141	0.0000166	0.0000679	< 0.0000302	0.000423
Removal Efficiency	> 98.78	99.47	99.36	99.02	> 99.98	99.98
Run 3						
Fuel	< 0.0022	0.0227	0.0023	0.0063	0.1323	1.756
Stack Emissions	< 0.0000304	0.000464	< 0.0000121	0.0000583	< 0.0000304	0.000668
Removal Efficiency	> 98.62	97.96	> 99.47	99.08	> 99.98	99.96

TABLE 2-4
RUN-BY-RUN TESTS SUMMARIES
FACILITY B
JULY 1995

	Rep 1	Rep 2	Rep 3	Average
Concentration, gr/DSCF				
Filterable Particulate	1.54E-03	7.60E-04	8.27E-04	1.04E-03
Arsenic	< 2.53E-07	< 2.10E-07	< 2.13E-07	< 2.25E-07
Barium	6.03E-06	4.52E-06	4.24E-06	4.93E-06
Cadmium	< 1.01E-07	2.29E-07	2.15E-07	< 1.82E-07
Chromium	7.10E-07	5.72E-07	6.90E-07	6.57E-07
Hexavalent Chromium	< 3.54E-07	< 3.50E-07	< 3.42E-07	< 3.49E-07
Lead	< 2.53E-07	< 2.10E-07	< 2.13E-07	< 2.25E-07
Zinc	4.06E-06	3.79E-06	4.26E-06	4.04E-06
Concentration, gr/DSCF @ 12% CO2				
Filterable Particulate	0.00293	0.00149	0.00155	0.00199
Arsenic	< 4.83E-07	< 4.14E-07	< 3.99E-07	< 4.32E-07
Barium	1.15E-05	8.90E-06	7.95E-06	9.45E-06
Cadmium	< 1.93E-07	4.51E-07	4.03E-07	< 3.49E-07
Chromium	1.35E-06	1.13E-06	1.29E-06	1.26E-06
Hexavalent Chromium	< 6.74E-07	< 6.88E-07	< 6.41E-07	< 6.68E-07
Lead	< 4.83E-07	< 4.14E-07	< 3.99E-07	< 4.32E-07
Zinc	7.72E-06	7.45E-06	7.99E-06	7.72E-06
Concentration, gr/DSCF @ 7% O2				
Filterable Particulate	0.00249	0.00126	0.00131	0.00169
Arsenic	< 4.10E-07	< 3.48E-07	< 3.37E-07	< 3.65E-07
Barium	9.75E-06	7.49E-06	6.70E-06	7.98E-06
Cadmium	< 1.64E-07	3.80E-07	3.40E-07	< 2.95E-07
Chromium	1.15E-06	9.47E-07	1.09E-06	1.06E-06
Hexavalent Chromium	< 5.72E-07	< 5.79E-07	< 5.40E-07	< 5.64E-07
Lead	< 4.10E-07	< 3.48E-07	< 3.37E-07	< 3.65E-07
Zinc	6.55E-06	6.27E-06	6.73E-06	6.52E-06
Emission Rate, lb/hr				
Filterable Particulate	0.376	0.203	0.219	0.266
Arsenic	< 6.19E-05	< 5.61E-05	< 5.63E-05	< 5.81E-05
Barium	0.00147	0.00121	0.00112	0.00127
Cadmium	< 2.48E-05	6.12E-05	5.69E-05	< 4.76E-05
Chromium	1.73E-04	1.53E-04	1.83E-04	1.70E-04
Hexavalent Chromium	< 9.28E-05	< 9.19E-05	< 8.63E-05	< 9.03E-05
Lead	< 6.19E-05	< 5.61E-05	< 5.63E-05	< 5.81E-05
Zinc	9.91E-04	1.01E-03	1.13E-03	1.04E-03

TABLE 2-5
PERCENT REMOVAL EFFICIENCIES, lb/hr
FACILITY B
JULY 1995

	Arsenic	Barium	Cadmium	Chromium	Lead	Zinc
Run 1						
Fuel	< 0.0030	0.0372	0.0031	0.0143	0.1191	2.607
Stack Emissions	< 0.0000619	0.00147	< 0.0000248	0.000173	< 0.0000619	0.000991
Removal Efficiency	> 97.91	96.05	> 99.20	98.79	> 99.95	99.96
Run 2						
Fuel	< 0.0029	0.0362	0.0033	0.0117	0.1196	2.499
Stack Emissions	< 0.0000561	0.00121	0.0000612	0.000153	< 0.0000561	0.00101
Removal Efficiency	> 98.06	96.66	98.15	98.70	> 99.95	99.96
Run 3						
Fuel	< 0.0030	0.0379	0.0034	0.0146	0.1252	2.686
Stack Emissions	< 0.0000563	0.00112	0.0000569	0.000183	< 0.0000563	0.00113
Removal Efficiency	> 98.13	97.05	98.34	98.74	> 99.96	99.96

3.0 PROCESS DESCRIPTION AND OPERATION

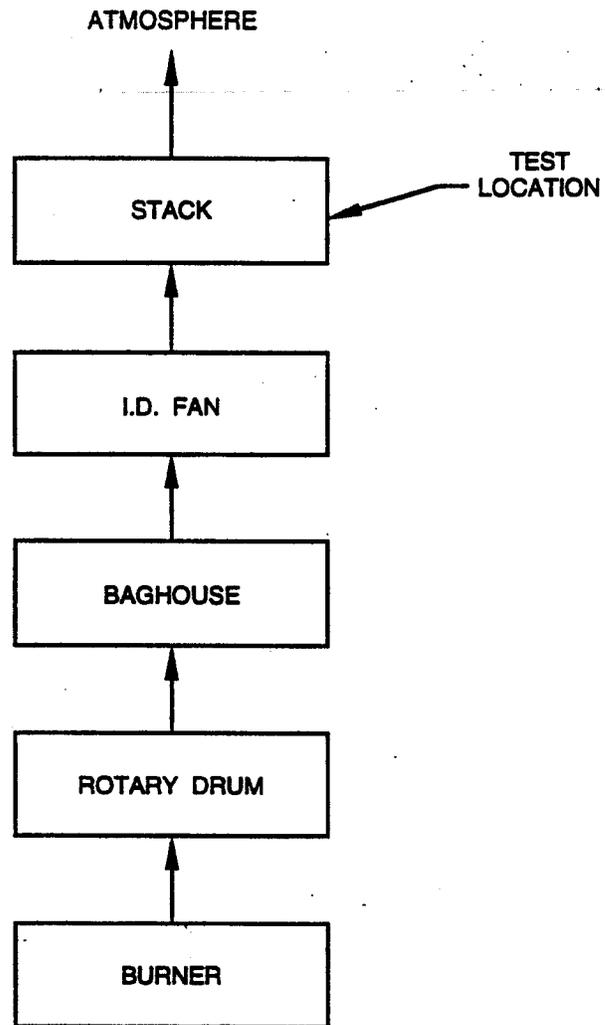
3.1 General

Facility A is an Astec, Inc. rotary drum mix asphaltic concrete plant. This facility has the capability of burning #2 and #4 fuel oil or natural gas. The plant can produce 350 tons per hour of asphaltic concrete paving material.

Facility B is an Astec, Inc. rotary drum mix asphaltic concrete plant. Testing was conducted with the plant operating near the rated capacity of 400 tons per hour.

3.2 Source Air Flow

Figure 3-1 is an air flow schematic showing the passage of flue gases exhausted from the asphalt plants. The air flow schematic is identical for both Facility A and Facility B.



Air flow schematic identical for Facilities A and B.

FIGURE 3-1. ASPHALT PLANT AIR FLOW SCHEMATIC

4.0 SAMPLING AND ANALYTICAL PROCEDURES

4.1 General

All sampling and analytical procedures were those recommended by the United States Environmental Protection Agency. This section provides brief descriptions of the sampling and analytical procedures.

4.2 Sampling Points

The number and location of the sampling points were determined according to the procedures outlined in EPA Method 1. As shown in **Figure 4-1**, Facility A's stack cross section was divided into 24 equal areas with six sampling points on each of four axes. As shown in **Figure 4-2**, Facility B's stack cross section was divided into 24 equal areas with six sampling points on each of four axes.

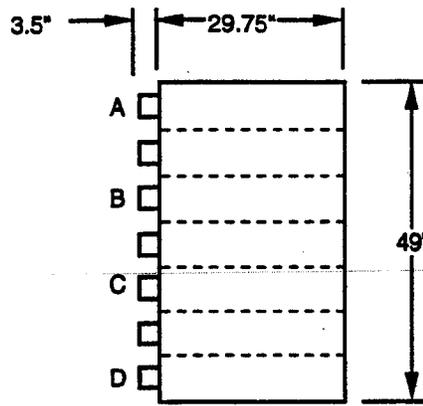
4.3 Cyclonic Flow Check

A Type S Pitot tube assembly, Magnehelic gauges, and a universal protractor (angle finder) were used to determine the flow angles at each of the sampling or velocity traverse points. At each point, the Pitot tube was positioned at a right angle to the air flow. The angles were determined by rotating the Pitot tube until a null reading was obtained on the Magnehelic gauges. When the null reading was obtained, the angle of the Pitot tube was recorded.

4.4 Volumetric Air Flow Rates

4.4.1 Flue Gas Velocity

The flue gas velocity and volumetric flow rate were determined according to the procedures outlined in EPA Method 2. Velocity head measurements (ΔP) were made using Type S Pitot tubes conforming to the geometric specifications outlined in EPA Method 2. Accordingly, each has been assigned a coefficient of 0.84. Differential pressures were measured with Magnehelic gauges of appropriate range. Flue gas temperatures were measured with chromel-alumel thermocouples equipped with hand-held digital readouts.



TRAVERSE POINTS

- 4 AXES
- 6 POINTS PER AXIS
- 24 TOTAL POINTS

SECTION K-K

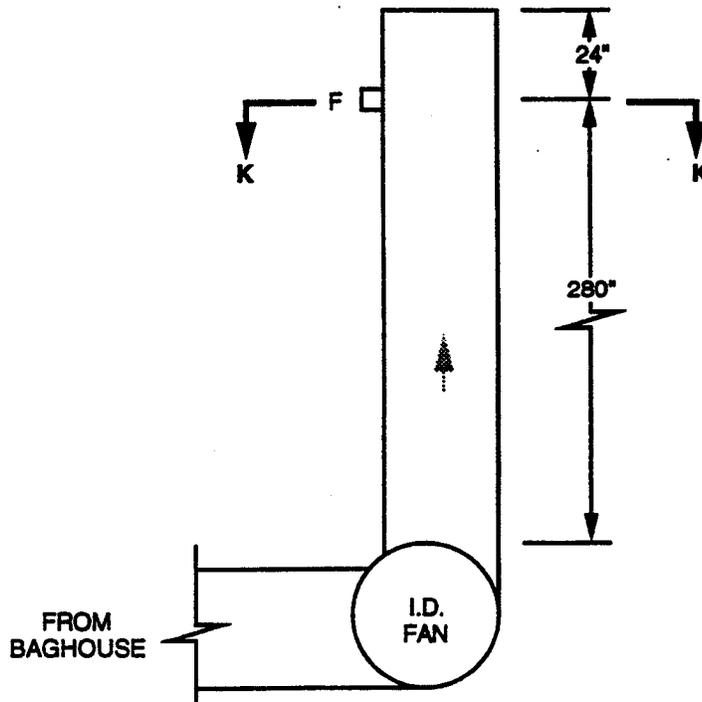
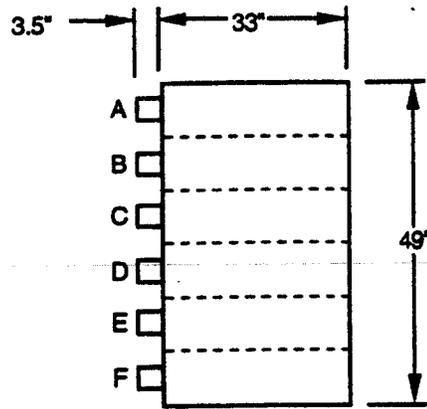


FIGURE 4-1. FACILITY A STACK TEST LOCATION



TRAVERSE POINTS

- 6 AXES
- 4 POINTS PER AXIS
- 24 TOTAL POINTS

SECTION K-K

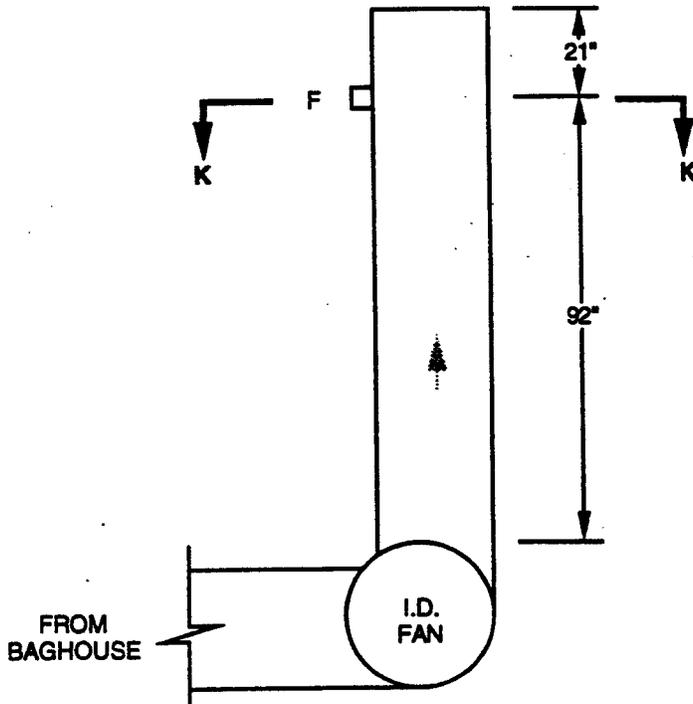


FIGURE 4-2. FACILITY B STACK TEST LOCATION

4.4.2 Flue Gas Composition

Sample Collection. Flue gas samples were collected using the multipoint, integrated sampling technique outlined in EPA Method 3. A stainless steel probe and a peristaltic pump delivering 500 to 750 mL/min of flue gas were used to fill a Tedlar bag. Moisture was removed by means of a knockout jar located prior to the pump. Sampling was of the same duration (except purges following port changes) as the pollutant emissions runs.

Sample Analysis. Analysis for carbon dioxide and oxygen was performed using an Orsat apparatus. The analytical results were used to determine the flue gas composition and excess air.

4.4.3 Flue Gas Moisture Content

The moisture content was determined in conjunction with the appropriate pollutant emissions methods discussed in the following sections.

4.5 Emissions Determinations

4.5.1 Particulate and Metals

Sample Collection. Samples were withdrawn isokinetically from the source using a combined EPA Method 5 and EPA Method 29 sampling train. The sampling train consisted of a glass nozzle, a heated glass probe with a Type S Pitot tube attached, a filter, four chilled impingers, and a metering console. The particulate sample was collected on a Pallflex 2500QAT-UP quartz filter maintained at a temperature of $248^{\circ}\text{F} \pm 25^{\circ}\text{F}$. The first impinger remained empty, the second and third impingers each contained 100 mL of 5% nitric acid (HNO_3)/10% hydrogen peroxide (H_2O_2), and the fourth contained preweighed silica gel. Each run was a minimum of two hours in duration with a minimum sample volume of 60 dry standard cubic feet. Each of the 24 points was sampled for 5 minutes, resulting in net run times of 120 minutes.

Sample Recovery. A Teflon spatula and Teflon coated tweezers were used to remove the filter from the filter holder and place it in a 250 mL glass jar. The reagents were returned to the original bottles, weighed, the weights recorded on the labels, and the liquid levels marked. The silica gel was returned to the original container, weighed, and the weight recorded on the label. The volume of water vapor condensed in the impingers and the volume of water vapor collected in the silica gel were summed and entered into moisture content calculations.

The nozzle, probe, and fronthalf of the filter holder were rinsed with 100 mL of acetone into a 500 mL jar followed by rinsing with 100 mL of 0.1N HNO_3 into a second 500 mL jar. A Teflon probe brush was used for cleaning the probe.

The backhalf of the filter holder and the first, second, and third impingers were rinsed with 100 mL of 0.1N HNO_3 into the 1000 mL jar containing the $\text{HNO}_3/\text{H}_2\text{O}_2$ reagent.

Sample Analyses. EPA Method 5 analytical procedures were used to analyze the filter and fronthalf acetone rinse for particulate.

For the metals analyses, the fronthalf acetone and HNO₃ rinses were evaporated to near dryness in a Teflon beaker. The filter, loose particulate, 3 mL of concentrated HNO₃, and 5 mL of concentrated HF were added to the beaker. The sample was digested on a hot plate until brown fumes were evident, indicating the destruction of organic matter. After the addition of concentrated HNO₃, the reagent and impinger rinses were evaporated to near dryness in a Teflon beaker on a hot plate. After cooling, 3 mL of concentrated HNO₃ and 5 mL of concentrated HF were added to the beaker and the sample was fumed on a hot plate to destroy organic residue. The prepared filter and HNO₃/H₂O₂ reagent samples were combined, brought to a final volume of 100 mL with 10% HNO₃, and analyzed for all metals with a Perkin Elmer 3030 atomic absorption analyzer using the appropriate SW-846 methods. Duplicate metals analyses were performed for approximately 10% of the emissions samples.

4.5.2 Hexavalent Chromium

Samples were withdrawn isokinetically from the source using the sampling train outlined in the EPA draft hexavalent chromium (Cr⁺⁶) method.

Sample Collection. The sampling train consisted of a quartz nozzle, a pump/sprayer assembly for continuously recirculating the reagent to the nozzle, a quartz probe with a Type S Pitot tube attached, five chilled impingers (four Teflon and one glass), and a metering console.

The first impinger contained 150 mL 0.1N potassium hydroxide (KOH), the second and third impingers each contained 75 mL of 0.1N KOH, the fourth impinger remained empty, and the fifth impinger contained preweighed silica gel. Each of the 24 points was sampled for 5 minutes, resulting in net run times of 120 minutes.

A posttest nitrogen purge was used as a safeguard against conversion of hexavalent chromium to trivalent.

Sample Recovery. Following the nitrogen purge, the KOH reagent was returned to the original container, weighed, the weight recorded on the label, and the liquid level marked. The silica gel was returned to the original container, weighed, and the weight recorded on the label. The volume of water vapor condensed in the impingers and the volume of water vapor collected in the silica gel were summed and entered into moisture content calculations. All sample exposed portions of the sample train were first rinsed four times with DI water into the jar containing the KOH reagent followed by rinsing three times with 0.1N HNO₃ into a separate jar. The combined KOH reagent and DI water rinse were then pressure filtrated into a graduated cylinder to remove insoluble matter which could cause hexavalent conversion.

Sample Analysis. The combined KOH reagent/DI water rinse were analyzed for Cr+6 using ion chromatography coupled with a post-column reactor (IC/PCR).

4.6 Equipment Calibration

Pertinent calibration data are provided in **Appendix E.**

5.0 QUALITY ASSURANCE/QUALITY CONTROL

5.1 General

Entropy, Inc. (EI) is committed to the continued implementation of a Quality Assurance Program to assure the quality of sampling and analytical procedures of environmental measurement data. The Quality Assurance measures taken during this test project equal or exceed the minimum QA/QC recommendations as set forth by the U.S. Environmental Protection Agency (EPA) for a particular method.

The following sections outline the QA program implemented by EI to justify the validity of test procedures. As applicable, the QA system for the various test programs addresses the following areas:

- Preventive Maintenance & Equipment Calibration
- Sample Processing
- Analytical Instrument Calibration
- Blanks and Spiked Samples
- Internal/External System Checks
- Data Reduction & Validation
- QA/QC Summary

5.2 Preventive Maintenance and Equipment Calibration

An effective preventive maintenance program decreases downtime and thus increases data completeness and quality. Pretest and posttest equipment calibrations are conducted in a manner and at a frequency which meets or exceeds U.S. EPA specifications.

Each item transported to the field is inspected to detect equipment problems which may originate during periods of storage. All equipment returning from the field is cleaned, repaired, reconditioned, and recalibrated as necessary. Routine maintenance on equipment (dry gas meters, pumps, Magnehelics, manometers, Pitot tubes, and nozzles) is carried out periodically for leaks, corrosion, dents, or any other damage. Table 5-1 shows the activities for equipment calibration.

**TABLE 5-1
IN-HOUSE EQUIPMENT CALIBRATION**

Apparatus	Calibration Method And Frequency	Specifications	Corrective Action
Type S Pitot Tubes	Standards contained in EPA Method 2	Coefficient of 0.84 ± 0.02	Refurbish or recalibrate
	Visual inspection prior to shipment to test site and again prior to each day of testing		
Manometers	Leak checked before and after each field use		Adjust or replace
Magnehelic Gauges	Initially calibrate over full range	0-10" water column	
	After each field use, checked against inclined manometer at average settings encountered during testing	Within $\pm 5\%$	Repair and Recalibrate
Thermometers - Impinger - Dry Gas Meter - Filter Box	After purchase and prior to each field use, using ASTM Hg-in-glass thermometer	Impinger = $\pm 2^\circ\text{F}$ DGM = $\pm 5.4^\circ\text{F}$ FB = $\pm 5.4^\circ\text{F}$	Adjust, determine correction factor, or reject
	After purchase and prior to each field use, using ASTM mercury-in-glass thermometer		
Thermocouple/ Potentiometer	After purchase. 3-point (ice bath, boiling water, and hot oil) using ASTM Hg-in-glass thermometer	$\pm 1.5\%$ of absolute temperature	Adjust, determine correction factor, or reject
	Before and after each field use, compared to ASTM Hg-in-glass thermometer at ambient conditions		
Dry Gas Meter and Orifice	Full calibration (every 6 months) over wide range of orifice settings to obtain calibration factor (isokinetic meter box)	DGM = ± 0.02 from avg. coeff. for each run Orifice = $\pm 0.15"$ H ₂ O over delta H range of 0.4"-4.0"	Adjust or replace
	10-minute quick calibration before sending to test site and again prior to each day of field use (isokinetic)	$\pm 3\%$ of full calibration γ $\pm 5\%$ of full calibration γ	Use if no backup Do not use
	Calculate γ_{qa} * on-site for each test run to determine if the meter gamma (γ) has changed (EPA Method 5 Section 5.3.2 Alternate Procedures as approved by Administrator)	Average γ_{qa} must be within $\pm 5\%$ of full calibration γ	Perform post test calibration at average delta H and highest vacuum encountered during testing to determine if meter gamma has changed (isokinetic)
	If γ_{qa} fails or is not acceptable to the Administrator, a post test calibration will be performed at average delta H and highest vacuum encountered during testing to determine if meter gamma has changed (isokinetic)	$\pm 5\%$ of full calibration Gamma (initial or recalibration) that yields the lowest sample volume for the testing is used for calculations	Recalibrate or replace
Dry Gas Meter Transfer Standard	Annual calibrations conducted in triplicate using EPA wet test meter. Calibrations conducted at 7 flow rates from 0.25 to 1.40 cfm.	$\pm 2\%$ of average factor for each calibration run	Adjust and recalibrate

* See Appendix D for EMTIC guideline document

**TABLE 5-1 (Continued)
IN-HOUSE EQUIPMENT CALIBRATION**

Apparatus	Calibration Method And Frequency	Specifications	Corrective Action
Barometer	Before and after each field use against an aneroid barometer	$\pm 0.1''$ mercury	Adjust to agree
	Reference barometer adjusted for elevation differences		
Probe Nozzle	Average of 5 I.D. measurements using a micrometer. Visual inspection before and after each field use	Difference between high and low measurement $\leq 0.004''$	Repair and recalibrate

5.3 Sample Processing

Entropy, Inc. employs systems which ensure the integrity of an environmental sample from the time of acquisition, through analysis, and ultimately to proper disposal. These systems are necessary to allow valid conclusions to be drawn from analytical results separated in time and space from the sampling operation. In addition, these systems recognize that samples are occasionally of value even after analytical results have been reported.

Samples are collected, transported, and stored in clean containers which are constructed of materials inert to the analytical matrix. Containers are used which allow air tight seals. When necessary, containers are employed which prevent photochemical reactions. All sample containers are labeled with the following information:

- Unique source identifier
- Sample run identifier
- Analyte identifier
- Sample matrix identifier
- Sample analyst identifier

Additional information relating to the sample is recorded on the data sheet for the sampling run that afforded the subject sample. Accordingly, the sampling data sheet contains all the information listed above, plus the date and time the sample was acquired and supplemental information such as observations pertinent to the quality of the sample. For condensed samples, e.g., samples in liquid media, the sample levels are marked on the outside of the container; this mark is used to indicate sample loss, and as such, may serve as a reference in adjusting results accordingly.

For transport from the field to the laboratory, samples are stored in sealed containers and secured in a fashion which minimizes movement and thus prevents breakage of containers. Containers used for transporting glass are packed with foam. Samples which require chilling are kept cold until analyzed.

Samples remain in the custody of the sampler, from acquisition until conveyance to the sample custodian. All custody transfers are signed and documented on a record of custody form, which remains with the sample until turned over to the custodian.

Analytical data are identified in a manner identical to that of the sampling data. Accordingly, all data generated from the analysis of samples are documented with the following information:

- Source identifier
- Sample run identifier
- Analyte identifier
- Sample matrix identifier
- Analyst identifier
- Analysis date

Portions of samples remaining after analysis are returned to their original sample containers. These samples are stored in designated storage areas until their destruction is authorized.

5.4 Instrument Calibration

Instrument calibration is one of the most important functions in generating precise and accurate quality data. All of the contract laboratories involved in the analytical testing for the test program maintain rigorous QA programs for instrument calibration.

5.5 Blanks and Spikes

Field blanks, method blanks, trip blanks, lab-proof blanks and filter blanks are obtained, digested and analyzed when applicable. The blanks reflect the background contamination obtained from the various sources during the sampling and analysis. Thus, data adjustment or correction can be made accordingly.

In most cases, it is not necessary to digest and analyze the method blanks, reagent blanks or the lab-proof blanks unless the field blank shows a high level of contamination. If a high level of contamination is present, it is imperative to individually analyze the above blanks to help determine the cause of contamination.

Spiked samples are used to check on the performance of a routine analysis or the recovery efficiency of a method. During spiking, a known amount of stock solutions of the substance of interest is added to the sample prior to sample extraction, digestion, and analysis.

5.6 Internal/External System Audit Checks

System and performance audits are routine elements of all Entropy QA/QC programs.

Internal Systems Audit: The following sampling equipment checks were conducted prior to sample collection.

- All sampling equipment was thoroughly checked to ensure clean and operable components.
- Equipment was inspected for possible damage from shipment.
- The oil manometers or Magnehelic gauges were leveled and zeroed.
- The temperature measurement systems were checked for damage and operability by measuring the ambient temperature.

Performance Audits: Performance audits of the laboratory are conducted prior to the processing of any compliance samples for analysis. Audit materials typically include samples available from the EPA prior to new source testing. Also, samples of known concentration are prepared in-house or obtained from the EPA for Internal QA checks.

External Systems Audits: Entropy is subject to a system audit each time a test is conducted for any Air Pollution Control agency. This procedure entails an EPA observer on-site to do qualitative evaluation of performance to demonstrate compliance with the applicable regulations.

5.7 Data Reduction and Validation

The test team leader is responsible for reviewing and validating data as they are acquired. Each team leader has extensive knowledge of sampling methodology and the characteristics of the process being measured and is capable of evaluating the accuracy, representativeness, and completeness of raw data on-site. Action to replace inadequate data can be taken immediately.

Data obtained during calibrations and test runs are recorded on standardized forms which are checked twice for completeness and accuracy by the QA Director or his designated representative. Data reduction and consistency are achieved by using the standardized forms and using Entropy's in-house computer facilities.

5.8 QA/QC Summary

All chemicals used were American Chemical Society (ACS), High Performance Liquid Chromatography (HPLC), or pesticide grade. The deionized, distilled water utilized met or exceeded the American Society for Testing and Materials (ASTM) specifications for Type-I reagent water. Pretest and posttest leak checks were conducted on each sampling train.

Acetone reagent blanks were analyzed for each of the test conditions. The acetone reagent blank for Facility A, Condition I was analyzed for particulate with 2.39 mg/53 mL detected. The acetone reagent blank for Facility A, Condition II was analyzed for particulate with 0.84 mg/30 mL detected. The acetone reagent blank for Facility B was analyzed for particulate with 5.53 mg/35 mL detected.

Field blanks were prepared and analyzed for metals; a matrix spike was conducted; and duplicate analyses were conducted. Tables 5-2 and 5-3 present the results for Facility A Conditions I and II, respectively. The results for Facility B are presented in Table 5-4.

**TABLE 5-2
METALS BLANKS, MATRIX SPIKES,
AND DUPLICATE ANALYSES RESULTS
FACILITY A, CONDITION I
JULY 1995**

	Field Blank, μg^a	Matrix Spike Recovery, % ^a	First Analysis, μg	Second Analysis, μg^b	Relative % Difference ^c
Arsenic	< 1.00	90.2	< 1.00	< 1.00	NA
Barium	5.25	90.7	6.630	6.88	1.85
Cadmium	< 0.400	107	2.490	2.51	0.40
Chromium	1.75	94.9	3.380	3.30	1.20
Lead	< 1.00	90	5.900	5.89	0.08
Zinc	12	106	72.0	72.0	0.00
Chromium (VI)	< 1.1	94.8	< 1.5	< 1.5	NA

(a) Conducted on repetition 3.

(b) Conducted on repetition 2.

(c) Not applicable if one or both results are below the detection limit.

**TABLE 5-3
METALS BLANKS, MATRIX SPIKES,
AND DUPLICATE ANALYSES RESULTS
FACILITY A, CONDITION II
JULY 1995**

	Field Blank, μg^{a}	Matrix Spike Recovery, % ^a	First Analysis, μg	Second Analysis, μg^{b}	Relative % Difference ^c
Arsenic	< 1.00	93	< 1.00	< 1.00	NA
Barium	4.51	97.3	4.67	4.66	0.107
Cadmium	< 0.400	99.7	0.552	0.550	.181
Chromium	1.84	93.4	2.00	2.050	1.235
Lead	< 1.00	96	< 1.00	< 1.00	NA
Zinc	< 10	104	14.00	14.00	0.00
Chromium (VI)	1.12	94.8	< 1.5	< 1.5	NA

- (a) Conducted on repetition 3.
 (b) Conducted on repetition 2.
 (c) Not applicable if one or both results are below the detection limit.

**TABLE 5-4
METALS BLANKS, MATRIX SPIKES,
AND DUPLICATE ANALYSES RESULTS
FACILITY B
JULY 1995**

	Field Blank, μg^{a}	Matrix Spike Recovery, % ^a	First Analysis, μg	Second Analysis, μg^{b}	Relative % Difference ^c
Arsenic	< 1.00	90.8	< 1.00	< 1.00	NA
Barium	10.4	88.3	21.2	21.8	1.40
Cadmium	< 0.400	104	1.10	1.08	0.92
Chromium	2.61	93.1	2.77	2.67	1.84
Lead	< 1.00	90.9	< 1.00	< 1.00	NA
Zinc	< 1.00	102	18.00	18.00	0.00
Chromium (VI)	0.821	102	< 1.5	< 1.5	NA

- (a) Conducted on repetition 3.
 (b) Conducted on repetition 2.
 (c) Not applicable if one or both results are below the detection limit.

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**METALS EMISSIONS FROM THE COMBUSTION
OF USED OIL FUEL**

PHASE I, LITERATURE SEARCH AND SURVEY

Report Prepared for:

Used Oil Recycling Coalition
Washington, D.C.

Report Prepared by:

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April 5, 1994

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SECTION 1 SUMMARY AND RECOMMENDATIONS

1.1 STUDY APPROACH

The Used Oil Recycling Coalition (UORC) has contracted with Entropy, Inc. to evaluate metals emissions from used oil combustion. The project is divided into two phases.

- Phase I - Metals Emission Data Literature Search and Marketers/Processors Survey
- Phase II - Emission Testing of Selected Combustion Processes

The objective of Phase I is to summarize pertinent data and to determine if there are significant gaps in the available technical information regarding the emissions of lead, barium, cadmium, chromium, arsenic and zinc from the combustion of used oil. The results from Phase I will be used to determine if the Phase II emission testing is needed, and if so, the types of combustion sources and types of used oil that are most important.

An emission inventory for used oil combustion sources was compiled during the Phase I work to evaluate the emission quantities of each source category. This inventory was based on (1) a survey distributed by the National Oil Recyclers Association (NORA) and summarized by Entropy and (2) information regarding the metals retention and collection efficiency at the various types of combustion processes.

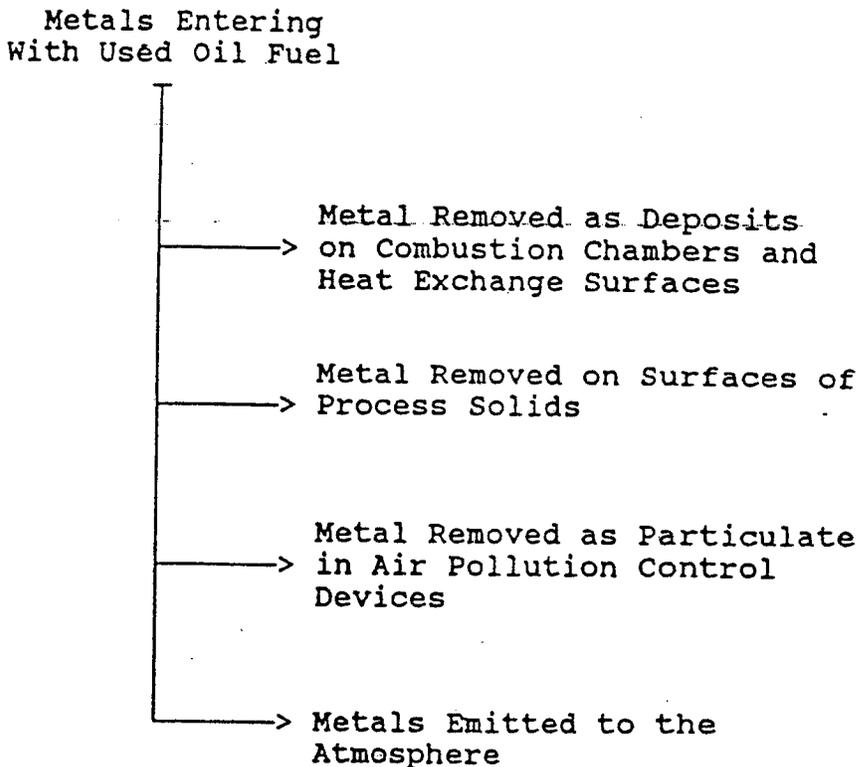
1.2 PHASE I CONCLUSIONS

Entropy, Inc. conducted a comprehensive literature search to compile information concerning air emissions resulting from the combustion of used oil in various types of boilers, industrial processes, and space heaters. The literature search included research studies published by government agencies and the private sector, data provided by Coalition members, and information provided by used oil marketers and processors contacted as part of the NORA survey. The general conclusions are listed below.

1. Due to significant reductions in the concentrations of some of the metals in used oils, most of the metals emission test data obtained prior to 1985 is not representative of present day emissions.
2. Due to the lead-in-gasoline phase-down requirements, lead levels in automotive used oil after processing have decreased substantially. Average levels are now in the range of 40 ppm, well below the pre-1985 levels of 200 to 1000 ppm.

Summary and Recommendations

Figure 1-1. Metals Partitioning



The lead emission estimates in Table 1-1 are based on source-by-source partitioning factors and total used oil fuel consumption rates. The used oil fuel data is based in part on the NORA sponsored survey of used oil marketers and processors. The respondents to this survey accounted for 570 million gallons of used oil in 1993. Of this total, 204 million gallons were used or sold as fuel. A total of 100 companies responded to this survey.

The NORA survey did not include the used oil fuels burned in space heaters since that fuel is usually burned by the organization generating the used oil and is not processed or marketed by one of the surveyed companies. Entropy has estimated that an additional 69 million gallons of used oil is consumed as fuel in space heaters.

While the NORA survey was one of the largest surveys of used oil marketers and processors that has been conducted, it is

Summary and Recommendations

impractical to survey all of the companies processing and burning used oil fuel. Accordingly, Entropy has applied a multiplication factor to the source-by-source consumption data provided by the NORA survey to estimate total U.S. consumption rates. A multiplication factor of 3.583 has been used for this purpose. This multiplication factor is based on the assumption that 800 million gallons of used oil per year are used as fuel in the United States.

The data in Table 1-1 provides a useful relative indicator of the significance of each source category for the emission of lead. Emission rates for the other metals included in the scope of the study can be estimated by using a ratio of the average metals concentrations used in developing these emission estimates. These metals concentrations are the weighted averages of the 204 million gallons of used oil fuel described in the responses to the NORA survey.

The partitioning of the other metals is not necessarily the same as lead. Accordingly, there are differences in the fractions of each metal which are emitted. These differences may affect the relative importance of each source category as a source of metal emissions.

Lead	40.36 ppm
Barium	10.0 ppm
Arsenic	1.19 ppm
Cadmium	1.60 ppm
Chromium	8.83 ppm
Zinc	917.0 ppm

Based on the emission inventory, several conclusions have been reached regarding the need for further evaluation of metals emissions from the various source categories.

- Asphalt plants are the largest single category of sources which are burning used oil. They consume approximately 43% of the total used oil collected and used as fuel in the United States and there are indications that the consumption rates are increasing. Metals removal in baghouse controlled asphalt plants is very high. There is considerable uncertainty regarding the capability of wet scrubber controlled plants to efficiently collect metals-containing particles.

SECTION 2

PROJECT PURPOSE, TECHNICAL APPROACH, AND SCOPE

2.1 PURPOSE OF THE USED OIL AIR EMISSIONS STUDY

The main objective of the Used Oil Recycling Coalition (UORC) Air Emissions Study is to compile accurate lead air emissions data for a variety of combustion sources utilizing used oil as a fuel.

The Coalition recognizes that other elements and compounds potentially emitted during used oil combustion may also be of concern. Accordingly, a secondary objective of this project is to compile accurate emissions data for other metals including barium, cadmium, chromium (Total and Cr⁺⁶), arsenic, and zinc.

2.2 PROJECT TECHNICAL APPROACH

The project is divided into two phases. A detailed literature search was conducted as Phase I. As part of this work, tests relevant to used oil combustion were reviewed, and data on trends in used oil composition was obtained. An emission inventory approach was used in compiling the Phase I data. The presently available data concerning used oil composition, quantities burned in combustion processes, and metals partitioning factors were used to estimate pollutant emissions from each category of the used oil combustion process.

The information compiled in Phase I will be reviewed by the Coalition to identify important gaps, if any, in the available technical information. These gaps could be addressed by surveys of Coalition members and/or additional air emission tests of selected combustion sources.

If UORC decides to continue with Phase II, Entropy, Inc. will conduct air emissions tests at facilities firing used oil fuel. These test programs would include the following basic elements.

- Used oil fuel sampling to characterize the as-fired fuel contaminants
- Gas stream sampling at the stack or air pollution control system outlet to measure emissions of contaminants
- Gas stream sampling at the inlet to the air pollution control system to evaluate the metals concentrations in the submicron size range

Project Purpose, Scope, and Technical Approach

The used oil combustion air emission data literature search was begun by conducting computerized searches for relevant technical articles, government sponsored research projects, and other publications. The following computerized literature searches were conducted.

- National Technical Information Service (NTIS)
- ARIES (U.S. Government Research Publications)
- Congressional Research Service
- ~~Lexis-Nexis System~~
- JANUS System
- State of California, Publications Department
- Electric Power Research Institute, Documents Department
- U.S. EPA, Pollution Prevention Clearinghouse

This material was supplemented by reference lists and limited searches provided by the American Petroleum Institute, Eastern Research Group, Inc., and the U.S. Army Corp. of Engineers Construction Engineering Research Laboratory. Many of the technical articles, research reports, manuals, and newspaper articles cited in these literature searches were purchased and reviewed. Additional documents were obtained from the Used Oil Recycling Coalition.

The comprehensive literature search revealed that there were a large number of documents concerning used oil in general, but very few were relevant to used oil combustion-related emissions. In an attempt to identify the existence of previous combustion-related studies, Entropy initiated a telephone survey of individuals and organizations active in the used oil business and air pollution control business. A partial list of the organizations contacted is listed below.

- Used oil marketers or processors who responded to the NORA survey (approximately 15 organizations contacted)
- Used Oil Recycling Coalition members listed by the UORC Project Manager
 - Edison Electric Institute
 - American Petroleum Institute
 - Cement Kiln Recycling Coalition
 - Waste Oil Heaters Manufacturing Association
- Electric Power Research Institute (Palo Alto and Washington D.C.)
- Lubricant Manufacturers and Consultants
 - Castrol
 - Ozimek, Inc.
 - Pennzoil, Inc.

Project Purpose, Scope, and Technical Approach

The initial review of the articles and other materials received indicated that there was little information of direct relevance to this study. Accordingly, the scope of the literature search was expanded to include the burning of virgin oils and the burning of hazardous wastes. The primary sources of information in these two categories were published articles and seminar proceedings. The search included the following materials.

- Air & Waste Management Journals (10 years)
(formally Air Pollution Control Association)
- Air & Waste Management Conference Proceedings (10 years)
- Hydrocarbon Processing (limited number of issues)
- Environmental Progress (6 years)
- Chemical Engineering Progress (6 years)
- Environmental Science and Technology (6 years)
- AIChE Journal (10 years)
- The Chemical Engineer (3 years)
- Oil & Gas Journal (1 year)
- World Oil (2 years)
- Combustion Institute Proceedings (8 years)
- Atmospheric Environment (6 Years)

This search identified several used oil related articles which had escaped listing in computerized databases due to the types of keywords chosen by the author. Furthermore, several virgin oil and hazardous waste combustion-related articles were obtained.

The remainder of the literature search involved the review of the documents and the references cited in the documents. Several additional documents were obtained in this manner.

Entropy has made a determined effort to identify and obtain technical information concerning air emissions from the combustion of used oil. The authors believe that most of the useful materials have been compiled. However, due to the volume of non-relevant articles, publications, and manuals, it is possible that one or more useful documents has escaped detection. If so, the Phase I report will be amended when the Phase II work is completed.

Overall, the presently available database concerning used oil combustion can be characterized as very limited and out-of-date. Many of the out-of-date studies have been reviewed in detail to demonstrate why they should no longer be used in evaluating metals emissions from used oil combustion.

SECTION 3

COMPOSITIONS AND QUANTITIES OF USED OILS

Many of the studies concerning air pollution emissions from the combustion of used oil were conducted prior to 1985. Since that time, significant changes in the compositions of used oil could make some or all of the conclusions based on these studies out-of-date and not representative of present-day conditions. Accordingly, Entropy has evaluated shifts in used oil composition.

The 1993 survey conducted by the National Oil Recyclers Association is one of the major sources of information concerning used oil compositions. Additional information was obtained by contacting respondents to the NORA survey, by contacting lubricant additive manufacturers, and by reviewing the technical literature. Several conclusions are based on this survey of used oil compositions and quantities.

- Lead levels in mixed used oil streams have dropped significantly due to the phaseout of lead-in-gasoline which began in 1985. Lead levels during the 1992-1993 time period were between 20 and 60 ppm. Some of the lead which is now present may be attributable to erosion of passenger car and heavy duty vehicle metal parts.
- Barium levels in mixed used oil streams have dropped significantly due to the elimination of barium as a component in lubricant dispersants. Barium concentrations are now less than 10 ppm.
- Zinc levels in mixed used oil have remained approximately the same since the 1985 time period. Zinc is present due to its continued use as a detergent in lubricants manufactured for passenger cars and heavy duty vehicles. Used oil zinc levels range between 400 and 1200 ppm.
- Cadmium and chromium levels continue to be present at pre-1985 levels of 1 to 10 ppm. The presence of these metals are due to wear of metal parts in passenger and heavy duty vehicle engines.
- Arsenic levels continue to be quite low. No information was found concerning the possible sources of arsenic.

Compositions and Quantities of Used Oil

Table 3-1. Vehicular Oil Generation Rates⁴⁵

Subcategory of Used Oil Generator	New Oil Sales 10 ⁶ Gals.	Used Oil Generation Factor	Used Oil Quantity, 10 ⁶ Gals.
On-Road			
Passenger Cars	441.6	0.67	295.9
Commercial Cars	158.9	0.66	104.7
Trucks and Buses	139.7	0.59	82.4
			483.0
Off-Road			
Farm	74.1	0.59	43.7
Construction	68.8	0.59	40.6
Mining	45.5	0.59	26.8
Government	11.7	0.63	7.4
Aviation	12.7	0.47	6.0
			124.5
Hydraulic Fluids			
On-Road	79.0	0.10	7.9
Off-Road	111.4	0.75	83.6
Greases & Other	108.0	0.00	0.0
			91.5
	TOTALS	0.599	699.0

Bider et al⁴⁵ has estimated that the total quantity of these industrial oils reaching the used oil management system is 567,000,000 million gallons. As in the case with the crankcase oils, these estimates are based on new oil sales and an estimated used oil generation factor. The data and assumptions which are the basis of the industrial oil estimate are presented in Table 3-2.

Compositions and Quantities of Used Oil

The five references used by Bider et al. to estimate the used oil generation rate factors were published in 1974, 1978, 1980, and 1982 (two publications). Accordingly, some of the information is much older than indicated by the 1983 base year of the Bider et al. study.

More recent data was compiled by Temple, Barker, & Sloane (TBS) for the U.S. Environmental Protection Agency. This data indicates that the total crankcase used oil generated for 1988 was 847,000,000 gallons (Bider estimate for 1983 was 699,000,000 gallons). The TBS estimate⁴⁶ was based in part on a used oil generation factor of 60.4% which was slightly higher than the value used by Bider et al.⁴⁵. Temple, Barker, & Sloane assumed that the 1988 quantity of used crankcase oil generated by do-it-yourselfers (DIY) was essentially unchanged from the 1983 data of Bider et al. The differences between the estimates of crankcase oil by TBS and Bider et al. were entirely due to non-DIY's.

The industrial used oil generation rates estimated by TBS for 1988 were 504,000,000 gallons which is 8.8% higher than the quantity estimated by Bider et al for 1983. TBS assumed an industrial oil generation factor of 49.9% in calculating the used oil quantity. The industrial used oils represented 40% of the total used oil estimates calculated by Bider et al. and 37% of those calculated by TBS.

Entropy has used the TBS data of 847,000,000 gallons of crankcase oil and 504,000,000 gallons of industrial oil per year since these are the most recent estimates available. A total used oil fuel consumption level of 800,000,000 million gallons has been assumed based on these TBS estimates. This is approximately 59% of the total crankcase oil and industrial oil generation rate.

A number of changes since 1988 are probable. The use of used oil for road oiling has been prohibited in response to regulations promulgated by State and local governments. Accordingly, the quantity of used oil entering the used oil management system and available for either re-refining or energy recovery should have increased. TBS estimated that road oiling accounted for 34,000,000 gallons of used oil use in 1983⁴⁶. Furthermore, there have been improvements in do-it-yourself oil disposal that should have increased the quantities of used oil entering the national used oil management. Accordingly, the total oil quantity figures prepared by TBS and used later in this study may be low.

Compositions and Quantities of Used Oil

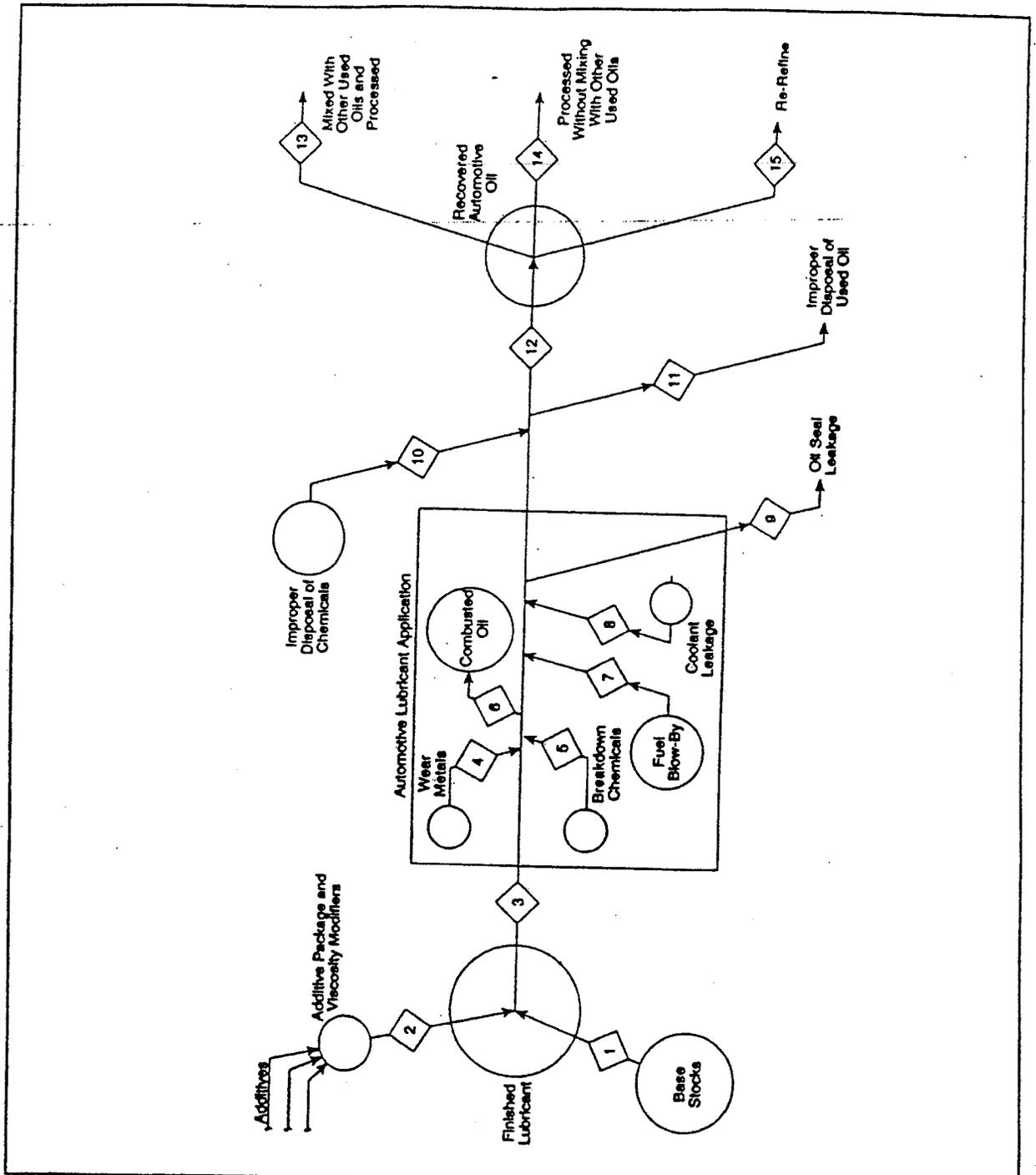


Figure 3-1. Factors affecting used oil composition

Compositions and Quantities of Used Oil

3.2.2 Crankcase Used Oils

The used oil drained from passenger vehicles and heavy duty vehicles includes the crankcase oil and smaller quantities of other oils such as hydraulic oil (primarily brake fluid), transmission oil, and diesel engine oil. These materials are recovered by service stations, rapid-change services, department stores, and do-it-yourselfers. It is logical to assume that the various types of oil enter the used oil management system together. The general model presented in Figure 3-1 will be used to characterize important used oil characteristics and trends which have a direct impact on the environmental consequences of used oil combustion.

Lubricant Formulations

Lubricants are composed of one or more base stock oils and a number of additives. These additives generally comprise 10 to 20% by weight of the finished lubricant^{48,49}.

The overall purpose of crankcase lubricants is to improve engine durability, enhance fuel economy, and reduce environmental emissions. The main lubricant material is the base oil itself. However, there are considerable variations in the base oil composition and characteristics depending on the source of the oil. None of the base oils are sufficient without additives for modern passenger cars or heavy duty diesel engines. As engine technology has advanced and environmental requirements have tightened, there has been a steady advancement in lubricant formulation. This is indicated by the chronology of lubricant milestones shown in Figure 3-2.

There are several major categories of additives used in formulating an engine lubricating oil.

Detergents

Dispersants

Inhibitors

- Anti-wear additives
- Anti-forming additives
- Anti-oxidation additives
- Friction modifiers
- Pour point depressants

Viscosity modifiers

Compositions and Quantities of Used Oil

metal cation. The most common metal cations are calcium, magnesium, and sodium⁴⁹. Barium and other heavy metals are no longer used⁴⁹.

Dispersants are chemically similar to detergents. However, they do not have metal cations⁴⁹. They adsorb on the surfaces of particles to keep them in suspension and, thereby, reduce engine deposits. They are much more capable of controlling particles than detergent molecules.

Inhibitors are used to reduce engine wear, corrosion, rust, and oxidation. They interrupt free radical oxidation chain reactions and form protective films on metal surfaces. One of the main inhibitors is zinc dithiophosphate (ZDTP)⁴⁹. Other types of chemicals used as inhibitors include sterically hindered phenols for free radical oxidation reaction control, phosphorus compounds for friction reduction, silicon compounds for antiformal protection, and sulfurized fatty acids for friction reduction⁴⁹.

Viscosity modifiers are used to produce multigrade oils which perform properly over a wide temperature range. High molecular weight polymers are used for this purpose⁴⁹. The most common types are polyhydrocarbons and polymethacrylates⁴⁹.

As indicated in Figure 3-3, the various additives are usually pre-blended into a performance additive package which is then combined with viscosity modifiers and base oils by the lubricant producer.

There can be between five and fifteen separate compounds comprising the performance additive package. The resulting motor oil composition is shown in Table 3-3⁴⁹.

Table 3-3. Motor Oil Composition⁴⁹

	Passenger Car Motor Oil	Heavy Duty Diesel Oil
Base Stock	84.8	85.2%
Performance Package	9.2	10.8
Viscosity Modifier	6.0	4.0

Compositions and Quantities of Used Oil

The zinc levels in the final lubricating oil average 0.12 to 0.13% by weight (1200 to 1300 ppm by weight)^{50,51}. These levels appear to be relatively similar to those detected in the past.

Base Oil Stocks

As indicated in Table 3-3, the base oil comprises a large fraction of the total passenger car motor oil. Accordingly, the concentration of metals and other pollutant precursors is important for these materials. No data was found which directly relates to the metals content in these base stocks. Accordingly, they will be evaluated qualitatively by assuming that they are similar in composition to a distillate oil. Data for distillate oil are presented in Table 3-4.

Table 3-4. Average Concentrations of Contaminants in Distillate Oil⁵²

Component	Concentration (ppm)
Ash	25
Chlorine	100
Sulfur	2400
Barium	0.5
Cadmium	1.3
Chromium	1.3
Lead	1.8
Zinc	3.6
Arsenic	0.8

It is apparent that there are slight quantities of lead and barium entering the lubricant with the base stocks if these are similar to distillate oil. Furthermore, cadmium and chromium in the base oil stock could contribute to the 1 to 10 ppm levels observed in automotive used oil.

Fuel Combustion Product Blow-by

It is generally believed that the piston blow-by of lead compounds from gasoline were primarily responsible for the high lead levels in used oils drained from passenger vehicles. The lead-in-gasoline phase down requirements mandated by Federal regulations promulgated on March 7, 1985 have had a direct and

Compositions and Quantities of Used Oil

Lubricating Oil Leakage

Lubricating oil that is lost due to leakage from seals is lost to the entire used oil management system. Due in part to the improvements in lubricating oil seal additives, the fraction of oil lost in this manner is approximately 0.5% of the total according to Capon and Haycock⁴⁹.

Crankcase Used Oil Characteristics

The lead concentration of used oil has decreased substantially during the last 10 years. This is indicated by the relatively low levels of 20 to 90 ppm reported in essentially all of the survey forms returned by respondents to the NORA survey. For example, the average lead concentration of used oil received by Evergreen Oil was 64.14 ppm for the September 1992 to September 1993 time period⁵⁴.

The trend in the lead content of the used oil during the last 10 years is shown in Figure 3-4. This figure displays the tested lead data from a variety of references^{45,55-62} over this time period. The high levels prior to 1986 were due primarily to the blow-by lead-containing gasoline. The present levels are probably due primarily to metal wear and slight quantities of lead-containing used oil remaining in tanks and other inventories.

The barium content has also decreased substantially over the past 10 years. This is due to the replacement of barium as a dispersant in lubricating oils. The decrease is indicated by the data from a variety of studies^{45,56-59,61} conducted over the 1980 to 1993 time period as shown in Figure 3-5.

The zinc content has remained relatively constant over the last ten years, probably due to the continued use of this material as a detergent additive to the lubricating oil. The zinc data is compiled in Figure 3-6.

The lead and barium concentrations shown in Figures 3-4 and 3-5 are generally supported by data obtained by SAIC⁶¹ for the U.S. Environmental Protection Agency. SAIC collected a limited number of samples and analyzed for metals in the TCLP filtrate. The results for the six categories which are relevant to crankcase oil are summarized in Table 3-6.

Compositions and Quantities of Used Oil

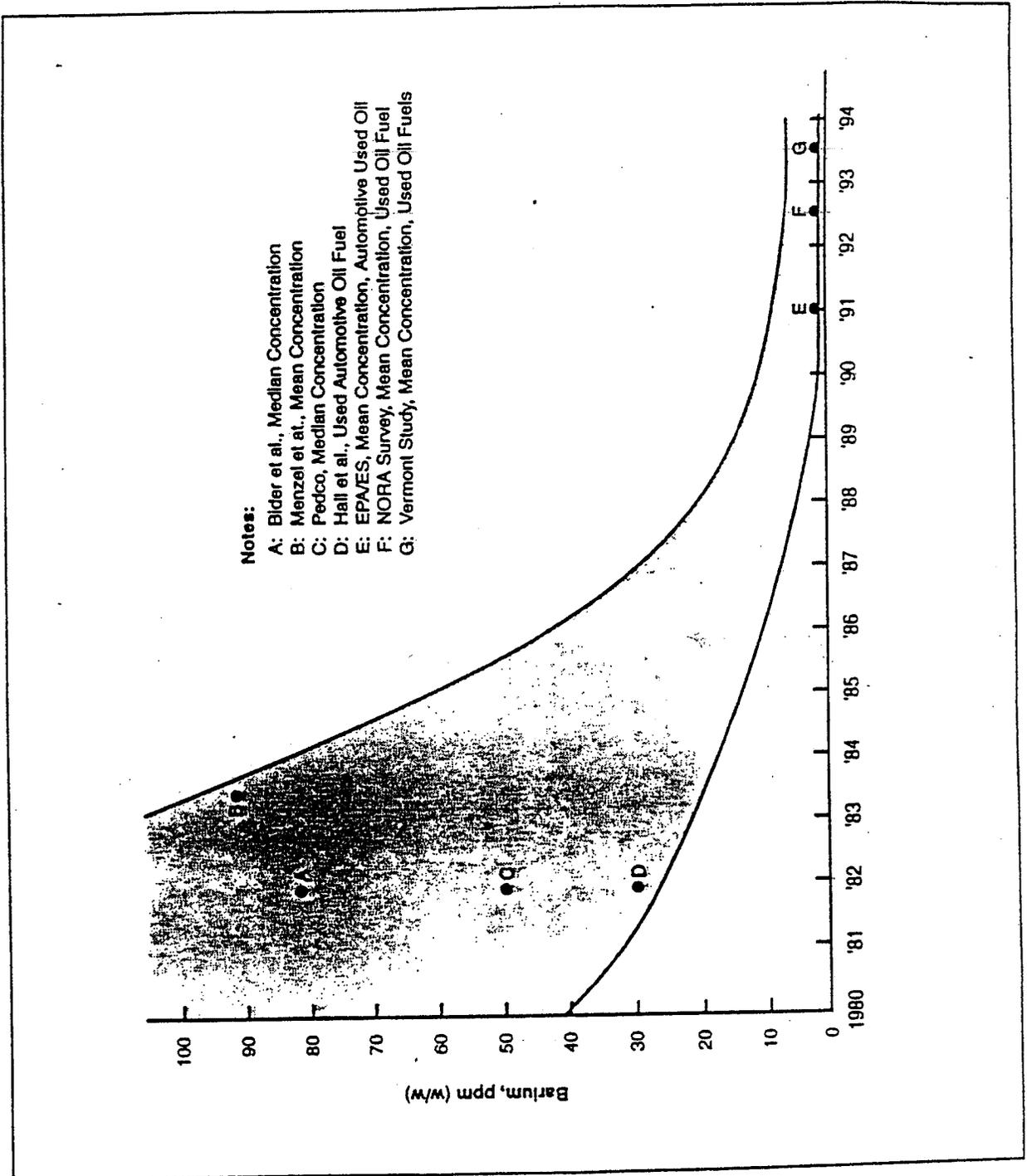


Figure 3-5. Barium Content of Used Oils

Compositions and Quantities of Used Oil

SAIC sampled both the vehicles and the used oil storage tanks. The tanks were sampled to determine if the used oil were contaminated during storage.

The data reported in this study only concerned the material that could pass through the filter. The contractor did not attempt to analyze any solids retained on the filters. Eliminating the solids analyses reduced the overall project analytical costs. However, this approach probably reduced the indicated metals concentrations since some of the materials are present as solids in the used oil. Quality assurance checks of twenty-one samples, did, in fact, indicate that some of the solid levels had moderate-to-high levels of barium and lead. Accordingly, some of the data shown in Table 3-6 may indicate lower-than-actual metals concentrations.

Table 3-6. EPA Analysis, 1989⁶¹

Source of Samples	Metals Concentration in TCLP Filtrate, ppm ¹				
	As	Ba	Cd	Cr	Pb
Automotive Crankcase	< 1	< 10	1.3	5.7	33.2
Automotive Crankcase Storage Tanks	< 2.4	13.2	1.8	4.4	95.4
Diesel Trucks/Buses	3.0	8.1	0.5	2.6	2.3
Diesel Truck/Buses Storage Tanks	4.9	15.9	1.0	5.1	40.1
Heavy Duty Equipment	2.7	< 10	1.9	1.5	1.4
Heavy Duty Equipment Storage Tanks	0.4	9.9	0.4	0.8	17.8

- Note: Many of the values shown were tabulated from sets of data reported as < minimum detectable. The value of the minimum detectable was used for each of the data points.

Compositions and Quantities of Used Oil

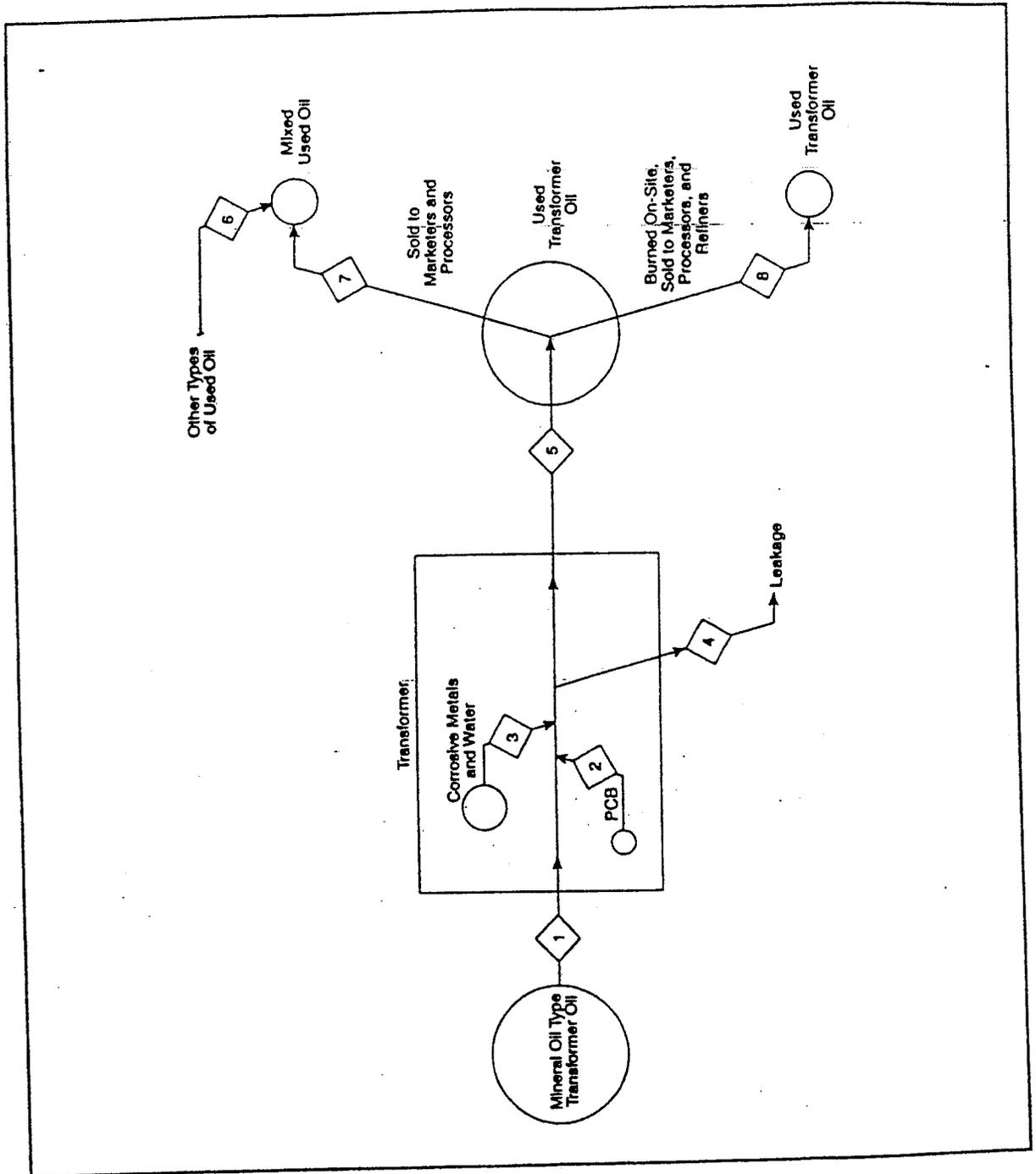


Figure 3-7. Transformer Oil

Compositions and Quantities of Used Oil

by emulsifying the oil with 60 to 95% water. The total quantity of oil generated in 1983 was 264 million gallons⁴⁵.

There is very little data available concerning the contaminant levels in metalworking and hydraulic oils. The data provided in the EPA/SAIC study is presented in Table 3-8. The metals concentrations are relatively low since metal wear is minimal in these types of oil applications. Also, there are no fuel-related contaminants.

Table 3-8. Metals Concentrations in Hydraulic Oils and Metalworking Oils, ppm⁶¹

	Hydraulic	Metalworking
Arsenic	< 1.0	2.1
Barium	25.9 ¹	< 10.0
Cadmium	1.4	0.3
Chromium	0.9	0.7
Lead	1.5	1.6

- Note: High average value is due to one very high concentration sample.

The majority of these used oils are sold to marketers, processors, and re-refiners. Some of this material is processed separately, rather than entering the mixed used oil system.

Marine Oils

The primary source of used marine oil is the bilge/ballast water that is pumped ashore when the ship enters port. The used oil is usually processed to reduce water and sludge and then burned on-site for energy recovery. In military bases, the used oil may also include materials generated by aircraft fueling and maintenance. However, low flashpoint jet fuels such as JP-4 are not added to the used oil since this would be unsafe to burn in conventional boilers.

The only available data for marine used oil were included in the EPA/SAIC study. This is summarized in Table 3-9.

Compositions and Quantities of Used Oil

Summary of Contaminants in Used Industrial Oils

Ten of the 100 respondents to the NORA survey reported receiving between 50% to 100% of their used oil from industrial sources. The mean concentrations of metals were as follows:

Lead	35.8	ppm
Chromium	16.8	ppm
Cadmium	1.83	ppm

With the exception of the lead data, these concentrations are relatively similar to the data generated as part of the EPA/SAIC study⁶¹. The high lead concentrations calculated using the NORA data may be due to the processing of crankcase oils with industrial oils at many of the facilities that submitted NORA forms.

Obviously, more data is necessary to characterize industrial used oil composition at the present time. This data is especially important since industrial oils account for 31 to 40% of the total used oil generated and since it is probable that some of industrial used oils are not mixed with crankcase used oils prior to combustion or re-refining.

3.3 SUMMARY - USED OIL COMPOSITION

Based on the presently available information, the data summarized in Table 3-11 will be used to represent the composition of used oils generated by both the automotive and industrial sectors. This data has been calculated using the weighted average concentrations reported on the NORA survey. This data appears to be consistent with the EPA/SAIC data and with the general trends in gasoline and lubricant formulations. The data has been compared with the data of Bider et al. to illustrate general changes in used oil composition since 1983.

SECTION 4

METAL EMISSIONS FROM USED OIL COMBUSTION

Metals compounds such as lead are not destroyed in combustion processes. They are transformed and partitioned into (1) solids retained in the combustion device, (2) flyash generated during combustion, (3) solid phase product streams (as in asphalt plants and cement kilns), and (4) vapor phase materials which are mixed with the effluent gas stream. Most of the vapor phase material ~~nucleates to form flyash particles while the gas stream cools in heat recovery portions of the boiler.~~ The separation of metals into the different material streams is termed "partitioning." One of the main objectives of this section is to evaluate existing data on metals partitioning during used oil firing.

Once in the particulate form, the metals can be efficiently removed in air pollution control systems. A second objective of this section is to compile data concerning factors that influence the collection efficiency for metal compounds.

Used oil is burned in a variety of combustion sources. For example, the heat input rates for space heaters are less than 0.5 million Btus per hour while the heat input rates for many utility sized oil-fired boilers can be more than 700 million Btus per hour. Many of the combustion variables which potentially affect metals partitioning and particulate removal efficiency vary widely over the different types and sizes of the combustion processes. Important variables include gas stream temperatures, gas stream oxygen concentrations, gas stream residence times in high temperature zones, and entrained solids content in the gas streams. Accordingly, differences in the air emissions from the various combustion processes are expected.

Previous air emissions studies conducted for sources burning used oil and similar fuels have been reviewed as part of the Phase I literature search and evaluation. Conclusions include the following.

- There are very few air emission studies of used oil combustion systems.
- The studies that have been conducted have concerned fuels which are not representative of present-day used oil. Some of the tests were conducted on malfunctioning units or under unusual operating conditions.

Air Emissions from Used Oil Combustion Processes

Table 4-1. Used Oil Specifications (40 CFR Part 279)

Constituent	Maximum Allowable
Arsenic	5 ppm
Cadmium	2 ppm
Chromium	10 ppm
Lead	100 ppm
Flash Point	100 °F
Halogens	4,000 ppm ¹

- Note: See §279.10 concerning used oils with halogen levels greater than 1,000 ppm.

Off-specification used oil can only be burned in boilers, industrial furnaces, space heaters, and other combustion processes that satisfy the requirements of §279.12. These combustion processes include but are not limited to the following.

- Industrial furnaces
 - Cement kilns
 - Lime kilns
 - Aggregate kilns
 - Phosphate kilns
 - Coke ovens
 - Blast furnaces
 - Smelting, melting, and refining furnaces
 - Pulping liquor recovery furnaces
- Boilers
- Space heaters
- Hazardous waste incinerators

To qualify as a boiler, the unit must recover thermal energy from the combustion gases and generate steam, heated fluids, or heated gas. The combustion chamber and the primary energy recovery section must be an integral part of the design. This requirement disqualifies modular type two-chamber incinerators and multi-chamber incinerators. However, the definition includes a wide range of boilers used for space heating (residential, commercial and industrial boilers) and for steam generation (industrial and utility).

Air Emissions from Used Oil Combustion Processes

Heat input is limited by the U.S. EPA regulation (§279.23) to a rate of 500,000 Btus/hr which is equivalent to approximately 3.5 gallons of used oil per hour. The combustion gases are vented directly to the atmosphere. There are no air pollution control devices.

Space heaters are used to burn used oil generated on-site or collected from household do-it-yourselfers. Usually, the used oil is burned as is, without processing to remove water and sludge and without blending with virgin oil⁵⁸. Used oils contaminated with chlorinated solvents should not be burned since they will cause corrosion. Low flash point wastes, such as gasoline, should also not be used since they could cause explosions⁶⁶.

Apartment House, Commercial, Hospital, and School Boilers

For simplicity, these units will be collectively termed "residential/commercial" or "commercial" boilers. They are used strictly for space heating. Heat input capacities can be as high as 15,000,000 Btus/hr⁵⁴. There are two types of units commonly used: (1) cast-iron, and (2) firetube boilers. In the cast-iron furnaces, a single oil fired burner is mounted in either a steel shell or a refractory lined combustion chamber. Hot water can be generated by forcing water to pass through a series of metal sections above the combustion chamber. In firetube boilers, an oil burner is mounted in a small combustion chamber near the bottom of the boiler. Hot combustion gases are forced to pass through several banks of boiler tubes immersed in boiler feedwater. Steam is accumulated at the top of the firetube boiler. Neither type of residential/commercial boiler is usually equipped with air pollution control systems.

Industrial Boilers

These provide steam for space heating or for process operations. One or more oil burners are mounted in water tube lined refractory combustion chambers. Most small units do not have air pollution control systems. Most moderate-to-large installations have low efficiency multi-cyclone collectors. Heat input capacities range from 10,000,000 to more than 400,000,000 Btus/hr. All new or modified units with a capacity greater than 10,000,000 Btus/hr (approximately 70 gallons of oil per hour) are subject to 40 CFR Part 60, Subpart Dc if they commenced construction or were modified after June 9, 1989. Subpart Dc limits sulfur dioxide emissions (due to sulfur in the fuel) but has no substantial limits on particulate emissions when burning

Air Emissions from Used Oil Combustion Processes

constructed or modified after June 11, 1973. Accordingly, it applies to essentially all operating units.

Cement and Lime Kilns

These are very large refractory lined combustion chambers designed to dry, calcine, and pyroprocess (cement plants) the kiln feed. A single large oil burner is used for heat input. Gas temperatures in the kiln exceed 3000°F. Gas residence times at high temperature are very long. High efficiency particulate control systems are used on cement and lime kilns. Particulate emissions from cement and lime kilns are subject to SIP regulations and NSPS regulations (40 CFR Part 60, Subparts F and HH). The NSPS for cement kilns applies to all units which commenced construction or were modified after August 17, 1971. The effective date for the lime kiln NSPS was May 3, 1977.

Steel Mill Processes

Used oil can be fired in a variety of oil burners as part of blast furnaces, sintering machines, or basic oxygen furnaces. These are all large processes which operate at high gas temperatures. Emissions from used oil combustion are mixed with metallurgical fume and other process related emissions. These processes are controlled with high efficiency air pollution control systems. All combustion sources and metallurgical processes in steel mills are subject to the applicable SIP regulations. In addition, the basic oxygen furnaces and electric arc furnaces are subject to NSPS regulations (Subparts N, Na, AA, and AAa) promulgated between June 1973 through August 1983.

Pulp Mill Recovery Boilers

The main purpose of the recovery boiler is to recover the sodium chemicals necessary to digest wood pulp. The lignins and other alkaline-soluble organics separated from the cellulose fibers during digestion are concentrated in the chemical-containing black liquor. These non-cellulose organics provide the main fuel for the recovery boiler. Used oil can be used to supplement the black liquor guns used to operate the boiler. Recovery boilers are equipped with high efficiency electrostatic precipitators. Recovery boilers have heat input rates equivalent to large utility boiler systems. Gas temperatures and gas residence times are relatively long. Pulp Mill Recovery Boilers are subject to 40 CFR Subpart BB which requires high efficiency particulate control, low total reduced sulfur (TRS) emissions, and continuous emission monitoring. Subpart BB applies to

Air Emissions from Used Oil Combustion Processes

Table 4-2. Sales of Used Oils for Fuels
(NORA Survey, 100 Respondents)

Industrial Category	Used Oil Combustion	
	Gallons/Year	% of Total
Asphalt Plants	87,462,094	42.8
Cement/Lime Kilns	9,798,500	4.8
Utility Boilers	25,780,000	12.6
Industrial Boilers	28,300,085	13.9
Commercial Boilers (Apartment House, Hospital, School, and Store)	351,000	0.2
Steel Mills	24,115,000	11.8
Pulp & Paper Mills	7,921,500	3.9
Marine Boilers	10,605,250	5.2
Other	9,725,340	4.8
TOTAL	204,058,970	100.0

The resulting elemental metals and metal compounds will convert from the vapor phase to the solid phase as the combustion gas stream cools during recovery of thermal energy⁷⁰⁻⁷⁴. The temperature at which the various metal species convert from the vapor state depends on their vapor pressure. A vapor pressure curve for a variety of metal species of interest in used oil combustion is provided in Figure 4-1. Each line on this figure presents the vapor pressure data for a single metal compound or elemental metal. As the temperature decreases, the concentration of the species that can remain as a vapor in the gas stream decreases.

Air Emissions from Used Oil Combustion Processes

These mechanisms are relevant to this study primarily because they yield particles which are usually very small. Particles generated by homogeneous nucleation are often in the range of 0.05 to 0.2 microns. Heterogeneous nucleation occurs primarily on the surfaces of particles in the 0.1 to 0.5 micron range. Particles generated by other mechanisms are usually in a much larger size range of 0.5 to > 20 microns.

The particles created by heterogeneous and homogeneous nucleation are predominately in the size range of 0.05 to 0.5 microns. This is the particle size range in which some types of air pollution control systems are least efficient. For example, venturi scrubbers (used on asphalt plants) have a minimum efficiency between 0.1 and 0.3 microns. Electrostatic precipitators (used on cement kilns, lime kilns, recovery boilers, and some oil-fired utility boilers) have a minimum efficiency between 0.1 and 0.5 microns.

The overall process of vaporization of metal species in high temperature zones, followed by nucleation onto the surfaces of very small particles as the gas stream cools, shifts the metals to the small, difficult-to-control size range. Small particles have high concentrations of volatile metal species while large particles have relatively low concentrations. This process is termed "enrichment" of the small particle size range.

Conversely, metal species and inorganic materials which are not very volatile tend to accumulate primarily in the large size ranges.

The various metal species of interest in used oil combustion processes have been grouped into three categories with respect to their volatility (Table 4-3). The metal species in the highly volatile group are the most difficult to collect in air pollution control systems.

Air Emissions from Used Oil Combustion Processes

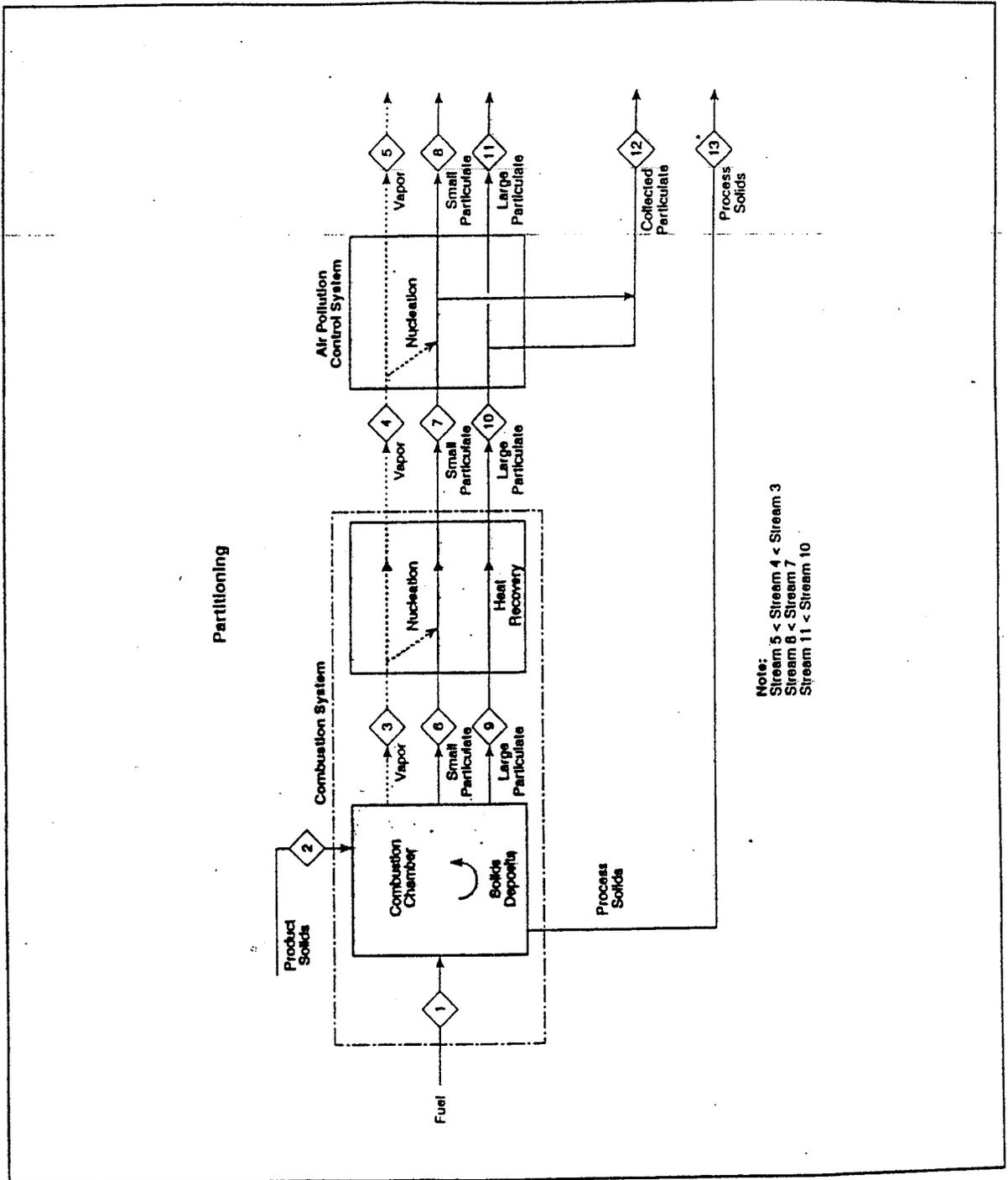


Figure 4-2. Partitioning of Metal Species

Air Emissions from Used Oil Combustion Processes

Entropy has obtained three air emissions studies concerning space heaters. All of these were conducted in the 1982 to 1983 time frame prior to the introduction of present-day space heaters. Therefore, most of this data is no longer relevant. Furthermore, used oil composition has changed significantly since 1983 due to the lead-in-gasoline phasedown and due to advances in lubricant additive formulation.

Due to these changes, these early studies have not been summarized completely. Only the information which is relevant to present day space heaters is discussed in the following sections.

4.2.1 EPA/Battelle Columbus Laboratories Study^{57,76}

This test program involved a single atomizing burner design (Dravo Hastings Thermoflo, Model 20-WO) and a vaporizing pot space heater (Kroll Model W400L). The vaporizing pot unit was discontinued by the manufacturer shortly before these tests were conducted. The atomizing burner unit used low pressure atomizing air and was similar to presently available designs.

Air emissions tests were conducted using used automobile crankcase oil and used diesel truck crankcase oil. The concentrations of metal contaminants in these used oil fuels are summarized in Table 4-4.

The oils used in this study had lead levels which are 7 to 80 times higher than present lead concentrations in used oil. The barium concentrations in this old study also were well above present barium concentrations.

Mass balances for various metals were determined by comparing metals emission rates and used oil metal feed rates. Metals emissions rates were calculated from the gas flow rates, and the metals concentrations data were determined by two separate techniques: the SASS train and a dilution tunnel. The metal feed rates were calculated using the used oil firing rate and the metals concentrations.

The mass balance results indicated that metals emissions were less than input rates in most cases. For example, the zinc emission rates during tests of both types of used oil were approximately one-half of the total zinc input rates. These results suggest that a fraction of each of the metals is retained as solids deposits within the combustion chamber and on the heat exchange surfaces.

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another major alloying element in stainless steel. These problems were eliminated in the EPA multi-metals sampling train developed by the U.S. EPA and Entropy several years after this study was conducted by Battelle Columbus.

The emissions data for the air atomizing type space heater indicated that the unit was operating well during the test. Table 4-5 shows that the carbon monoxide concentrations ranged from 16.7 to 25 ppm.

Table 4-5. General Test Conditions, Air Atomizing Burner Type Space Heater⁵⁷

Test Conditions	Automobile Crankcase Oil	Diesel Truck Crankcase Oil
Stack Gas Temperature, °F	642	630
Oxygen Concentration, %	4.8	4.8
Excess Air, %	27.9	28
Carbon Monoxide Concentration, ppm	25	16.7
Unburned Hydrocarbon Concentration, ppm	3.1	2.1
Particulate Emissions, mg/M ³	224.4	223.4

4.2.2 British Columbia Research Corporation Study⁷⁸

Emission tests on 6 used oil-fired space heaters were conducted by the British Columbia Research Corporation for the Government of the Northwest Territories (Canada). Five Lanair type vaporizing pot heaters and a low pressure air atomizing type space heater were tested. U.S. EPA Reference Method 5 was used to sample the combustion gases. The filters were digested in nitric acid, filtered, and analyzed by inductively coupled plasma - mass spectroscopy (ICP-MS). Only the test conducted on the air atomizing unit is relevant to the UORC study.

The metals emission rates and the used oil metals concentrations for the air atomizing unit are summarized in Table 4-6. The retention factors for the metals could not be calculated since

Air Emissions from Used Oil Combustion Processes

particulate matter emitted contained 97% of the total lead emissions. The less than 0.6 micron fraction contained 74% of the total lead emissions. This is consistent with the expected homogeneous and heterogeneous nucleation mechanisms discussed earlier in this section. It is apparent that lead volatilizes and nucleates even in the relatively limited temperature and residence time environment of a space heater.

The retention of lead within the combustion chambers was high in all five units tested. As indicated in Table 4-7, the percentages of metals emitted were 18% to 38%.

Table 4-7. Percentages of Lead Emitted⁹

Test Site	Test No.	Percentage of Lead Emitted
1	A	33
	B	28
	C	24
2	D	30
	E	24
3	F	18
	G	24
4	H	34
	I	27
5	J	38
	K	35

Very high lead levels were found in the deposits in the combustion chambers. At test site 1 (laboratory), the lead deposits in the combustion chamber were 32% of the total. The lead levels in the heat exchanger and the exhaust box decreased to 12.7% and 9.8% respectively. High lead levels were also detected in the boiler scrapings from test sites 2 and 3.

The data of Periera et al. is generally consistent with the lead retention results from the study of Hall et al. In both cases, a major fraction of the lead remained in the combustion chamber. This means that air emissions are reduced proportionally.

The total particulate emissions from the five units tested during the Periera et al. study ranged from 250 to 438 mg/M³ in all but

Air Emissions from Used Oil Combustion Processes

between the combustion gas stream and internal deposits. It is especially important to determine the extent to which these deposits can serve as a "sink" or "source" of lead emissions during short term emission tests of space heaters.

The particle size distribution of lead-containing particles generated in space heaters is probably quite small. Most of the lead emitted to the atmosphere is in the submicron range. More data is necessary to confirm the distribution of lead and other metals as a function of particle size.

4.3 RESIDENTIAL/COMMERCIAL BOILERS

These boilers are used for space heating at apartment houses, businesses, hospitals, and schools. The boilers generate hot water or steam. The heat input capacities range from 0.4 million Btus/hr to 25 million Btus/hr⁴⁵. There are three basic design types.

- Cast-iron
- Firetube
- Water tube

Cast-iron boilers derive their name from the water heating sections used for recovering heat from the flue gases. Small, round cast-iron units are larger but nevertheless similar in appearance (externally) to old-style wood-fired stoves used for residential heating. They have a series of hollow sections above and around the combustion chamber for the circulation of water. The hot combustion gases pass upward through the center of the unit and around the hollow sections. Round cast iron boilers have the following components which are arranged vertically.

- Ashpit
- Firepot
- Crown section
- Intermediate sections
- Dome section

Water circulates from section to section through a set of push nipples connecting the sections. After passing through the boiler, the combustion gases enter the outlet breeching and are discharged to the atmosphere through a flue.

Many cast-iron boilers are constructed in a square or rectangular shape. The water circulating sections are stacked vertically above the combustion chamber. The hot gas combustion products

Air Emissions from Used Oil Combustion Processes

fans are used to move the combustion gases through the boiler and tube banks. Units designed for commercial applications usually do not have air pollution control systems. However, they are subject to the air quality regulatory requirements discussed above.

Small sized commercial boilers are usually operated in an on-off mode controlled by building temperature monitors. Emissions of organics (possible adsorbents for metals) are greatest during the start-up and shut-down periods due to the cold gas temperatures in the combustion chamber. Moderate-to-large commercial units often operate with more stable boiler loads due to the size of the building being heated and the economical feasibility of more sophisticated boiler controls.

The oil burners used in this boiler size category include rotary cup atomizers, mechanical atomizers, and air atomizers. In all three cases, the oil is dispersed as fine droplets to facilitate rapid oxidation.

4.3.1 GCA Corporation Emission Test Study

In 1984, the U.S. EPA, Industrial Environmental Research Laboratory sponsored a set of emission tests at six commercial sized boilers. The emission tests were conducted by GCA⁶². The study concerned the destruction efficiencies of chemical contaminants such as chlorinated organics which could be present in used oil. As part of the study, the fate of metals in the used oil were also evaluated. The metals portion of the test program work is relevant to the UORC Phase I project.

In order to control the highly variable concentrations of organic contaminants, GCA used a 4000 gallon oil supply tank. A supply of used oil was purchased, analyzed, and then spiked with four volatile chlorinated organic compounds and four semivolatle chlorinated organic compounds. The resulting concentrations were 3,000 to 5,000 ppm for each compound. This is important since the levels of chlorinated compounds were several orders of magnitude higher than the levels present in typical used oil fuels. Reactions between the chlorinated compounds and metal species in the used oil tank and during combustion could lead to the formation of metal chlorides which are inherently more volatile than the oxide form and the elemental form. Accordingly, the partitioning of the metal species measured in this study may not be representative of commercial boilers firing a more conventional used oil fuel.

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Table 4-9. GCA Test Data for Commercial Boilers⁶²

	Emission Test Site					
	A	C	D	E	F	G
Fuel, gal./hr.	3.22	24.05	13.14	14.6	23.2	23.1
Gas flow, DSCM ³ /hr.	382	1,543	1,479	2,342	1,460	1,652
Stack Temp., °F	357	437	268	199	575	203
Oxygen, %	9.5	10.2	12.4	16.9	8.8	7.1
CO, ppm	220	47	350	28	28	48
Particulate lbs/10 ⁶ Btu	0.17	0.41	0.38	0.39	0.28	0.39
As, ug/M ³	11.2	655	26.1	106	251	286
Cd, ug/M ³	31.2	102	8.3	182	350	81
Cr, ug/M ³	62.2	166	112	230	205	263
Zn, ug/M ³	5,150	33,700	3,134	12,100	26,800	27,000
Pb, ug/M ³	9,680	72,400	5,390	20,300	49,800	51,000

Note: Site A, cast-iron boiler, mechanical atomizer, serving an office building
 Site C, Horizontal return tube type firetube boiler, rotary cup atomization, serving a greenhouse
 Site D, Scotch firetube boiler, air atomization, serving an office building
 Site E, Scotch firetube boiler, rotary cup atomization, serving a greenhouse
 Site F, Scotch firetube boiler, air atomization, serving a greenhouse
 Site G, Scotch firetube boiler, air atomization, serving a greenhouse

Air Emissions from Used Oil Combustion Processes

The metal mass balance data is too weak to support any conclusions regarding metal retention in commercial boilers. There is too much data scatter, and the results do not clearly match the volatilities of these elements.

The high cadmium results indicate one or more of the following problems.

- Cadmium release from internal deposits
- Cadmium contamination from the sampling train
- Inaccurate cadmium analyses in the used oil
- Inaccurate emission test results

The emissions tests were conducted using the appropriate U.S. EPA reference methods and using applicable quality assurance procedures for the emission sampling and sample analysis. However, the operating conditions of the unit being tested were not fully described. Basic combustion parameters like oxygen concentration and stack temperature were abnormal in some cases. Basic combustion parameters such as combustion chamber draft were not recorded. The emission tests were conducted under the assumption that short term emission tests can characterize emissions of species that are both retained and released from internal surfaces. No attempt was made to confirm that equilibrium conditions were established with respect to the internal mass transfer mechanisms prior to the tests. Overall, this study was extremely well executed from the standpoint of the air emission tests. However, the units being tested were apparently (1) fired under highly suspect operating conditions, (2) fired with fuel having highly unusual levels of chlorinated compounds, and (3) evaluated using short term tests with unknown retention conditions.

It should be noted that some qualitative information concerning lead behavior can be obtained from the results. Particle size analyses performed during some of the tests (sites A, G, and E) have been plotted in Figure 4-3. In all three cases shown, more than 80 percent of the lead emissions were in particles less than 1 micron in diameter. This indicates that lead vapor is nucleating homogeneously and/or heterogeneously to form submicron particles in the commercial boiler.

Air Emissions from Used Oil Combustion Processes

4.3.2 Summary - Commercial Boilers

Entropy identified and reviewed only one available air emissions test program for commercial boilers. This emission data is not representative of boilers firing present-day used oils. Some of the units appeared to be operating improperly during the tests. Due to limitations of the data, it is not possible to accurately evaluate partitioning of the metals between the flyash and boiler deposits. The particle size data suggests that the lead emissions are predominantly in the submicron range.

4.4 INDUSTRIAL BOILERS

Industrial boilers range in capacity from 5 million Btus/hr to more than 250 million Btus/hr. Small units are usually firetube boilers. These can have capacities up to approximately 15 million Btus/hr. Watertube type boilers are generally used for heat input capacities greater than 15,000,000 Btus/hr to more than 400,000,000 Btus/hr. Both types of boilers have been described in Section 4.3.

Industrial boilers used for space heating usually operate throughout the heating season. Boiler loads are much more stable than commercial boilers. Facilities having more than one boiler in the heating plant can adjust for steam demand changes by starting or shutting down one of the boilers. This normally allows the boilers that are operating to be near full load and thereby operate in the most thermally efficient manner. Any oil-fired boiler capable of firing No. 5 or No. 6 oil can be readily adapted to burn used oil. Some burner system modifications would be necessary to adapt a No. 2 burner for used oil.

There is no information available concerning the extent to which industrial boiler operators blend used oils with virgin oil prior to firing. Also, it is not known whether or not used oil firing occurs during start-up.

The types of air pollution control systems used on industrial boilers depend on the heat capacity of the boiler. Existing boilers are subject to fuel burning source particulate regulations (included in the SIPs) which require lower emissions from large units.

Also new or substantially modified boilers greater than 10 million Btus/hr (most industrial boilers) are subject to the New Source Performance Standard 40 CFR Part 60, Subpart Dc

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This data is of interest only because it demonstrates that the concept of metals retention within the combustion chambers of oil-fired boilers has been recognized for more than twenty years. The fraction of lead emitted was as low as 20% in one of the tests, and it was usually in the range of 40 to 50%.

4.4.2 Summary - Industrial Boilers

Air emissions data for used oil firing in industrial boilers is extremely limited. There are qualitative indications that lead retention in the boiler does occur. However, accurate partitioning factors for lead and other metals cannot be based on the data, all of which is more than twenty years out-of-date.

4.5 MARINE BOILERS

These are similar in size and performance to small industrial boilers. Most marine boilers are firetube designs. Air pollution control systems are not used on these boilers.

While at sea, the marine boilers operate at relatively stable loads, especially if there are several boilers in use. However, very low boiler loads are possible when ships are docked. Marine boilers must be capable of high turndown rates in order to operate at the very low steam demands which exist at such times. High opacity emissions are possible if the unit is not adjusted properly. During these periods, some metal emissions are possible. Occupied areas close to harbors could be impacted by these emissions. However, it should be noted that the relatively "cold" conditions in the boiler at low load should favor metal retention due to the adsorption of metal species vapors on the soot-coated heat exchanger surfaces. Accordingly, only a fraction of the total metals in the used oil would be emitted. No air emission tests were identified concerning marine boilers.

4.6 UTILITY BOILERS

Used oil can be burned in both oil-fired and coal-fired utility boilers. The types of used oil burned include but are not limited to vehicle crankcase oil, transformer oil, and turbine oil.

Utility scale coal-fired and oil-fired boilers are watertube boilers with a large number of burners arranged in rows. Combustion gases pass upwards through a boiler tube-lined

Air Emissions from Used Oil Combustion Processes

In the case of oil-fired units, the used oil can be fired in separate burners or blended with virgin oil prior to firing. Many oil-fired units are equipped with multi-cyclone collectors for removal of large sized particulate matter. Some units are equipped with high efficiency particulate control systems.

No air emission test data were found concerning utility scale boilers firing used oils. Testing is warranted based on the used oil consumption data indicated by the NORA survey (Table 4-1). Utility boilers are the third largest consumer of used oils supplied by marketers, processors, and blenders.

4.7 ASPHALT PLANTS

Asphalt plants consume approximately 40% of the used oil fuels generated in the U.S. according to the results of the 1993 NORA survey. The National Asphalt Paving Association (NAPA) has estimated that the industry consumes as much as 200 million gallons per year²⁴. That consumption rate has increased during the last few years.

Used oil is used in asphalt plants to dry and heat the aggregate prior to its mixing with asphaltic binder. There are two main types of plants: (1) hot mix, and (2) drum mix.

A simplified schematic of a hot mix plant is shown in Figure 4-4. Aggregate of various size gradations is metered out of bins in proportions necessary to produce the grade of asphaltic concrete specified by the customer (usually State DOT). The aggregate must be dried and heated to 250 to 325°F in order to ensure proper coating with the asphaltic binder. Heating and drying are performed in a small rotary drier with a single oil-fired burner. The portion of the rotary drier on the opposite side from the burner has side-mounted scoops to shower the aggregate across the combustion gas stream as the drum rotates. The hot aggregate is then transported by a hot bucket elevator to the hot bins and hot screens. The size proportions are readjusted, and the aggregate is dumped into a pug mill for mixing with the asphaltic binder.

The hot combustion gases entrain fine aggregate dust in the rotary dryer. These particulate emissions are controlled by a pulse jet baghouse or a medium pressure drop venturi scrubber. In many plants, fugitive dust captured from the hot screens and the elevator are also ducted to the particulate control system.

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A drum plant performs aggregate drying/heating and binder application in the rotary drum. There are no hot bins, hot screens, or pug mill. After passing part of the way through the rotary drier, the dried and heated aggregate is coated with binder using an injection pipe which extends in from the cold side of the drier. The placement of the injection pipe is adjusted to minimize volatilization of the asphaltic binder. The hot gases are ducted to a pulse jet baghouse or a medium pressure drop venturi scrubber.

Most asphalt plants have oil burners which can be readily adapted for used oil firing. The used oil increases the metals emissions to the particulate control system. However, it is important to note that the used oil is not the only source of metals. The aggregate itself has low concentrations of many of the metals addressed in this project. These low concentrations are important simply because of the large aggregate dust loadings to the air pollution control system.

There are two air emissions studies of asphalt plants firing used oils. These are summarized in the following sections.

4.7.1 Harris and Schlickerieder Study⁴⁵

Harris and Schlickerieder of A.D. Little, Inc. conducted a study of a hot mix plant under the sponsorship of the Massachusetts Department of Environmental Quality Engineering (DEQE). The report states that it was conducted in part because the Commonwealth of Massachusetts had determined that asphalt plants consumed approximately one-half of the used oil generated in the State. Furthermore, the State had determined that much of the data published prior to 1983 was inadequate to support regulatory decisions.

The tests were conducted in accordance with a trial burn plan developed by A.D. Little and reviewed by both the DEQE and the Massachusetts Asphalt Paving Association. U.S. EPA Reference Method 5 was used for particulate sampling, and the metals were analyzed using ICP and atomic absorption (AA). The used oil fuel was a blended mix of two used oil supplies. Prior to the tests, trichloroethylene was added to yield a concentration of 9,400 ppm. The resulting used oil composition is summarized in Table 4-12.

Plant operations during the test appeared to be normal for the specific facility and representative of the industry in general.

Air Emissions from Used Oil Combustion Processes

aggregate do not pose an environmental hazard since they are incorporated into the hardened asphaltic concrete.

4.7.2 Baker et al. Study⁸⁶

This study was reported in the Background Information Document (BID) for the BIF Regulations (Volume II Industrial Furnaces). However, as of this time, Entropy has not been able to obtain a copy of the draft report (dated 1983) which is cited as the source of emissions data. Accordingly, only the data and information included in the BID can be evaluated.

The air emissions tests were conducted at two plants. One was a 400 ton per hour drum mix plant equipped with a baghouse. This was fired entirely with a processed industrial used oil. The second plant was a 76 ton per hour unit equipped with a scrubber. It was fired with 100% processed crankcase oil. The production data included in reference⁸⁶ indicates that both plants were operating normally during the test program.

At both plants, metals concentrations were measured in the used oil feeds, the aggregate feeds, the asphaltic binder, the baghouse inlet dust, and the stack emissions. U.S. EPA Method 5 was used for sampling at the baghouse inlet and the stack.

Baker et al. attempted to measure the metal-specific control efficiencies of the baghouse and scrubber. In order to isolate the fraction of the metals due to the used oil, they analyzed the aggregate dust prior to the drier. Mass balance calculations were then performed using the dust loadings generated in the drier. The results of these calculations are shown in Table 4-14 for Plant #1 and in Table 4-15 for Plant #2.

Mass balance calculations of the type shown in Table 4-14 and 4-15 are vulnerable to a number of problems in obtaining representative samples and accurate analyses of several different types of materials. Furthermore, the aggregate stream is at least one hundred times larger than the used oil stream. Despite these inherent limitations, the data in these two tables do indicate the following.

- Used oils can be major contributors to the metals listed in these two tables.
- The removal efficiencies for all of the metals are relatively similar.
- The removal efficiencies for the metals are different for the scrubber controlled plant.

Air Emissions from Used Oil Combustion Processes

4.7.3 Summary - Asphalt Plants

The limited data available indicates that metals in used oil fuels burned in asphalt plant driers are captured with high efficiency at units equipped with well operated baghouses. Emissions of all of the metals may be less than 1% of the total input quantities present in the used oil.

A plant with a wet scrubbing systems may have lead emissions which were 50 to 75% of the total input quantities. This may be due to the presence of lead and other volatile metal species in the difficult-to-control submicron size range. The single study identified concerning wet scrubber equipped asphalt plants is not sufficient to characterize metal collection efficiencies.

Metal removal efficiencies may be high in the asphalt industry due to the characteristics of the combustion process. The metals vaporized in the burner flame have ample opportunity to nucleate on the surfaces of aggregate dust circulating through the combustion gas stream. The aggregate surface temperatures are much lower than the dewpoint temperatures for the metal vapors. In fact, the aggregate temperatures are far below the normal surface temperatures of the boiler tubes and combustion chamber surfaces of boilers. Accordingly, condensation of these vapors is likely on the aggregate dust. Metal emissions are further reduced by fabric filters used in many plants. Since fabric filter efficiency is high even in the submicron range, metal vapor which nucleates homogeneously will also be captured.

There are practical limits to the firing of used oils in asphalt plants. Used oil fuels with high concentrations of chlorinated compounds could cause severe HCl-related corrosion of the ductwork and air pollution control equipment.

4.8 CEMENT KILNS

Portland Cement kilns pyroprocess feed materials (limestone, sand, and iron oxide) to yield tricalcium silicate, tricalcium aluminate, tetracalciumaluminate-ferrite, and a variety of other component compounds. The feed materials are blended in the proper stoichiometric proportions and fed into a large, refractory lined rotary kiln. The kiln is fired by a single burner which can be easily adapted for used oil firing. Fuel costs represent an important fraction of the overall cost of producing portland cement. There are a number of Portland Cement kiln designs.

Air Emissions from Used Oil Combustion Processes

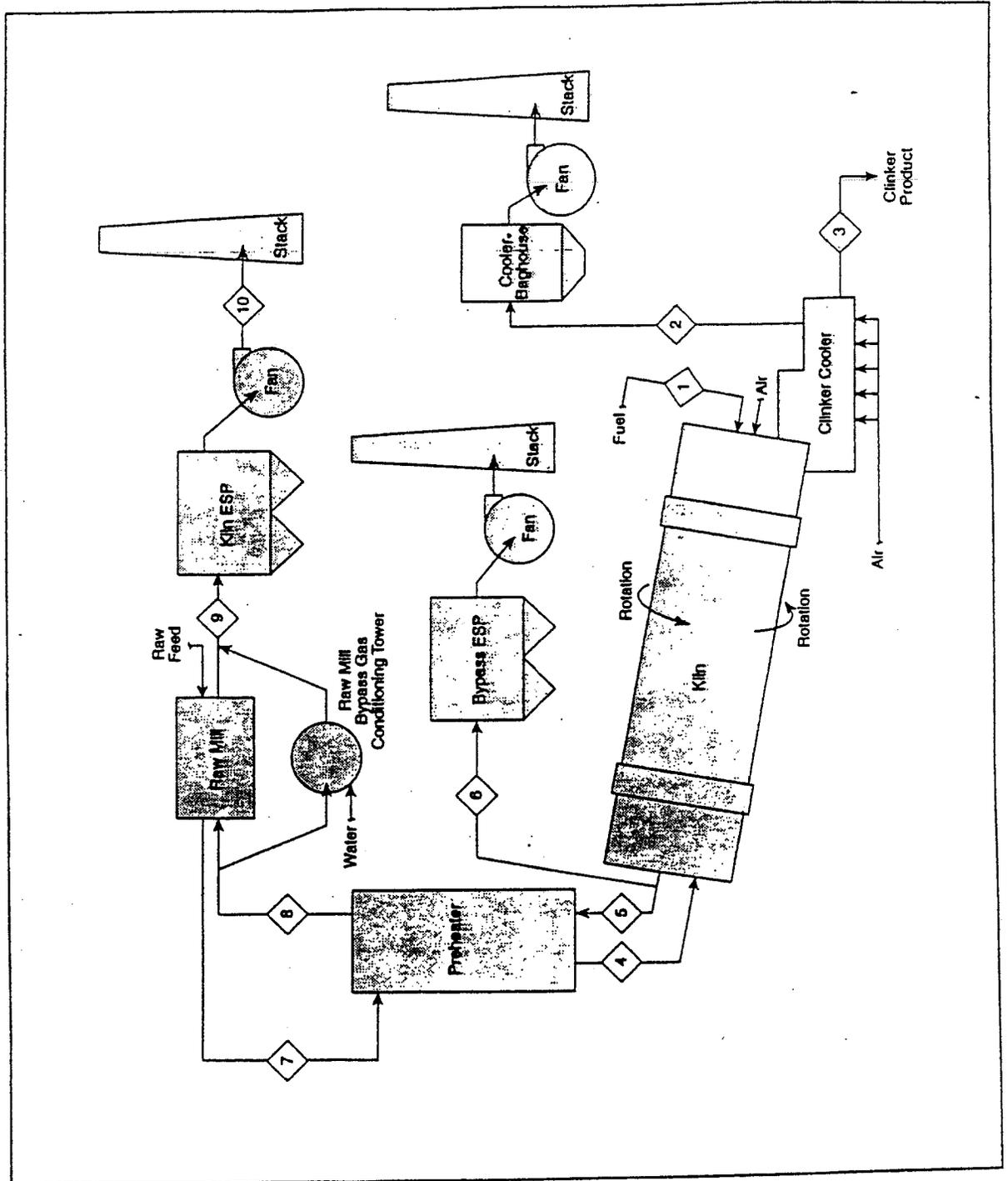


Figure 4-5. Preheater Type Portland Cement Plant

Air Emissions from Used Oil Combustion Processes

The gas stream passes in a counterflow direction from the solids. The gas temperatures reach peak levels of 3000 to 3400°F for several seconds. They remain at high temperatures throughout the kiln and preheater tower. Due to the high temperatures and long gas residence times, essentially all of the metals of interest in the Phase I study are volatilized. As the combustion gas stream cools passing up through the kiln, the nonvolatile elements can be captured by the feed materials and partially processed solids moving in a counterflow direction. Some of the metal species can react with the partially processed feed materials and be immobilized⁷³. These materials will exit the kiln with the clinker. The moderately volatile metal species can remain in the vapor state until they reach the preheater tower. As the gas stream cools moving up through the series of cyclones, the metal vapors nucleate heterogeneously on the surfaces of the feed material particles.

The metals emitted from the combustion of used oil are partitioned into the clinker stream exiting the kiln, the feed materials passing downward toward the kiln, and the particulate exiting the preheater tower and going to the particulate control system. A high efficiency particulate control system is needed due to the high solids loadings resulting from entrainment of particulate in the preheater tower and raw mill. Both reverse air fabric filters and electrostatic precipitators are used.

The metal vapors which condensed heterogeneously in the preheater tower can be re-volatilized as the feed material particles cascade downward and are exposed to increasingly higher gas temperatures. The process of re-volatilization in the high temperature area near the bottom of the preheater tower or the kiln and nucleation in the cold temperature area at the top of the preheater can set up a loop for concentrating the metal species and compounds such as sodium and potassium. There is no means of escape for this materials unless a portion of the kiln gases are drawn off and treated in a separate air pollution control system. This is termed the alkali bypass system since the main objective is to purge the kiln system of sodium and potassium that can not be present at high concentrations in the clinker product. A major fraction of the metals released during used oil firing can exit the kiln system through the alkali bypass gas stream. An electrostatic precipitator is used for high efficiency collection of the particulate matter in the alkali bypass stream.

Portland Cement plants are well suited for used oil firing. All of the metals in the oil should be vaporized in the firing end of

Air Emissions from Used Oil Combustion Processes

difficult-to-control size range of 0.1 to 0.5 microns. Electrostatic precipitators are least efficient in this size range.

Table 4-16. Metal Mass Emission Rates⁶⁷

Metal	Mass Flow Rates, Lbs./hr.	
	Fuel Total	Stack Emissions
Cadmium	0.13	0.005
Mercury	0.009	0.001
Lead	2.396	0.055
Selenium	0.08	0.027

Note: This is a secondary reference. No data is available concerning plant or control device operating conditions.

4.8.2 Dellinger et al.⁷³

The Scientific Advisory Board (SAB) on Cement Kiln Recycling has prepared a comprehensive report on the performance of cement kilns burning hazardous wastes. The portions of the report concerning the partitioning and collection of metals is relevant to the Phase I UORC project.

A general model of metals behavior in cement kilns has been prepared by Dellinger et al. This model was based on the volatilities of the various metal species, the temperature profiles in the equipment, and the cement plant design characteristics. The model has been used to predict metals partitioning into the clinker, the cement kiln dust (CKD) captured by the particulate control systems, and the emissions to the atmosphere. The model results have been compared to air emission data obtained in a variety of earlier test programs.

Comparisons of the model results and the emission data for lead and chromium at two separate plants are shown in Figures 4-7 through 4-10 from the SAB report. This data indicates that most of the lead (moderately volatile) is partitioned to the cement kiln dust which is captured by the particulate control systems.

Aii Emissions from Used Oil Combustion Processes

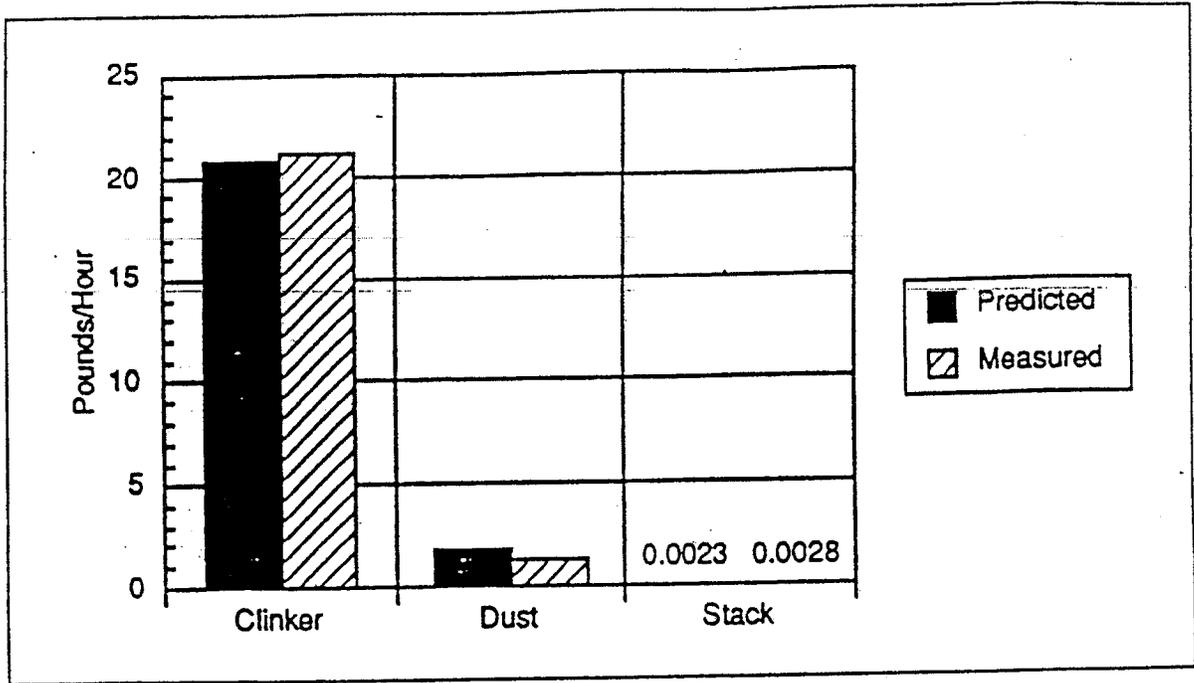


Figure 4-9. Predicted and Actual Chromium Partitioning, Plant "P"

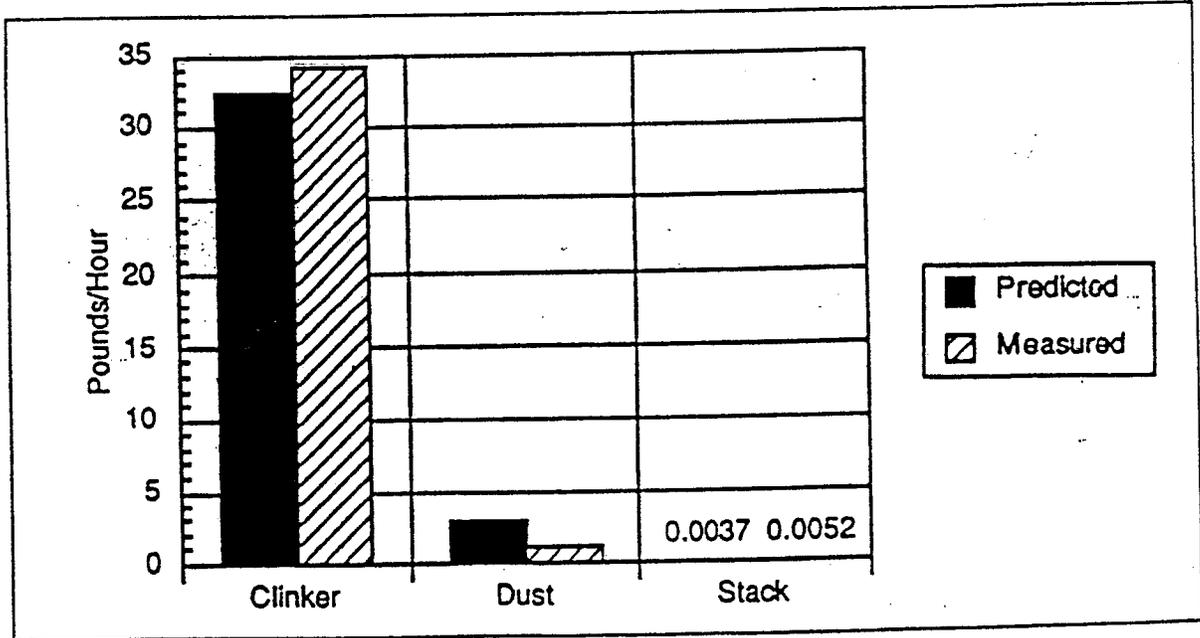


Figure 4-10. Predicted and Actual Chromium Partitioning, Plant "O"

Air Emissions from Used Oil Combustion Processes

of coal, tires, and liquid hazardous wastes. The liquid hazardous wastes were spiked with metals for approximately 48 hours prior to emission testing and sampling in order to "condition" the process. This was useful in ensuring that changes in the preheater-kiln concentration loops would not affect the metals partitioning and collection efficiency test results.

In preparing the mass balances, Roth did not include the metals contents in the incoming raw feed and in the coal. The overall efficiency of metals removal was determined simply by comparing the total emission values for the main stack, bypass stack, and clinker cooler (Figure 4-5) with the metals input levels from the spiked hazardous waste and the tires. The results of these mass balance calculations are shown in Table 4-18.

Table 4-18. Metals Removal Efficiencies¹⁸

	Condition 1, high metals spiking			Condition 2, low metals spiking		
	Stacks ¹	Input ²	Eff., %	Stacks ¹	Input ²	Eff., %
Arsenic	0.00034	0.49	99.93	0.00017	0.14	99.88
Barium	0.0058	13.08	99.96	0.0036	13.16	99.97
Cadmium	0.0011	1.32	99.91	0.00077	0.48	99.84
Chromium	0.0024	8.28	99.97	0.0029	8.70	99.97
Lead	0.0183	14.94	99.88	0.0078	11.68	99.93
Mercury	0.0069	0.09	92.38	0.0079	0.05	84.40
Zinc	0.0134	37.08	99.96	0.0084	28.88	99.97

1. Total stack emissions from three stacks
2. Metals input from hazardous waste, tires, and spiked material

The data presented by Roth¹⁸ are consistent with the metal emission factor estimates presented by SAB⁷³. These studies indicate that the emissions of lead and other metals included in the scope of the Phase I UORC study are quite low.

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They determined that the quantities of arsenic entering with the kiln feed and coal were several orders of magnitude greater than that entering with the hazardous waste fuel (<1 to 8.8 ppm). Most of the arsenic became part of the cement kiln dust, and a small amount became trapped in the clinker.

The large majority of the barium entering with the kiln feed, coal, and hazardous waste became part of the clinker. Unlike many other elements, the source of cadmium was almost exclusively the hazardous waste fuel. All of the cadmium became part of the cement kiln dust.

The raw feed dust entrained in the combustion gas streams was considered to be the major source of chromium reaching the particulate control devices. Chromium entering the kiln with the hazardous waste fuel is effectively captured in the kiln and is incorporated into the clinker stream.

The authors conclude that lead has a strong tendency to concentrate in the cement kiln dust. As a volatile material, it can participate in volatilization-nucleation loops. Accordingly, lead emissions to the particulate control systems are subject to variations in input rates when there are operational changes that effect this concentration cycle.

4.8.7 Summary - Cement Kilns

There have been numerous detailed studies of hazardous waste firing in cement kilns. The data provided by these studies regarding metals behavior support the following conclusions.

- The emissions of lead, cadmium, chromium, barium, arsenic, and zinc are very low. Less than 1% of the metals entering with the waste fuel are emitted in the combined effluents from the main kiln stack, the alkali bypass stack, and the clinker cooler stack.
- The high metal removal efficiencies are due to the capture of the low volatility metal species in the clinker and the high efficiency control of cement kiln dust.

It should also be noted that used oils have considerably lower lead, barium, and chloride concentrations than the hazardous wastes tested in the studies discussed. In some cases, the quantities of metals entering with the used oil could be

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Data is needed concerning the specific types of combustion devices and metallurgical processes firing used oil, the factors which limit the types of used oil burned, and the air emissions resulting from used oil firing.

4.10 OTHER COMBUSTION PROCESSES

There are a number of other industrial combustion processes and furnaces that could utilize used oil fuels.

- Pulp mill recovery boilers
- Lime kilns
- Lightweight aggregate kilns
- Sulfur recovery furnaces

Air emissions data during used oil firing is needed for all of these source categories. The most important of these is the pulp mill recovery boilers since the NORA survey indicated that they account for several percent of the total used oil fuel consumption.

Emission Estimates

pollution control devices, a zero percent removal efficiency for the emitted particles has been used. These partitioning factors and the control efficiency have been entered on Table 5-1.

The NORA survey did not provide information concerning the quantities of used oil burned in space heaters. The organizations involved in used oil marketing and processing would usually not have information on used oil consumption for space heaters since these units operate on used oil generated on-site or locally without processing. For the purposes of this study, Entropy has assumed that 6,500 units are sold each year and that the average life of space heaters is 10 years. Accordingly, the total population of operating space heaters is estimated at 65,000. The used oil consumption has been estimated based on an average heater capacity of 0.3 million Btus/hr. and an average operating time of 500 hours per year. This yields a total used oil consumption rate of 69 million gallons per year for space heaters in the U.S.

5.1.2 Commercial Boilers

The used oil consumption rate for commercial boilers reported in the NORA survey was 351,000 gallons. This has been multiplied by a factor of 3.583 to account for used oil consumers not included in the NORA survey. This results in a total U.S. consumption of approximately 1,300,000 gallons in apartment house, commercial building, and school boilers.

The lead emission rate for this source category is based on a lead retention in the combustion chamber of 50%. As in the case of space heaters, it is assumed that 49% of the lead leaves the combustion system as particulate, and 1% leaves as vapor. A zero percent control efficiency has been assumed for the particulate since the lead-containing particles are too small to be collected by low efficiency control systems. All of the vapor phase lead is assumed to be emitted.

5.1.3 Industrial Boilers

The partitioning factors and control efficiency factors for industrial boilers are identical to those chosen for space heaters and commercial boilers.

The total used oil consumed in the population of sources represented by the NORA survey was 28,300,085 gallons. This has been multiplied by 3.583 to yield a total U.S. consumption of approximately 101,400,000 gallons per year in industrial boilers.

Emission Estimates

5.1.6 Asphalt Plants

The consumption of used oil at asphalt plants indicated by the NORA survey was 87,462,094 gallons. The total U.S. consumption of used oil by asphalt plants has been estimated at 313,400,000 gallons based on the multiplication factor discussed earlier.

The lead emission rate estimate for asphalt plants is based on a lead capture efficiency of 20% on the aggregate passing through the drier. Most of the remaining lead (79%) has been assumed to nucleate on particles entrained in the gas stream. As in the case with the other source categories, it is also assumed that 1% of the lead remains in the vapor state.

A lead-containing particle removal efficiency of 75% has been assumed for the asphaltic concrete industry. This relatively low value takes into account the 99+% efficiencies expected for fabric filter controlled units and the 60% removal efficiency estimated for lead-containing particles in wet scrubber controlled plants. The actual performance of asphalt plant wet scrubbers is probably greater than the 60% value chosen. Accordingly, the actual emissions may be lower than indicated in Table 5-1.

5.1.7 Cement Plants

The dominant factor in the case of cement plants is the overall particulate control efficiency for the main kiln gas stream, the alkali bypass gas stream, and the clinker cooler gas stream. The efficiency for metal-containing particulate has been assumed to be 95%. This takes into account the reduced efficiency of electrostatic precipitators in the 0.1 to 0.5% range. In calculating the emissions, it has been assumed that 20% of the metals are captured in the clinker and are not entrained in any of the gas streams.

The total consumption of used oil at cement plants reported in the NORA survey was 9,798,500 gallons. The total U.S. consumption by cement plants has been estimated at 35,100,000 gallons based on the results of the NORA survey.

5.1.8 Steel Mills

An overall collection efficiency of 95% for lead-containing particles has been used for steel mill operations. This factor takes into account the efficiency of the air pollution control

Emission Estimates

Due to the number of assumptions necessitated by the lack of firm data, these calculations provide only an order-of-magnitude (or "ballpark") estimate of emissions. However, several conclusions can be based on a comparison of the estimates for the various sources. These are discussed in the following sections.

5.2.1 Space Heaters

Space heaters are an important source of lead emissions due to the limited retention in the combustion chamber and the lack of an air pollution control. Also, emissions from these units could create locally high concentrations of metal-containing particulate due to the limited dispersion characteristics of the stacks.

Information is needed to confirm the metals retention levels of typical air atomizing space heaters presently on the market. Also, data is needed concerning the numbers of operating units, the capacities of these units, and the average operating hours per year. The Vermont Study will provide the needed data.

5.2.2 Commercial Boilers

This category appears to be relatively unimportant due to the low consumption rates for used oil. However, these units have very limited emission dispersion capability due to the low stacks, low gas temperatures, and close proximity to densely populated areas.

5.2.3 Industrial Boilers

This category of sources is important due to the relative large quantities of used oil consumed and the uncertainty regarding metals retention in the boiler. It is also possible that emission testing would indicate that certain metals such as chromium and barium are generated primarily in large particle size ranges which are collected with modest efficiency by the multi-cyclone collectors used on large industrial boilers. Air emission testing should be conducted at one or more typical industrial boilers.

5.2.4 Marine Boilers

Marine boilers do not have as great an environmental impact as industrial boilers since they consume less used oil fuel and

Emission Estimates

since some of the emissions occur away from populated areas. Air emissions data generated for industrial boilers would also be helpful in further evaluating marine boiler emissions.

5.2.5 Utility Boilers

This is one of the most important source categories. The utility boiler sector is a major used oil consumer as indicated by the estimated firing rate of 92.3 million gallons per year.

Furthermore, there is uncertainty regarding the extent to which metals are retained in the combustion chambers. There is also uncertainty regarding the metal-containing particulate control efficiency at oil-fired units with only low efficiency particulate control systems.

Air emission testing of one or more utility boilers is recommended. This test should be conducted on oil-fired unit with a low efficiency particulate control system.

5.2.6 Asphalt Plants

Asphalt plants are clearly one of the most important source categories burning used oil. They now utilize approximately 43% of the total used oil fuel supply, and the rate of consumption has been increasing for the last several years based on information supplied by NAPA⁸². There is considerable uncertainty regarding the emissions rates of lead and other metals from asphalt plants controlled with wet scrubbers. The low efficiency estimate used in Table 5-1 was necessary due to the probability that a major fraction of the metal-containing particulate is in the difficult-to-control submicron size range. Air emission testing at one or more asphalt plants is recommended. Hot mix and/or drum mix plants with a venturi wet scrubber should be tested. Particle size distributions of the metal-containing particles should be measured at the inlet and outlet of these units to further evaluate the removal capability of the medium pressure drop venturi scrubbers typically used on asphalt plants.

5.2.7 Cement Plants

The previously generated data concerning hazardous waste firing clearly indicates that metals are retained and collected at high efficiency at cement kilns. No air emissions testing of cement kilns is recommended. If additional data is needed regarding

Emission Estimates

- The speciation of Cr^{+3} and Cr^{+6} in "typical" used oil
- The conversions of the chromium valance states during combustion and in industrial furnaces/processes
- The particle size distributions of low volatility elements such as barium and chromium
- The extent to which low concentrations of chlorine affect the volatility of lead and other metals in used oil being burned.

Phase II Emission Test Recommendations

should be analyzed for lead, barium, cadmium, chromium (total and Cr⁺⁶), arsenic, zinc, and total chlorides.

The units should operate for several days using the used oil supply to "condition" the ductwork and air pollution control systems. U.S. EPA Reference Method SW 846-0012 (multi-metals) should be used for sampling the stack emissions from the wet scrubber systems. This train uses from four to seven impingers containing solutions of acid hydrogen peroxide and acidic potassium permanganate. These reagents collect gaseous metal emissions effectively. Analyses are performed using inductively coupled argon plasma emission spectroscopy (ICAP), atomic absorption spectroscopy (AA) or graphite furnace atomic absorption spectroscopy (GFAA). The emissions of total chromium and hexavalent chromium should be measured using U.S. EPA Reference Method SW 846-0013.

Metals sampling should also be conducted at the inlets to the wet scrubber systems. This data can be used in conjunction with the stack test data to evaluate the overall metals removal efficiency of the scrubbers. The inlet data can also be used to evaluate the fraction of each metal partitioned to the entrained particulate stream and to the asphaltic concrete. Sampling of the asphaltic concrete should not be attempted since it would be difficult to obtain accurate analyses in the case of the drum mix plant due to the addition of the asphaltic binder in the drum.

As part of the test program, the particle size distributions at the inlet and outlet of the scrubbers should be determined using cascade impactors. Each of the impactor stages should be analyzed for lead, arsenic, and barium. Due to the metal surfaces of the cascade impactors, these tests are not useful for the analysis of low concentrations of chromium and zinc. The weight distributions of lead and arsenic should be used as an indicator of the behavior of moderately volatile metals in the asphalt plant. The weight distribution of barium should be used as an indicator of the behavior of low volatility metals.

Plant operating data should be recorded during the tests to demonstrate that it was operating in a normal manner. This data includes the aggregate temperatures leaving the drum, the production rate, the type of asphaltic concrete produced, and the type of binder used.

6.2 UTILITY BOILERS

There are two types of utility boilers of interest: (1) units in which used oil is fired in conjunction with virgin oil, and (2)

Phase II Emission Test Recommendations

deposits at various locations in the boiler should be obtained soon after the used oil air emissions tests. This data would be helpful in confirming the retention of metals in the combustion chamber and on the surfaces of the heat recovery equipment.

The operating conditions of the boiler should be carefully documented during the test. The necessary data includes but is not limited to the following.

- Air pollution control system operating parameters
- Stack opacity as indicated by the continuous emissions monitor and by visible emission observations
- Boiler oxygen (economizer outlet) and carbon monoxide concentrations
- Boiler load
- Boiler gas temperatures
- Types and quantities of fuel fired for approximately two weeks prior to and during the tests
- Soot blowing practices prior to and during the tests

6.3 INDUSTRIAL BOILER

The air emission test on an industrial boiler should be conducted. The unit should be designed for burning oil fuel and have a rated heat input capacity between 10 and 100 million BTUs per hour. Some of the other criteria include the following.

- The operating company should be willing to participate in the test program.
- One unit should be 100% oil fired and equipped with multi-cyclone collectors. The used oil firing rate should be sufficient to allow measurement of possible metals emissions.
- The units should fire used oil on a continuous basis, or they should be able to fire used oil for one to two weeks prior to the test program to ensure that all of the internal surfaces are at an equilibrium condition with respect to conditioning.
- Travel costs should be minimized.

The tests would be very similar to those discussed with respect to utility boilers. However, there is no need for testing prior to a control device since it is assumed that metals-containing particles are not collected efficiently in these units.

REFERENCES

1. Hall, Robert. U.S. EPA, Air Energy and Environmental Laboratory, Personal Communication, 1993.
2. Daughbill, David. U.S. Army Industrial Hygiene Laboratory, Personal Communication, 1993.
3. Scott, Paul. U.S. Air Force, Air Quality Branch, Office of Environmental Health Laboratory, Personal Communication, 1993.
4. Ripley, Dennis. U.S. Department of Energy, National Institute of Petroleum and Energy Research, Personal Communication, 1993.
5. Campbell, Craig. Cement Kiln Recycling Coalition, Personal Communication, 1993.
6. Sedman, Charles. U.S. EPA, Air Energy and Environmental Laboratory, Personal Communication, 1993.
7. Maxwell, William, U.S. EPA, Office of Air Quality Planning and Standards, Personal Communication, 1993.
8. Manning, Justice. U.S. EPA, Technology Transfer Office, Personal Communication. 1993.
9. Perry, Charles. U.S. EPA, Hazardous Waste Laboratory. Personal Communication. 1993
10. Villahermosa, Lewis. U.S. Army R&D Center, Fuels and Lubricants Branch, Personal Communication, 1993.
11. Ross, Charles. Carolina Power and Light. Personal Communication, 1993.
12. Johnson, Chris, Southern California Edison. Personal Communication, 1993.
13. Cho, Paul. Electric Power Research Institute. Personal Communication, 1993.
14. Pines, Eydie. U.S. EPA, Personal Communication, 1993.
15. Weitzman, Leo. Weitzman Associates, Inc., Personal Communication. 1993.

References (Continued)

35. Necessary, D.E. Necessary Oil, Personal Communication, 1993.
36. Lewis, Gary. Personal Communication, 1993.
37. Noble, James. Noble Oil, Personal Communication, 1993.
38. Savoie, Marty. U.S. Army Corps. of Engineers, Construction Engineering Research Laboratory, Personal Communication, 1993.
39. Ranson, Randall. American Boiler Manufacturers Association, Personal Communication, 1993.
40. Jones, Brad. American Petroleum Institute, Personal Communication, 1993.
41. Green, Doug. Piper & Marbury/Edison Electric Institute, Personal Communication, 1993.
42. Brintle, David. Entropy, Inc., Personal Communication, 1993.
43. Gambird, Neil. Todd Combustion, Personal Communication, 1993.
44. McSurley, Gary. Sunwest Energy, Personal Communication, 1993.
45. Bider, William, et al. *Composition and Management of Used Oil Generated in the United States*. U.S. EPA Publication EPA/530-SW-013, PB85-180297, November 1984.
46. Temple, Barker, and Sloane, Inc. *Generation and Flow of Used Oil in the United States in 1988*. Presented at the Government Institutes/NORA Conference, November 28, 1989.
47. Wilson, Michaelle. *Lead in Used Oil Issues Paper, Sources of Lead: Fuel and Oil Additives*. Report prepared for the U.S. EPA, Contract No. 68-WO-0027, June 30, 1993.
48. Hegberg, Bruce A., William H. Hallenbeck, and Gary R. Brenniman. *Used Oil Management in Illinois*. Report Submitted to the University of Illinois Center for Solid Waste Management and Research, Office of Technology Transfer. NTIS Document PB91-236422, July 1991.
49. Copan, W.G., and R.F. Haycock. *Lubricant Additives and the Environment*. Paper CEC/93/SP02 presented at the Fourth International Symposium on the Performance Evaluation of Automotive Fuels and Lubricants. May 5-7, 1993.
50. Shepand, Thomas J; Lubrizol Corporation. Letter to Mr. Brad Jones, American Petroleum Institute, November 23, 1993.

References (Continued)

64. Ross, Charles and Steve Lund, Carolina Power and Light. Personal Communication, 1993.
65. Clean Burn, Inc. Model CB-90-Aa. Undated.
66. Clean Burn, Inc. *Operator's Manual, Clean Burn Models CB-90-AH and CG-90-BH with "CB-90-HS" Burner*. August 1992.
67. Barton, R.G. and W.R. Seeker. *Behavior of Metals in Medical Waste Incinerators*. Paper 90-38.5, Air and Waste Management Association, Pittsburgh, Pennsylvania, June 24-29, 1990.
68. Barton, R.G., W.D. Clark, and W.R. Seeker. *Fate of Metals in Waste Combustion Systems*. Combustion Science and Technology, Volume 74, Page 327-342, 1990.
69. Srinivasachar, S., Joseph R. Morency, and Barbara E. Wysiouzil. *Heavy Metal Transformations and Capture During Incineration*. Paper 92-41.07, 85th Annual Air and Waste Management Association, Kansas City, Missouri, June 21-26, 1992.
70. Buonicore, Anthony. *Experience with Air Pollution Control Equipment on Hazardous Waste Incinerators*. Paper 90-33.2. 83rd Annual Meeting of the Air and Waste Management Association, Pittsburgh, Pennsylvania, June 24-29, 1990.
71. Rizeq, R. G., Wyman Clark, and W.R. Seeker. *Engineering Analysis of Metals Emissions from Hazardous Waste Incinerators*. Paper 92-42.05, 85th Annual Meeting of the Air and Waste Management Association, Kansas City, Missouri, June 21-26, 1992.
72. Rizeq, R.G., D.W. Hansell, W. Clark, and W.R. Seeker. *Predictions of Metals Emissions from Hazardous Waste Incinerators and Comparison to Test Results from a Full Scale Facility*. Energy and Environmental Research Corporation.
73. Dellinger, H.B., D.W. Pershing, and A.F. Sarofin. *Evaluation of the Origin, Emissions, and Control of Organic and Metal Compounds from Cement Kilns Co-Fired with Hazardous Waste*. A report of The Scientific Advisory Board on Cement Kiln Recycling. June 8, 1993.
74. Gossman, David., Myron Black, and Mark Ward. *The Fate of Trace Metals in the Wet Process Cement Kiln*. Proceedings of Waste Combustion in Boilers and Industrial Furnaces. Air and Waste Management Association Publication SP-72, Pages 70-93, 1990.
75. Mantech, Mike. Clean Burn Inc. Personal Communication, 1993.

References (Continued)

87. U.S. EPA. *Background Information Document for the Development of Regulations to Control the Burning of Hazardous Wastes in Boilers and Industrial Furnaces, Volume II Industrial Furnaces*, January 1987.
88. Roth, Andrew J. *BIF Metals stack Emissions, Removal Efficiencies, and Fate in a Conditioned Preheater-type Cement Kiln*. Paper 92-41.02. Presented at the 85th Annual Meeting & Exhibition of the Air & Waste Management Association. Kansas City, Missouri. June 21-26, 1992.
89. Bolstad, Jon N. and John Chehaske. *Test Results of Hazardous Waste Combustion in two Cement Kilns*. Paper 85-68.2, 78th Annual Meeting of the Air Pollution Control Association. Detroit, Michigan, June 16-21, 1985.
90. Hansen, Eric R. *Effect of Spiking Method on Cr⁺⁶ Behavior in a Cement Kiln*. Ash Grove Cement Company.